MEASUREMENTS OF SELECTED C_2-C_5 HYDROCARBONS IN THE BACKGROUND TROPOSPHERE: VERTICAL AND LATITUDINAL VARIATIONS

D.H. EHHALT, J. RUDOLPH, F. MEIXNER, and U. SCHMIDT

ABSTRACT. Meridional cross sections of the concentration of light hydrocarbons are reported. They were obtained from 20. April to 10. May, 1980, during the French research flight STRATOZ II, and cover the latitudes between 60° N and 60° S and the altitudes between 800 mb and 200 mb. The mixing ratios of ethane, ethene, acetylene, propane, propene, n-butane, i-butane, n-pentane, and i-pentane range between 2.0 and 0.02 ppb. Globally, a decrease in concentration with increasing altitude and - in most cases - with decreasing latitude is observed. In addition the 2-dimensional concentration fields show structures of different scales. In particular, isolated maxima of high concentrations are found in the upper troposphere. They point to fast vertical transport between the boundary layer and the upper troposphere. In the present case these maxima seem to be correlated with large scale meteorological systems, such as low pressure regions or the Inter Tropical Convergence Zone. It is argued that the NMHC provide a set of tracers well suited to the detection of fast vertical transport.

KEY WORDS. Nonmethane hydrocarbons, trace gases, remote troposphere, vertical and latitudinal variation, vertical transport, aircraft observation

1. INTRODUCTION

The importance of non methane light hydrocarbons for the chemistry of the urban atmosphere has been long recognized. In contrast their possible role in the photochemistry of the background troposphere has long been overlooked. Methane, which is by far the most abundant hydrocarbon species, was thought to sufficiently represent the hydrocarbons in chemical models of the background atmosphere (Levy, 1971; Logan et al., 1981). In the meantime measurements of non methane light hydrocarbons, NMHC, in the background atmosphere have become available (Robinson, 1978; Singh et al., 1979; Cronn and Robinson, 1979; Singh et al., 1982; Rudolph et al., 1981a, 1981b, 1982a; Ehhalt and Rudolph, 1984; Rasmussen et al., 1983; Hov et al., 1984). They gave mixing ratios for the C_2-C_5 hydrocarbons on the order of one ppb or less. Even at mixing ratios that low nonmethane hydrocarbons become significant, because they

react much faster than CH_4 - mainly with the OH radical, which provides the major sink reaction for most hydrocarbons. In fact, in some remote locations of the northern midlatitudes more carbon in form of NMHC than in form of CH_4 is processed in atmospheric reactions (Rudolph et al., 1980). The NMHC also generate additional intermediate and product species in the background atmosphere, such as acetaldehyde, acetic acid and peroxy acetylnitrate (Singh and Hanst, 1981), and thus open new chemical pathways.

In this paper we would like to stress another important aspect of the NMHC, namely their role as tracers for fast vertical transport. This role is based on the facts, that the NMHC are emitted at the earth's surface and are ubiquitous in the planetary boundary layer, that they are little soluble in water and thus not rained out, and that they have a wide range of relatively short lifetimes - from about one

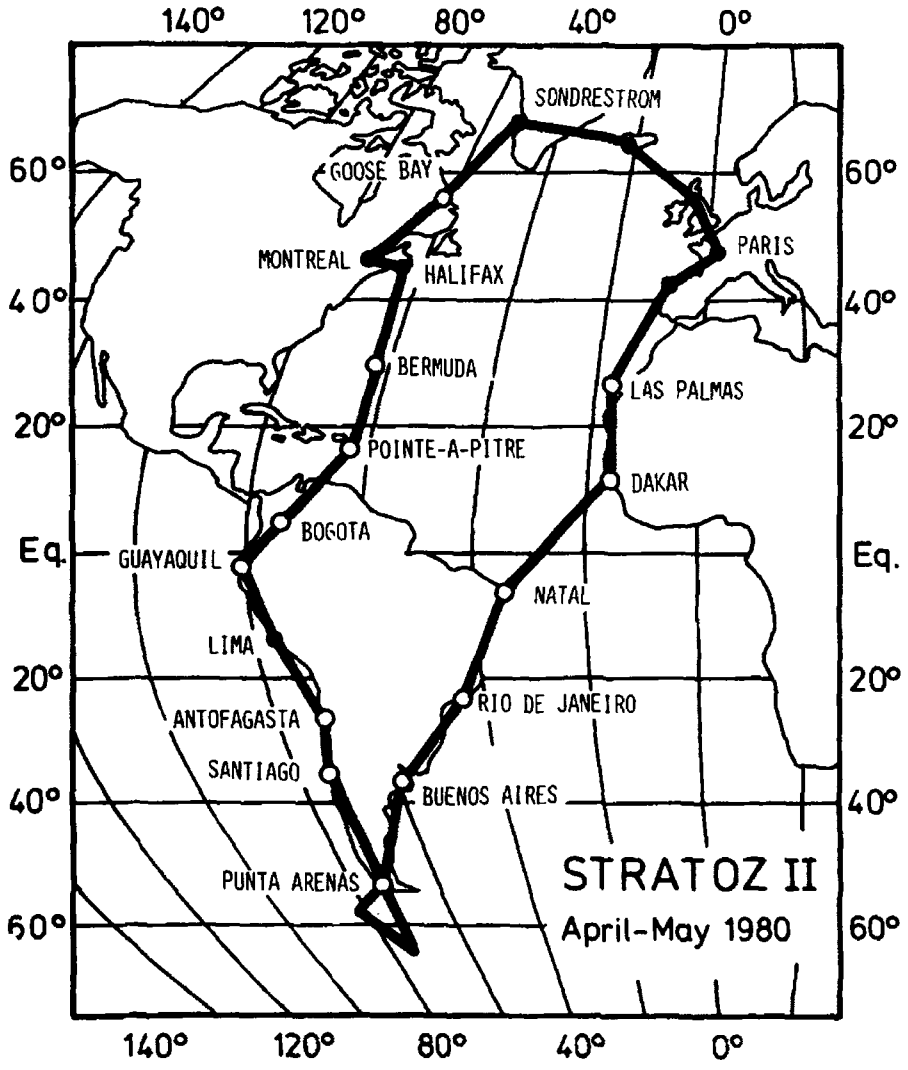


Figure 1. Flight track of the STRATOZ II experiment.

day for ethene or propene to about two months for ethane. The short lifetimes cause steep mean vertical concentration gradients and air parcels which were recently lifted from the boundary layer should be easily identified by their elevated NMHC concentrations. Moreover, the relative concentration of the various NMHC in an air parcel can serve as a finger print characterizing their source or source area.

In the following we attempt to illustrate the utility of the NMHC as a set of tracers for vertical motions using data which we have obtained during the "STRATOZ II" flight of the Caravelle research aircraft of the French Centre d'Essais en Vol at Bretigny. The mission started in Paris on the 20. April and returned on the 10. May 1980. The flight track is shown in Figure 1. The plane landed about every 3000 km, which allowed the sampling of vertical profiles during the approach to or take off from the airports, whose positions are indicated by the dots in Figure 1. The sampling pattern has been published by Schmidt et al. (1982a). The data allow for the first time a 2-dimensional view of hydrocarbon distributions. They will be presented and discussed in form of meridional cross sections.

2. EXPERIMENTAL

Air samples at ambient pressure were collected in evacuated stainless steel containers of 2 l volume equipped with metal bellow valves. The containers were carefully cleaned and pretreated to avoid sample contamination or losses. The procedure has been described by Ehhalt et al. (1976). The sample containers allowed storage for two months without detectable changes in the mixing ratios of the light hydrocarbons. Fifteen such containers were attached to a common inlet line which was connected to the air intake mounted on top of the cabin in the forward part of the wing section of the aircraft. A detailed description of the air intake and exhaust and inlet line preparation was given by Schmidt et al. (1982b). The samples were analysed in the laboratory with a Packard 419 gaschromatograph equipped with a flame ionisation detector and a 6 m x 0.8 mm column packed with porous silica (Spherosil XOB 075). The column was operated at programmed temperatures increasing from -80 °C to 150 °C. A precolumn of Spherosil and Carbosieve at -100 °C was used to enrich the hydrocarbons prior to injection. The details of the gaschromatographic analysis have been published by Rudolph et al. (1981c). The hydrocarbons measured were ethane, ethene, acetylene, propane, propene, n-butane, i-butane, n-pentane and i-pentane. The detection limits varied between 20 ppt and 50 ppt depending on the available sample volume and the individual compound. Neither the sample containers nor the analytical procedure caused detectable blank values. Due to the outgassing of a polymer gasket in the container valve the concentrations of C_2H_4 and C_3H_6 in the working standard increased as a function of time. The form of this function is unknown, because the absolute calibrations of the working standard were spaced about a year apart. Thus the actual C_2H_4 and C_3H_6 concentrations in the working standard at the time of the measurement of the STRATOZ II samples were uncertain, and the mixing ratios of C_2H_4 and C_3H_6 given below, could be too low by a

factor of two. They should be, however, mutually consistent, because the samples were measured within a few weeks.

In addition to the C_2-C_5 hydrocarbons CO, CH_4 , $CFCl_3$, CF_2Cl_2, and N_2O were measured. The results have been reported by Schmidt et al. (1982a).

3. RESULTS

Altogether 110 air samples were collected during STRATOZ II, most of which were also analysed for NMHC. They cover the altitude range between 200 mb, the maximum altitude of the aircraft, and 800 mb, the lowest pressure level chosen to prevent the collection of contaminated air samples in the vicinity of the airports. The data are available in tabulated form in Schmidt et al. (1982b). In the present paper the NMHC data are summarized in form of meridional cross sections (Figures 2 through 10). For clarity the figures do not contain the individual data points, but rather the isolines of constant mixing ratio interpolated between them. Such interpolation always implies a certain measure of subjectivity. In order to minimize a bias in the displayed data, we were careful not to transfer information from one meridional cross section to the other - nor did we incorporate information from previous measurements. Each figure is separated in a southbound and northbound section. The southbound section is based on the flights between Sondrestrøm, Greenland, and Puntas Arenas, Chile, the northbound section on the flights between Puntas Arenas and Paris. The latter also includes the flights between Paris and Sondrestrøm; but note that these took place at the beginning of the mission about two weeks prior to the other northbound flights (see Figure 1). Few samples were taken over Europe, the resulting gap is indicated by the vertical dashed lines in Figures 2 through 10. Finally we note that the mixing ratios of the shortest lived species, C_2H_4 and C_3H_6, showed larger spatial scatter than that of the other NMHC. Their isopleths are, therefore, more uncertain than those of the others.

In the following we describe the general features of the meridional NMHC distributions. These are common to all or a larger subset of the measured NMHC. Firstly, the NMHC distributions all show strong latitudinal gradients. For the NMHC with low carbon numbers, $C \leq 3$, the latitudinal pattern is simple. The highest mixing ratios occur around 50° N. The mixing ratios decrease at all altitude levels from northern midlatitudes towards the equator, and they continue to decrease into the southern hemisphere (Figures 2 through 6). During the southbound flights the mixing ratios also decrease north of 50° N leading to upward bulging, domeshaped isolines at this latitude. This pattern corresponds closely to the single maximum at 40° N in the latitudinal distribution of the low alkanes found in surface air over the Atlantic (Rudolph et al., 1981a, 1982a).

The pentanes show a more complex latitudinal distribution with maximum mixing ratios at three latitudes. This is most clearly visible for i-pentane (Figure 10). In addition to the upward bulging isolines at 50° N it shows another equally strong bulge at the equator during

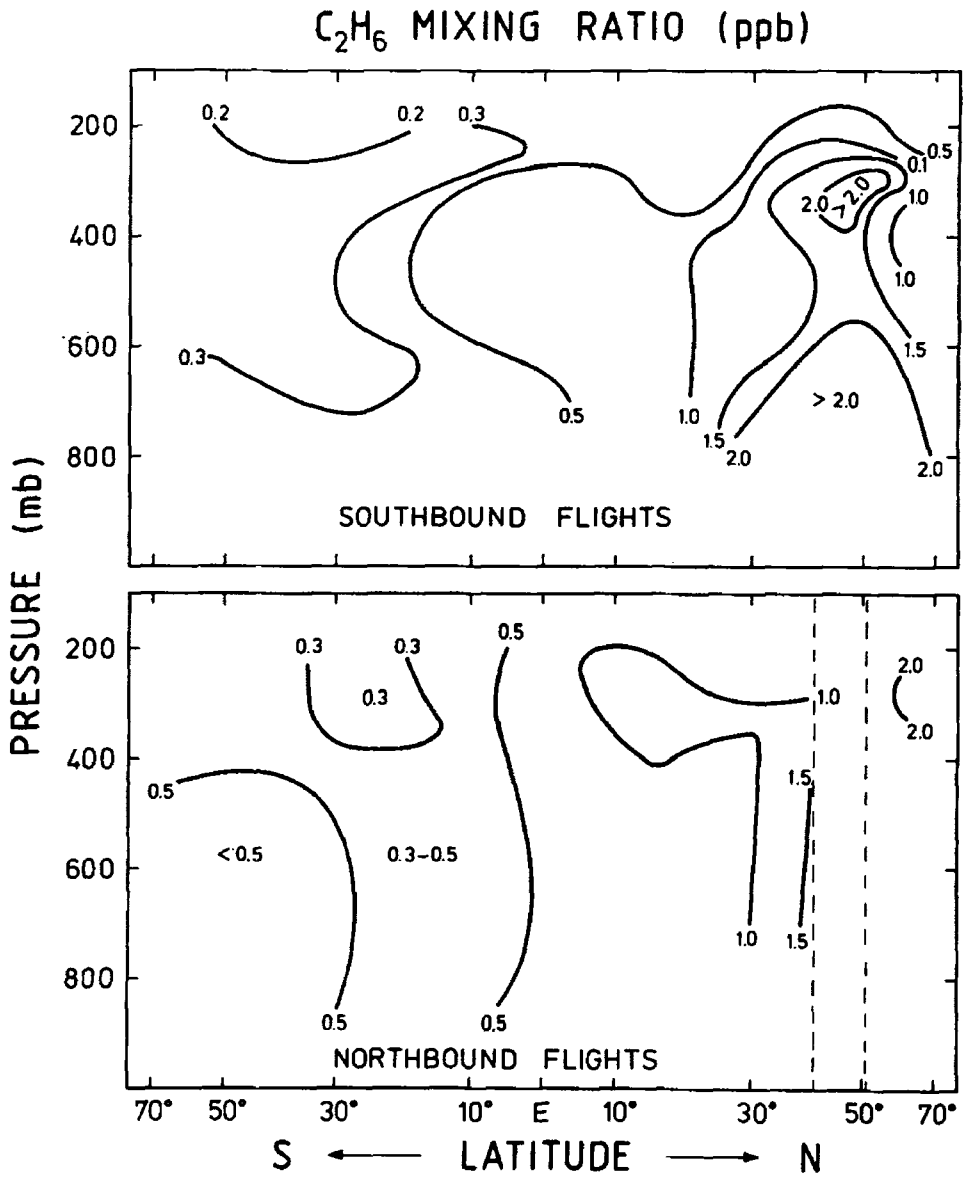


Figure 2. Latitude-altitude cross section of the C_2H_6 mixing ratio obtained during STRATOZ II. The contours of constant mixing ratio are given in ppb.

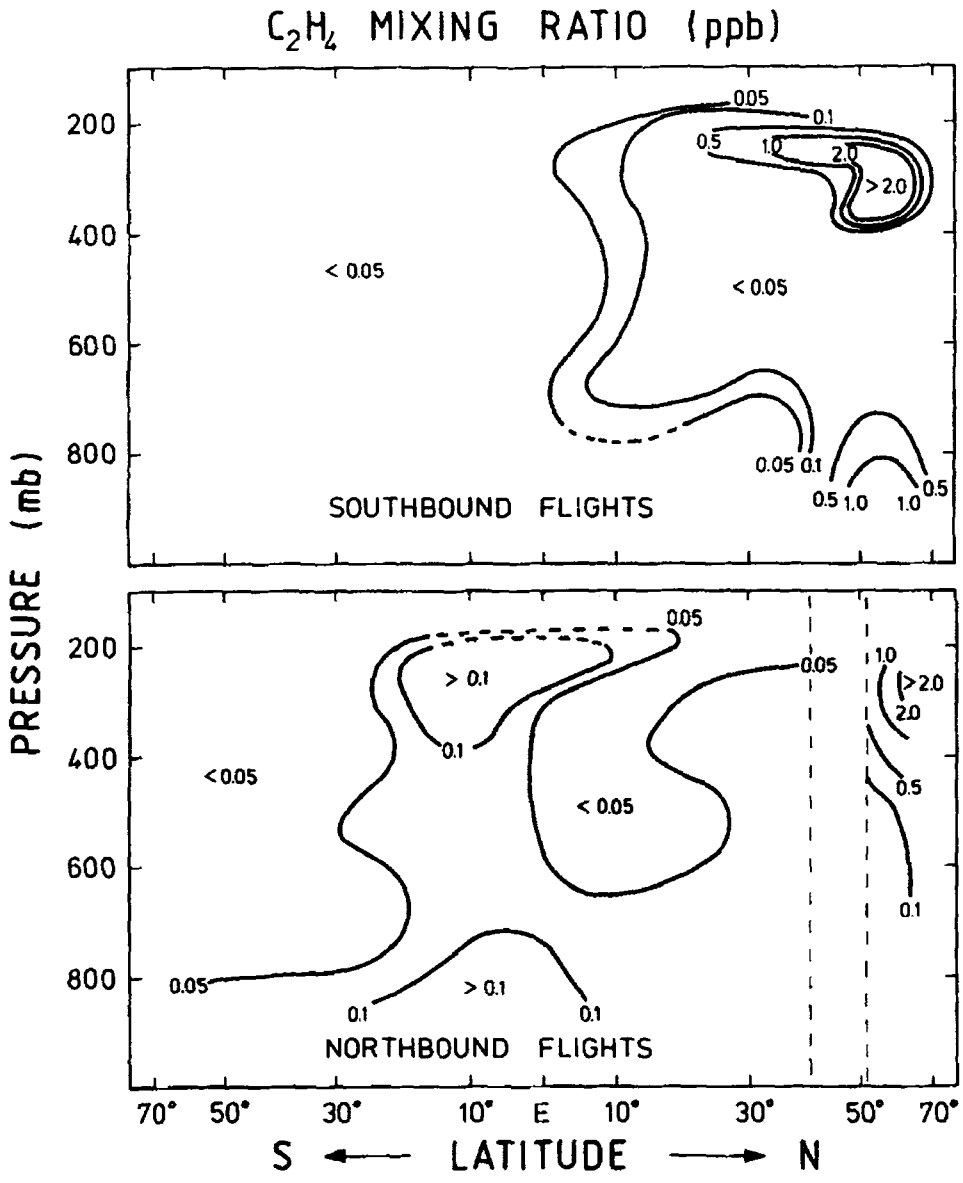


Figure 3. Latitude-altitude cross section of the C_2H_4 mixing ratio obtained during STRATOZ II. The contours of constant mixing ratio are given in ppb.

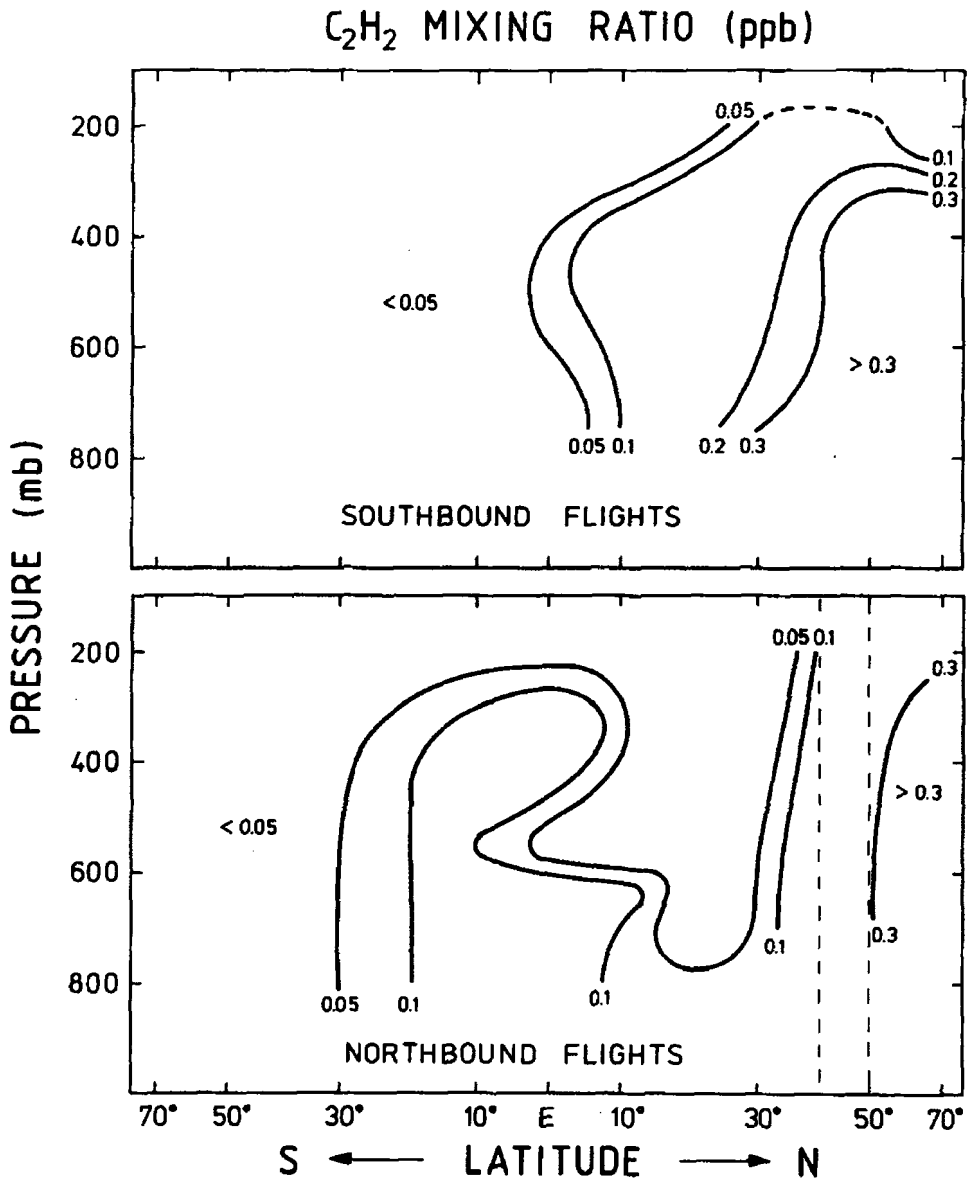


Figure 4. Latitude-altitude cross section of the C_2H_2 mixing ratio obtained during STRATOZ II. The contours of constant mixing ratio are given in ppb.

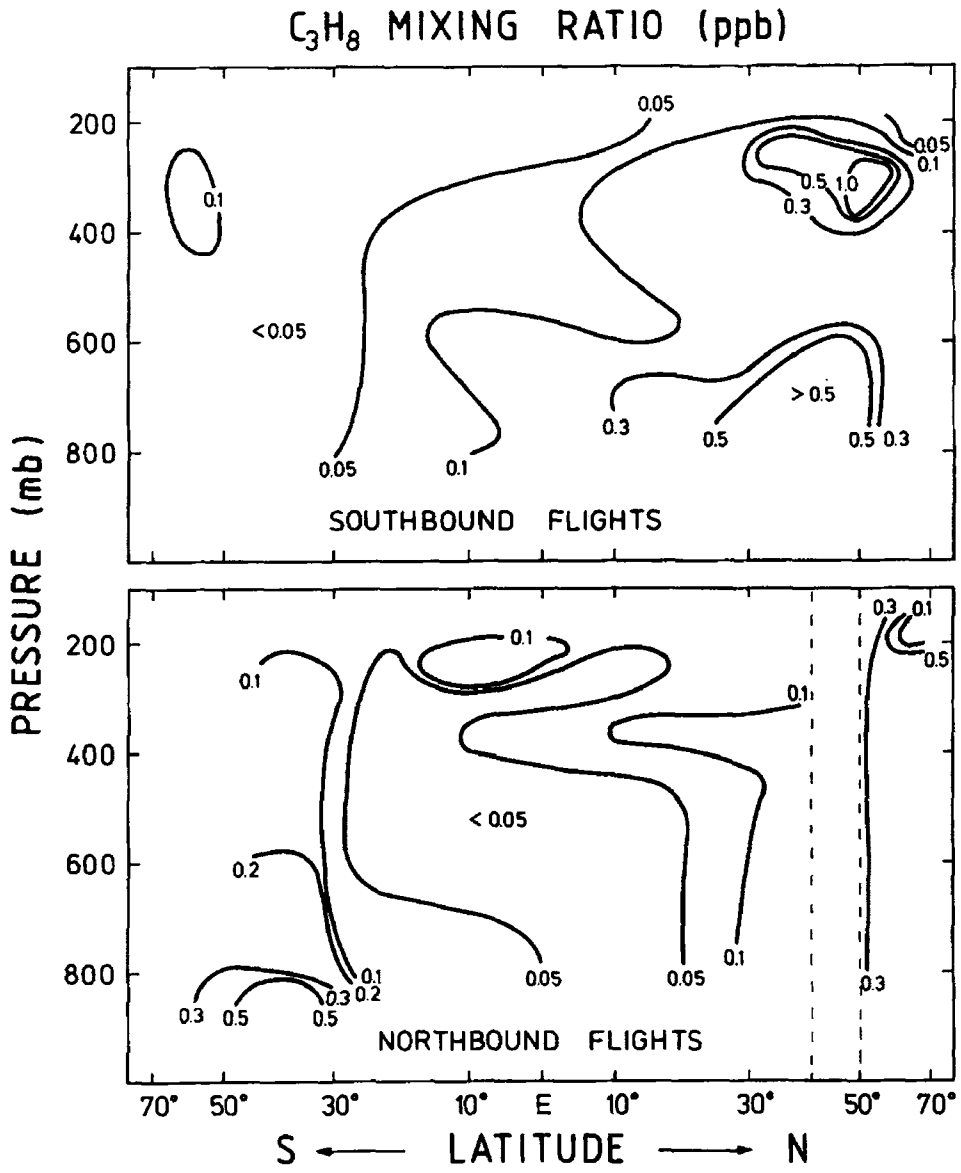


Figure 5. Latitude-altitude cross section of the C_3H_8 mixing ratio obtained during STRATOZ II. The contours of constant mixing ratio are given in ppb.

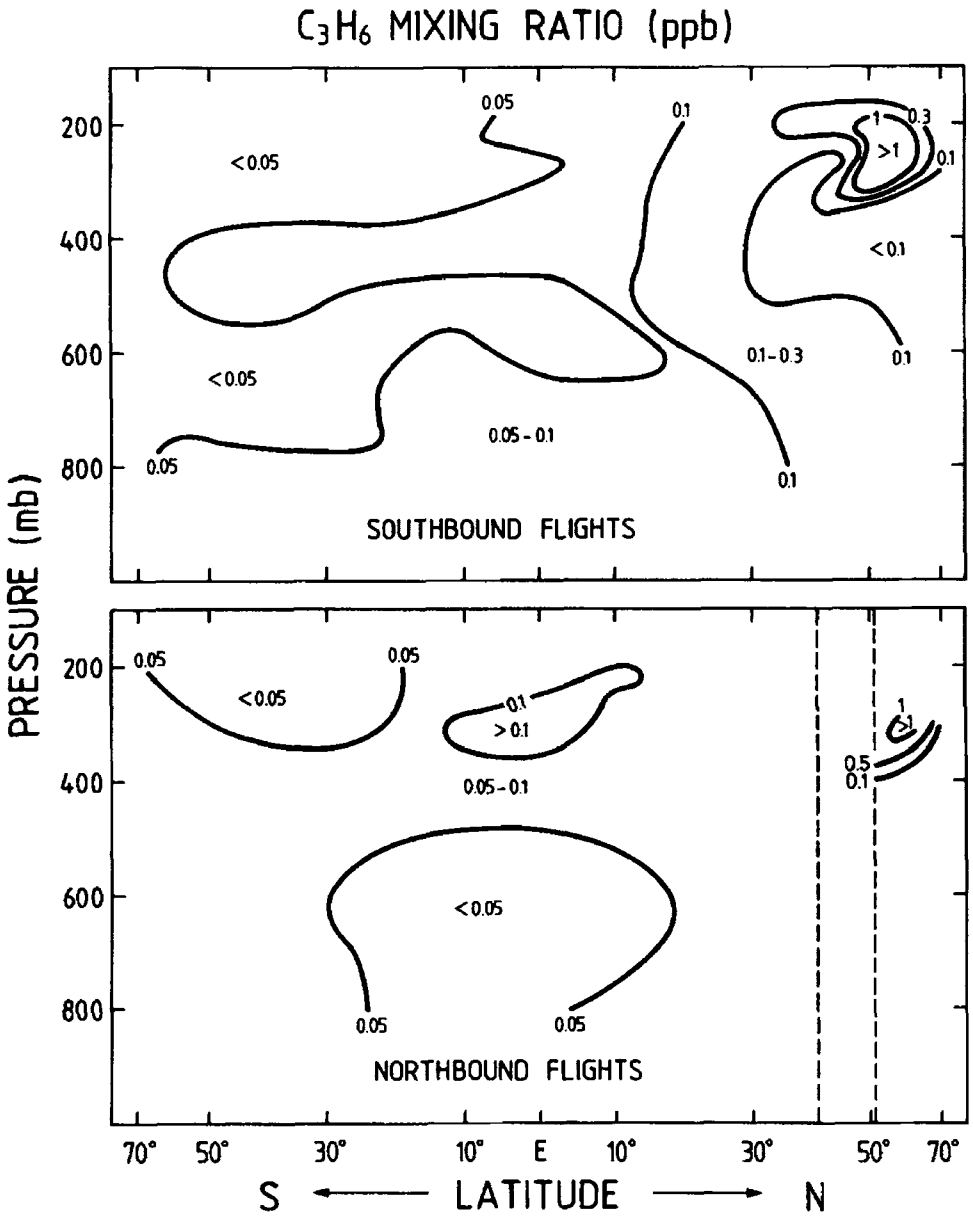


Figure 6. Latitude-altitude cross section of the C_3H_6 mixing ratio obtained during STRATOZ II. The contours of constant mixing ratio are given in ppb.

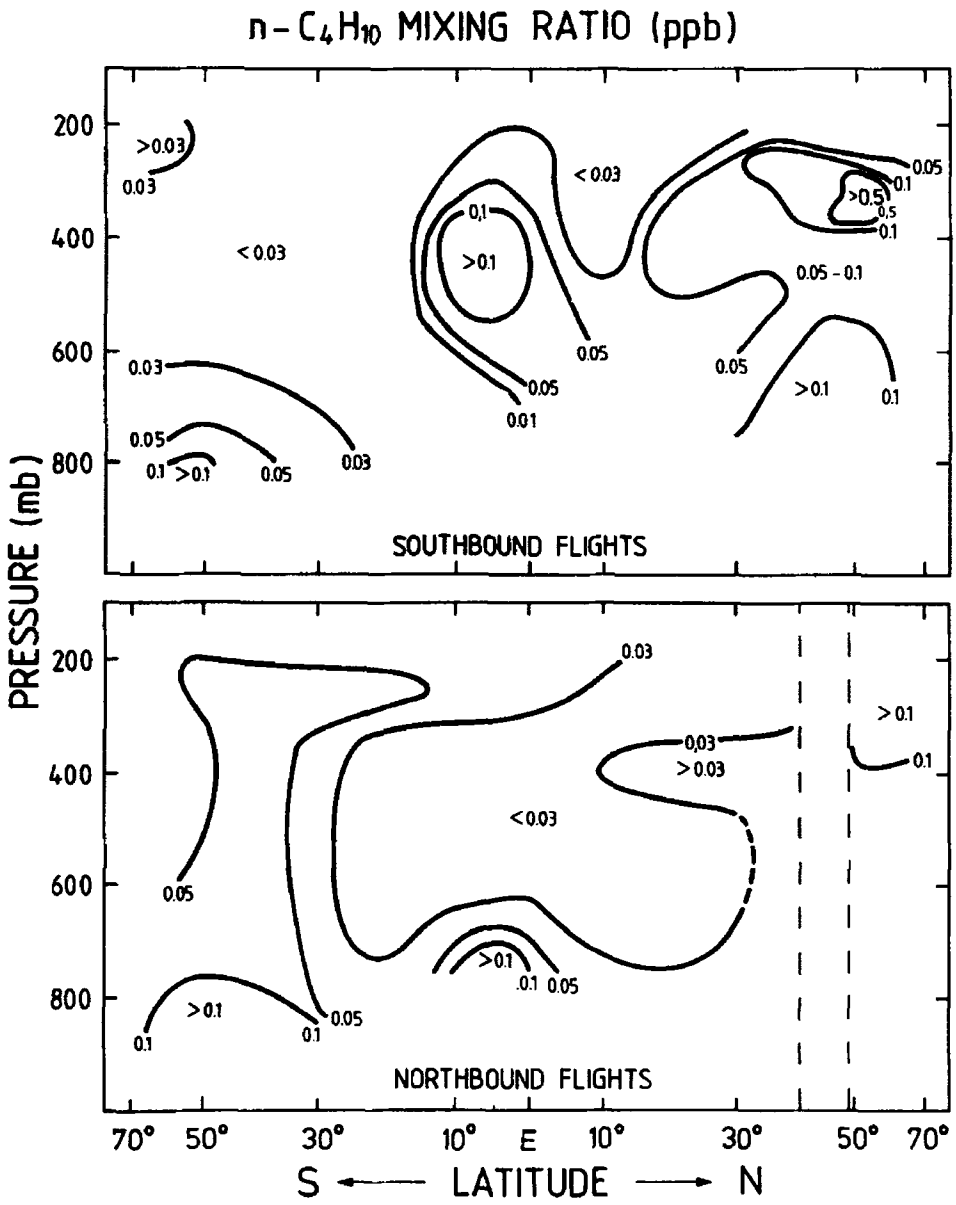


Figure 7. Latitude-altitude cross section of the n-C_4H_{10} mixing ratio obtained during STRATOZ II. The contours of constant mixing ratio are given in ppb.

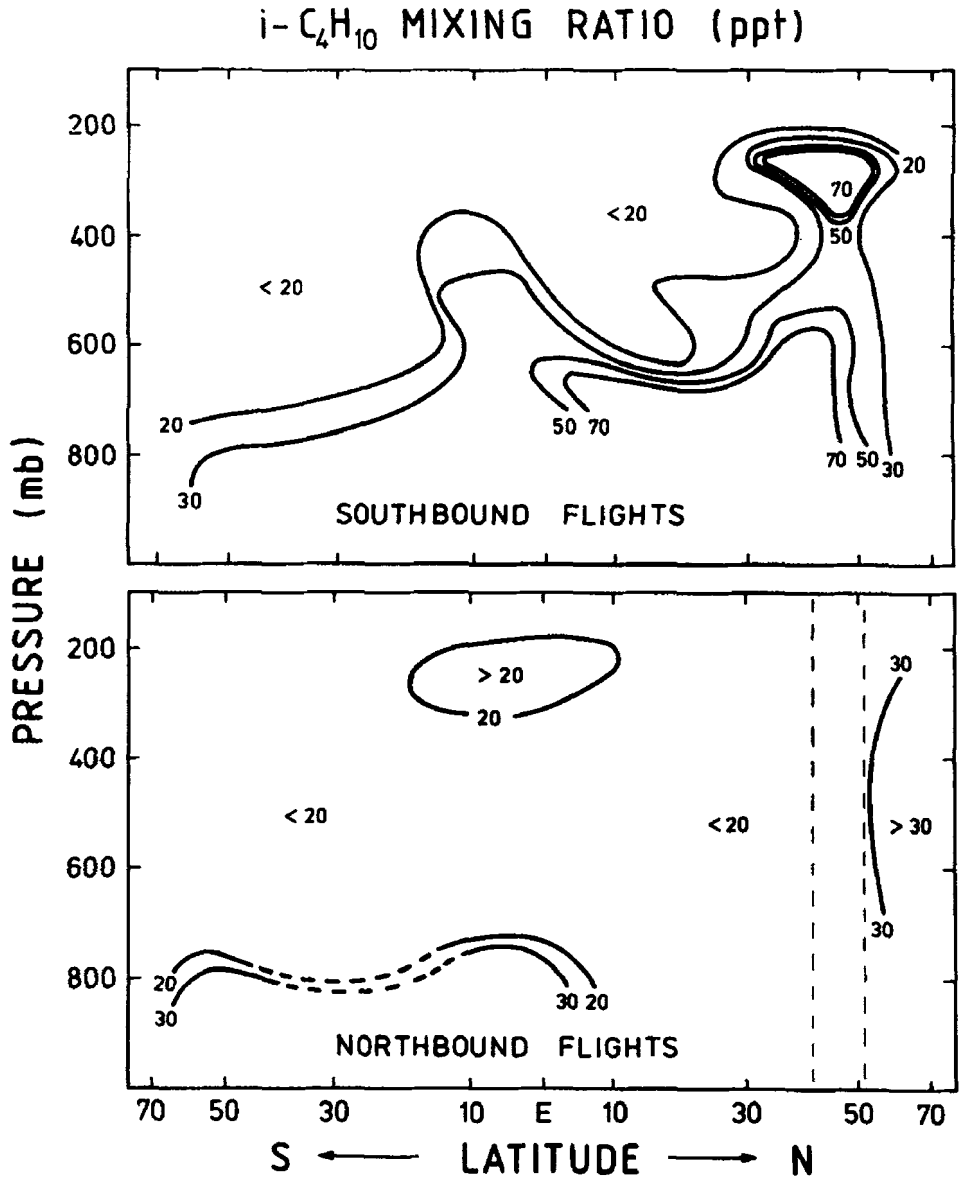


Figure 8. Latitude-altitude cross section of the i-C_4H_{10} mixing ratio obtained during STRATOZ II. The contours of constant mixing ratio are given in ppt.

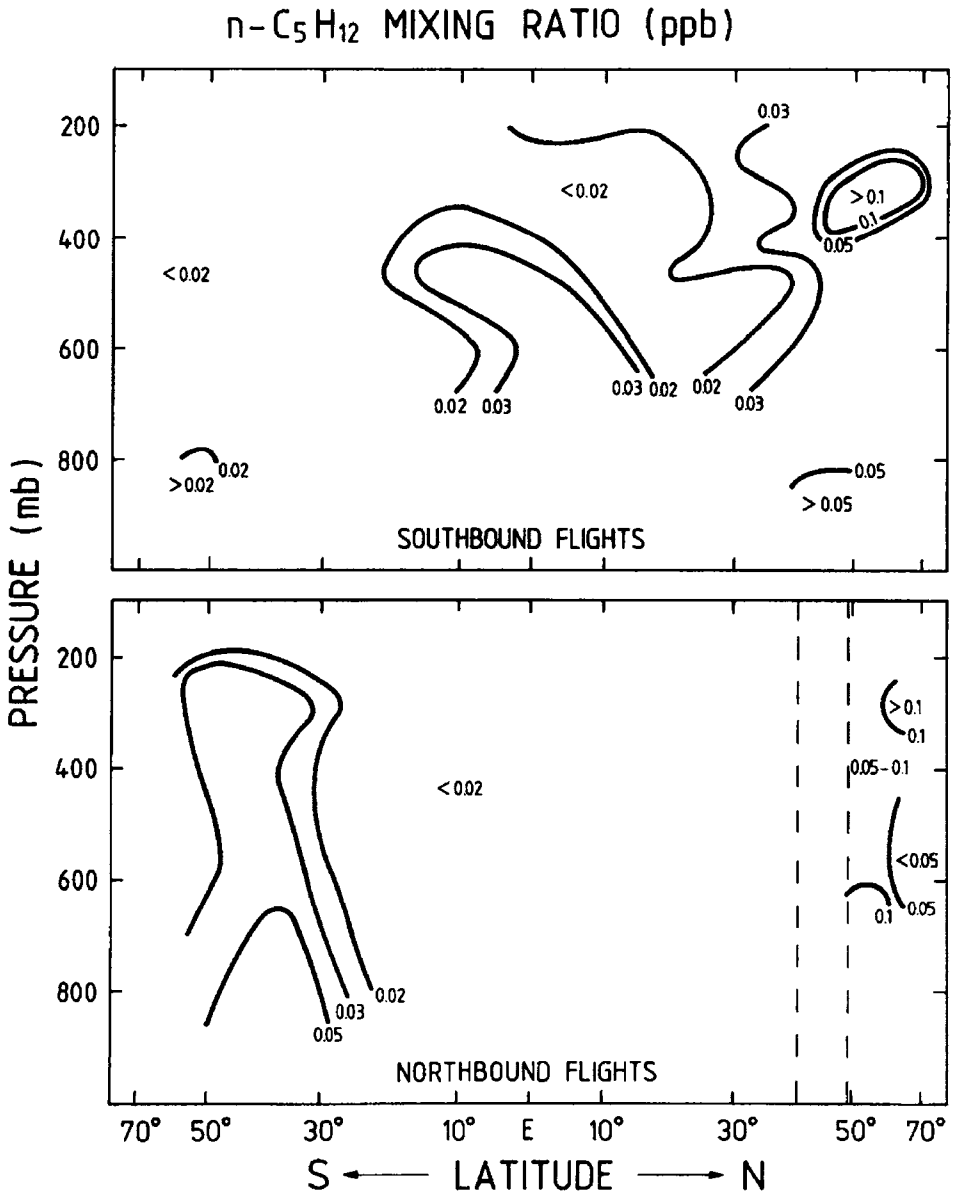


Figure 9. Latitude-altitude cross section of the n-C_5H_{12} mixing ratio obtained during STRATOZ II. The contours of constant mixing ratio are given in ppb.

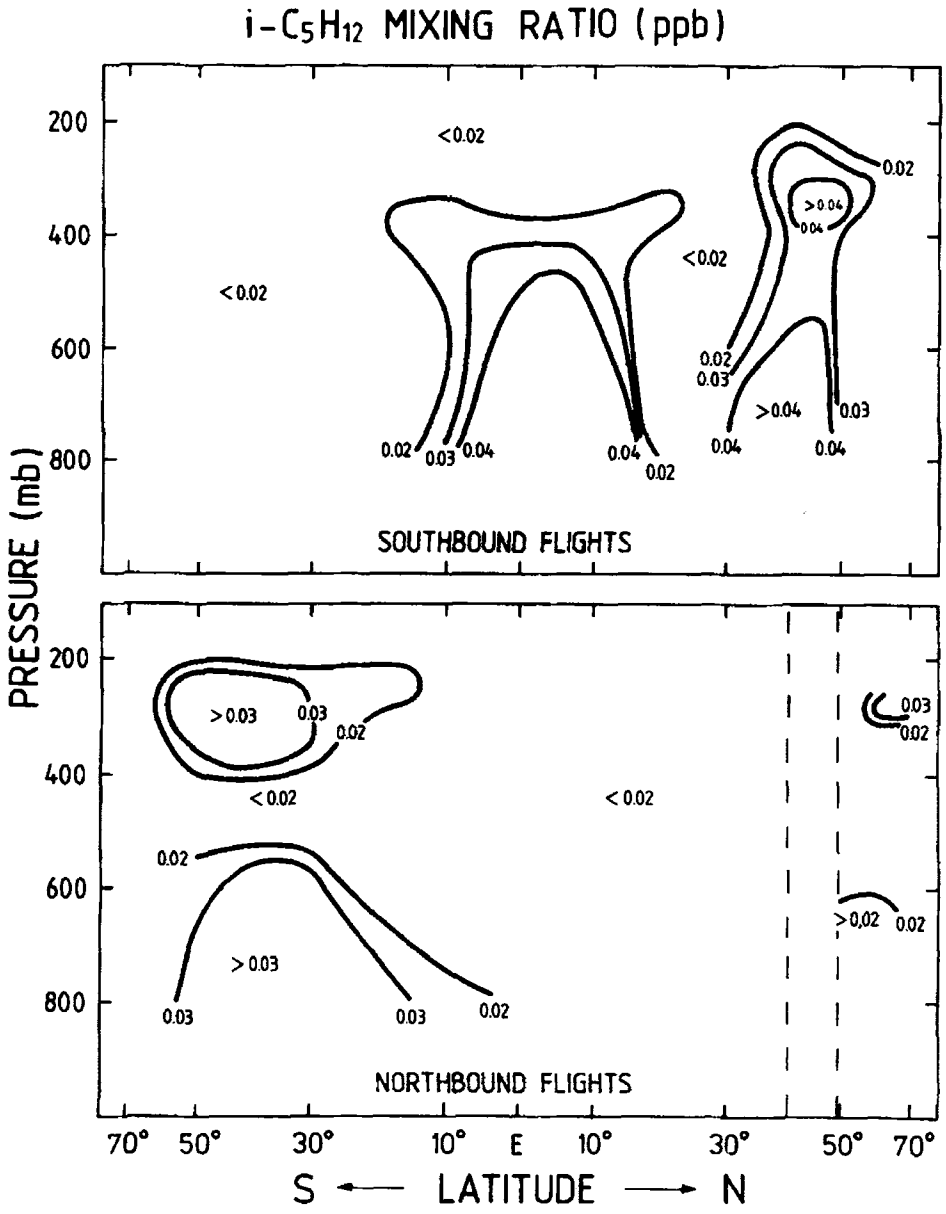


Figure 10. Latitude-altitude cross section of the i-C_5H_{12} mixing ratio obtained during STRATOZ II. The contours of constant mixing ratio are given in ppb.

the southbound flights, and a third at 40° S during the northbound flights. N- and i-butane show a transition between the simple and the complex pattern: Their latitudinal distributions also show the three maxima, but the one at 50° N is so dominant that there remains a general decrease from north to south. Looking closely, one observes even for C_2H_2 and C_3H_8 slight maxima at the equator or in the southern hemisphere.

The second general observation is a vertical decrease in the mixing ratio of the NMHC with increasing altitude. This is expected because the NMHC are emitted at the earth's surface.

There are, however, a number of exceptions from that general vertical decrease, namely, isolated patches of high NMHC mixing ratios in the upper troposphere. Most NMHC show such an isolated maximum over the equator during the northbound flights, and another one around 60° N. But the most conspicuous feature is the cell in the upper troposphere at around 50° N which was observed during the southbound leg. It very distinctly shows maximum mixing ratios for all NMHC except C_2H_2. On the whole, one is left with the general impression of large spatial and temporal variability, despite the regular latitudinal and vertical gradients also observed in the present meridional NMHC distributions. This is emphasized by a comparison of the separate meridional cross sections obtained for the southbound and northbound flights, respectively. Apart from the regular gradients mentioned above they show little similarity indicating at least temporary zonal gradients in the mixing ratios. In particular, the measurements north of the equator show lower values during the northbound leg than during the southbound leg indicating cleaner air over the Eastern Atlantic than over the Western Atlantic.

4. DISCUSSION

As indicated in Figure 1 the flight route skirted the continents and the sampled air masses are exspected to be influenced by the largely continental sources of NMHC. Moreover, the NMHC concentrations at northern latitudes exhibit significant annual variations (Singh and Salas, 1982; Rasmussen et al., 1983; Hov et al., 1984) causing seasonal changes in the meridional distribution of NMHC. Thus, the meridional cross-sections provided in Figures 2 to 10 should not be construed as global averages, although they tend to show the most persistent global features. They rather represent a more or less instantaneous snapshot of the atmosphere, which is subject to the momentary airflow, which itself is quite likely far from the mean state of the atmosphere. The resulting deviations from the mean NMHC mixing ratio fields reflect these motions, and the observed variability contains, at least in principle, a good deal of information on the transport processes and regional sources. In the following we briefly investigate the more conspicuous examples of likely deviations from the mean. The most obvious one is the isolated maximum at 10 km altitude and 50° N. It was observed on the 24. April 1980 during the southbound flights from Sondrestrøm to Goose Bay, and Goose Bay to Montreal. The highest mixing ratios were observed in three samples, whose positions are shown in Figure 12. The

maximum is a distinct feature in all NMHC distributions except that for C_2H_2. For some NMHC, notably C_2H_4 and C_3H_6, the mixing ratios exceed those found at the lowest altitudes. Such common behavior points to a common mechanism. It is quite tempting to assume that this maximum is caused by exhaust emissions of commercial jet aircraft. The flight path of our Caravelle aircraft followed over large parts the trans-atlantic flight pattern of that day. It is even conceivable that the Caravelle was following another plane relatively closely and thus encountered high levels of pollution. There is, however, a serious inconsistency in that explanation when we use the frequency pattern of the NMHC as a fingerprint of the origin of the NMHC. For example, the ratio of CO to NMHC (C_2-C_5) within the cell of maximum mixing ratios, expressed as the ratio of carbon atoms, (C_{CO}/C_{NMHC}), amounts to about 15. A jet engine, however, emits very few NMHC in the C_2-C_5 range (cf. Fig. 11). Most of the emitted hydrocarbons have carbon numbers above 7, and the ratio of CO to NMHC (C_2-C_5) in jet exhaust is very large, namely about 100 (NAS, 1976; Oliver et al., 1978). This seems to rule out a large contribution by jet exhaust. On the other hand most of the NMHC emitted by a gasoline engine are in the range C_2-C_5 (cf. Figure 11), and C_{CO}/C_{NMHC} in gasoline

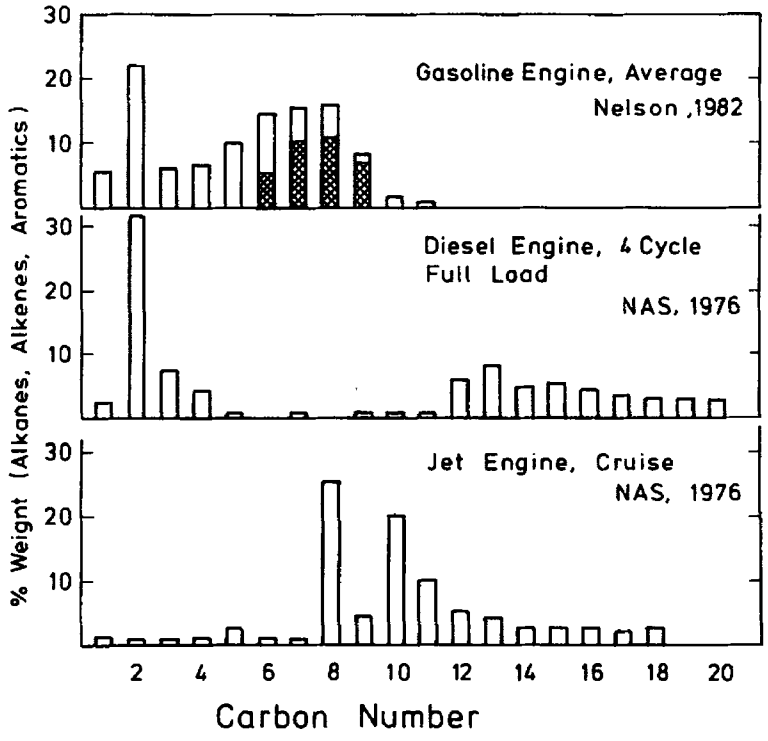
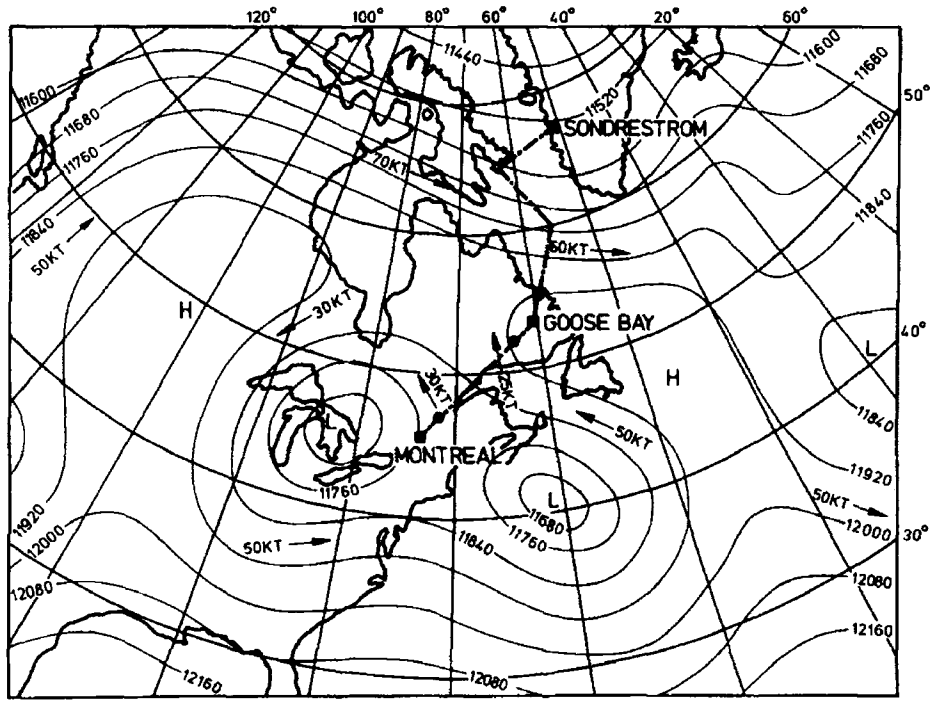


Figure 11. The distribution of hydrocarbons in the exhaust of a gasoline engine, a diesel engine and a jet engine, under specified operating conditions. Hydrocarbons with the same carbon number are lumped together. The full portion of the bars for the gasoline engine indicates the fraction of aromatic compounds.

engine exhaust is much lower, namely about 10. This value is also observed in the boundary layer as a whole. Thus, the NMHC observed in the maximum show a frequency pattern more consistent with boundary layer air. Surface air as the source of the NMHC maximum in the high troposphere is also supported by the fact that CO, CH_4 and CF_2Cl_2 also showed such a maximum (Schmidt et al., 1982a).

If this interpretation is correct, there must be rather fast transport processes to carry the high concentrations of NMHC to these altitudes, as the lifetimes of the alkenes, C_2H_4 and C_3H_6, are on the order of one day only. For example, an extended front with high-reaching convection could pump boundary layer air quickly to altitudes close to the tropopause. Such an explanation is indeed possible in the present case. Figure 12 shows the constant pressure surfaces at 200 mb. It exhibits two areas of low pressure, one over the Great Lakes and another offshore the Canadian coast. They extended all the way to the surface and were associated with cyclones and, at least in the case of the latter, with strong frontal activity. This activity could have provided the fast vertical transport from the surface to 300 mb, the height of the NMHC maximum. The circulation at 200 and 300 mb would certainly have allowed the uplifted air to reach the points of sampling.



200mb surface, 24-04-80, 12:00 UT

Figure 12. 200 mb pressure surface over Eastern North America on 24. April 1980, the date, when the very high NMHC mixing ratios were sampled in the upper troposphere. The flight track is indicated by the dash-dotted line. The full circles indicate the positions of the high concentration samples. Note the jet stream around 60° N (after Karcher et al., 1982).

It is noted that the observed maximum most likely represents the superposition of two separate transport events. The two high measurements shortly before and after Goosebay are associated with the low pressure region and surface front over the Western Atlantic. The high data point before Montreal, on the other hand, is more likely caused by the low over the Great Lakes.

In any case, the observed cell of maximum NMHC mixing ratios represents a large deviation from the expected mean. This is emphasized in Figures 13 and 14, where vertical profiles of C_2H_6 and C_2H_4 at 50° N extracted from the STRATOZ II data are compared to measurements made over the Eifel, a mountain region in Germany, and 1 D model calculations, although it is clear, that a 1 D model, whose vertical transport is parameterized by eddy diffusion, is unable to generate such a maximum, and will always predict monotonically decreasing NMHC mixing ratios with altitude. For C_2H_6, which is relatively longlived, with an atmospheric lifetime of about 2 months, the relative deviation from the model or from the previous measurements is not that large. However, for the shortlived C_2H_4 the deviation becomes very large. The mixing ratios

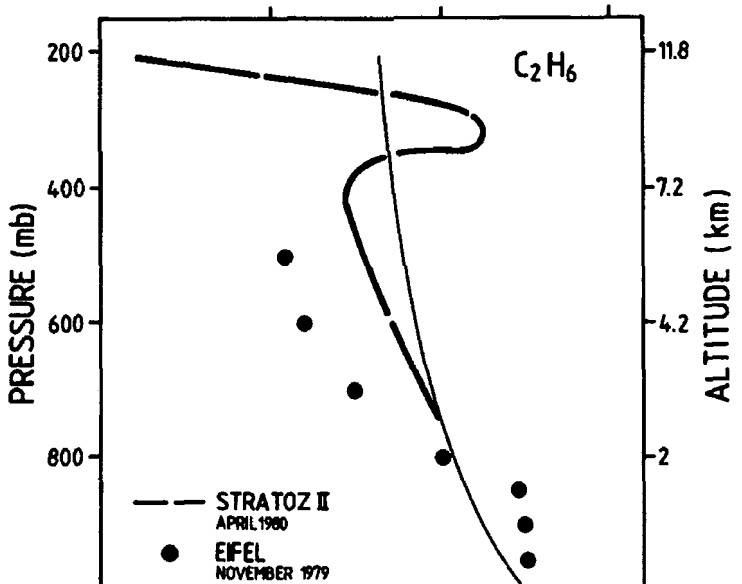


Figure 13. Vertical profiles of the C_2H_6 mixing ratio at 50° N latitude. The full dashed curve is based on STRATOZ II data (cf. Figure 2). The full circles represent the average of 3 flights over the Eifel mountains, West Germany, in November 1979 during strong westerly winds and clean air (Rudolph et al., 1982b). The thin full line is a model calculated profile from Chameides and Cicerone (1978).

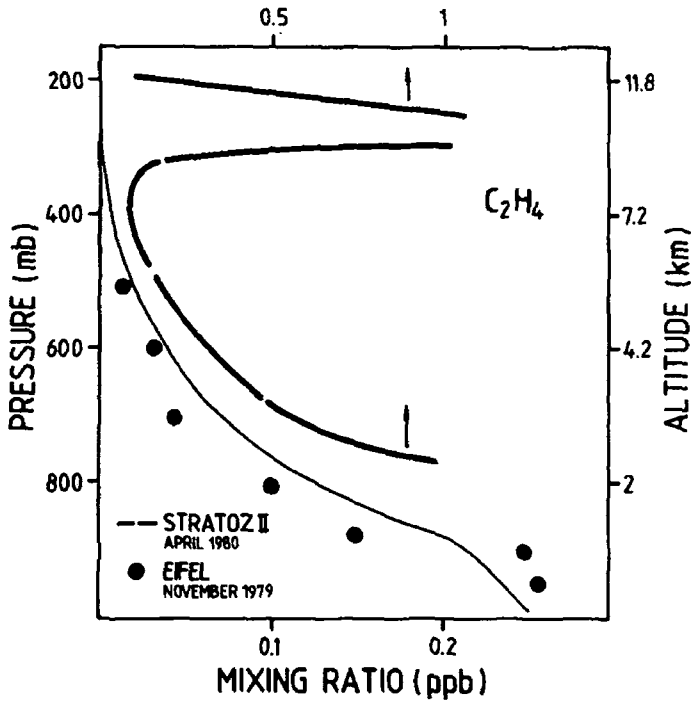


Figure 14. Vertical profiles of the C_2H_4 mixing ratio at 50° N latitude. The full dashed curve is based on STRATOZ II data (cf. Figure 3). The full circles represent the average of 3 flights over the Eifel mountains, West Germany, in November 1979 during strong westerly winds and clean air (Rudolph et al., 1982b). The thin full line is a model calculated profile from Fishman and Carney (1984). Note the different scales for the experimental data.

observed in the maximum are 3 orders of magnitude higher than those predicted by the model of Fishman and Carney (1984) for 10 km altitude, although that model describes the measurements over Germany quite well and parallels also the lower part of the STRATOZ II profile. This large deviation rules strongly against diffusive transport and illustrates quantitatively the need for fast direct transport between boundary layer and the upper troposphere in the present case.

The other instance during the STRATOZ II mission where high NMHC mixing ratios were observed at high altitudes was found at 63° N, close to Keflavik, Iceland, on the 20.4.1980. The maximum is included in the northbound flights. It is based on one sample only and therefore not as well supported as the former example. In this case part of the rising motion can be demonstrated by meteorological data. Figure 15 shows the back trajectory of the sampled air mass, which moved in an anticyclonic semi-circle starting at 20° to 10° W longitude and 45° to 50° N latitude this position was occupied on the 18.4.1980, 12:00 UT. During the horizontal motion, which was reconstructed based on an isobaric trajec-

tory analysis, the air mass experienced also a strong vertical lift. As estimated the isentropic movement of the 315 - 317 K surfaces along these trajectories, it rose from 500 mb to 282 mb, the sampling level. The starting position was covered by a wide field of stratiform clouds. From satellite images the presence of altocumulus (Ac) and altostratus (As) could be identified at levels from 3 to 6 km, while the surface (ship) observations reported stratus and stratocumulus clouds at levels above several hundred meters. Although the convective character of that cloud type is generally moderate, it is, no doubt, sufficient to provide the necessary transport from the boundary layer to 500 mb. The winds at 850 mb were from the north east, as reported by radiosonde stations and indicated by the small arrows in Figure 15. This would trace the sampled air back to the United Kingdom, Ireland and France and the observed maximum over Keflavik would reflect the high NMHC mixing ratios in the boundary layer over Western Europe.

A third cell of maximum mixing ratio at 200 mb over the equator during the northbound flights is also visible in most NMHC distributions. Its mixing ratios are lower than those found in the high tropospheric cells at northern latitudes. This is not unexpected, since the boundary layer mixing ratios of C_2-C_5 alkanes in the tropics are generally also lower than those at northern midlatitudes (Rudolph et al., 1981a; 1982a; see also Figures 2 - 10). Compared to the local surface values the upper tropospheric maximum in the tropics is about as strong as the others.

Although they represent deviations from the mean, such cells do not seem a rare occurrence. During STRATOZ II we observed three of them and during a mission in 1974 Seiler and Fishman (1981) observed one case in a similar meridional cross section of CO. Since the maxima observed here also contain high mixing ratios of shortlived NMHC, it appears that fast transport processes, which inject surface air directly into the upper troposphere, are relatively common. Clearly, transport by cumulonimbus towers, especially when they occur in larger, organized systems, is a very likely mechanism to explain the observed cells.

To elaborate on the last point we investigate one more case, namely the upward bulge of the mixing ratio isolines over the tropics for the butanes and pentanes during the southbound flights. The meteorological situation is sketched in Figure 16, which also shows the flight legs during which the high mixing ratios were observed. They occurred south of 10° N, which nearly coincided with the boundary of the Inter Tropical Convergence Zone (ITCZ) on the 29.4.1980. The area was covered with cumulonimbus reaching the tropopause level, i.e. considerably higher than the ceiling of the aircraft. (It is conceivable that the outflow layer of these clouds formed another cell of maximum NMHC mixing ratios above the accessible altitudes). The ITCZ was still encountered the following day when the plane continued its flight from Bogota to Guayaquil and then to Lima. It appears, therefore, quite probable that the strong vertical mixing caused by the activity of the ITCZ is responsible for the domeshaped lines of constant mixing ratio across the equator. It also points to level surface sources for the butanes and pentanes.

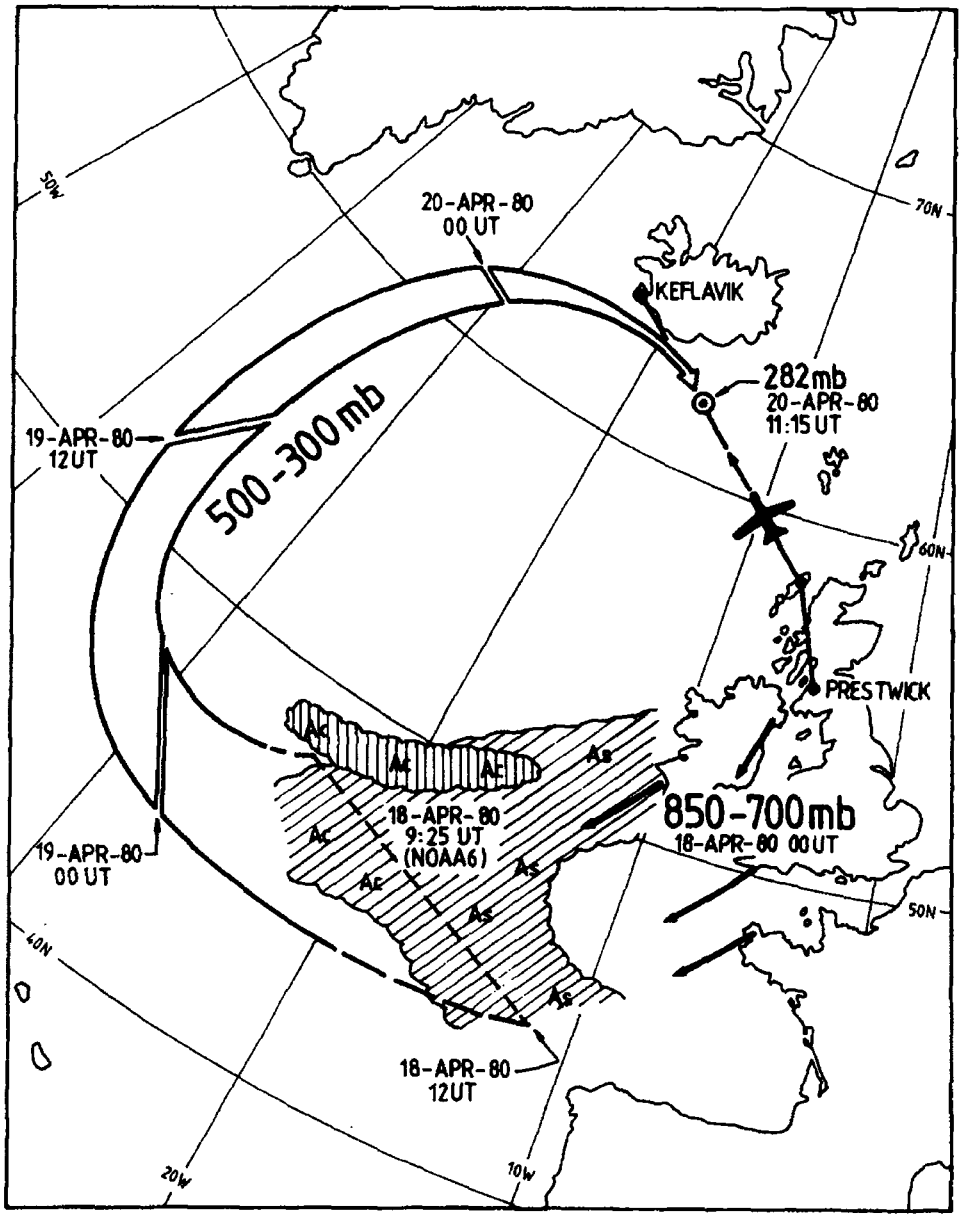


Figure 15. Approximate trajectory of the air sampled on 20. April 1980 south of Iceland. The inner circle respresents the isobaric trajectory at 500 mb, the outer circle that at 300 mb. The position of the high NMHC concentration sample is indicated by the open circle. The cloud cover distribution is based on satellite imagery (NOAA 6, IR, VIS). These, surface and upper air charts, as well as radio sonde soundings were obtained from the Deutscher Wetterdienst, FRG.

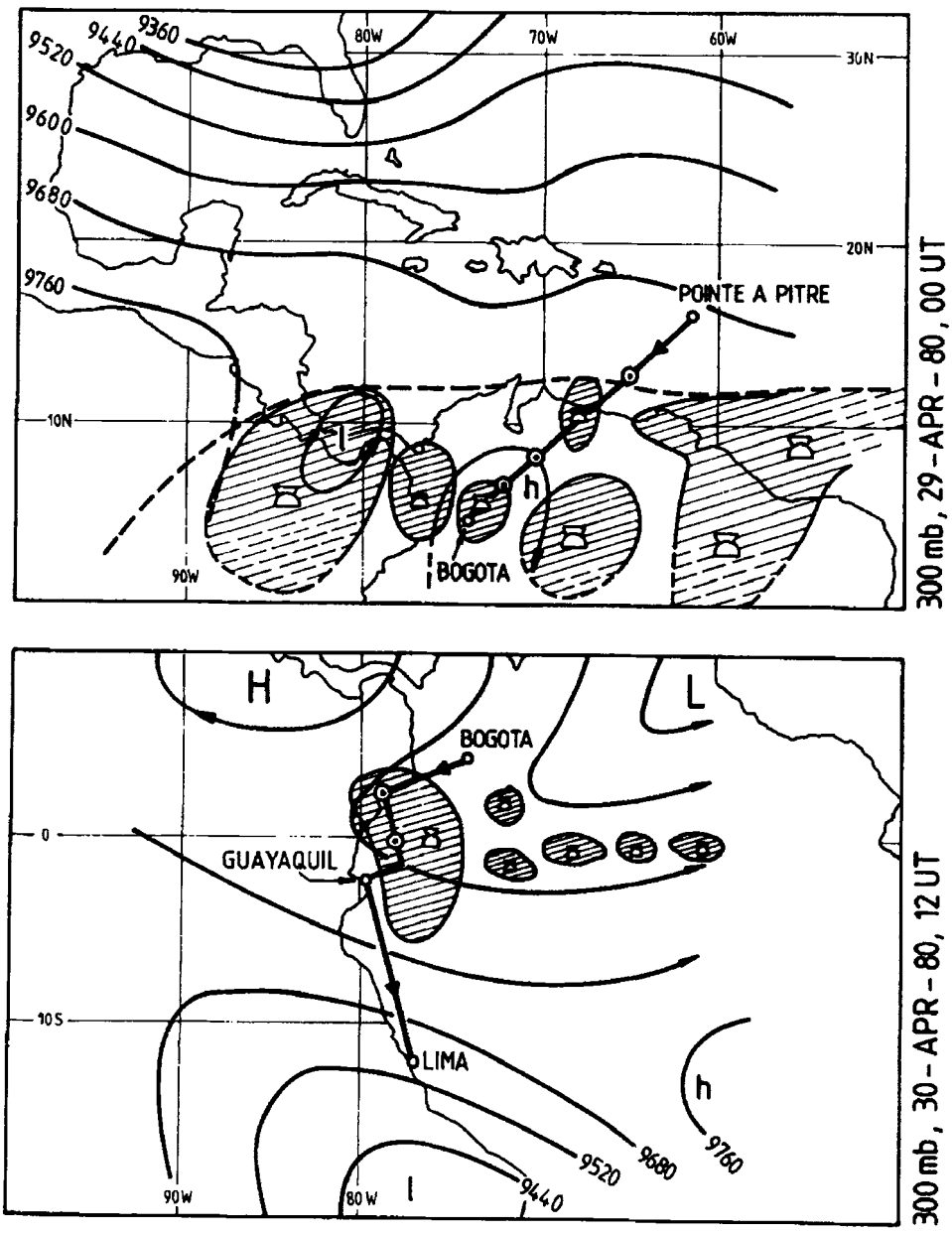


Figure 16. 300 mb surfaces over Middle and South America on the 29. and 30. April 1980. The flight track is indicated by the heavy line, the northern boundary of the ITCZ by the dashed line, the sampling points en route by the dotted circles. The lines marked by arrows represent the stream lines at 300 mb and are deduced from actual wind observations. The shaded areas mark the individual regions of ITCZ activities with high reaching cumulonimbus (after Karcher et al., 1982).

There are more examples of apparent deviations from the expected mean distribution. They express themselves as smaller scale wiggles in the isolines. Because of the resulting large variability it is difficult to derive a mean distribution. The only clear average features emerging from the present measurements are those already mentioned: A general decrease in mixing ratio with altitude, a maximum of C_2-C_5, NMHC mixing ratios at northern midlatitudes and generally lower mixing ratios in the tropics and in the southern hemisphere. These features were also known from previous measurements. The maximum at northern midlatitudes points to strong sources in the industrialized countries. In these latitudes, because of their high mixing ratios, the NMHC are more important to the atmospheric chemistry than CH_4, certainly in the planetary boundary layer, but occasionally, maybe even often, also in the free troposphere. For example, at a mixing ratio of 1 ppb, as observed on the 24.4.1980 at 50° N 200 mb, the reaction of propene alone converts more molecules per unit time and volume than that of methane. It is probably useful as a cautionary note to remind ourselves that most experimental investigations as well as model interpretations of atmospheric chemistry were made for these latitudes, where the influence of NMHC cannot be neglected.

5. CONCLUSION

The occurrence of high mixing ratios of NMHC (and of other trace gases) in the high troposphere appears to be relatively common and, at least in some of the cases presented, it is consistent with the idea that these maxima are caused by the outflow of high reaching clouds (cf. Gidel, 1983; Chatfield and Crutzen, 1984). In any case they demand an efficient and fast mechanism of direct transport from the boundary layer to the upper troposphere. Moreover, some of these maxima were observed close to areas of enhanced tropospheric-stratospheric air mass exchange: in one case the ITCZ; in the other a strong, nearly zonal polar jet stream at 60° N (cf. Figure 12) associated with a marked tropopause fold just north of Goose Bay (Karcher et al., 1982). This raises the possibility of an injection of short-lived trace species into the stratosphere - one which is much faster than hitherto suspected. Clearly, more measurements of this kind, preferably at additional longitudes and seasons, are required, to substantiate the existence of such fast transport and to reliably establish the mean meridional NMHC distribution. It is also clear from the measurements presented that the NMHC form a set of tracers well suited for detecting fast vertical transport. Some further measurements are in progress. In June 1984 we participated in STRATOZ III which repeated the flight route of 1980. The measured NMHC concentrations are currently evaluated.

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