Tellus (1990), *42B*, 408–422

Seasonal variation of hydrocarbons in the free troposphere at mid-latitudes

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(Manuscript received 7 April 1989; in final form 17 May 1990)

ABSTRACT

The free tropospheric concentrations of several light hydrocarbons and ozone have been measured throughout most of the year in air flows approaching the UK from unpolluted areas of the Northern Hemisphere. The measurements were made using an aircraft at altitudes between 1500 and 3000 m and concurrent measurements of halocarbons confirmed that the air had not passed recently over potential sources of hydrocarbons. Most of the hydrocarbons show a clear seasonal pattern with a summer minimum and winter maximum, but propene and ethene, which are very short-lived in the atmosphere and have oceanic sources, show no seasonal pattern. The halocarbon concentrations also exhibit no seasonal pattern but ozone shows a spring maximum. The results for ethane and propane, which have a common anthropogenic source, are consistent with a summer to winter average OH radical concentration ratio of about 4 to 7 and a travel time for source area to sampling point of about 20 days. It is suggested that the presence of large concentrations of non-methane hydrocarbons on an extensive scale will influence the seasonal pattern of ozone observed in large parts of the northern hemisphere.

1. Introduction

Hydrocarbons of many types are emitted into the atmosphere from both natural and man-made sources. They are removed by reaction with hydroxyl radicals and other oxidants such as ozone and nitrate radicals, but the hydroxyl reaction predominates for most species.

Emission of hydrocarbons has a substantial influence on the production of ozone in the troposphere. This process begins with the photolysis of nitrogen dioxide but the presence of other molecules, such as hydrocarbons, is necessary for substantial ozone concentrations to accumulate (see Demerjian et al. (1974)):

$$NO_2 \xrightarrow[\lambda < 400\ nm]{h\nu} NO + O \quad (1)$$

$$O + O_2 + M \longrightarrow O_3 + M \quad (2)$$

$$O_3 + NO \longrightarrow NO_2 + O_2 \quad (3)$$

$$C_2H_6 + OH \longrightarrow C_2H_5 + H_2O \quad (4)$$

$$C_2H_5 + O_2 \longrightarrow C_2H_5O_2 \quad (5)$$

$$C_2H_5O_2 + NO \longrightarrow C_2H_5O + NO_2 \quad (6)$$

$$C_2H_5O + O_2 \longrightarrow CH_3CHO + HO_2 \quad (7)$$

$$HO_2 + NO \longrightarrow OH + NO_2 \quad (8)$$

The hydroperoxy radicals produced in reaction (7) and organic peroxide radicals produced, in the case of ethane oxidation, in reactions (4) and (5) oxidize NO to NO_2 without consuming ozone in reaction (3). The NO_2 produced then can photolyse to produce ozone by reactions (1) and (2).

Many different hydrocarbons, with different reactivities, are involved in similar reaction chains, leading to ozone production (Demerjian et al., 1974). In the polluted boundary layer, this causes the phenomenon of photochemical air pollution where the amount of ozone produced

can be shown to be closely correlated with the nature and extent of hydrocarbons available for hydroxyl radical oxidation (Hough and Derwent, 1988).

In the free troposphere, it has been estimated that similar amounts of ozone can be generated by in-situ photochemistry to that transferred from the stratosphere (Fishman et al., 1979). The main source of HO_2 and RO_2 in this case was considered to be carbon monoxide and methane oxidation but it is also possible that non-methane hydrocarbons could make a contribution if the sum of their concentration is high enough (Liu, 1988). The role of non-methane hydrocarbons will also be emphasised since their atmospheric lifetimes are much more similar to the nitrogen oxides, which must be present to produce ozone.

Measurements of non-methane hydrocarbons have been made in polluted atmospheres for pollution assessment purposes (Bos et al., 1978; Sexton and Westberg, 1984). Measurements are far fewer in the more remote parts of the atmosphere although there are indications that substantial concentrations of low molecular weight species exist from time to time (Ehhalt et al., 1985; Bonsang et al., 1988; Penkett, 1982; Hov et al., 1984), and indications from boundary layer measurements that the concentrations of many species are seasonally dependent (Hov et al., 1984; Blake and Rowland, 1986; Singh and Salas, 1982).

In order to collect data in a systematic way on the concentrations of hydrocarbons in the atmosphere over the UK, an experimental programme is being carried out involving the collection of air samples from an aircraft. The program has three major aims which are:

(i) measurement of hydrocarbons in plumes spreading from discrete sources, such as London, for the experimental determination of hydrocarbon fluxes from source areas;

(ii) investigation of hydrocarbon consumption and ozone production by photochemistry in urban plumes;

(iii) measurements of hydrocarbons in the free troposphere in air of oceanic origin reaching the UK throughout the year.

This paper describes some preliminary work done on the third aim made over the years 1982 to 1986. The observations enable us to draw important conclusions about the seasonal variation of hydroxyl radical chemistry at mid to high latitudes and to speculate about the role of anthropogenically emitted non-methane hydrocarbons in the ozone budget of the northern hemisphere.

2. Experimental

The experiment was conducted using an aircraft to collect air samples, usually in the free troposphere, for their analysis either at the Harwell Laboratory (AERE) or the Central Electricity Research Laboratories (CERL). Various other measurements were made in-situ.

2.1. Aircraft and flight plans

The sampling vehicle was a Handley-Page Jetstream, a twin turbo-prop aircraft, owned and operated by the Cranfield Institute of Technology, and based at the Cranfield airfield, about 65 km north of London. It has a maximum endurance of about 4 h and, flown unpressurized, an operational ceiling of about 3300 m. It has been extensively instrumented by CERL for chemical and physical measurements and much of the data is continuously recorded on magnetic tape during flights for subsequent computer analysis at CERL. During the clean air flights, only ozone of the inorganic gases continuously monitored, was normally above the detection level of the measuring instruments available, (2 ppbv SO_2, 5 ppbv NO_x, 1 ppbv ozone). The air intakes on the aircraft were forward of the engines and the low concentrations of NO and NO_2 suggested minimal contamination.

Table 1 gives dates and locations of flights whose background air samples are reported here.

At the beginning of the project, samples were considered to represent background air when they were taken in areas upwind of local sources during flights made for other purposes. Samples were excluded if they would obviously be from air which had traversed major continental sources in the recent past. As interest grew in the characteristics of background air, opportunities were sought to make flights to measure background air specifically (see Table 1) from November 1984 onwards. These are now regularly made in air flows following the passage of a cold front, that is

Table 1. *Dates and locations of flights*

Flight no.	Date	Location	No. of background air samples
1	8 December 1982	Bristol Channel	2
2	12 July 1983	London	2
3	16 August 1983	North Sea	2
4	21 November 1984	Eastern England	8
5	2 May 1985	North of Ireland	8
6	18 July 1985	Western Approaches to English Channel	10
7	18 September 1985	North of Ireland	12
8	31 October 1985	North Sea (off Firth of Forth)	12
9	26 March 1986	West English Channel and West of Scillies	6[a]

[a] Samples taken on both sides of a warm front.

in a polar or Arctic air mass flow. Samples are collected either in the western approaches to the English Channel, or off St. David's Head, Pembrokeshire, or north of Ireland, depending on the wind direction. One or two flights have been made over the North Sea, off the Firth of Forth, when the synoptic situation indicated an air flow coming down to the west of Scandinavia. The trajectory for one such flight is shown in Fig. 1. We have sought to avoid very unstable, showery conditions so as to minimize the possibility of sampling air recently convected up from the surface to the sampling altitude, which was normally near the aircraft's operational ceiling. We have also sought to avoid circumstances in which the sampled air could have been re-circulated around a low pressure centre.

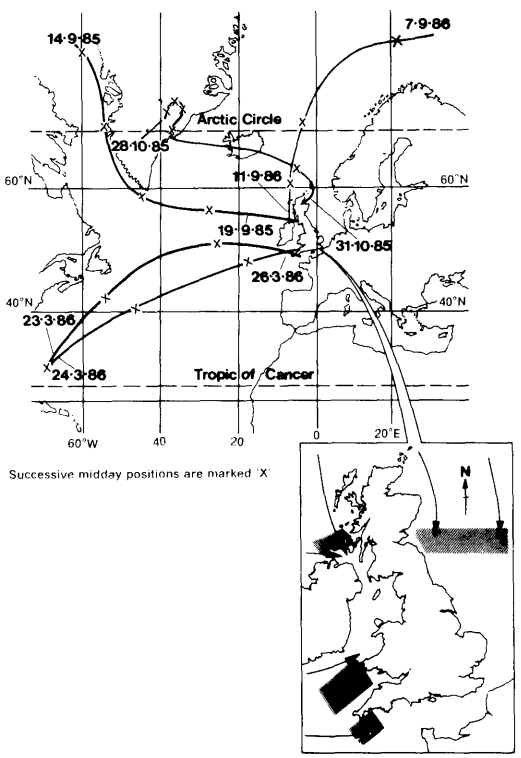

Fig. 1. Typical 700 mb wind-back trajectories for clean air sampling flights. (Computed by the Meteorological Office, Bracknell.)

2.2. *Collection of air samples*

Air samples for organic analysis were collected in 1.6 litre internally electropolished stainless steel bottles supplied by Professor R. A. Rasmussen of the Oregon Graduate Center. Until the flight of 26 July 1984, a pack of 6 aluminium bottles was used, with the samples pumped to about 2 atmospheres above atmospheric pressure by a single PTFE sealed stainless steel bellows pump. This gave a total volume for analysis of about 3 litres at STP. The results indicated a need for a greater number of samples to be taken on each flight, and from the flight of 21 November 1984 onward a pack of twelve stainless steel bottles was used. In this case the sample was pumped by two of the metal bellows pumps in series to 4–5 atmospheres above atmospheric pressure, giving a total volume for analysis of 5–6 litres at STP.

Bottles were flushed by the pumps for 4–5 min before filling. Filling took about 40 s or 2.5 km of flight track.

2.3. *Analysis of hydrocarbons and halocarbons*

The hydrocarbons were analysed by gas chromatography with flame ionization detection (GC/FID). Preconcentration by liquid argon trapping was necessary because of their low atmospheric concentrations. Typically 1 litre of sample at STP was passed through a cold trap (at −186°C) packed with fine glass beads, after drying with a column of potassium carbonate. The trap was warmed to 50°C and the condensed hydrocarbons were then flushed into the chromatograph in 90 s using a gas sampling valve. The following chromatographic conditions were used for the different hydrocarbons and halocarbons; nitrogen was used as carrier gas in all cases.

(i) *Aliphatic hydrocarbons.* These were analysed using a 2.5 m long, 6 mm diameter column of OPN/Porasil (J. J. Chromatography Ltd.). The column was run isothermally at −10°C to resolve ethane and ethylene and then isothermally at 60°C for the other hydrocarbons (acetylene to cyclohexane).

(ii) *Benzene.* This was analysed on a 62 m long 0.53 mm internal diameter quartz capillary column, with 50 m coated with BPI and 12 m with BP20 (SGE Ltd.). The temperature programme for analysis started at −50°C and was increased to 100°C at 10°C/min; it was then held at 100°C for 15 min.

(iii) *Halocarbons.* These were analysed by gas chromatography with electron capture detection (GC/ECD) using direct injections of 2 mls of air. The column was 2.5 m in length and 6 mm diameter packed with 10% DC200 (12,500 cS) on Diatomite C-AW (J. J. Chromatography Ltd.) and was run isothermally at 40°C.

Blank runs were made on all columns using clean nitrogen to check for analytical artefacts and determine the degree of contamination of the analysis by the analytical system.

2.4. *Standardization*

Concentrations of gaseous aliphatic hydrocarbons were determined by comparison with commercial standards in the ppm range. These were checked against standards made up from pure hydrocarbons diluted into a 1 m^3 aluminium chamber. Aliphatic and aromatic hydrocarbon vapour standards were prepared by dispensing vapours at known pressures into a cell of known volume before dilution in the aluminium chamber. Typically 1 ml injections of ppm range standards were made into the concentrator system used for the air samples. These gave an identical response to injections made directly on to the head of the column indicating that no loss was occurring in the concentration step. Concentrations of halocarbons were determined by direct comparison with air samples used as long term standards and stored in high-pressure containers. The concentrations in the standards were determined using the vapour transfer system described above and a double dilution into a 100 litre chamber and the 1 m^3 chamber (Penkett et al., 1979).

3. Results and discussion

3.1. *Seasonal patterns of observation*

A summary of the means and standard deviations for 10 hydrocarbons, CFC11 and ozone over a sampling period from March to December is shown in Table 2. Most of the monthly values are averages of 6 or more individual estimates but the December values were obtained from just two samples in December 1982, and the August ones, similarly, from two samples taken in the vicinity of an active cold front in 1983. Individual plots of concentrations obtained throughout the same period are also shown in Figs. 2 to 6. For clarity, the data are plotted as bars showing the monthly ranges with ticks indicating the monthly means. The standard deviations for most hydrocarbons are typically 10% of the mean, indicating that the degree of variability was very small. Samples collected by us in polluted air show a much higher degree of variability.

The data patterns are very similar for many hydrocarbons with a summer minimum and a pronounced winter maximum. This includes ethane, acetylene, propane, normal and iso butane, n-pentane, n-hexane and probably benzene. The concentrations of ethane reported here and the amplitude of the seasonal cycle are very similar to that reported by Blake and

Table 2. *Monthly statistics of background air hydrocarbon concentrations (pptv)*

Month	Ethane	Acetylene	Propane	i-butane	n-butane	n-pentane	n-hexane	Ethylene	Propene	Benzene	CFC11	Ozone
March	2280 ± 306	418 ± 71	662 ± 177	133 ± 52	235 ± 77	68 ± 38	<90 .	162 ± 12	72 ± 15	88 ± 17	223 ± 1	49 ± 6
May	2526 ± 117	342 ± 23	490 ± 32	51 ± 7	139 ± 8	<30 .	<100 .	145 ± 40	46 ± 15	141 ± 29	218 ± 6	65 ± 4
July	1235 ± 50	108 ± 36	109 ± 11	15 ± 0	18 ± 3	<30 .	<80 .	134 ± 42	35 ± 6	79 ± 28	223 ± 2	59 ± 4
Aug.	1175 ± 64	190 .	131 ± 13	46 ± 8	63 ± 8	<50 .	<70 .	240 ± 28	92 ± 16	<100 .	202 0	25 ± 3
Sept.	1249 ± 60	111 ± 7	189 ± 15	19 ± 3	35 ± 10	<30 .	<90 .	178 ± 47	19 ± 7 .	59 ± 21	221 ± 2	38 ± 4
Oct.	1753 ± 82	311 ± 42	590 ± 49	123 ± 14	242 ± 37	117 ± 20	93 ± 33	149 ± 25	46 ± 14	139 ± 22	225 ± 2	38 ± 1
Nov.	2568 ± 146	649 ± 74	964 ± 81	209 ± 18	415 ± 33	193 ± 24	92 ± 16	265 ± 60	24 ± 8	203 ± 33	227 ± 2	32 ± 1
Dec.	2505 ± 205	1385 ± 21	1440 ± 127	195 ± 7	430 ± 14	275 ± 49	130 ± 42	200 .	30 0	. .	199 ± 1	33 0

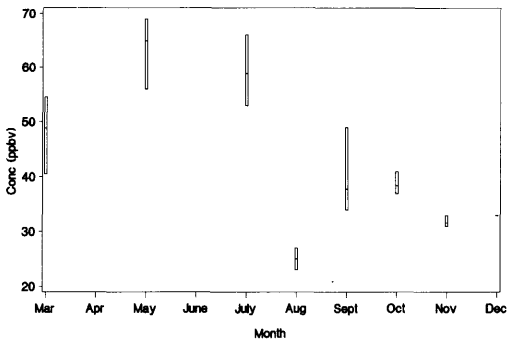

Fig. 2. Seasonal variation of clean air ozone.

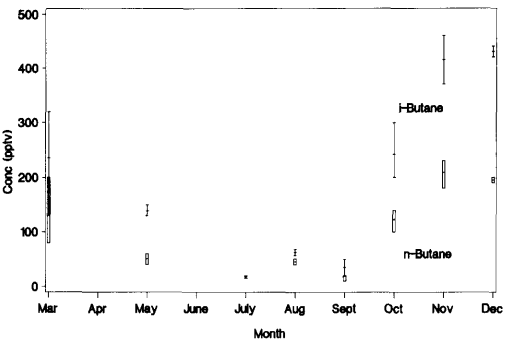

Fig. 5. Seasonal variation of clean air i-butane and n-butane.

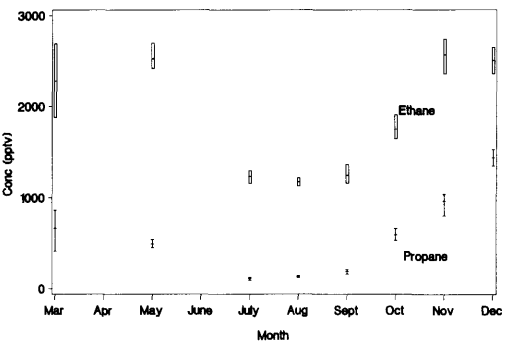

Fig. 3. Seasonal variation of clean air ethane and propane.

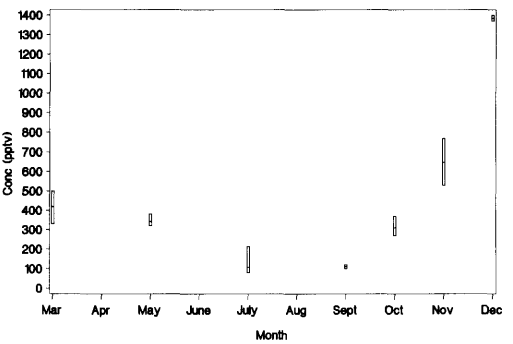

Fig. 6. Seasonal variation of clean air acetylene.

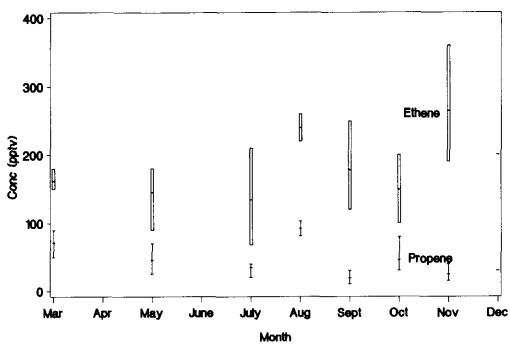

Fig. 4. Seasonal variation of clean air ethene and propene.

Rowland (1986). The size of the seasonal oscillation may be related to reactivity of the individual hydrocarbon with hydroxyl, with ethane showing the lowest percentage variation. Ethylene and propene, however, which are both very reactive molecules with respect to hydroxyl and ozone, do not show much variation in concentration between summer and winter.

The different hydrocarbons measured in these experiments may have different sources. It is likely that ethane, acetylene, propane, the butanes and benzene have largely anthropogenic sources since the winter ratios of the other species to acetylene are somewhat lower than those we have measured in urban plumes close to source (see also Sexton and Westberg, 1984). The ethane/acetylene ratio is highest in the summer whereas those of propane and the butanes are lowest. Given that acetylene is more reactive to OH than ethane but less than propane and the butanes, this is reasonable if they come from a common source area. The source of the olefins though is more likely to be natural (Rudolph and Ehhalt, 1981).

The concentration of CFC11 ($CFCl_3$) measured simultaneously with the hydrocarbons, is also shown in Table 2. The values are consistent with those expected in clean air at about 50°N in the year of sampling (Brice et al., 1982). Thus the lowest value (199 pptv) was obtained in December 1982 at the beginning of the experiment. The value of 203 pptv was obtained 8 months later in 1983, other values between 218 and 227 pptv were obtained between November 1984 and October 1985 when the CFC11 concentration in the atmosphere would have increased due to continuing release as a result of commercial usage. The set of CFC11 values clearly indicates that all hydrocarbon measurements relate to clean air conditions with little or no sign of contamination from regional sources. In particular the spread of values obtained in any one sampling exercise is very small.

It follows from this that the hydrocarbon concentrations in the same air are also characteristic of air which has not recently been affected by regional anthropogenic input. These hydrocarbons will then be of two sorts; those with local sources, such as the ocean, and those with long enough lives to survive the length of time since the last passage of the air over a major source area. It is striking, in this regard, that winter hydrocarbon concentrations in the free troposphere over the North Atlantic, are often within a factor of two of those observed spreading from sources such as London during the summer. Given the dilution which must take place as a result of vertical mixing between the source areas and our observation points, this suggests that hydrocarbons must accumulate in the winter troposphere. Two obvious causes of this accumulation are: increased input to the atmosphere from increased winter emissions, and decreased removal from it by decreased reactivity. Both of these possibilities are considered below. It should be said that the high winter concentrations observed in the free troposphere are most unlikely to be the result of sampling or analytical artefacts since these would also give rise to high values in the summer flights.

The large difference between winter and summer values in air having a northerly or Arctic origin (Table 2) is also mirrored in air sampled either side of a warm front in March 1986 (Table 3). Air with a polar maritime origin in the cold sector had hydrocarbon concentrations somewhat typical of winter values, whereas air in the warm sector, which had a tropical maritime origin, was similar to air sampled in the summer flights. This is a very interesting observation showing that the trace gas composition of air remote from sources can be very variable, depending on its previous chemical history. It further suggests that interesting experiments on the chemistry of the remote troposphere can be carried out over the oceans.

Ozone data is also shown in Tables 2 and 3 and in Fig. 2. In general the concentrations are higher than values which are measured at ground level at a similar latitude (PORG, 1987). This no doubt reflects the remoteness of the air from the Earth's surface, where it is removed by deposition processes. Based upon this rather limited data set, a maximum of 65 ppbv is observed in May, with lowest values being observed in the winter months November and December. By March the concentration is increasing with polar air having higher concentrations than tropical air of clean origin (Table 3). The low value observed in August 1983 may possibly be caused by photochemical decomposition in the presence of low NO_x concentration (Fishman et al., 1979; Liu, 1988). Unfortunately the detection limit of the NO_x instrument on board the aircraft would not allow measurements to be made but the low hydrocarbon levels measured would indicate very low values for NO and NO_2 in the summer (see also Isaksen et al., 1985).

The cause of the seasonal variation observed in hydrocarbon concentrations in the clean free troposphere may be associated with a variation in the source strengths of natural emissions or anthropogenic emissions, or more likely with seasonal differences in chemical reactivity or transport characteristics.

3.2. Seasonal variation of emissions

There have been limited studies so far on the natural sources of hydrocarbons into the atmosphere, although it is known that almost all of the hydrocarbon species we have reported have oceanic sources in varying degrees (Rudolph et al., 1980; Rudolph and Ehhalt, 1981; Ehhalt et al., 1985; Bonsang et al., 1988; Wilson et al., 1970). Virtually no information is available at present on the pattern of emissions through the

Table 3. *Air concentrations from samples taken on either side of a warm front on 26 March 1986; organic concentrations in pptv, detection levels indicated with "<"*

Sample	Ethane	Acetylene	Propane	i-butane	n-butane	n-pentane	n-hexane	Ethylene	Propene	Benzene	CFC11	Ozone ppbv
Samples taken before warm front												
1	1880	330	410	80	130	30	<90	180	50	90	222	54
2	2110	390	550	100	180	50	<90	150	60		223	54
3	2330	430	700	140	250	60	<90	160	80	70	222	55
4	2690	500	860	190	320		<90	160	80	110	224	46
5	2560	500	850	200	320	130	<90	170	70		224	45
6	2110	360	600	90	210	70	<90	150	90	80	222	41
Samples taken after warm front												
7	1430	130	170	20	29	<30	<90	200	80		219	42
8	1410	120	170	20	30	<30	<90	130	60		218	41
9	1470	130	180	20	30	<30	<90	260	120		219	42
10	1470	140	170	20	30	<30	<90	120	60		219	43
11	1880	130	400	70	160	70	<90	200	110	40	210	45
12	1480	130	180	20	20	<30	<90	210	90	40	219	45

year. There is also very little data in the literature on the expected seasonal variation on the anthropogenic light hydrocarbon emissions and there also are major differences of opinion on annual average emissions (see Tables 4 and 5). Considering the main emission categories, if natural gas leakage (ethane and propane), were chiefly from leaking joints in gas mains, this might not vary much from season to season. On the other hand, solvent evaporation, especially

Table 4. *Proportions of some UK hydrocarbon emissions*

	Source of data					
	Derwent & Hov (1979)		Hough (1986)		PORG (1987)	
	Species total ktonnes	Species total %	Species total ktonnes	Species total %	Species total ktonnes	Species total %
emission category						
petrol exhaust	426.92	48.08	744.51	56.81	255.70	32.96
diesel exhaust	3.29	0.37	2.26	0.17	13.00	1.68
vehicle fuel evaporation	66.63	7.50	82.87	6.32	88.40	11.39
stationary combustion	.	.	2.18	0.17	24.70	3.18
solvent evaporation	96.67	11.00	117.77	8.99	242.60	31.27
industrial processes	23.43	2.64	32.48	2.48	27.20	3.51
petroleum industry	109.68	12.35	135.95	10.37	92.00	11.86
natural gas leakage	160.26	18.05	192.48	14.69	32.30	4.16
emission category total	887.88	100.00	1310.51	100.00	775.90	100.00

Table 5. *Proportions of some UK hydrocarbon emissions*

	Source of data					
	Derwent & Hov (1979)		Hough (1986)		PORG (1987)	
	Emission category total ktonnes	Emission category total %	Emission category total ktonnes	Emission category total %	Emission category total ktonnes	Emission category total %
Species						
ethane	103.79	11.69	128.30	9.79	21.60	2.78
ethylene	60.97	6.87	106.80	8.15	60.80	7.84
acetylene	53.20	5.99	91.83	7.01	44.10	5.68
propane	32.29	3.64	32.00	2.44	5.40	0.70
propene	34.17	3.85	51.32	3.92	33.20	4.28
i-butane	48.65	5.48	70.87	5.41	32.60	4.20
n-butane	107.75	12.14	158.62	12.10	78.50	10.12
2-me-butane	195.89	22.06	278.60	21.26	218.80	28.20
n-pentane	109.91	12.38	155.01	11.83	131.90	17.00
toluene	141.26	15.91	237.15	18.10	149.00	19.20
emission category total	887.88	100.00	1310.51	100.00	775.90	100.00

from those solvents used in paints, might be expected to have a summer maximum. Surprisingly, surveys indicate very little variation of motor vehicle mileage in the UK between summer and winter (M. Williams, Warren Spring Laboratories, 1987 private communication) so the primary source may be seasonally invariant. In the UK at least (R. G. Derwent, private communication), the largest evaporative emissions from vehicles by mass occur in the spring and autumn, due to evaporation of the extra light components of the winter fuel, and mass emissions are lowest in the summer. The effect on tropospheric burdens, of such variations in evaporative emissions will differ from one source region to another, and it is just possible that we are seeing contributions from such effects in the butanes and conceivably, propane. Such arguments could not apply to the observed seasonal variations of ethane and acetylene, nor would they explain the observed winter pattern.

3.3. Ethane and propane chemistry

There have been many studies of the hydroxyl radical chemistry of hydrocarbons (Kerr and Calvert, 1984; Baulch et al., 1986) and when combined with a knowledge of the seasonal variability of atmospheric hydroxyl radical concentration (Isaksen et al., 1985; Crutzen, 1982), this does provide a sensible interpretation of the concentration patterns observed.

The bimolecular rate constants for reactions of hydrocarbons with hydroxyl radicals derived from laboratory studies and the resulting pseudo-unimolecular half-lives in the atmosphere in summer and winter conditions, are shown in Table 6. The summer and winter conditions are

Table 6. *Rate constants and half-lives for some reactions of hydrocarbons with OH, ozone and NO_3*

		Half-life (days)	
	OH rate const. (cm^3 $molecule^{-1}$ s^{-1})	Winter $T = 260°K$ $OH = 3 \times 10^5$ cm^{-3}	Summer $T = 278°K$ $OH = 1.3 \times 10^6$ cm^{-3}
ethane	$2.7 \times 10^{-13} \exp(-1260(1/T - 1/298))$	184	31
ethylene	$8.4 \times 10^{-12} \exp(8.4(1/T - 1/298))$	3	1
acetylene	$6.1 \times 10^{-12} \exp(-650/T)$	53	10
propane	$1.2 \times 10^{-12} \exp(-800(1/T - 1/298))$	33	6
propene	$2.9 \times 10^{-11} \exp(540(1/T - 1/298))$	0.7	0.2
i-butane	$2.4 \times 10^{-12} \exp(-390(1/T - 1/298))$	13	3
n-butane	$2.6 \times 10^{-12} \exp(-560(1/T - 1/298))$	14	3
pentane	$4.1 \times 10^{-12} \exp(-530(1/T - 1/298))$	8	2
hexane	$5.7 \times 10^{-12} \exp(-530(1/T - 1/298))$	6	1
benzene	1.2×10^{-12}	22	5

OH rate constants taken from Kerr and Calvert (1984) unless stated otherwise.
Rate constant for acetylene taken from Hough (1986).

	Ozone rate const. (298°K) (cm^3 $molecule^{-1}$ s^{-1})	Half life[a] (days)	NO_3 rate const. (298°K) (cm^3 $molecule^{-1}$ s^{-1})	Half life[b] (days)
ethylene	1.75×10^{-18}	5	6.1×10^{-17}	4384
propene	1.13×10^{-17}	0.8	4.2×10^{-15}	64
isoprene	1.43×10^{-17}	0.6	3.2×10^{-13}	0.8
2meBut2ene	1.16×10^{-15}	0.01	3.1^{-11}	0.001

[a] Ozone concentration taken as 30 ppbv (9×10^{11} molecule cm^{-3}).
[b] NO_3 concentration taken as 1 pptv (3×10^7 molecule cm^{-3}).
Ozone and NO_3 rate constants taken from Cox (1988).

chosen to reflect temperatures in the air being sampled and OH concentrations which are typical and have a seasonal ratio indicated from our measurements (see later). This shows that substantial differences in atmospheric lifetimes will occur at different seasons leading to large differences in standing concentrations for most molecules. The exceptions may be the various hydrocarbons with a double bond which have appreciable rates of reaction with ozone and nitrate radicals. The lifetimes of these molecules will still be less in summer though because of more efficient hydroxyl radical removal.

It is interesting to consider the effect of chemistry alone on the concentrations of species whose half-lives are comparable with their travel times from source to "clean" sampling areas. The effect of source strength variations can be removed by considering a pair of hydrocarbons which have a common major source but differ in reactivity, such as ethane and propane. These two gases are emitted in large quantities from the use of natural gas (Table 4 and 5); they are also produced naturally (Ehhalt et al., 1985), but this is most probably of less consequence in the northern hemisphere. Measurements confirm much lower concentrations in the southern hemisphere, where natural emissions will predominate, see Singh and Salas (1982), Ehhalt et al. (1985) and Blake and Rowland (1986), than the winter concentrations reported here (Table 2).

Assuming that the hydrocarbon is removed by hydroxyl radical chemistry only, then it can be shown that for a pair of hydrocarbons denoted 1 and 2, at a fixed [OH] concentration:

$$C_1/C_2 = S_1/S_2 \exp(-(k_1 - k_2)[\mathrm{OH}]t) \qquad (9)$$

where C_1 and C_2 are the observed concentrations remote from sources, S_1 and S_2 are the concentrations recorded close to source, k_1 and k_2 are the rate constants for the reaction with OH (whose average concentration over the travel period is [OH]), and t is the travel or reaction time, (see Nutmagul and Cronn, 1985 for a similar method applied to aromatics).

In other work of this group, (to be published), the ethane/propane concentration ratio in urban (London) plumes in winter is close to 2, and given the low level of photochemical activity at the time of the year, this might be expected to be the source ratio (S_1/S_2), although current emission inventory estimates suggest a higher value of about 5:1, see Table 4.

Substituting into eq. (1) the observed value of the ratio (S_1/S_2) at source, the measured clean air concentration ratios in the free troposphere, (2.5–3 for the winter and 11.5–12 for the summer (Fig. 7)), and the rate constants (at 260°K for the winter and 278°K for the summer), and assuming the same travel time, t, summer and winter, gives ratios of summer to winter OH concentrations of about 4 to 7. The values depend strongly on the winter source and free troposphere ethane/propane ratios, much less on the temperatures chosen for the calculations, or indeed on the rate constants used. These values compare reasonably with model predictions (Cocks and Fletcher, 1988 and Fletcher, private communication). Alternatively, taking a winter average OH concentration of 3×10^5 molecules cm^{-3} and a summer average of 1.3×10^6 molecules cm^{-3} (i.e. an annual average of 8×10^5 molecules cm^{-3}), gives values for the travel time t, of about 20 days in the summer and 13–24 days in the winter (the winter values are very sensitive to the ethane/propane ratios). The calculated travel times are sufficient for the air to have reached the UK from very distant source areas, and at least half the time to travel around the world. The samples therefore almost certainly reflect well-mixed air, typical of large parts of the northern hemisphere at mid to high latitudes.

3.3.1. Transport processes. In this respect, 700 mb isobaric wind back trajectories have been computed for us by the Meteorological Office,

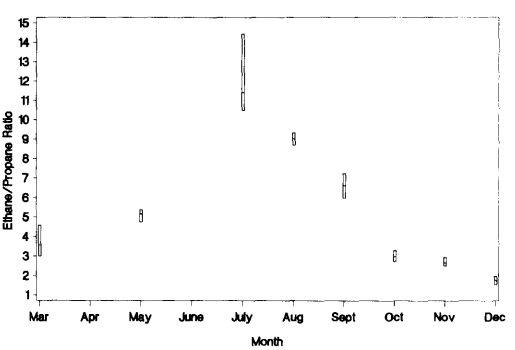

Fig. 7. Seasonal variation of the clean air ethane/propane ratio.

Bracknell for some of the flights. See Fig. 1 for typical trajectories. The trajectory calculations show that the air takes 3 to 5 days to traverse the Atlantic Ocean and neighbouring Arctic regions. Travel times of the length calculated would make the true origin of the air difficult to predict, but would argue for uniform concentrations of long-lived non-methane hydrocarbons in the free troposphere of the northern hemisphere at latitudes of 50°N.

Pathways from industrial source areas to arctic areas have been identified, both using seasonal average pressure and circulation patterns (Rahn, 1981; Raatz, 1989), and back trajectory calculations (Herbert et al., 1989). These are especially active during the winter and give rise to arctic haze episodes. This polluted air probably also contains high hydrocarbon concentrations. It is likely that such airstreams would not retain their identity until they had returned to temperate latitudes (Shaw, 1981). However a high frequency of flows of polluted air into the arctic during some period would presumably result in elevated general concentrations in the air in the arctic regions, which would be reflected in the concentrations in the air flowing out towards lower latitudes behind cold fronts. If these high-concentration episodes did indeed occur preferentially in the winter, they would impose a seasonality on the concentrations observed in the outflowing air, which would reinforce the chemical kinetic effects considered above. Such transport effects would apply equally to all long-lived hydrocarbon species of course, and kinetics would need to be invoked to explain the observed differences between them. Shaw (1981), considers 10 to 20 days to be a reasonable time for the transport of the polluted air across the arctic region, which is consistent with our estimates based on kinetics.

It will be noticed that the half life of ethane is long enough for it to persist, all year round, from one season to the next, and acetylene and even propane could be persistent in the winter, in which case a simple treatment of the results as controlled by a single passage from source to sampling region would not be appropriate, and the apparent good sense of the conclusions may be fortuitous.

We accept that the treatment we have given is very simple, but it does lead to reasonable OH concentrations, summer and winter, and sensible travel times, long enough to indicate that a large scale phenomenon is being considered.

3.4. Ethylene and acetylene

A comparison of ethylene with acetylene is also of interest (Fig. 8). They are emitted in similar quantities from anthropogenic sources (Table 4, Fig. 8) but their atmospheric reactivity is very different with half-lives of 1 and 10 days respectively, shown in Table 6 for 278°K. This would suggest a much larger ratio of winter to summer concentrations for ethylene than for acetylene, yet ethylene shows no major seasonal variation. In the absence of experimental artefacts the observations can most easily be accounted for by a large variable natural source which is also seasonally dependent and is in phase with the strength of the atmospheric sink due to hydroxyl radicals. This same logic also applies to propene. The natural source must be dominant, particularly in the summer since the ethylene concentrations are nearly equivalent to acetylene then, even though the atmospheric life-times of the olefins are much shorter. These observations support those reported by Rudolph et al. (1980); Rudolph and Ehhalt (1981) and Hov et al. (1984), who suggested that the most likely natural source was the ocean.

While explanations may be found in terms of the different transport histories of long-lived and short-lived (oceanic source) species, the variation in circumstances from one sampling to another then becomes of great importance, and we feel that the explanation given is probably the simplest and most general available.

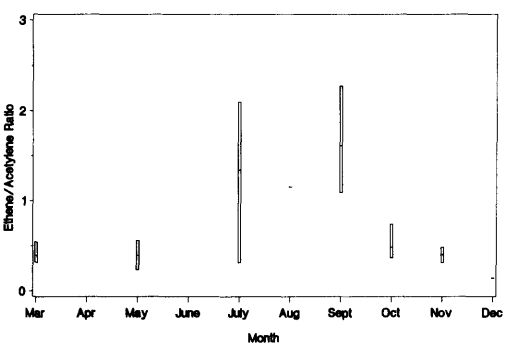

Fig. 8. Seasonal variation of the clean air ethene/acetylene ratio.

3.5. Ozone generation

Perhaps the most interesting feature of this large seasonal variation in the concentrations of non-methane hydrocarbons from anthropogenic sources is the accumulation of high concentrations in winter due to increased atmospheric life-times. Molecules such as butane for instance will probably have a winter lifetime of the order of two weeks in the free troposphere and acetylene will have a lifetime of about two months (see Table 6). By contrast summer lifetimes will be of the order of a few days in the polluted boundary layer for many hydrocarbons (Table 6), and therefore less material will survive long enough to achieve large scale dispersion away from sources.

On oxidation and removal from the atmosphere during the transition from winter to summer concentrations this hydrocarbon reservoir is capable of generating large amounts of ozone in the free troposphere, mostly in the spring months. Using only the molecules reported here (ethane, propane, acetylene, normal and isobutane) the difference between winter and summer average concentrations amounts to approximately 7.5 ppbv carbon, which is capable theoretically of generating about 7 ppbv of ozone, if sufficient NO_x is present (Hough and Derwent, 1988). We therefore suspect that a significant percentage (up to 20%) of the total ozone variation observed both in summer and winter in our free tropospheric measurements (Fig. 2) could well be produced by tropospheric chemistry, particularly in the spring when the hydrocarbon concentration is declining rapidly. This would agree with the finding of a maximum in the concentration of peroxyacetyl nitrate (PAN) in "clean" air in spring at a ground based site in Southern England (Penkett and Brice, 1986), Holland (Guicherit, 1988) and Northern Canada (Brice, Bottenheim and Anlauf, 1988). Undoubtedly ozone will be transferred from the stratosphere to the troposphere in considerable quantities and tropospheric ozone is generated from the oxidation of methane and carbon monoxide, but the contribution of non-methane hydrocarbons, which makes both PAN and ozone simultaneously, may be of great significance at certain times of year (see Penkett, 1988).

In summary, background air concentrations of hydrocarbons measured in these experiments depend on anthropogenic source strengths, reactivity with OH, travel times and oceanic sources. Some information is available on the first two but little is known about the others. Measurements of the type described here can help provide information on the two unknown parameters. The measurements also support the suggestion that non-methane hydrocarbons may at times contribute significantly to the generation of ozone in the clean troposphere.

4. Acknowledgements

The work was carried out in part at the Central Electricity Research Laboratories of the Technology Planning and Research Division and the paper is published with permission of the Central Electricity Generating Board. The work also formed part of the programme of environmental studies carried out at AERE Harwell funded by the Department of the Environment and the CEC.

Paper originally presented at the sixth international symposium of the Commission for Atmospheric Chemistry and Global Pollution (CACGP) at Peterborough, Ontario, Canada in August 1987.

Thanks are due to Mr. J. Crabtree, formerly of the Meteorological Office, Bracknell, for calculating some of the wind-back trajectories, for arranging the computation of the others, and for valuable discussions on the meteorological conditions obtaining during many of the flights.

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