NILU OR: 4/89

NILU OR : 4/89
REFERENCE: O-1314
DATE : JANUARY 1989
ISBN : 82-425-0004-5

HYDROCARBON MEASUREMENTS AT RURAL BIRKENES, SOUTH NORWAY, MAY 1987-MAY 1988

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SUMMARY

One year of measurement from May 1987-May 1988 of individual light hydrocarbons sampled at Birkenes in south Norway are presented. Spot samples were taken approx. every second day in steel canisters and analysed for C_2-C_5 hydrocarbons. Alkanes dominated the samples, with ethane and propane making up about 50% of the total on a C-basis. The concentrations of the alkanes and acetylene peaked in February 1988, while the alkenes had a secondary summer maximum as well. The maximum sum C_2-C_5 concentration measured was 52.6 ppbC. The individual hydrocarbons are quite well correlated with primary pollutants (NO_2 and SO_2) while there is no correlation with O_3 or sulphate aerosol.

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HYDROCARBON MEASUREMENTS AT RURAL BIRKENES, SOUTH NORWAY, MAY 1987-MAY 1988

1 INTRODUCTION

Non-methane hydrocarbons (NMHC) are important precursors of photochemical oxidants in the atmosphere. They also contribute to the transformation of nitrogen oxides (NOx) and sulphur dioxide (SO_2) to nitric acid and sulphate through their influence on the hydroxyl radical concentration (OH) and hydrogen peroxide (H_2O_2).

Non-methane hydrocarbons (NMHC) have a controlling influence on the occurrence of high ozone concentrations in the atmospheric boundary layer over Europe in episodes of a few days´ duration in the summer (Hov, 1988). In the free troposphere methane (CH_4) and nitrogen oxides control the chemical production and loss of ozone, while the abundance of NMHC is usually so low that their influence on ozone is minor (Isaksen and Hov, 1987). This implies that when the boundary layer production of ozone is slow, CH_4 and NOx also control the ozone concentration near the ground together with the downward flux from the stratosphere through the free troposphere, and ground removal.

For other species, like peroxyacetyl nitrate (PAN), the abundance and composition of NMHC have a controlling influence both in the atmospheric boundary layer and in the free troposphere. While ozone formation depends more on the reactivity and number of C-atoms of a given NMHC-species, PAN formation is strongly dependent on the formation of acetaldehyde, methylglyoxal or biacetyl to have acetyl peroxy radicals formed, and consequently the molecular structure of the NMHCs is important for PAN.

2 REVIEW OF HYDROCARBON MEASUREMENTS

A picture of the composition and distribution in time and space of individual NMHCs over Europe and elsewhere is slowly being built up through surface and aircraft measurements. Little exist of long-term measurements. The sampling and analytical techniques require usually manual involvement, consequently most measurements are taken on a campaign basis.

At Delft in the Netherlands atmospheric levels of non-methane hydrocarbons have been monitored since 1971 (Bos et al., 1978; Guicherit, 1988). Acetylene, which is mostly emitted by mobile sources, has an upward trend of 5-6%/a. The concentrations on a seasonal basis peak in the winter/early spring (at around 8-12 ppb of acetylene), with an early fall minimum which is approx. 50% of the late winter maximum.

In Delft, the 1976-1979 median NMHC (C_2-C_5) concentration was 390 ppbC, with 1.47 ppmC as 95 percentile and 1.79 ppmC as 98 percentile (Bos et al., 1978).

Rudolph et al. (1982a) reported measurements of the vertical distribution of C_1-C_5 hydrocarbons on several occasions over FRG and France. The mixing ratios fell significantly off above 2 km in particular for the most reactive species (C_3-C_5). The light hydrocarbons (ethane, propane and butane) had highest abundances, and were comparable on a C-atom basis.

Airborne measurements of the vertical distribution of NMHC over West-Europe by Tille et al. (1985) supported the conclusions by Rudolph et al. (1982a) for some flights, for others, e.g. over Norway in September 1981, increasing concentrations with height were found.

The latitudinal distribution of light hydrocarbons has been investigated by several authors. Atlantic measurements taken onboard F.S. Meteor have been reported by Rudolph and Ehhalt (1981), Rudolph et al. (1982b) and Ehhalt and Rudolph (1984), covering 75^0S-80^0N. Despite considerable scatter, there is a systematic latitudinal variation with a maximum concentration between 20 and 50^0N in the light alkanes and acetylene with a fall off northwards and southwards to equator and with particularly low concentrations around equator and into the southern hemisphere. There is no clear indication of a seasonal variation in the data. The measurements of propene and ethene were much more variable and Rudolph and Ehhalt (1981) and Ehhalt and Rudolph (1984) ascribed the abundance of these species in oceanic air fully to oceanic sources, quoting measurements showing that the ocean is supersaturated in C_3H_6 by a factor of 100. Atlantic measurements from "Polarstern" in February-April, 1983 (Rudolph et al., 1984) supported the conclusions from the Meteor cruise.

During the STRATOZ II and III flights in April-May 1980 and June 1984, respectively, profiles of the vertical and meridional variation of light hydrocarbons were obtained over the Atlantic and along both coasts of South-America (Ehhalt and Rudolph, 1984; Ehhalt et al., 1985; Rudolph, 1988). The mixing ratios of C_2H_6, C_2H_4, C_2H_2, C_3H_8, C_3H_6, n-C_4H_{10}, i-C_4H_{10}, n-C_5H_{12} and i-C_5H_{12} ranged between 2.0 and 0.02 ppb. There was a decrease in concentration with altitude and in general with decreasing latitude. Isolated maxima of high concentrations were found in the upper troposphere, and these maxima were attributed to fast vertical transport in large scale meteorological systems (low pressure regions or the ITCZ).

Blake and Rowland (1986) reported measurements of ethane at remote surface locations in the Pacific 71^0N-47^0S over several years and found a mid latitude maximum as well as a late winter-early spring maximum in the northern hemisphere, less of a seasonal variation in the southern hemisphere but with a fall minimum (March). Earlier, Singh et al. (1979) had shown measurements of a meridional C_2H_6 profile, also with a maximum between 30-60^0N.

Singh and Salas (1982) found significantly more ethane and propane in the northern hemisphere over the Pacific than in the southern hemisphere, while the hemispheric difference was only slight for propene and ethene.

Bonsang and Lambert (1985) measured C_2-C_6 hydrocarbons onboard a French cruise in November 1982 from France to Tasmania through the Panama Canal (50^0N-40^0S). Considerable scatter was found in concentrations, but there was a decreasing trend from north to south for long-lived species such as C_2H_6 and C_3H_8. The inter-hemispheric gradient was less apparent and even nonexistent for other species with shorter lifetimes.

Air samples collected over the Pacific during Gametag in June 1978 support the picture of a mid latitude northern hemisphere global maximum of C_2H_2 and C_2H_6, while C_2H_4 was variable at approx. the same level in both hemispheres (Rasmussen and Khalil, 1982). Rasmussen and Khalil (1983) showed that both benzene and toluene have a mid latitude northern hemisphere maximum in background surface air, and with a winter-spring maximum at the sampling sites (Niwot Ridge, Whiteface Mountain, NY, Cape Meares, OR, Pt. Banow, AL).

Surface and airborne measurements of individual light hydrocarbons have been reported by many authors for specific locations or covering local or regional aspects of their distribution. Rudolph and Khedim (1985) reported measurements from Deuselbach in the Federal Republic of Germany in October 1983, Perner et al. (1987) at Schauinsland, Jülich and Deuselbach, Cox et al. (1976) at Harwell in the UK, Hough and Derwent (1987) in the London urban plume and Bamber et al. (1984) around the British Isles from the M.R.F. Hercules aircraft.

Outside of Europe, Greenberg et al. (1985) measured light hydrocarbons in air samples from the Kenyan savannah, Dickerson et al. (1987) analysed air samples taken by aircraft near a midwestern US thunderstorm and Roberts et al. (1984) measured aromatic hydrocarbons at Niwot Ridge in Colorado. All these measurements were made on a campaign basis and provide information for a brief period of time.

Light hydrocarbons have been measured in the Arctic particularly at Pt. Barrow in Alaska and on Spitzbergen. Rasmussen et al. (1983) showed that the annual variation in light hydrocarbons like ethane and propane follows that of Arctic haze with a spring maximum and a summer minimum. Hov et al. (1984, 1988) showed that alkanes and aromatic species (benzene) peaked in the spring with a summer minimum, while ethene and propene had the opposite annual variation with a summer maximum. This was taken as an indication that the light alkenes have different sources compared to the light alkanes, following the suggestion by Ehhalt and Rudolph (1984) of a marine source of these gases. In Table 1 a summary is given of surface air measurements of NMHC at rural sites. The measurements summarized in Table 1 are mainly of alkanes and alkenes, aromatic species were not analysed in most of the samples because they change with time in the steel canisters used in most of the cases.

In the most righthand column in Table 1 an illustration is given of the estimated composition of UK anthropogenic VOC-emissions (Hough and Derwent, 1987).

From Table 1 it can be seen that all the cleanest locations (the high latitude sites, Deuselbach and the coastal sites in Maine and Florida) all have a high fraction of slowly reacting alkanes (ethane, propane and butane) and acetylene, while the alkenes are depleted. At the more polluted sites (Düren near Jülich in FRG and in the London urban plume including Harwell), the more reactive species like ethene and propene also make up a sizeable fraction of total, and n-butane and i-pentane are among the most important species on a C-atom basis.

Table 1: Measurements of non-methane hydrocarbons at rural sites (ppt).

Species	Ny-Alesund[1]	Ny-Alesund[3]		Ship M[3]	Pt. Barrow[5]	Deuselbach[6]	Düren[6]	Deuselbach[7]	Deuselbach[8]
	Spring 1983	Spring 1985	Spring 1986[4]	Spring 1985	Early spring 1982	23 Oct 1983	March 1984	May 1983	Jul-Aug 1981
C_2H_6	3 950	3 303	3 358	3 493	2 872	1 550	5 300	2 400	2 100
C_2H_4	156	617	290	766	75	600	6 600	450	1 000
C_2H_2	954	932	1 110	1 176	686	590	5 800	620	600
C_3H_8	2 156	2 551	2 389	2 799	1 260	720	2 800	500	850
C_3H_6	24	283	106	268		100	1 400	80	280
propyne	NA[2]	≈ 10	8	20		-	-	-	-
i C_4H_{10}	390	429	276	344		220	1 700	190	140
n C_4H_{10}	805	1 119	623	781		540	5 500	420	220
trans-2-butene	NA	33	NA	27					
iso-butene	NA	441	NA	559					
cis-2-butene	NA	15	NA	22					
n-pentane	339	361	NA	209		140	1 600	130	80
i-pentane	346	549	269	265		250	3 100	310	200
n-hexane	172	248	NA	153		51	800		
2,2-dimethyl-propane	NA	< 5	NA	< 5					
2,2-dimethyl-butane	NA	77	NA	47					
2-methyl-pentane	182	170	NA	90					
3-methyl-pentane	160	115	NA	67					
benzene	NA	NA	NA	NA	319	120	1 100		
toluene	NA	NA	NA	NA	69	180	2 500		
Sum (pptC)	≈ 28 000	≈ 34 500	≈ 22 000	≈ 31 600	≈ 13 400	≈ 15 200	≈ 12 900	≈ 13 300	≈ 13 600

Species	London plume[9] 21 June & 12 July 1983	Midwestern[10] U.S.	Kenya[11]	Belfast[12] Maine	Miami[12] Florida	Harwell[13] UK	Harwell[14] UK	Black Forest[16] June 1984	Fraction of UK NMHC emissions on a C-atom basis
C_2H_6	3 750		1 030	1 750	2 000	15 400	9 100	2 090	0.063
C_2H_4	2 020	450	1 490	1 000	250	3 100	2 430	1 890	0.056
C_2H_2	3 340		750	< 250	< 250			1 390	0.052
C_3H_8	1 800		670	670	670	5 400	2 810	650	0.016
C_3H_6	230	180	470	170	< 170	1 000	720	630	0.027
propyne	-	-	-	-	-	-	-	-	-
i C_4H_{10}	2 500		170	125	< 125	1 500	950	390	0.028
n C_4H_{10}	4 000		400	500	250	2 900	1 700	1 190	0.081
trans-2-butene									
iso-butene			300	< 125	< 125			150	0.019
cis-2-butene									
n-pentane	1 640	240	150	200	200			490	0.080
i-pentane	3 620	70	110	200	300			550	0.143
n-hexane			100					350	
2,2-dimethyl-propane									
2,2-dimethyl-butane									
2-methyl-pentane			55						
3-methyl-pentane			35						
benzene		160	230					430	
toluene		140	340					690	0.133
Sum (pptC)	≈ 76 600		≈ 19 600	≈ 13 500	≈ 13 000	≈ 73 000	≈ 44 300	≈ 36 200	≈ 0.698

Notes:
1) Mean of 10 samples (Hov et al., 1984).
2) NA: Not analysed.
3) Ship M: 66^0 N, 2^0 E (Hov et al., 1988) (19 samples on ship M, 23 in Ny-Ålesund).
4) 7 samples.
5) Rasmussen et al. (1983).
6) Rudolph and Khedim (1985).
7) Perner et al. (1987), average of 5 samples 18-20 May.
8) Perner et al. (1987), average of 4 samples 29 July-27 August.
9) Hough and Derwent (1987), average of 2 samples.
10) Dickerson et al. (1987) 15 June 1985, Oklahoma.
11) Greenberg et al. (1985), average of 13 samples (55-90% of total NMHC in each sample was identified).
12) Sexton and Westberg (1984 (coastal sites).
13) Cox et al. (1976), average of 20 samples in March 1973.
14) Cox et al. (1976), average of 5 samples in July 1973.
15) Based on the UK emission inventory and specification published by Hough and Derwent (1987).
16) Average of 5 samples in the Black Forest, FRG, 19-26 June 1984(Platt et al., 1988).

Less is known of the concentration, composition and distribution of $\geq C_6$ hydrocarbons, including aromatic compounds and natural hydrocarbons (isoprene and terpenes), due to the need for other sampling and analytical methods compared to $< C_6$ hydrocarbons. Solid adsorbent sampling is a well-known technique for determination of C_5-C_{15} substances in ambient air, while compound losses of compounds heavier than C_5 may occur both during sampling and storage if stainless steel canisters are used for sampling (Schmidbauer and Oehme, 1987).

A summary of some of the measurements of aromatic hydrocarbons reported by Roberts et al. (1984) at rural Niwot Ridge in Colorado is given in Table 2. The measurements were made using Tenax GC porous polymer for sampling followed by GC-FID analysis. The sum of the average concentrations of aromatic compounds is approx. 2 000 pptC, which indicates that these compounds probably make up only a minor fraction of the total NMHC at the site.

Table 2: Aromatic hydrocarbons at remote sites (see also Table 1 where some data for benzene and toluene are given) (in ppt by compound).

	Niwot Ridge, Colorado[1]	Northern hemisphere, Pacific[2]	Southern hemisphere, Pacific[2]	East Washington state[3]
benzene	160	49	10	226
toluene	130	20	5.6	133
o-xylene	13	14	6.6	
ethylbenzene	13	7.6	3.7	
m+p-xylene		25	13	

Notes:

1) Average of 23 tenax samples June-October 1981 (Roberts et al., 1984). The O_3- and NOx-levels were 46 and 0.53 ppb on the average, respectively.

2) Nutmagul and Cronn (1985), measurements between 42°N and 30°S in the eastern Pacific in October/November 1983 (average of many samples).

3) Rural site, average of samples taken between July 1982 and October 1983 (Nutmagul and Cronn, 1985). Benzene was higher in winter than in summer.

Nutmagul and Cronn (1985) measured aromatic hydrocarbons on a cruise in the eastern Pacific in October/November 1983 and their average numbers for the northern and southern hemisphere Pacific are also given in Table 2. For comparison, Bonsang and Lambert (1985) quote the following numbers for the marine background mixing ratios in the South Pacific Ocean: C_2H_6 (0.4 ppb); C_2H_4, C_3H_6, C_5H_{10} and n C_6H_{14} (0.2 ppb); C_3H_8, i C_5H_{12} and C_4H_8 (0.1 ppb) and n C_4H_{10} (0.05 ppb), which adds up to approx. 5.4 ppbC; the aromatic compounds in Table 2 for the South Pacific add up to about 400 pptC, or about 7% of the total NMHC on a C-basis.

The involvement of hydrocarbons of biogenic origin in photooxidant formation is not settled (Abelson, 1988). In particular in areas with an extensive coverage of deciduous trees, the isoprene emissions can be important during daytime in hot weather. Chameides et al. (1988) concluded from a case study in Atlanta, Georgia that biogenic hydrocarbons play an important role in photochemical smog formation. Based on measurements of hydrocarbons and NOx at the rural site Scotia in Pennsylvania, Trainer et al. (1987a) showed that natural NMHCs can have a significant impact on ozone formation in rural air. On specific days in July 1986, they found isoprene concentrations twice as high as anthropogenic C_3-C_{10} HC (up to 40 ppbC of isoprene).

There is some evidence in favour of the hypothesis that under low NOx-conditions, i.e. in a situation with only biogenic NOx-emissions, isoprene does not contribute to ozone formation. On the contrary, it perhaps leads to a slight O_3 reduction due to the formation of organic nitrates through the reaction of intermediate components in the isoprene decomposition with NOx. At present day emission levels of NOx e.g. in continental U.S. or Europe, isoprene contributes to O_3 formation (Jacob and Wofsy, 1988; Trainer et al., 1987a). Organic nitrates have been identified in the North Pacific at 50-100 pptC-levels of C_4+C_5 alkyl nitrates (Atlas, 1988).

The very low O_3 concentrations found in Montsouris near Paris hundred years ago (Volz and Kley, 1988) may perhaps be seen in this light: In an unpolluted, low NOx environment, isoprene emissions contribute to a suppression of ozone near the ground (the average Montsouris values for O_3 were ~ 10 ppb, opposed to a free tropospheric natural background of 10-25 ppb). This would also be in line with the self interest of biological systems - to protect themselves from toxic levels of O_3.

With present NOx emissions, isoprene contributes to O_3 formation and indirectly perhaps also to an increased oxidation of organic gases through OH. This may contribute to the observed increase in CO (Khalil and Rasmussen, 1988).

Measurements of natural hydrocarbons have been reported for Norway by Hov et al. (1983) where the sum of α- and β-pinene, camphene, carene, γ-terpinene, limonene and p-cymene was found to be in the range 8.8-70.7 ppbC for samples collected in adsorption tubes within a tree canopy.

In Table 3 is shown a summary of hydrocarbon measurements reported by Zimmerman et al. (1988) from the Amazon boundary layer in July and August, 1985.

Table 3: Summary of median mixing ratios (ppbC) and hydrocarbons in the Amazon boundary layer (Zimmerman et al., 1988).

	Altitude				
	All samples	30 m	61 m	152 m	305 m
Total terpenes	23	27	20	18	15
Total alkanes	7.9	7.5	7.0	7.3	7.9
Total alkenes	17.4	20.8	16.6	14.1	13.2
Total aromatics	8.4	6.6	6.7	6.5	9.8
Total biogenics	12.6	15.7	12.9	10.3	10.7
Total NMHC	46.4	52.3	51.6	36.8	40.1

The biogenic compounds are mainly made up of isoprene. The most reactive species (alkenes, terpenes, isoprene) fall off more rapidly with height than the more slowly reacting species, but the fall off with height is slight compared to what has been estimated for other locations (Hov et al., 1983; Trainer et al., 1987).

In Table 4 a summary is given of natural hydrocarbon measurements in Japan during the summer (Yokouchi and Ambe, 1988) and at Niwot Ridge during May-October 1981 and June-October 1982 (Roberts et al., 1983; 1985).

Table 4: Biogenic hydrocarbons in Japan (Yokouchi and Ambe, 1988) and at Niwot Ridge in Colorado (Roberts et al., 1983; 1985) (ppbC).

	Niwot Ridge[1]	Niwot Ridge night[2]	Japan, average wet season	Japan, average clear season
β-pinene	0.97	2.1	0.82	0.73
α-pinene	0.54	1.5	2.0	3.0
Δ^3-carene	0.51	1.0		
camphene	0.38	1.0	0.77	0.44
d-limonene	0.30	0.72		
isoprene			0.56	1.9

1) Average for May-October, 1981 and June-October, 1982, Roberts et al. (1983).

2) Roberts et al. (1985).

The higher concentrations measured at night at Niwot Ridge can be attributed to increased atmospheric stability at night.

The change in the atmospheric abundance of methane (CH_4) is of importance both for tropospheric O_3 and OH. In this paper the focus is on NMHC. Reference is made to Blake and Rowland (1988), Rasmussen and Khalil (1986) and Khalil and Rasmussen (1987).

3 MEASUREMENTS AT BIRKENES IN SOUTH NORWAY

Birkenes is located in a rural area approx. 20 km from the coast of south Norway north of Kristiansand, at 190 m a.s.l., at $50^0 23'$N and $8^0 15'$E. The annual precipitation was 1 305 mm in 1986. The station is part of the EMEP-network and has been in operation since November 1971. Precipitation chemistry, SO_2, NO_2, sulphate, nitrate and ammonium in air are measured on a daily basis. O_3 is measured on an hourly basis.

In connection with the Tropospheric ozone research (TOR) sub-project under Eurotrac which is a part of EUREKA, the site at Birkenes is being equipped to fulfil the measurement programme in TOR. As a part of that effort, the sampling of light hydrocarbons was started on a regular basis in May 1987. Manual samples using stainless steel (SS 304) bottles of 0.8 l volume together with a metal-bellow pump (Schmidbauer and Oehme, 1988) are obtained every second day, although there have been irregular intervals at times due to practical difficulties.

The stainless steel bottles of 0.8 l volume with electropolished internal surfaces were obtained from professor R.A. Rasmussen at Oregon Graduate Center, U.S.A. The canisters tolerate a pressure of maximum 16 bar, and are equipped with a single Nupro SS 4H metal-bellow sealed shut-off valve. Purging and filling of this bottle was carried out by repeated pressurizing and emptying. Contaminated bottles were cleaned by connecting them to a high-vacuum pump system. Blanks free for any traces of C_2-C_8 hydrocarbons were obtained even for bottles which had been exposed to high levels (ppm) by evacuating them for 72h at room temperature with a vacuum better than 5×10^{-7} torr (Schmidbauer and Oehme, 1988).

The quantitative analysis is described in detail by Schmidbauer and Oehme (1986, 1987). The canister with about 2.5 bar overpressure was connected to the preconcentration unit and all tubes were flushed with helium. 300-500 ml of air was preconcentrated on a cryotrap. The sample volume was then transferred to a tandem cryotrap submerged in liquid nitrogen. A drying tube was placed between the traps.

Condensed air (O_2, N_2) was removed from the trap by a helium flow. Afterwards the tandem trap was heated with hot water and after passing the drying tube and the second trap the sample was retrapped on a fused silica capillary submerged in liquid nitrogen.

A Carlo Erba 2400T gas chromatograph equipped with a flame ionization detector was used in the analysis. A fused silica capillary coated with aluminium oxide was used for the gas chromatographic separation. The temperature programme was as follows: 60^0C for 2 min., 60^0-190^0C at 15^0C/min., and a helium flow rate of 2 ml/min. This technique was suitable for samples with normal humidity content (< 70-80%) and allowed to detect C_2-C_6 hydrocarbons down to a few ppt.

Schmidbauer and Oehme (1988) found that there is little risk of irreversible losses due to wall adsorption in the canisters for C_2-C_6 hydrocarbons. The risk increases with increasing boiling point and polarity of the compound sampled. The blank values are low and comparable to the detection limit, and the samples can be stored for several weeks without changes in sample composition. The removal of the air humidity from the samples before analysis causes losses of the less volatile (> C_6) compounds.

Calibration gases from Scott Speciality Gases (S) (PA, U.S.A.) were used. These have previously been compared with gas mixes from Messer Griesheim (N), Düsseldorf, FRG (Hov et al., 1988).

The comparison showed that there was up to 51% difference for individual species between the calibration gases from the two suppliers. There was no systematic difference, for some species S was lower than N, and vice versa. The arithmetic mean of the ratios S/N of the individual species was very close to 1. The standard deviation was the same for both calibration gases relative to the mean, indicating that the differences in the mean were not due to the analytical procedures. Our experience is that the calibration gases from the two suppliers are consistent from batch to batch which indicates that the results obtained with different batches of gases but from the same supplier can be compared in absolute terms.

4 RESULTS

Altogether 143 samples were collected after one year starting 22 May 1987. Four of the samples were deleted from the series of measurements due to contamination of the steel flasks. The following compounds dominated in the samples and are discussed in the following: ethane, ethene, propane, propene, i-butane, acetylene, n-butane, 2-methylbutane (i-pentane), n-pentane.

In Figure 1 (a-d) is shown in 1a and 1b a cumulative plot of the absolute concentrations of each of the individual light hydrocarbons on a C-basis. Also indicated are the maximum concentrations in ppt for each compound and in pptC for the sum. Day number 1 corresponds to 22 May 1987. The peak concentration in the first 180 days (till mid November) was found on 30 July (sum = 39 250 pptC), while the annual maximum was found on 29 January 1988 (sum = 52 628 pptC). There is a lot of variation in the concentration throughout the year with a summer minimum and a winter maximum.

The relative composition of each sample is shown in Figure 1c-d, where the individual hydrocarbons in each sample are shown in a cumulative plot relative to the total in each sample (on a C-basis).

In Table 5 is shown the average composition of the samples over 90, 180 and 360 d as averaging time. From Figure 1c and d and Table 5 it can be seen that C_2H_6 and C_3H_8 which are the least reactive alkanes, make up about 50% of the total, butanes 19% and pentanes 11%, or 80% alkanes of the total, 13% alkenes and 6% C_2H_2.

Table 5: Relative composition of the samples on a C-basis averaged over 90, 180 and 360 days.

	Interval (d)						
Species	1-90	91-180	181-270	271-360	1-180	181-360	1-360
C_2H_6	0.26	0.23	0.21	0.23	0.26	0.22	0.25
C_2H_4	0.14	0.12	0.09	0.07	0.14	0.08	0.10
C_3H_8	0.17	0.24	0.23	0.28	0.21	0.26	0.25
C_3H_6	0.07	0.06	0.03	0.02	0.06	0.02	0.03
$i\text{-}C_4H_{10}$	0.06	0.05	0.06	0.06	0.05	0.06	0.05
C_2H_2	0.04	0.04	0.05	0.08	0.04	0.07	0.06
$n\text{-}C_4H_{10}$	0.14	0.13	0.14	0.14	0.14	0.14	0.14
$i\text{-}C_5H_{12}$	0.08	0.08	0.09	0.06	0.07	0.07	0.06
$n\text{-}C_5H_{12}$	0.05	0.05	0.10	0.06	0.04	0.08	0.05

The relative importance of the alkenes is higher in the first 6 months during summer and fall, than during the winter and spring. For the other species there is a tendency to have relatively more ethane during summer than winter, while the contribution of propane to the total was much higher in the spring than during the summer, fall or winter. This applies to acetylene as well.

The annual variation of each individual hydrocarbon and of the sum is shown i Figure 2a-j, where each individual sample is marked (+), as well as the running average over 30 d. The concentration marked in the upper right hand corner is the maximum 30 d running average concentration, to get the maximum concentration in one sample, Figure 1 must be consulted (e.g. for ethane the maximum single recording was 5 830 ppt, the maximum 30 d running average was 4 390 ppt). The individual measurements in Figure 2 are scaled to the same value as the running average (the maximum 30 d running average).

Ethane has an annual variation with a late January maximum and an early autumn minimum at about 25% of the winter maximum.

Ethene also peaks in late January, but there is a secondary maximum in July-August at about 50% of the winter maximum. Propane follows the same pattern as ethane, except that the summer/winter ratio is even smaller (about 0.20). Propene (Figure 2d) has 2 maxima, in July-August and in late January. The concentration is lowest in the spring. One may speculate that the summer peak has a different origin from the winter maximum. The winter maximum most likely is due to long range transport of pollutants. This is less likely for the propene summer maximum since propene is the most reactive of the light hydrocarbons sampled, and should not be enriched in long range transport, in particular not in the summer with high OH and O_3 which react with propene. The summer maximum in propene therefore most likely is due to fairly local release of propene, and the possibility of propene emissions from the coastal areas upwind of the site cannot be ruled out.

Iso-butane and n-butane both peak in late January and have a minimum around September 1987. There is an elevated level in July-August due to a few high values, but the summer level is typically 25% of the winter peak.

Acetylene is very low in the summer, only 10-20% of the peak value which is found in March, while there is a secondary maximum in

January. Iso- and n-pentane are also low in the summer, in particular n-pentane which in the summer is only 10-15% of the late January maximum.

The sum (Figure 2j) follows the variation of the most abundant species with a late January-February 1988 maximum for the year measured, and a much lower summer level at 20-30% of the total.

The scatter of individual measurements around the average as shown in Figure 2 gives an indication of the standard deviation around the mean in the measurements. The ratio of the standard deviation to the mean is seen to be higher in summer than in winter for all compounds, and the ratio in general increases going from low reactivity to high reactivity (Figure 3). This relationship between $\sigma/\bar{x}$ and reactivity has been established for other rural sites as well (see e.g. Hov et al., 1988).

The relationship between the individual hydrocarbons and the sum is further analysed in Figure 4 and Table 6. In Figure 4 the Pearson product-moment correlation coefficient between each individual hydrocarbon and the sum is shown averaged over the year and over the summer months. The coefficients are calculated from the expression

$$R_{jk} = \frac{S_{jk}}{\sqrt{S_{jj} \cdot S_{kk}}} \qquad j,k = 1,\ldots,18$$

where S_{jk} are the sums of squares and cross-products of deviations from means:

$$S_{jk} = \sum_{i=1}^{139} (x_{ij} - \bar{x}_j)(x_{ik} - \bar{x}_k) \qquad j,k = 1,2,\ldots,18$$

where $\bar{x}$ are the means, $j = 1,2,\ldots,18$.

In Figure 4 it can be seen that when all samples are included, the alkanes and acetylene have a high correlation with the total ($R \geq 0.8$, .72 for n-C_5H_{12}). For the alkenes the correlation is particularly poor for propene. Ethene and propene are decomposed through the reaction

Table 6: Pearson product-moment correlation coefficients for 18 different parameters on days when light hydrocarbons were analysed 22 May 1987-22 May 1988 (139 cases). The light hydrocarbons are spot samples, the ozone concentrations 24h mean ($\bar{O}_3$), maximum or minimum hourly concentration during the day (O_{3max} or O_{3min}), and NO_2, SO_2, SO_4^{2-}, ΣNO_3^- and ΣNH_4^+ are 24h averages.

	C_2H_6	C_2H_4	C_3H_8	C_3H_6	i-C_4H_{10}	C_2H_2	n-C_4H_{10}	i-C_5H_{12}	n-C_5H_{12}	ΣHC	$\bar{O}_3$	O_{3max}	O_{3min}	NO_2	SO_2	SO_4^{2-}	ΣNO_3^-	ΣNH_4^+
C_2H_6	1.00																	
C_2H_4	.35	1.00																
C_3H_8	.91	.43	1.00															
C_3H_6	.03	.74	.04	1.00														
i-C_4H_{10}	.70	.51	.71	.14	1.00													
C_2H_2	.86	.36	.88	-.09	.74	1.00												
n-C_4H_{10}	.71	.52	.69	.17	.98	.71	1.00											
i-C_5H_{12}	.55	.40	.48	.13	.84	.60	.86	1.00										
n-C_5H_{12}	.52	.26	.44	.03	.63	.59	.64	.87	1.00									
ΣHC	.88	.58	.87	.20	.91	.87	.91	.82	.72	1.00								
$\bar{O}_3$	.27	-.05	.17	-.18	.08	.25	.07	.01	.06	.13	1.00							
O_{3max}	.24	-.09	.13	-.20	.08	.20	.07	.00	.03	.10	.94	1.00						
O_{3min}	.35	.09	.30	-.08	.15	.36	.15	.07	.13	.25	.83	.65	1.00					
NO_2	.41	.17	.49	-.05	.30	.34	.29	.17	.13	.38	.09	.10	.17	1.00				
SO_2	.25	.07	.21	.00	.22	.17	.22	.16	.09	.22	-.15	-.07	-.19	.31	1.00			
SO_4^{2-}	.36	.17	.42	-.04	.27	.30	.27	.18	.12	.34	.08	.12	.09	.83	.26	1.00		
ΣNO_3^-	.22	.04	.23	-.02	.11	.12	.12	.06	.03	.16	+.02	.08	-.08	.55	.60	.50	1.00	
ΣNH_4^+	.18	.07	.23	-.01	.14	.09	.15	.09	.02	.17	-.08	-.01	-.13	.68	.50	.77	.84	1.00

with O_3 as well as with OH, while for the alkanes the OH-reaction is dominant, and the lifetime of ethene and propene is 10-100 times shorter than for the alkanes. There is also a significant difference in the sources. Ethane and propane originate from natural gas distribution and application, while the other species have petrol engine exhaust and motor vehicle evaporative loss as dominant anthropogenic sources. The difference in correlation for alkanes compared to alkenes originates therefore from a combination of different chemical lifetimes and different source distributions.

In Table 6 the correlations between pairs of hydrocarbons on an annual basis can be found, while in Table 7 the same correlations are shown when a 30 d running average is first applied for smoothing. It can be seen in Table 6 that ethene and propene are correlated (R= 0.74) while there is no correlation between propene and other hydrocarbons than ethene. The smoothing applied before Table 7 was calculated tends to reinforce the correlations in the cases when it also from Table 6 is given an indication that a linear regression can explain a significant fraction of the variance in the dependent variable, while a lack of correlation in Table 6 is not altered in Table 7. Iso- and n-butane are very well correlated, the same applies to i- and n-pentane and C_2H_6 and C_3H_8.

Table 7: Same as Table 6, but a 30 d running average was first applied for smoothing.

	C_2H_6	C_2H_4	C_3H_8	C_3H_6	i-C_4H_{10}	C_2H_2	n-C_4H_{10}	i-C_5H_{12}	n-C_5H_{12}	ΣHC	$\bar{O}_3$	O_{3max}	O_{3min}	NO_2	SO_2	SO_4^{2-}	ΣNO_3^-	ΣNH_4^+
C_2H_6	1.00																	
C_2H_4	.61	1.00																
C_3H_8	.98	.62	1.00															
C_3H_6	.08	.81	.11	1.00														
i-C_4H_{10}	.94	.76	.93	.29	1.00													
C_2H_2	.93	.41	.93	-.14	.87	1.00												
n-C_4H_{10}	.94	.76	.91	.29	.99	.85	1.00											
i-C_5H_{12}	.81	.65	.76	.24	.90	.74	.93	1.00										
n-C_5H_{12}	.81	.57	.75	.15	.86	.73	.89	.97	1.00									
ΣHC	.97	.72	.96	.23	.99	.90	.98	.89	.88	1.00								
$\bar{O}_3$	.27	-.18	.23	-.42	.08	.37	.03	-.16	-.12	.10	1.00							
O_{3max}	.17	-.30	.12	-.50	-.03	.27	-.07	-.24	-.18	.00	.98	1.00						
O_{3min}	.48	.12	.47	-.19	.36	.59	.30	.08	.06	.37	.89	.78	1.00					
NO_2	.69	.58	.75	.28	.67	.62	.68	.56	.51	.71	-.10	-.23	.21	1.00				
SO_2	.59	.55	.54	.26	.64	.43	.69	.72	.72	.65	-.40	-.43	-.24	.58	1.00			
SO_4^{2-}	.29	.08	.37	-.04	.16	.32	.16	-.01	-.05	.22	.24	.19	.38	.68	.17	1.00		
ΣNO_3^-	.10	.02	.17	.04	.03	.05	.05	-.04	-.02	.08	-.10	-.05	-.11	.41	.35	.69	1.00	
ΣNH_4^+	.02	-.07	.11	-.01	-.05	.02	-.04	-.16	-.17	-.01	.00	.06	-.02	.36	.18	.77	.95	1.00

The correlations shown in Table 6 are further illustrated in scatter plots in Figure 5a-d, where the sum of C_2-C_5 hydrocarbons is shown vs. propane and propene, respectively, and acetylene vs. propane and propene is shown. Even though acetylene and propane have different soures (petrol engine exhaust and natural gas, respectively), they correlate well which indicate that the source areas overlap at the same time as the chemical decay proceeds at comparable rates.

The hydrocarbon measurements have been kept together with the measurements of ozone (hourly concentrations), sulphate aerosol, sum nitric acid and nitrate in air and sum ammonia and ammonium in air (24h means) at Birkenes. These are measurements which are obtained on a regular basis through the EMEP programme (European Monitoring and Evaluation Programme). In Figure 6a is shown the daily mean concentration of ozone and the observed sum of light hydrocarbons.

The maximum daily mean O_3-concentration was 57.7 ppb (around mid May 1988). There is a spring maximum in the daily mean O_3-concentration and a fall-winter minimum in ozone. Tables 6 and 7 indicate that there is no correlation between O_3 and sum C_2-C_5. This is clearly illustrated in Figure 6b where the 30 d running average is applied. Sum C_2-C_5 has an annual variation with a Jan/Feb max, while O_3 tends to increase when sum C_2-C_5 drops and vice versa.

The sum of C_2-C_5 hydrocarbons follow the seasonal variation of the primary pollutants (SO_2, NOx) rather than of secondary pollutants like O_3 or sulphate aerosol (Figure 6c, d). Sulphate is seen to have a fall maximum (figure 6d) made up of 3 episodes of a few days´ duration (Figure 6c).

In Figures 6e-h the individual measurements of sum C_2-C_5, SO_2 and NO_2 are shown as well as the 30 d running averages. Both SO_2 and NO_2 have a highly episodic behaviour and are not correlated with sum C_2-C_5 for the individual samples (r = 0.22 and 0.38, respectively), while for the 30 d average there is a correlation (0.71 for NO_2 and sum C_2-C_5 and 0,65 for SO_2 and sum C_2-C_5). The somewhat smaller value for SO_2 is probably due to the shift in time for the maximum (Figure 6f).

A model interpretation of these measurements will be published later. A lagrangian long-range transport model for the EMEP grid with photooxidant chemistry has been used for the calculation of ozone and other photooxidants on an episode basis in Europe (see Hov, 1988).

An example of a 20 day calculation to Langesund which is a coastal, rural ozone site in South Norway about 150 km northeast of Birkenes, is shown in Figure 7, for the period starting 20 May 1982. Four days' long trajectories are calculated every 6h to the receptor site, and in Figure 7 is shown O_3, sum of airborne NMHC and total emitted NMHC along the trajectory arriving at the receptor site. There are two periods with elevated ozone: 27 May and 2-6 June. The maximum airborne NMHC concentration calculated was 37.3 ppbC, and the highest NMHC emissions along a single trajectory was 66 ppbC (in the model there is on the average 3.7 C-atoms in each HC-molecule). It can be seen that the NMHC-level typically was 10-50% of the maximum, which means that an average trajectory arriving at Langesund was calculated to contain less than 10 ppbC. Comparing the calculated results with the summer measurements in Figure 1a, the conclusion can be drawn that although two different years are compared, the model calculations are comparable with the measurements and much can be learnt from a model analysis of the measured data. Such work is underway (Hov, 1988; Eliassen et al., 1988).

5 ACKNOWLEDGEMENT

The measurements reported here were carried out with funds from the Norwegian Ministry of Environment. The data analysis was supported by the Nordic Council of Ministers.

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Figure 1: Cumulative plots of individual hydrocarbons as a function of time (a and b). The day number refers to 22 May 1987 as starting date. The concentrations given are maximum concentrations for the period covered in the graph. Concentrations are scaled on a C-basis to the sum C_2-C_5. The sequence of species is from the bottom: C_2H_6, C_2H_4, C_3H_8, C_3H_6, i-C_4H_{10}, C_2H_2, n-C_4H_{10}, i-C_5H_{12}, n-C_5H_{12}. The vertical lines indicate the days on which samples were taken. In Figure 1c and d similar diagrams are shown except that the composition of each sample is scaled to the sum C_2-C_5 in each sample.

Figure 2: Individual measurements (+) and 30 d running average (full line) of each of the individual hydrocarbons and of the sum C_2-C_5. The concentration used for scaling is indicated in the upper right hand corner and is the 30 d running average maximum.

Figure 3: The ratio $\sigma/\bar{x}$ (standard deviation divided by the mean) for summer (days 1-90) and winter (days 211-300) as a function of reactivity for each hydrocarbon as measured by the reaction rate coefficient k between HC and OH.

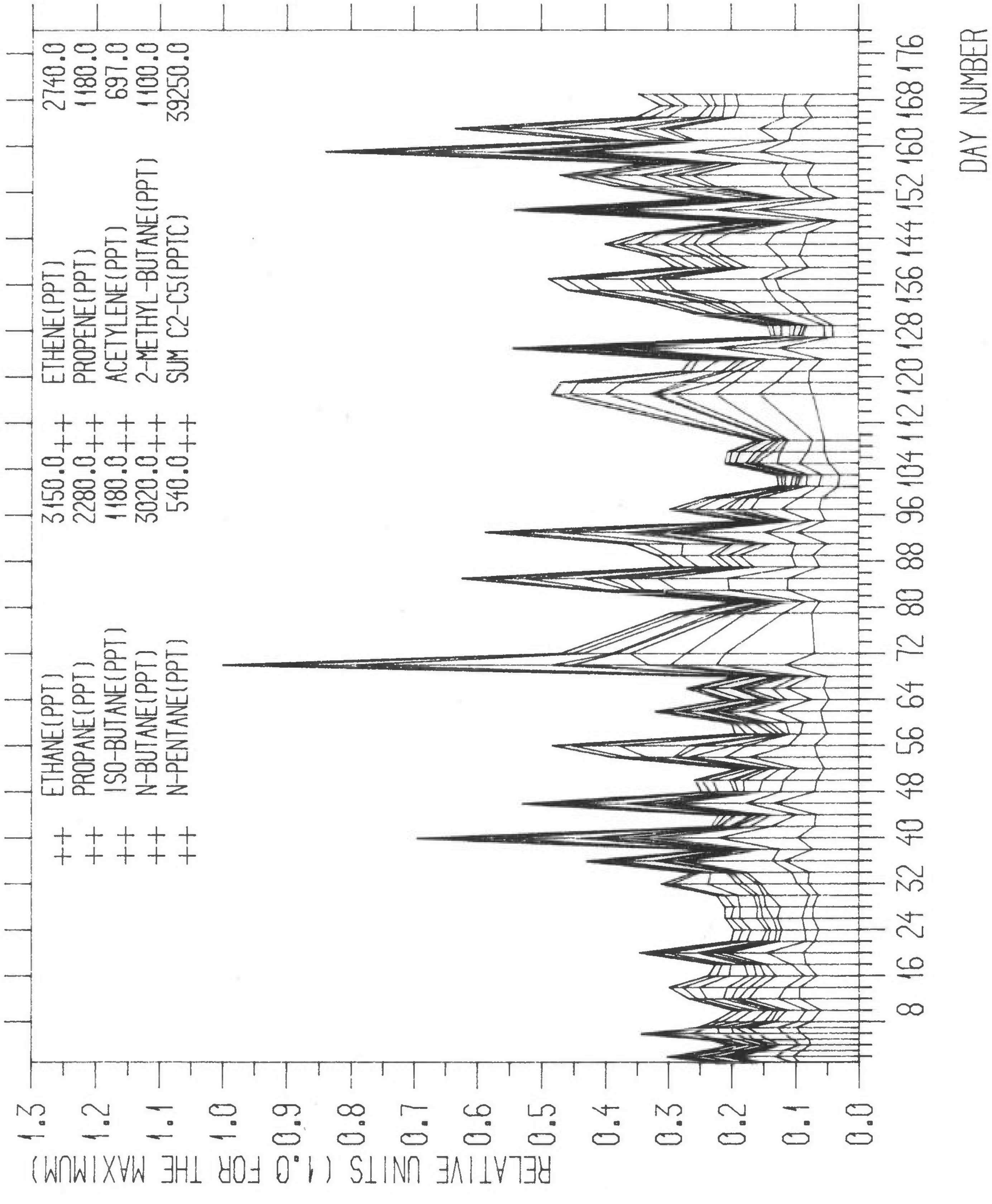
Figure 4: Correlation between an individual hydrocarbon C_i and the sum C_2-C_5 as a function of reactivity for the whole year 22 May 1987-22 May 1988 (full line) and summer 1987 (days 1-90) (dashed line).

Figure 5: Scatter diagrams for individual measurements of sum C_2-C_5 vs. C_3H_8 and C_3H_6 and acetylene vs. C_3H_8 and C_3H_6, based on one year´s samples. The correlation coefficient r is also shown.

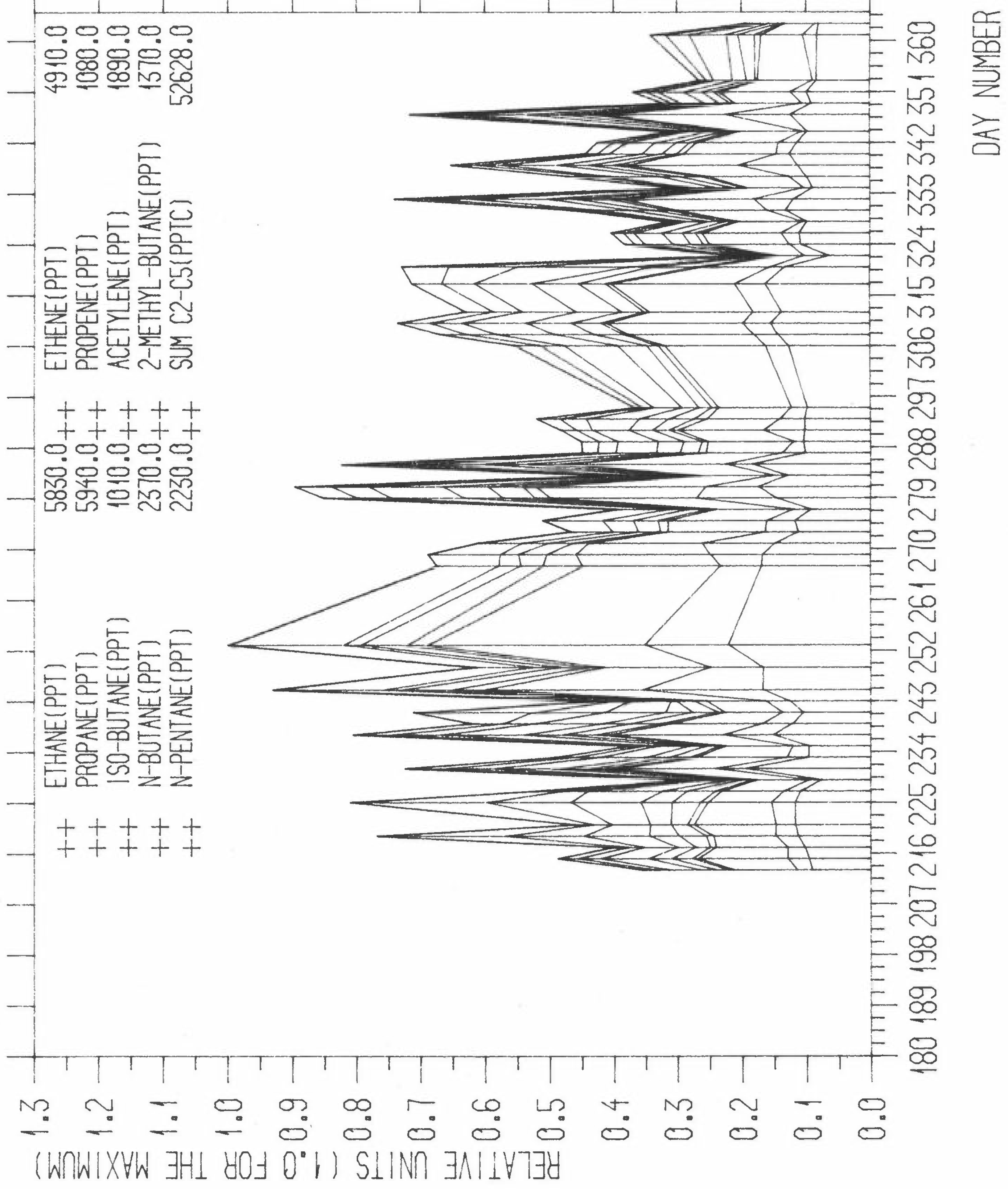
Figure 6: (a) The individual measurements of the sum C_2-C_5 and of ozone daily mean concentrations as a function of day number, (b) Same as (a) but using 30 d running average concentrations. (c) The individual measurements of the sum C_2-C_5 and of sulphate aerosol (24h values) as a function of day number, (d) Same as (c) but using 30 d running average concentrations. (e) and (g) same as (c) but with SO_2 and NO_2 in stead of sulphate, (f) and (h) same as (d) but for SO_2 and NO_2.
The maximum concentrations used for scaling (1.0 on the vertical axis) are indicated in the upper right hand corner.

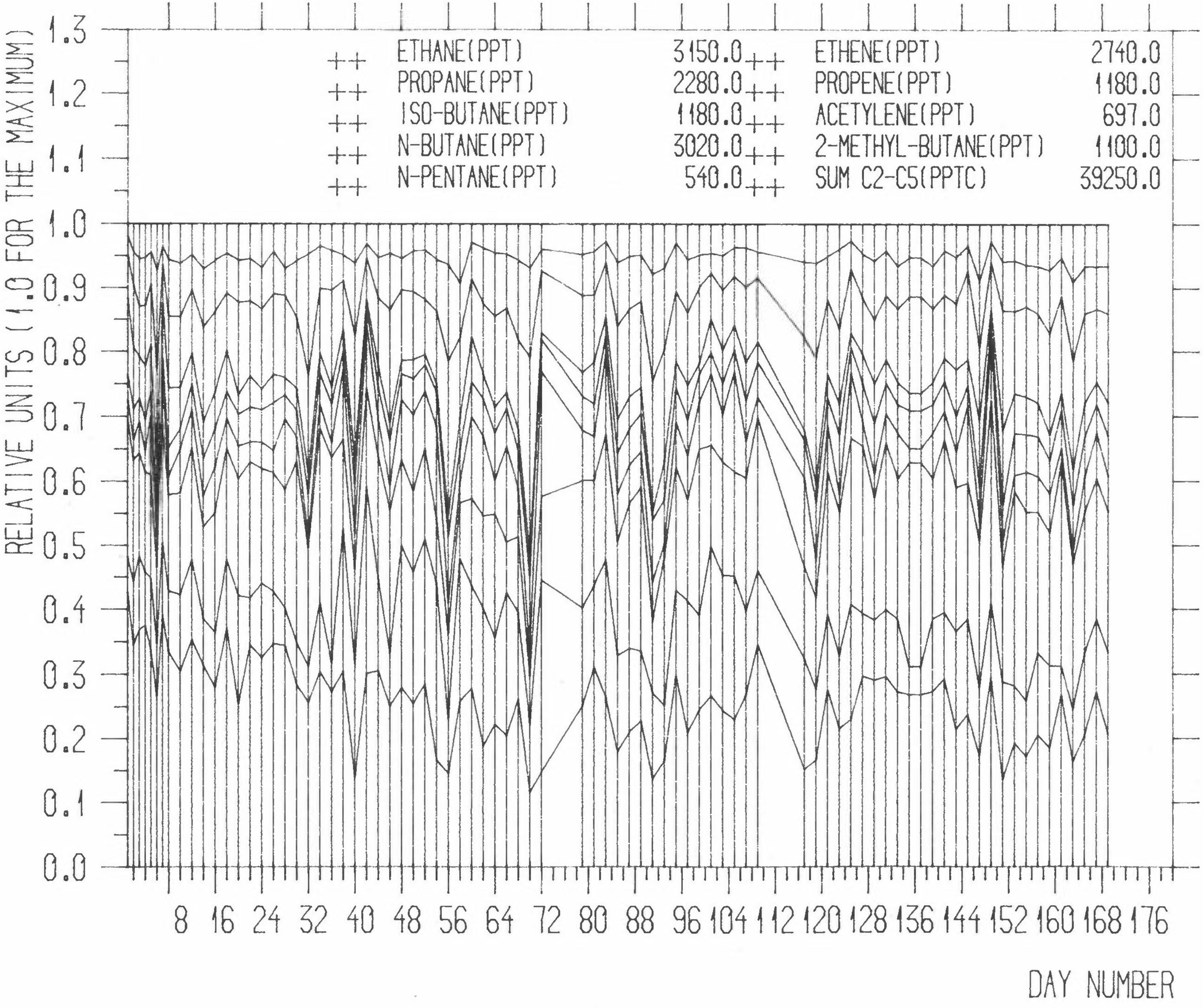
Figure 7: Model calculation of 20 days of photooxidant formation during transport to Langesund, a coastal, rural site in South Norway, from 20 May-9 June 1982. 6h-values for O_3 (relative to a maximum of 82.2 ppb), airborne NMHC (relative to a maximum of 37.3 ppbC) and emitted NMHC along each trajectory (relative to a maximum of 17.8x3.7 ppbC = 66 ppbC).

1a)


++ ETHANE(PPT) 3150.0 ++ ETHENE(PPT) 2740.0
++ PROPANE(PPT) 2280.0 ++ PROPENE(PPT) 1180.0
++ ISO-BUTANE(PPT) 1180.0 ++ ACETYLENE(PPT) 697.0
++ N-BUTANE(PPT) 3020.0 ++ 2-METHYL-BUTANE(PPT) 1100.0
++ N-PENTANE(PPT) 540.0 ++ SUM C2-C5(PPTC) 39250.0
RELATIVE UNITS (1.0 FOR THE MAXIMUM)
0.0
0.1
0.2
0.3
0.4
0.5
0.6
0.7
0.8
0.9
1.0
1.1
1.2
1.3
DAY NUMBER
8
16
24
32
40
48
56
64
72
80
88
96
104
112
120
128
136
144
152
160
168
176

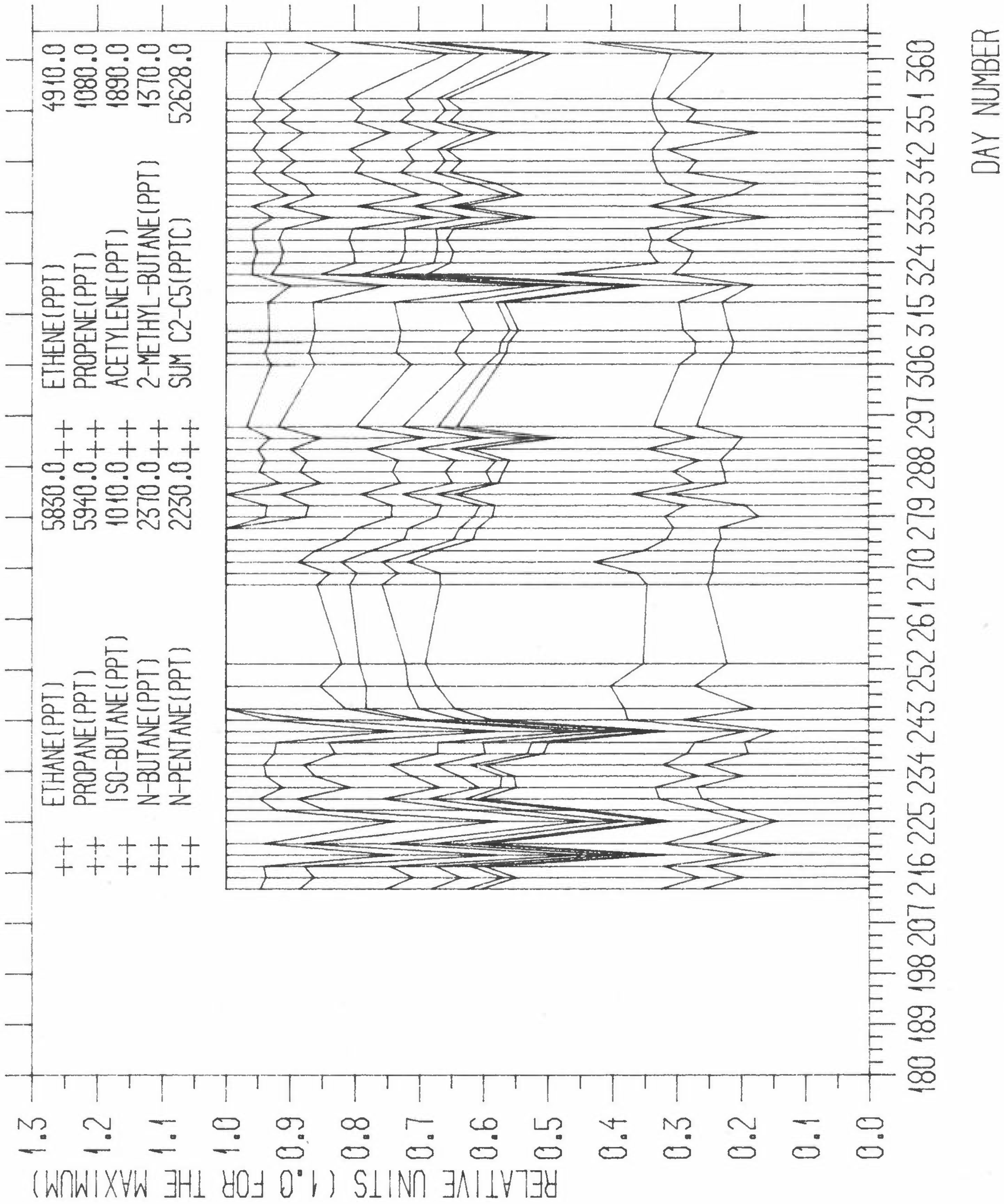
1b)


++ ETHANE(PPT) 5830.0 ++
++ PROPANE(PPT) 5940.0 ++
++ ISO-BUTANE(PPT) 1010.0 ++
++ N-BUTANE(PPT) 2370.0 ++
++ N-PENTANE(PPT) 2230.0 ++
ETHENE(PPT) 4910.0
PROPENE(PPT) 1080.0
ACETYLENE(PPT) 1890.0
2-METHYL-BUTANE(PPT) 1370.0
SUM C2-C5(PPTC) 52628.0
RELATIVE UNITS (1.0 FOR THE MAXIMUM)
0.0
0.1
0.2
0.3
0.4
0.5
0.6
0.7
0.8
0.9
1.0
1.1
1.2
1.3
180 189 198 207 216 225 234 243 252 261 270 279 288 297 306 315 324 333 342 351 360
DAY NUMBER

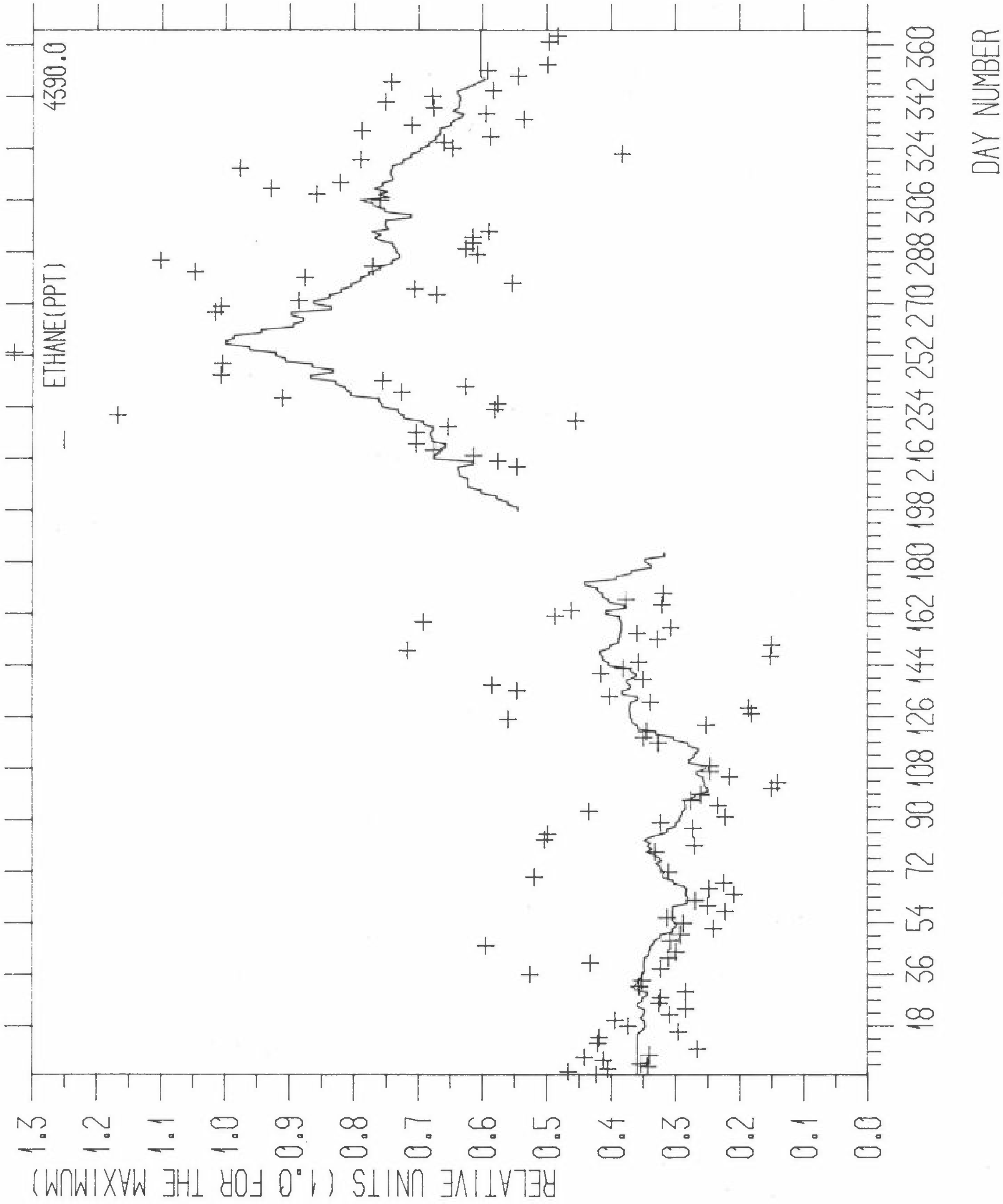

++ ETHANE(PPT) 3150.0
++ PROPANE(PPT) 2280.0
++ ISO-BUTANE(PPT) 1180.0
++ N-BUTANE(PPT) 3020.0
++ N-PENTANE(PPT) 540.0
++ ETHENE(PPT) 2740.0
++ PROPENE(PPT) 1180.0
++ ACETYLENE(PPT) 697.0
++ 2-METHYL-BUTANE(PPT) 1100.0
++ SUM C2-C5(PPTC) 39250.0
RELATIVE UNITS (1.0 FOR THE MAXIMUM)
1.3
1.2
1.1
1.0
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0.0
8
16
24
32
40
48
56
64
72
80
88
96
104
112
120
128
136
144
152
160
168
176
DAY NUMBER

1c)

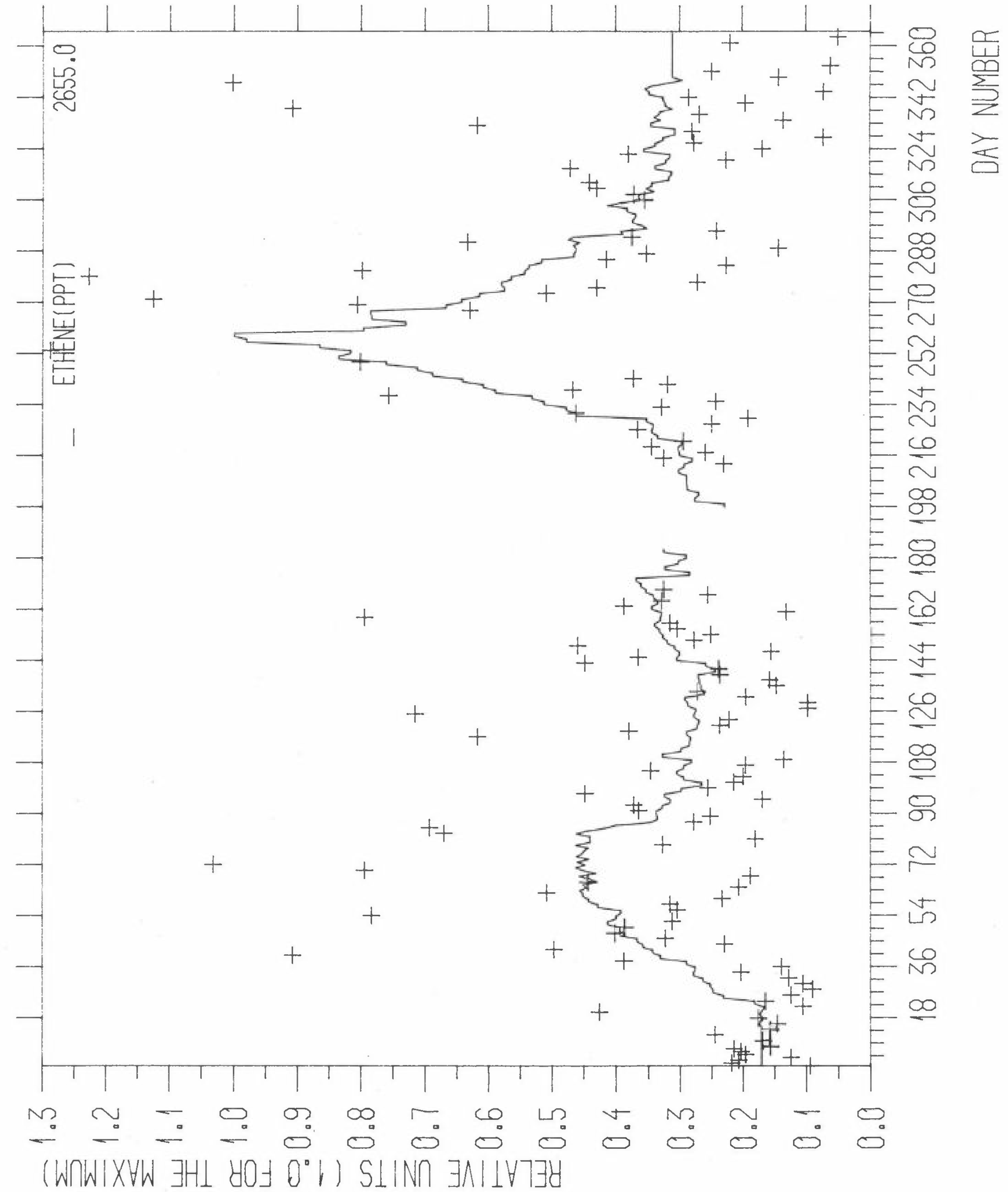
1d)


++ ETHANE(PPT)
++ PROPANE(PPT)
++ ISO-BUTANE(PPT)
++ N-BUTANE(PPT)
++ N-PENTANE(PPT)
5830.0 ++ ETHENE(PPT) 4910.0
5940.0 ++ PROPENE(PPT) 1080.0
1010.0 ++ ACETYLENE(PPT) 1890.0
2370.0 ++ 2-METHYL-BUTANE(PPT) 1370.0
2230.0 ++ SUM C2-C5(PPTC) 52628.0
RELATIVE UNITS (1.0 FOR THE MAXIMUM)
1.3
1.2
1.1
1.0
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0.0
180 189 198 207 216 225 234 243 252 261 270 279 288 297 306 315 324 333 342 351 360
DAY NUMBER

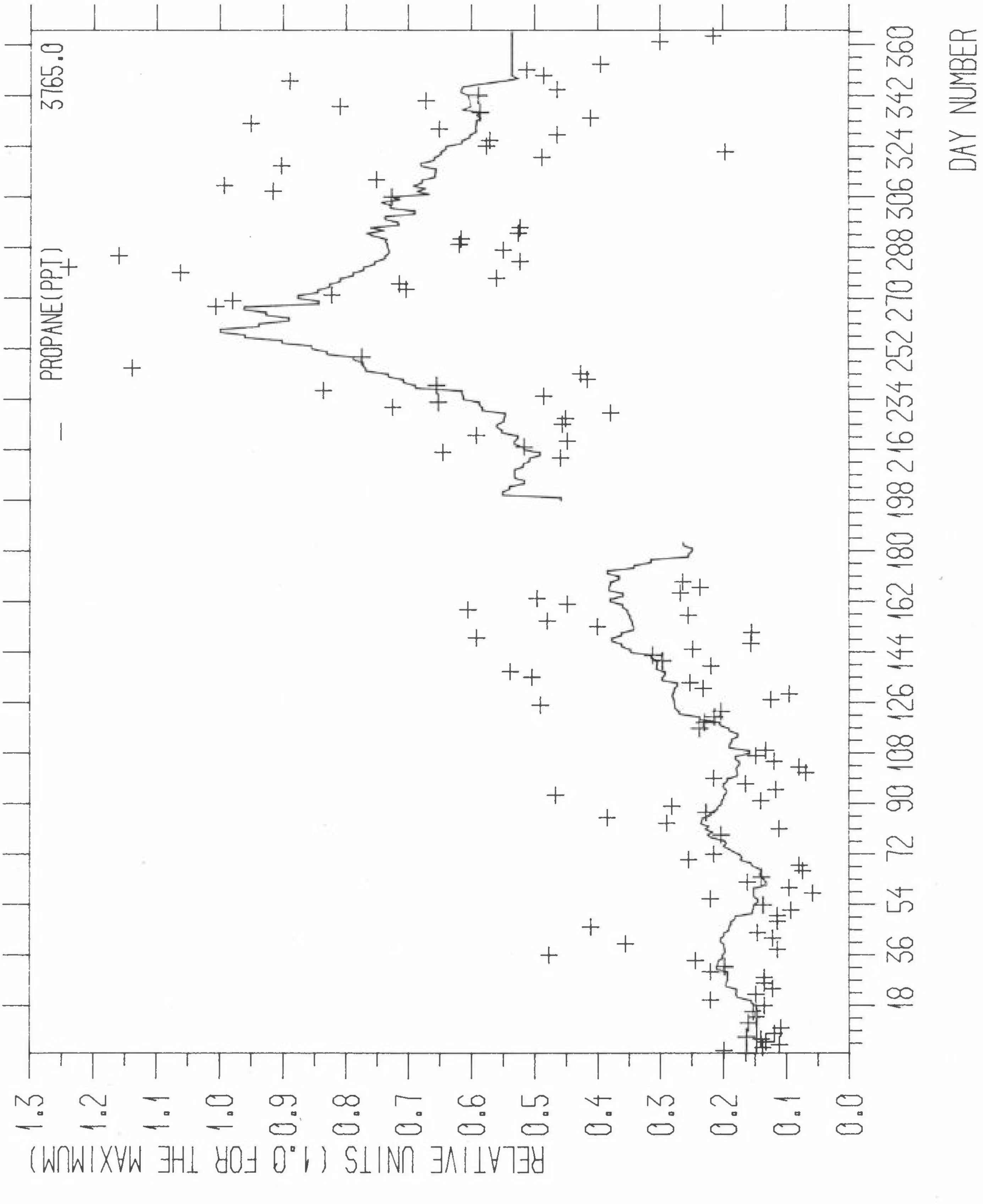
2a)


4390.0
ETHANE(PPT)
DAY NUMBER
18
36
54
72
90
108
126
144
162
180
198
216
234
252
270
288
306
324
342
360
RELATIVE UNITS (1.0 FOR THE MAXIMUM)
0.0
0.1
0.2
0.3
0.4
0.5
0.6
0.7
0.8
0.9
1.0
1.1
1.2
1.3

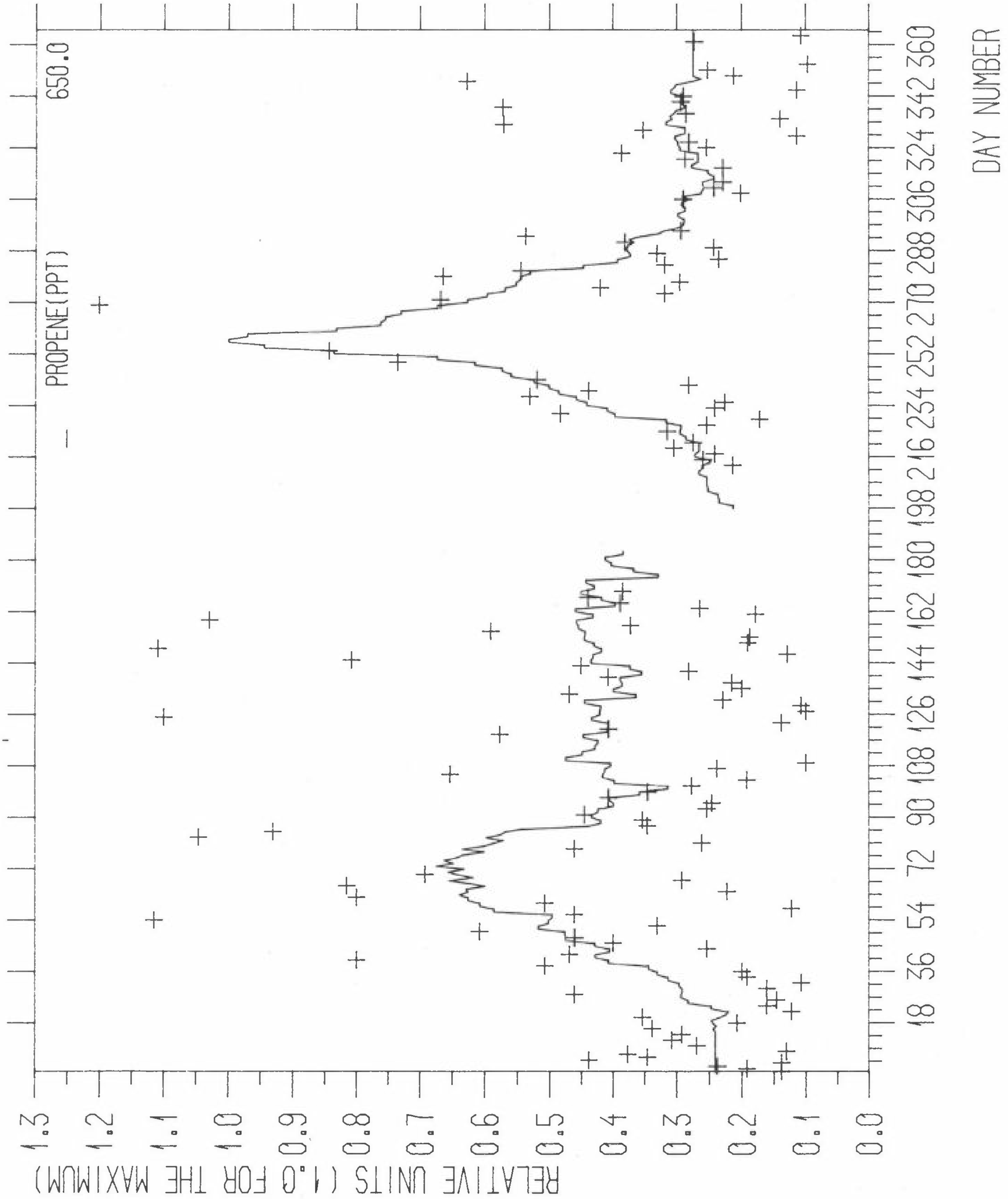
2b)


ETHENE(PPT)
2655.0
RELATIVE UNITS (1.0 FOR THE MAXIMUM)
0.0
0.1
0.2
0.3
0.4
0.5
0.6
0.7
0.8
0.9
1.0
1.1
1.2
1.3
DAY NUMBER
18
36
54
72
90
108
126
144
162
180
198
216
234
252
270
288
306
324
342
360

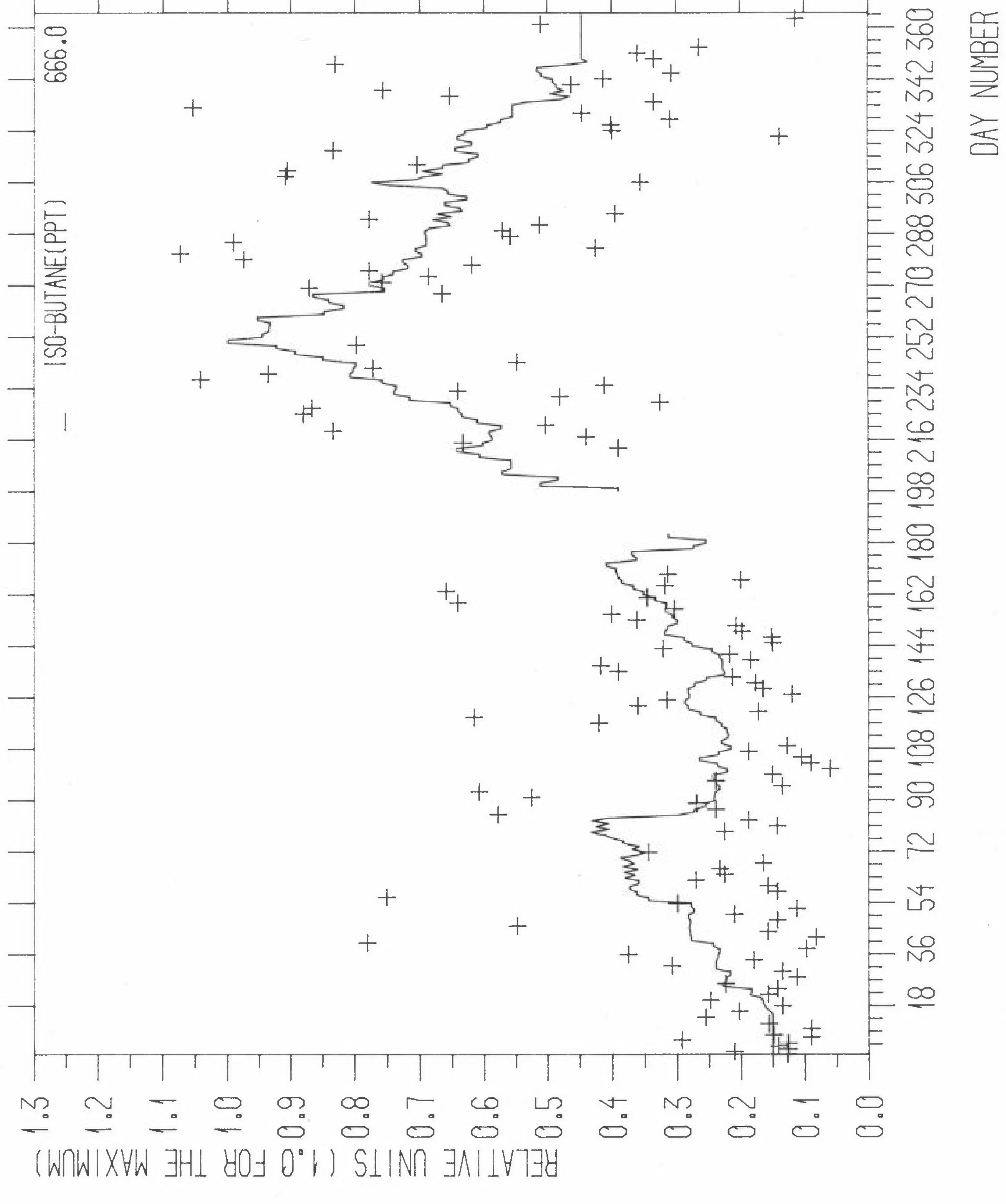
2c)


PROPANE(PPT)
3765.0
RELATIVE UNITS (1.0 FOR THE MAXIMUM)
0.0
0.1
0.2
0.3
0.4
0.5
0.6
0.7
0.8
0.9
1.0
1.1
1.2
1.3
DAY NUMBER
18
36
54
72
90
108
126
144
162
180
198
216
234
252
270
288
306
324
342
360

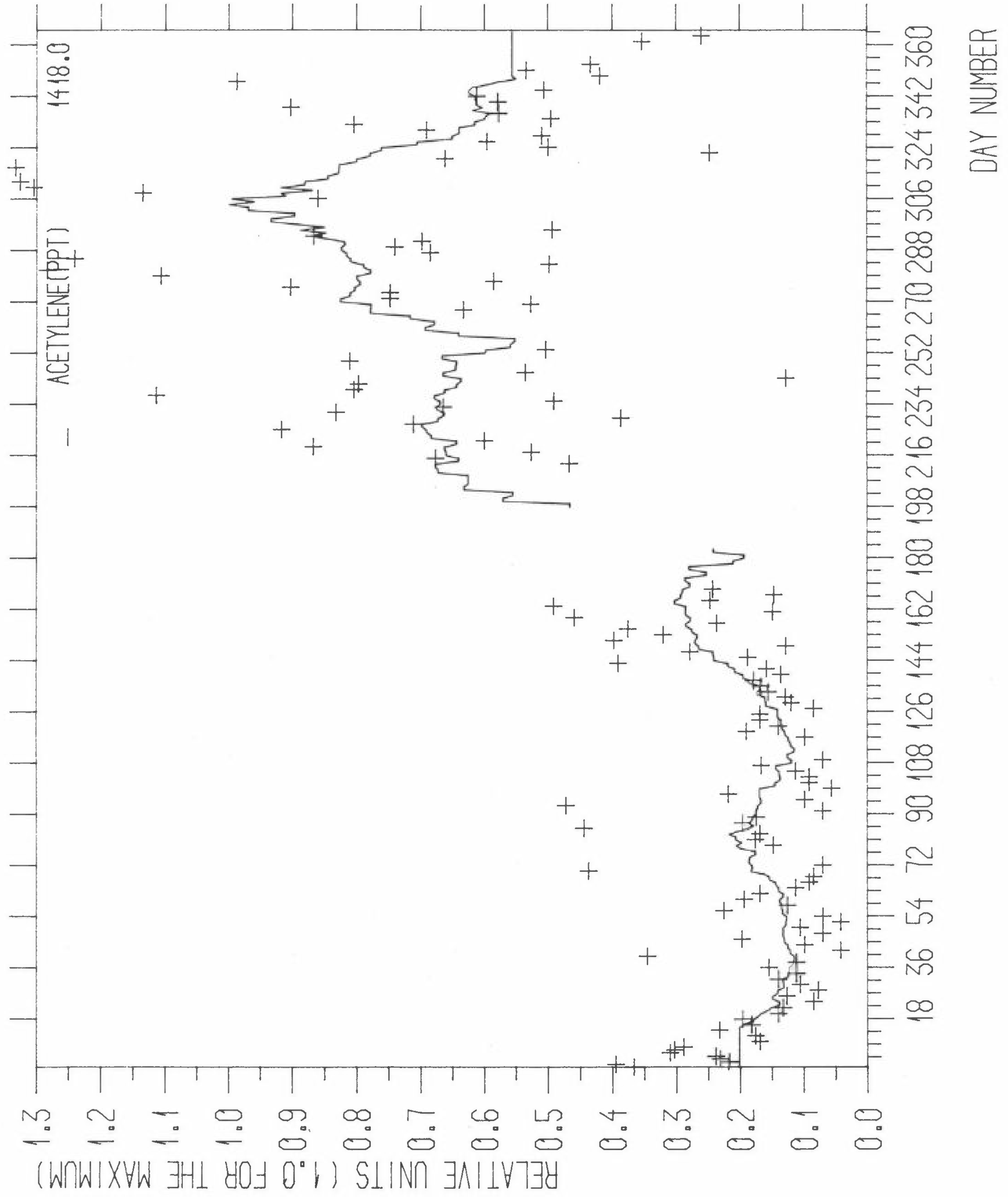
2d)


PROPENE(PPT)
650.0
DAY NUMBER
18
36
54
72
90
108
126
144
162
180
198
216
234
252
270
288
306
324
342
360
RELATIVE UNITS (1.0 FOR THE MAXIMUM)
0.0
0.1
0.2
0.3
0.4
0.5
0.6
0.7
0.8
0.9
1.0
1.1
1.2
1.3

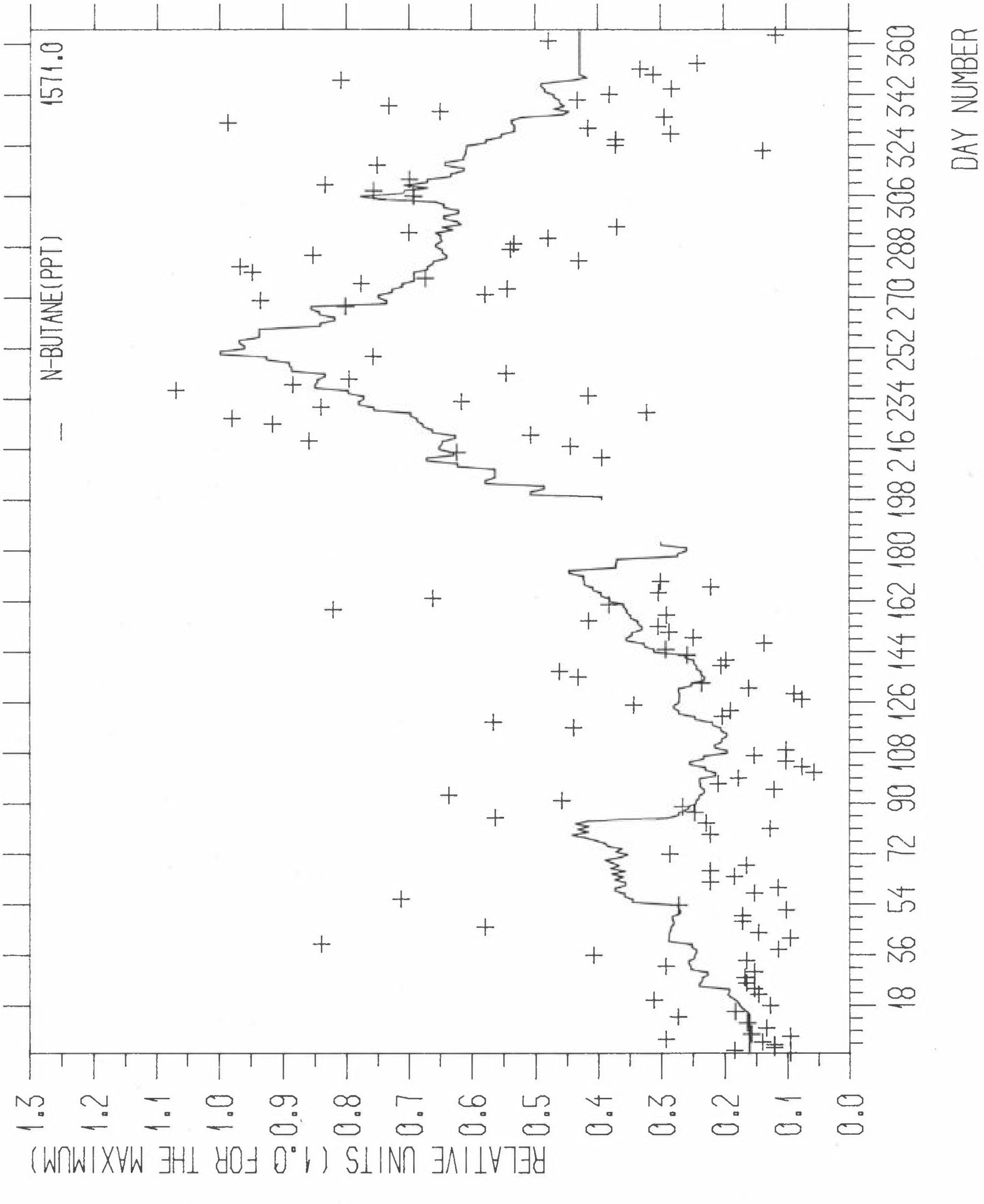
2e)


ISO-BUTANE(PPT)
666.0
RELATIVE UNITS (1.0 FOR THE MAXIMUM)
1.3
1.2
1.1
1.0
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0.0
DAY NUMBER
18
36
54
72
90
108
126
144
162
180
198
216
234
252
270
288
306
324
342
360

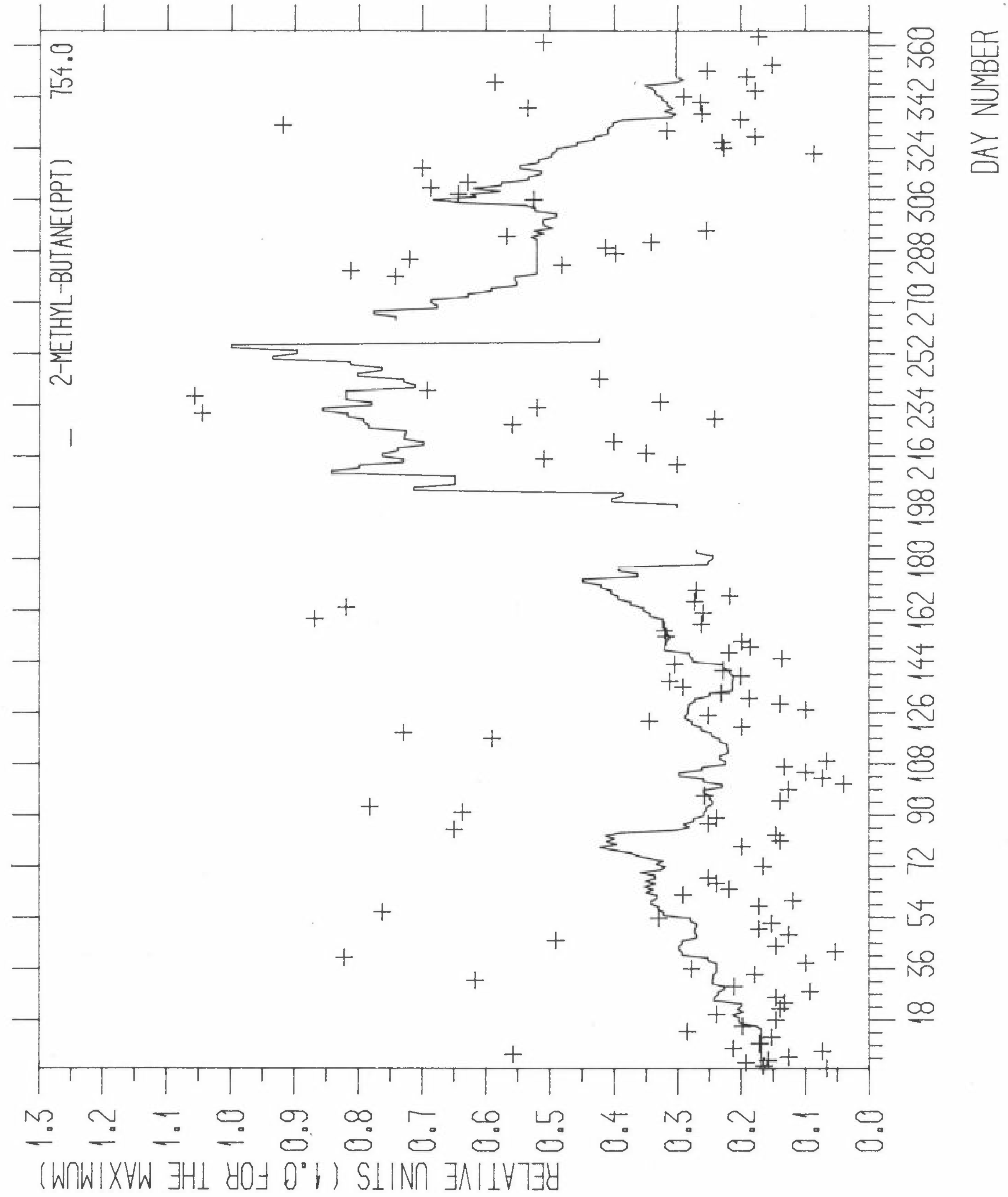
2f)


ACETYLENE(PPT)
1418.0
DAY NUMBER
18
36
54
72
90
108
126
144
162
180
198
216
234
252
270
288
306
324
342
360
RELATIVE UNITS (1.0 FOR THE MAXIMUM)
0.0
0.1
0.2
0.3
0.4
0.5
0.6
0.7
0.8
0.9
1.0
1.1
1.2
1.3

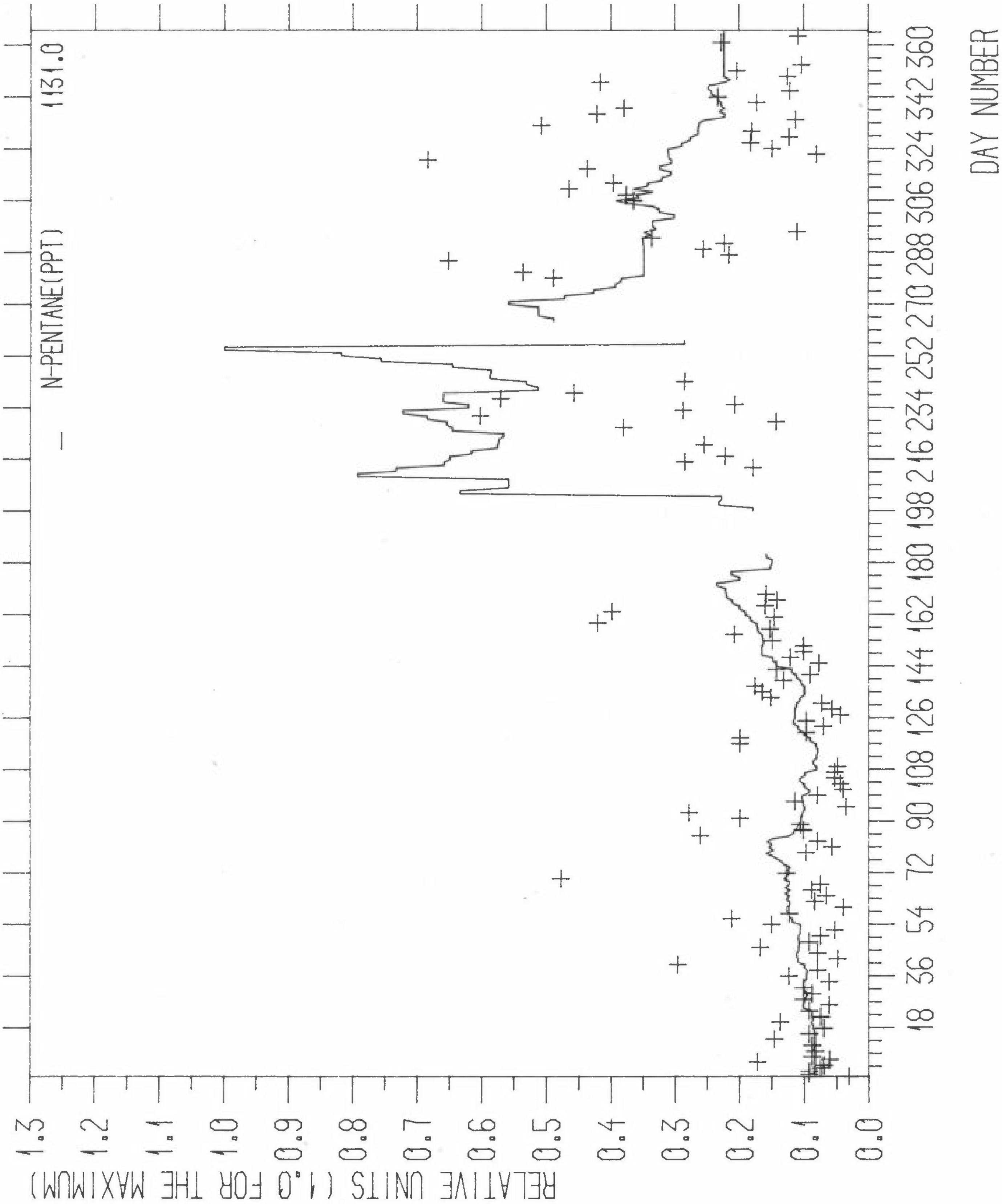
2g)


N-BUTANE(PPT)
1571.0
RELATIVE UNITS (1.0 FOR THE MAXIMUM)
0.0
0.1
0.2
0.3
0.4
0.5
0.6
0.7
0.8
0.9
1.0
1.1
1.2
1.3
DAY NUMBER
18
36
54
72
90
108
126
144
162
180
198
216
234
252
270
288
306
324
342
360

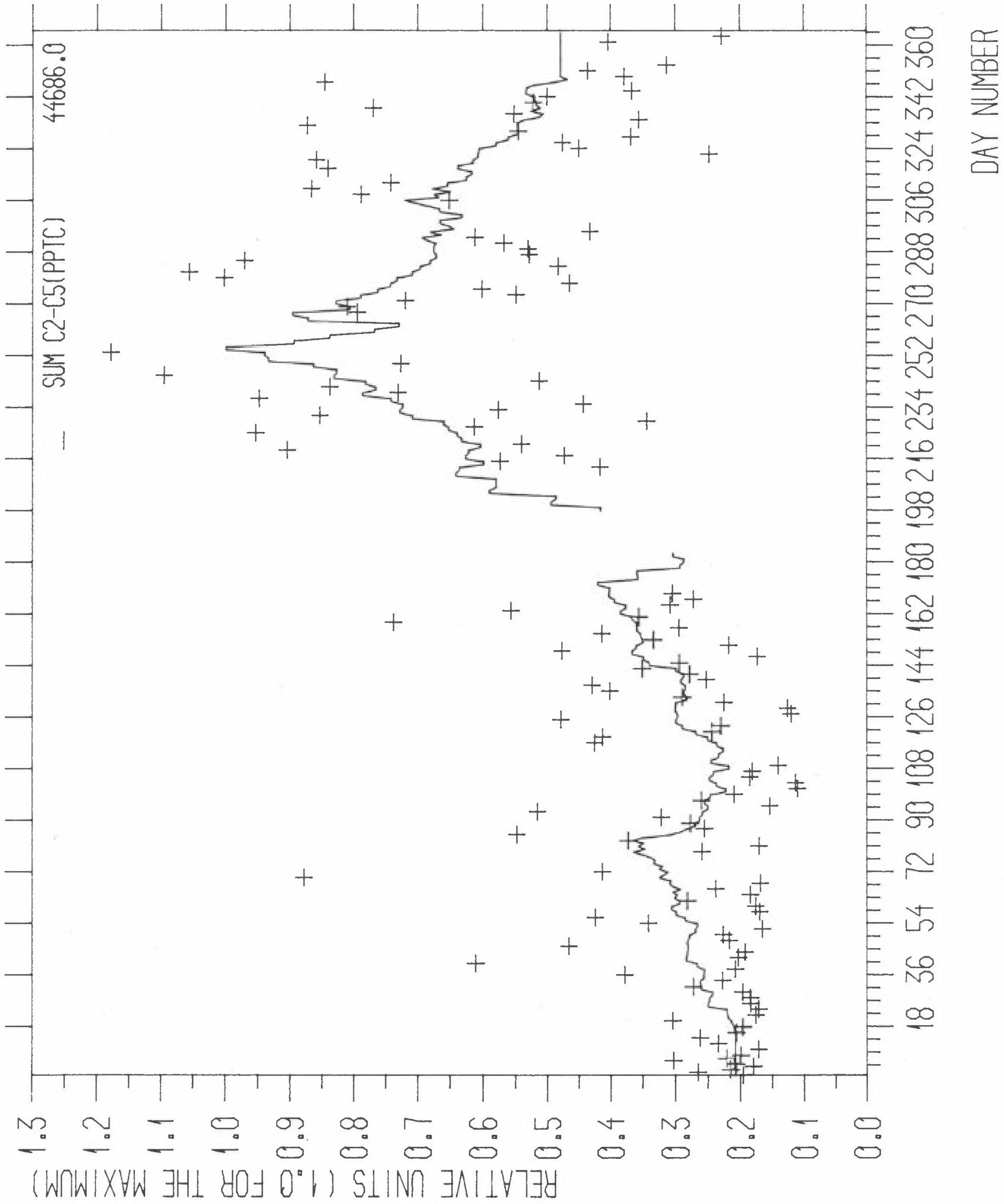
2h)


2-METHYL-BUTANE(PPT)
754.0
DAY NUMBER
18
36
54
72
90
108
126
144
162
180
198
216
234
252
270
288
306
324
342
360
RELATIVE UNITS (1.0 FOR THE MAXIMUM)
1.3
1.2
1.1
1.0
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0.0

2i)

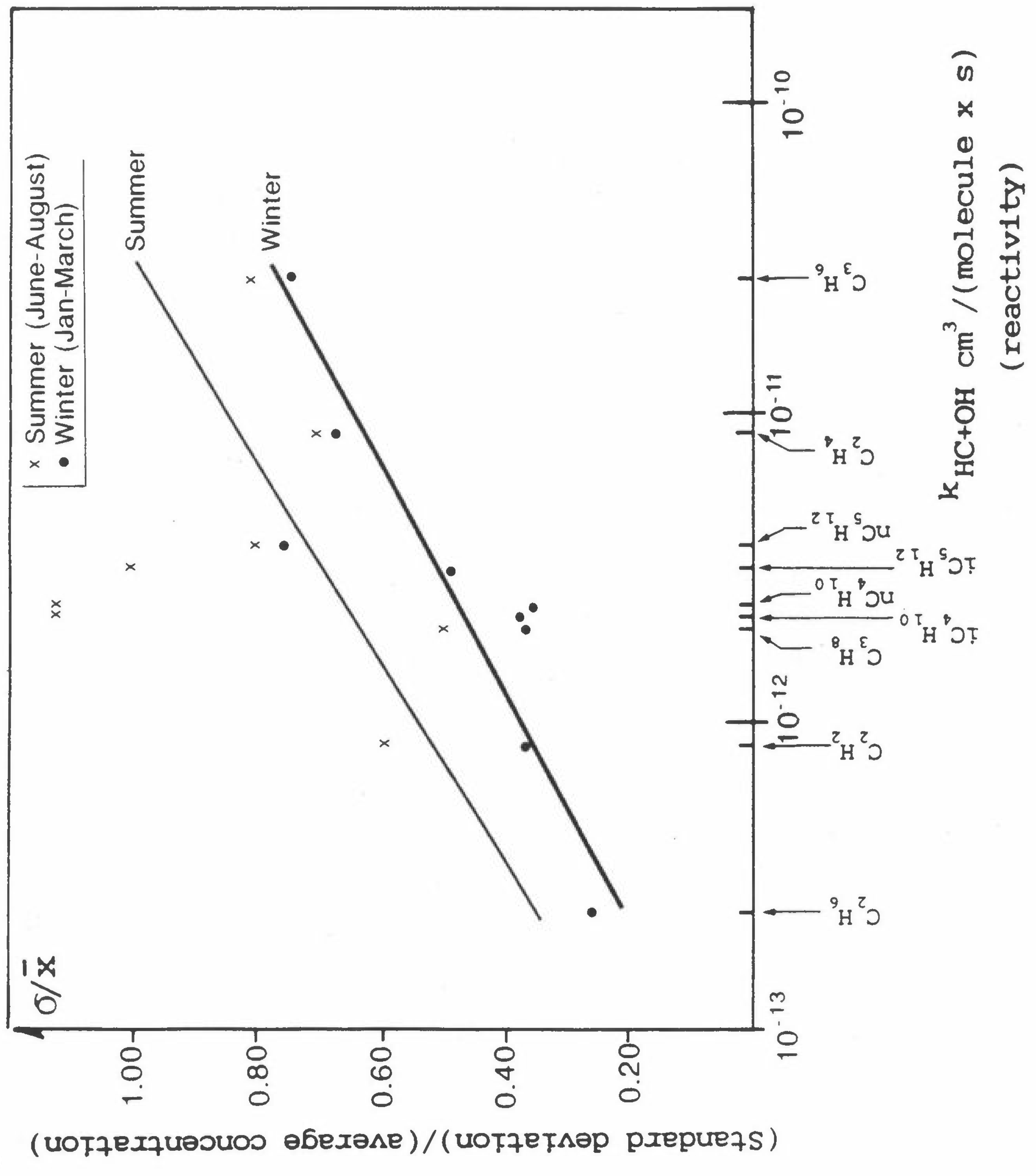

N-PENTANE(PPT)
1131.0
DAY NUMBER
18
36
54
72
90
108
126
144
162
180
198
216
234
252
270
288
306
324
342
360
RELATIVE UNITS (1.0 FOR THE MAXIMUM)
0.0
0.1
0.2
0.3
0.4
0.5
0.6
0.7
0.8
0.9
1.0
1.1
1.2
1.3

2j)

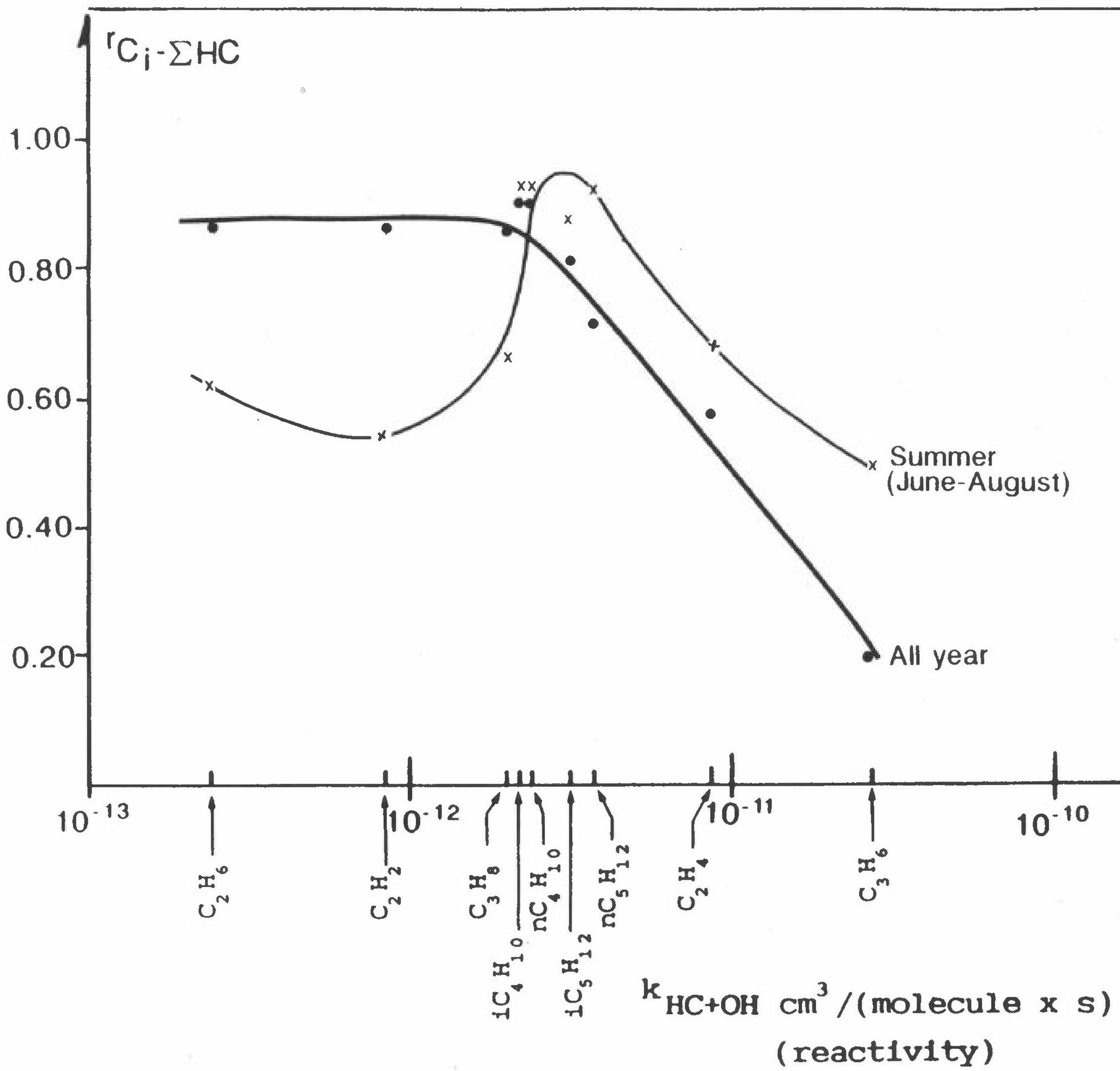


SUM C2-C5(PPTC)
44686.0
DAY NUMBER
18
36
54
72
90
108
126
144
162
180
198
216
234
252
270
288
306
324
342
360
RELATIVE UNITS (1.0 FOR THE MAXIMUM)
0.0
0.1
0.2
0.3
0.4
0.5
0.6
0.7
0.8
0.9
1.0
1.1
1.2
1.3

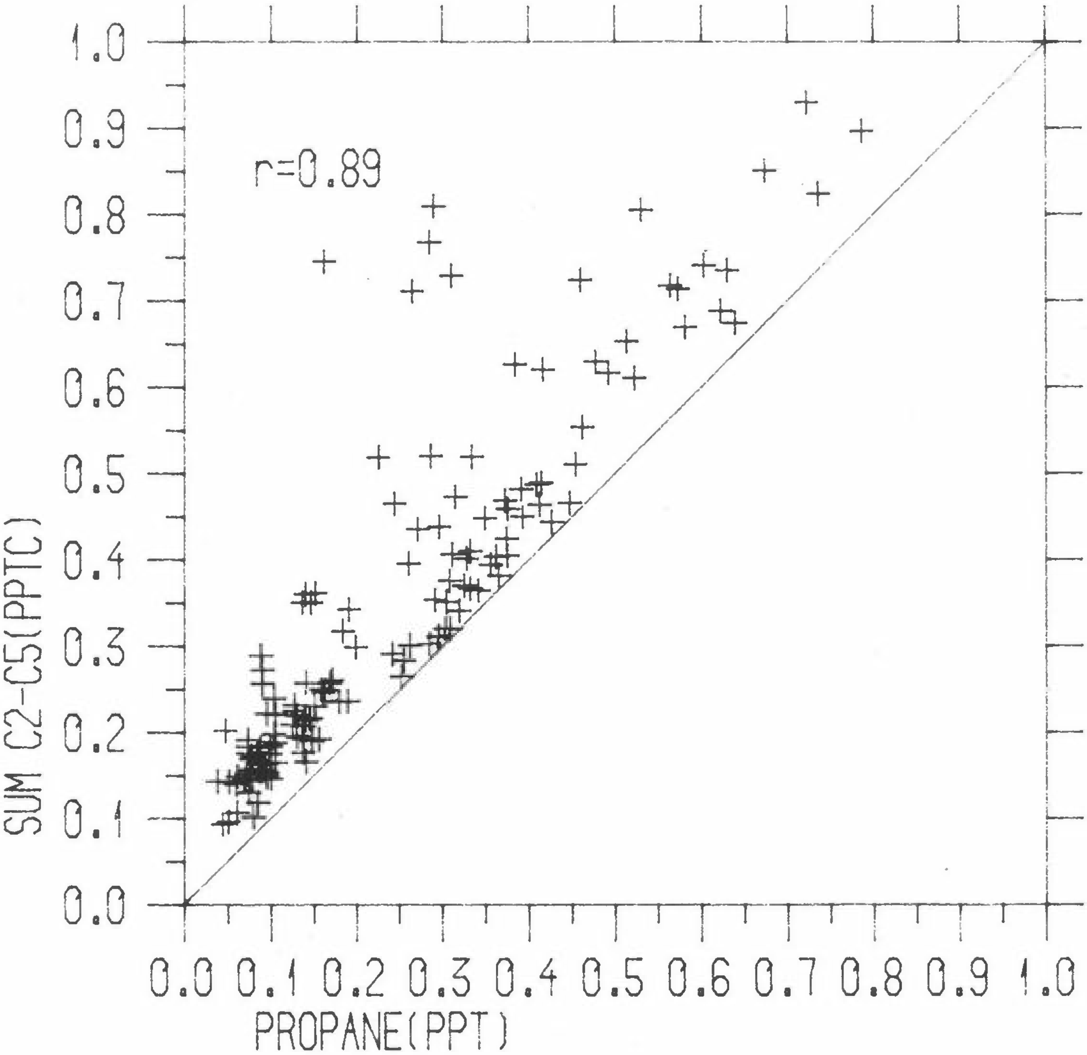
3)


× Summer (June-August)
● Winter (Jan-March)
Summer
Winter
$\sigma/\bar{x}$
1.00
0.80
0.60
0.40
0.20
(Standard deviation)/(average concentration)
10^{-13}
10^{-12}
10^{-11}
10^{-10}
C_2H_6
C_2H_2
C_3H_8
iC_4H_{10}
nC_4H_{10}
iC_5H_{12}
nC_5H_{12}
C_2H_4
C_3H_6
k_{HC+OH} cm^3/(molecule x s)
(reactivity)

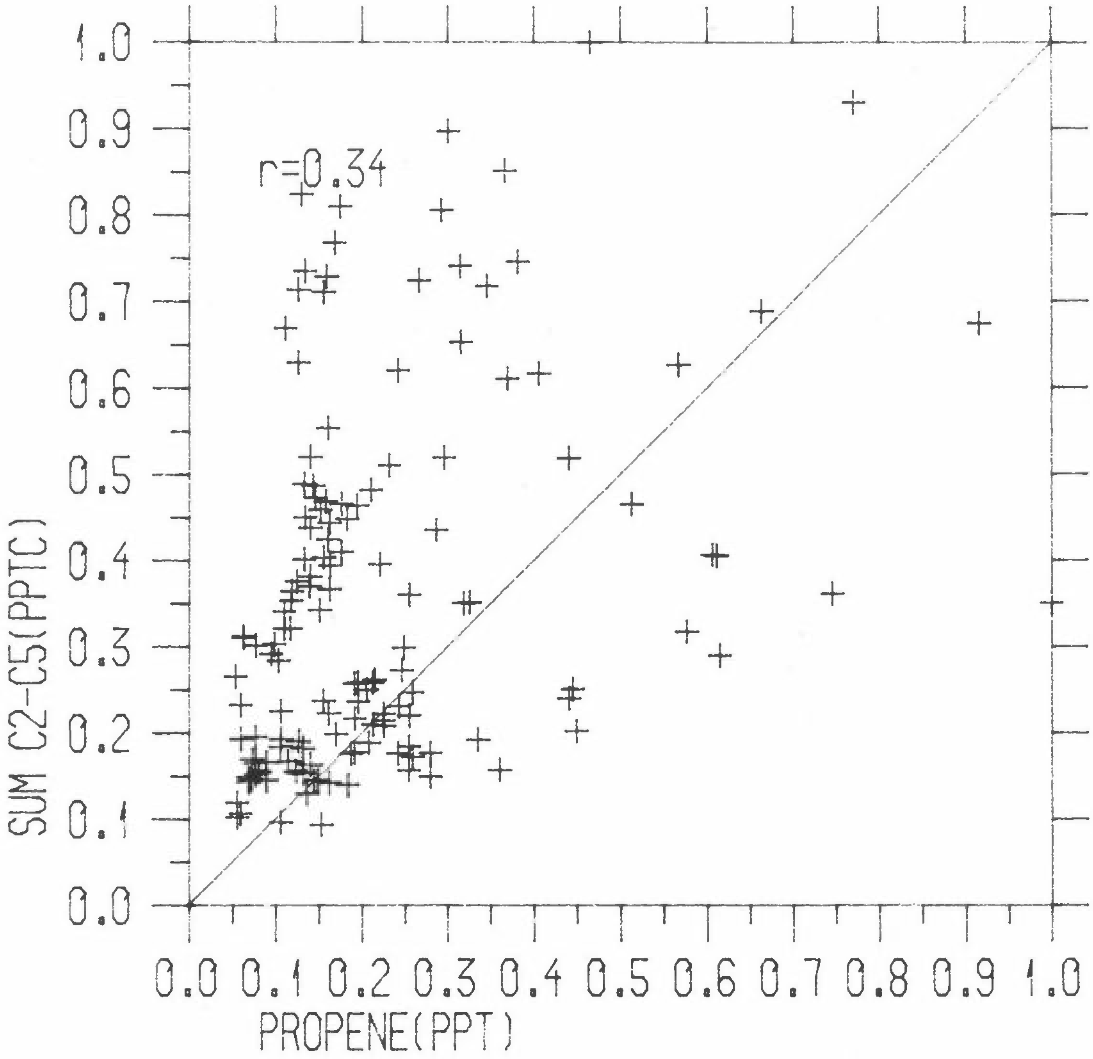
4)


$r_{C_i-\Sigma HC}$
1.00
0.80
0.60
0.40
0.20
Summer (June-August)
All year
10^{-13}
10^{-12}
10^{-11}
10^{-10}
C_2H_6
C_2H_2
C_3H_8
iC_4H_{10}
nC_4H_{10}
iC_5H_{12}
nC_5H_{12}
C_2H_4
C_3H_6
k_{HC+OH} $cm^3/(molecule \times s)$
(reactivity)

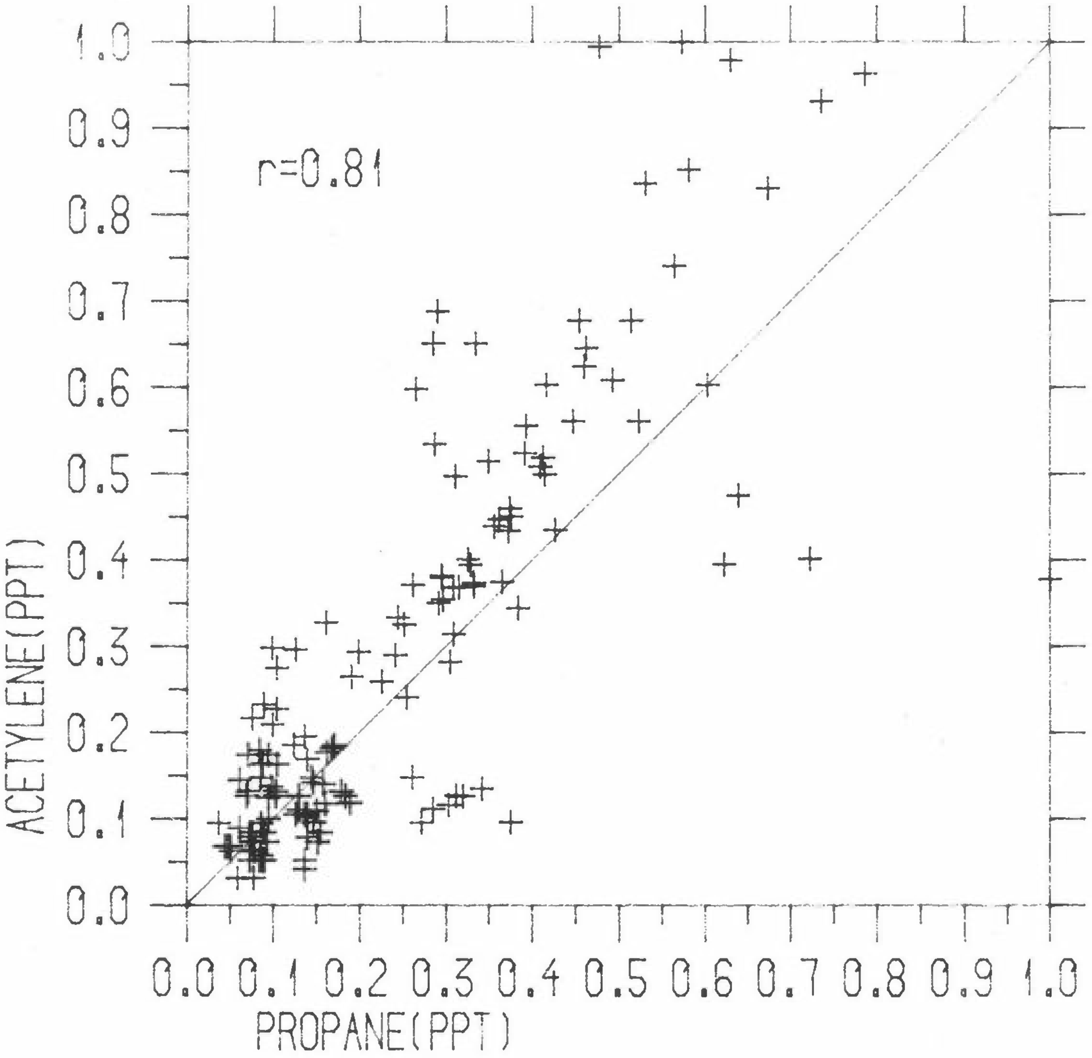
5a)



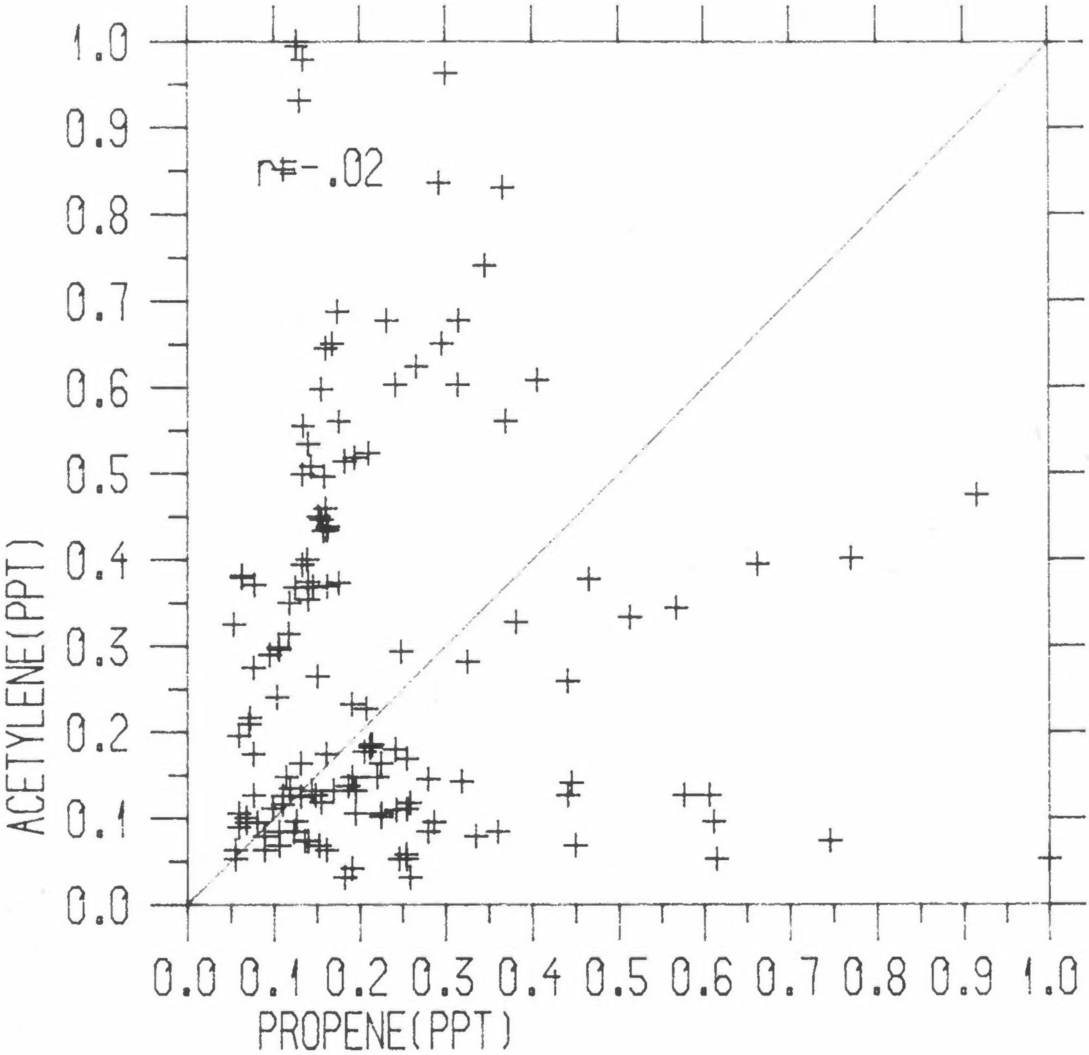
5b)



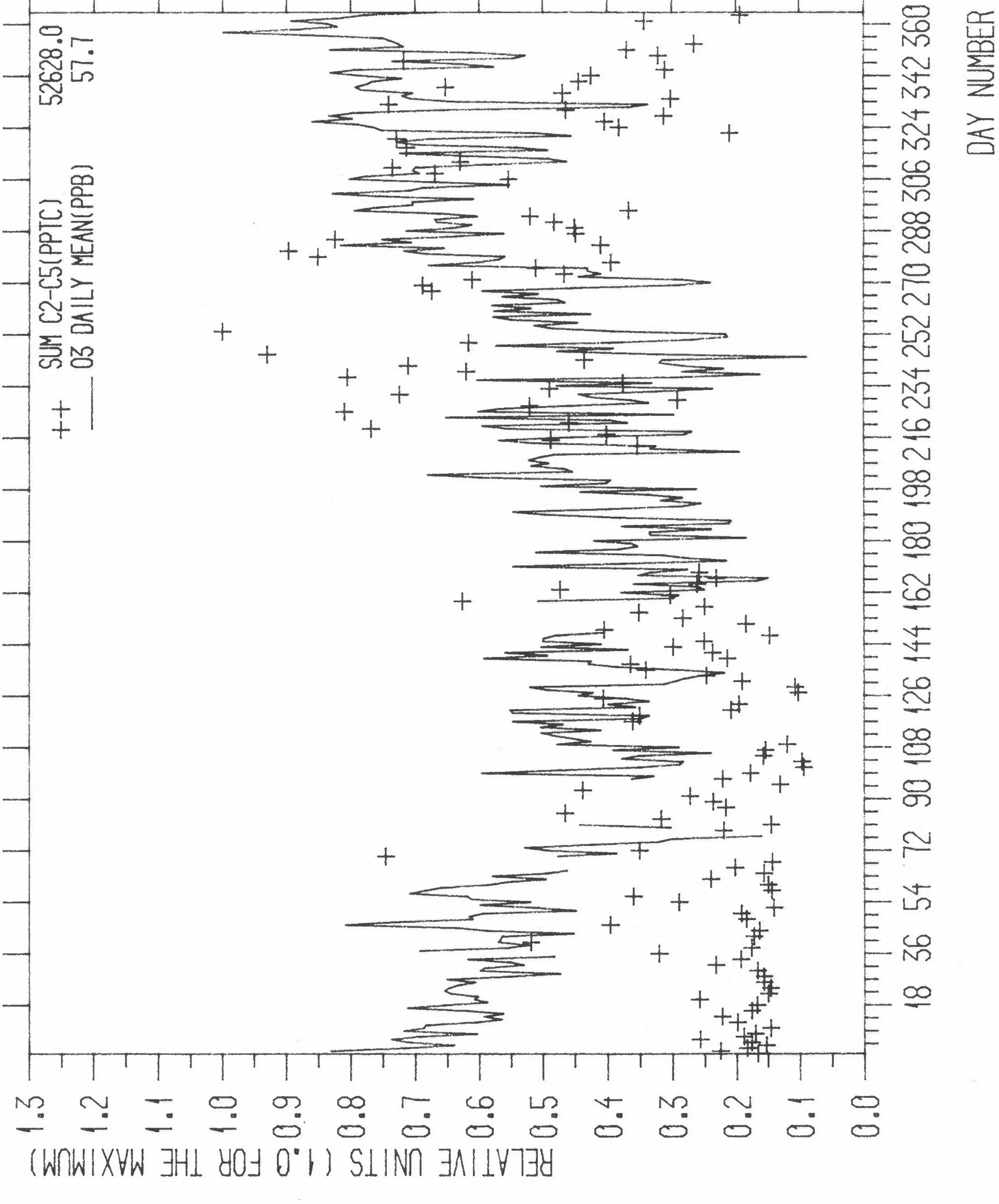
5c)



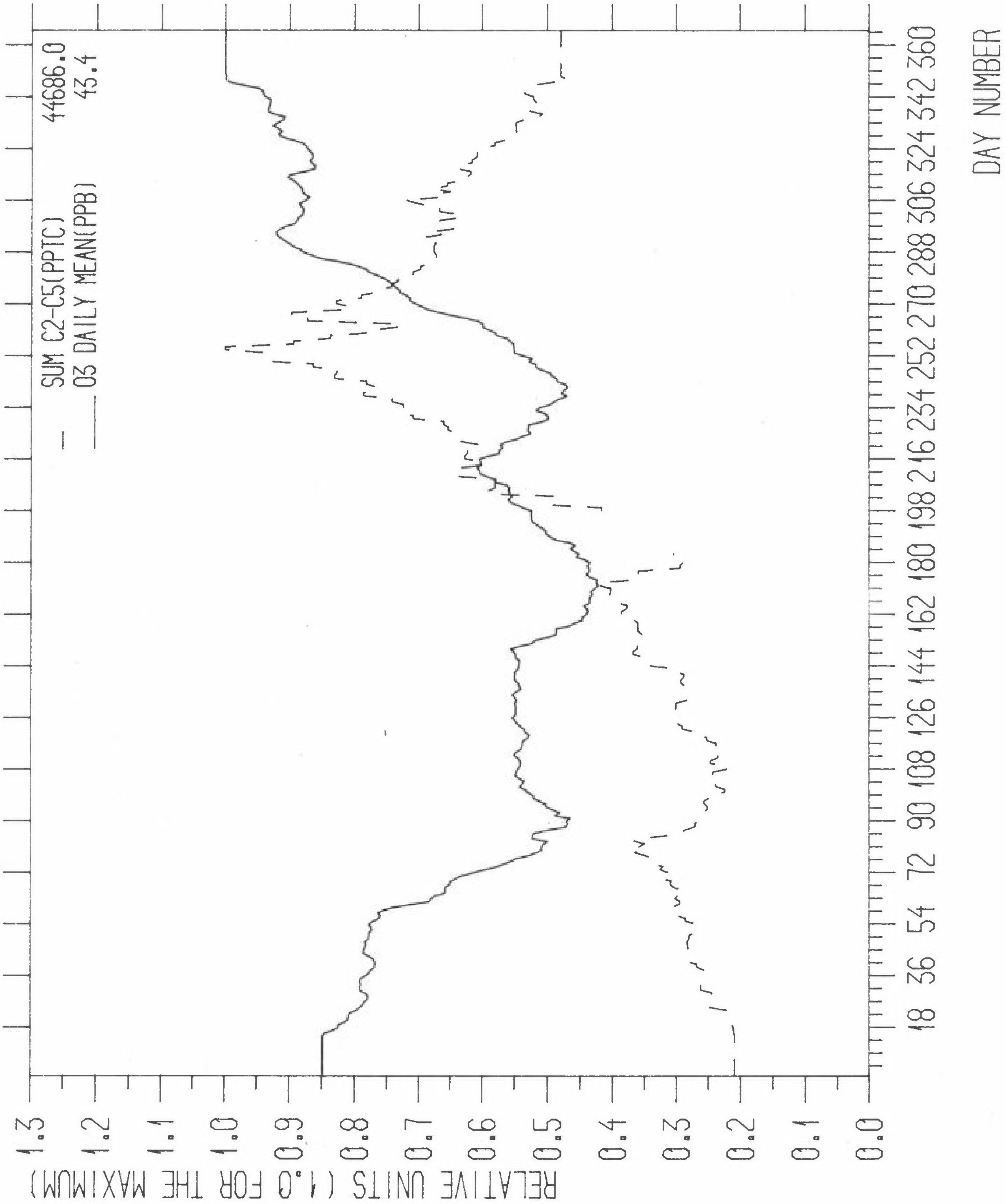
5d)



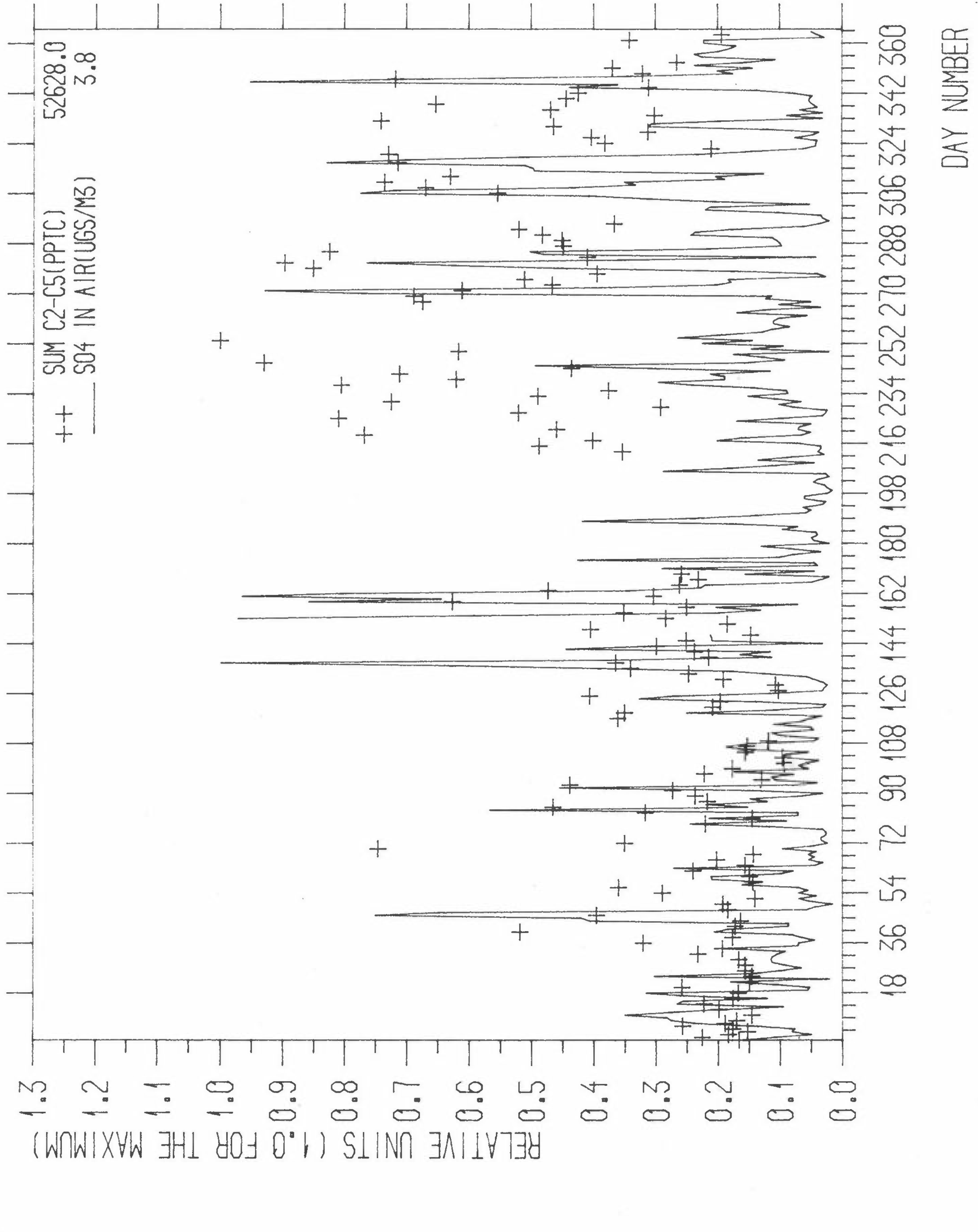
6a)


++ SUM C2-C5(PPTC) 52628.0
___ O3 DAILY MEAN(PPB) 57.7
RELATIVE UNITS (1.0 FOR THE MAXIMUM)
0.0
0.1
0.2
0.3
0.4
0.5
0.6
0.7
0.8
0.9
1.0
1.1
1.2
1.3
DAY NUMBER
18
36
54
72
90
108
126
144
162
180
198
216
234
252
270
288
306
324
342
360

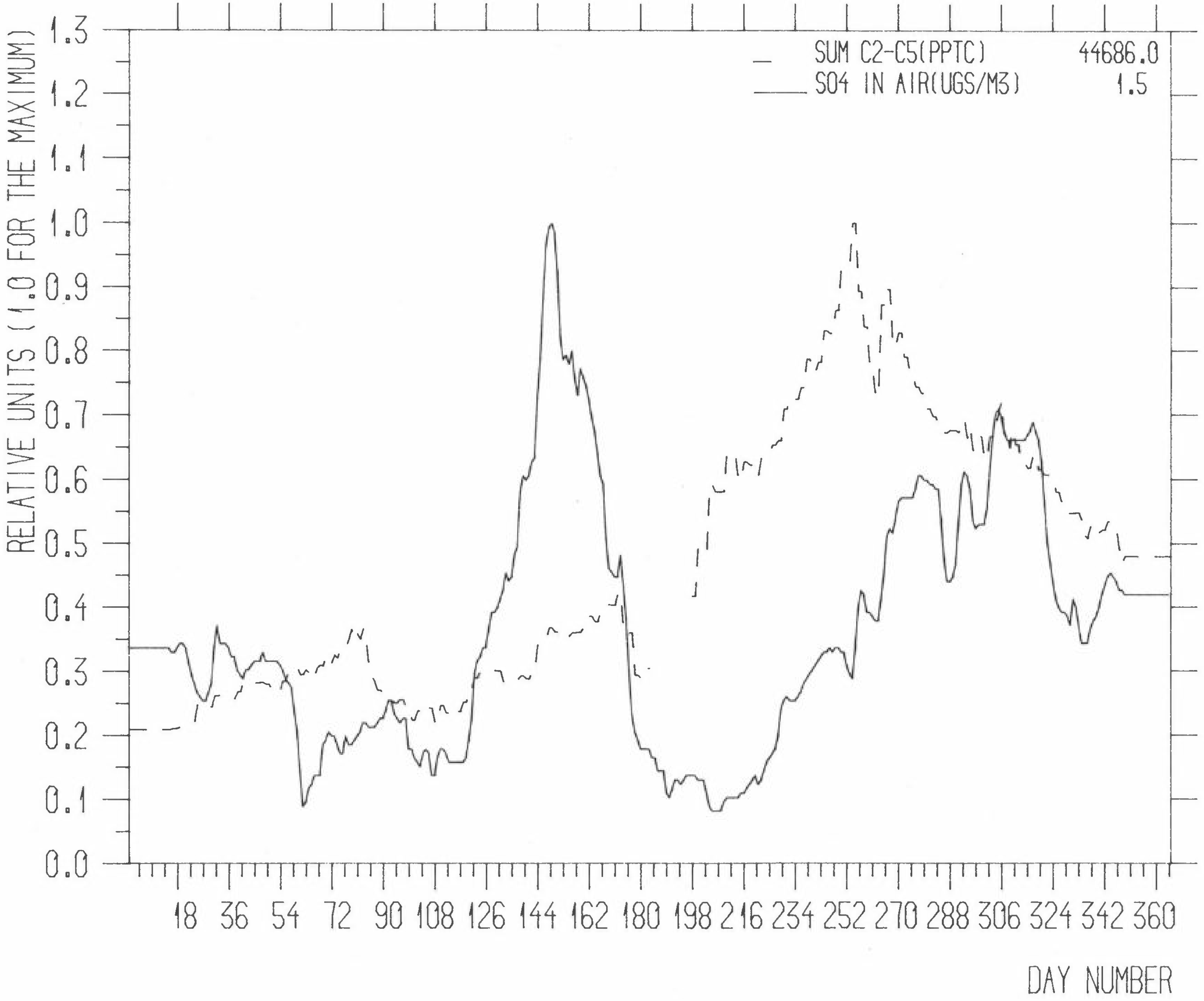
6b)


SUM C2-C5(PPTC) 44686.0
O3 DAILY MEAN(PPB) 43.4
RELATIVE UNITS (1.0 FOR THE MAXIMUM)
1.3
1.2
1.1
1.0
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0.0
DAY NUMBER
18
36
54
72
90
108
126
144
162
180
198
216
234
252
270
288
306
324
342
360

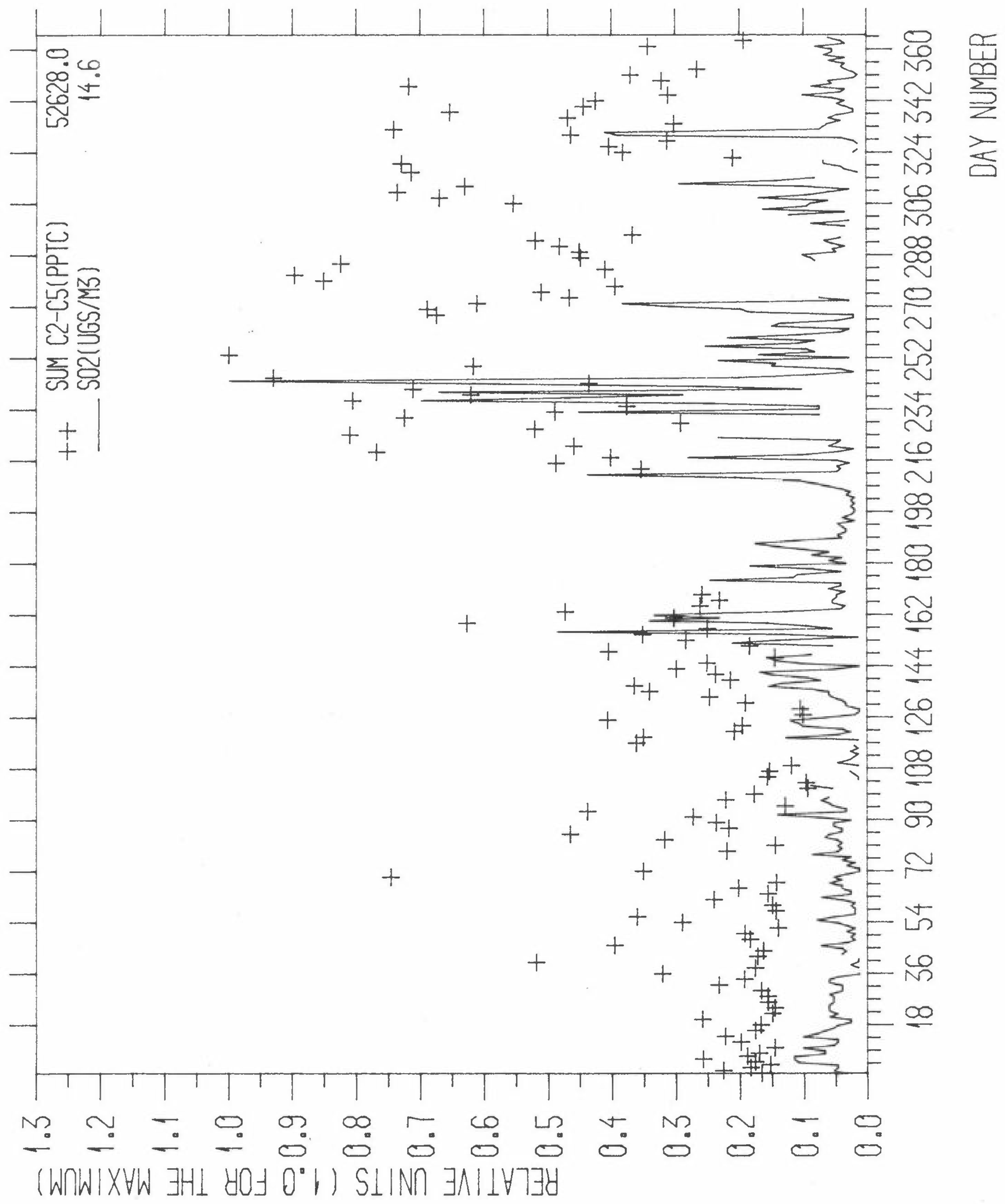
6c)


++ SUM C2-C5(PPTC) 52628.0
___ SO4 IN AIR(UGS/M3) 3.8
RELATIVE UNITS (1.0 FOR THE MAXIMUM)
0.0
0.1
0.2
0.3
0.4
0.5
0.6
0.7
0.8
0.9
1.0
1.1
1.2
1.3
DAY NUMBER
18
36
54
72
90
108
126
144
162
180
198
216
234
252
270
288
306
324
342
360

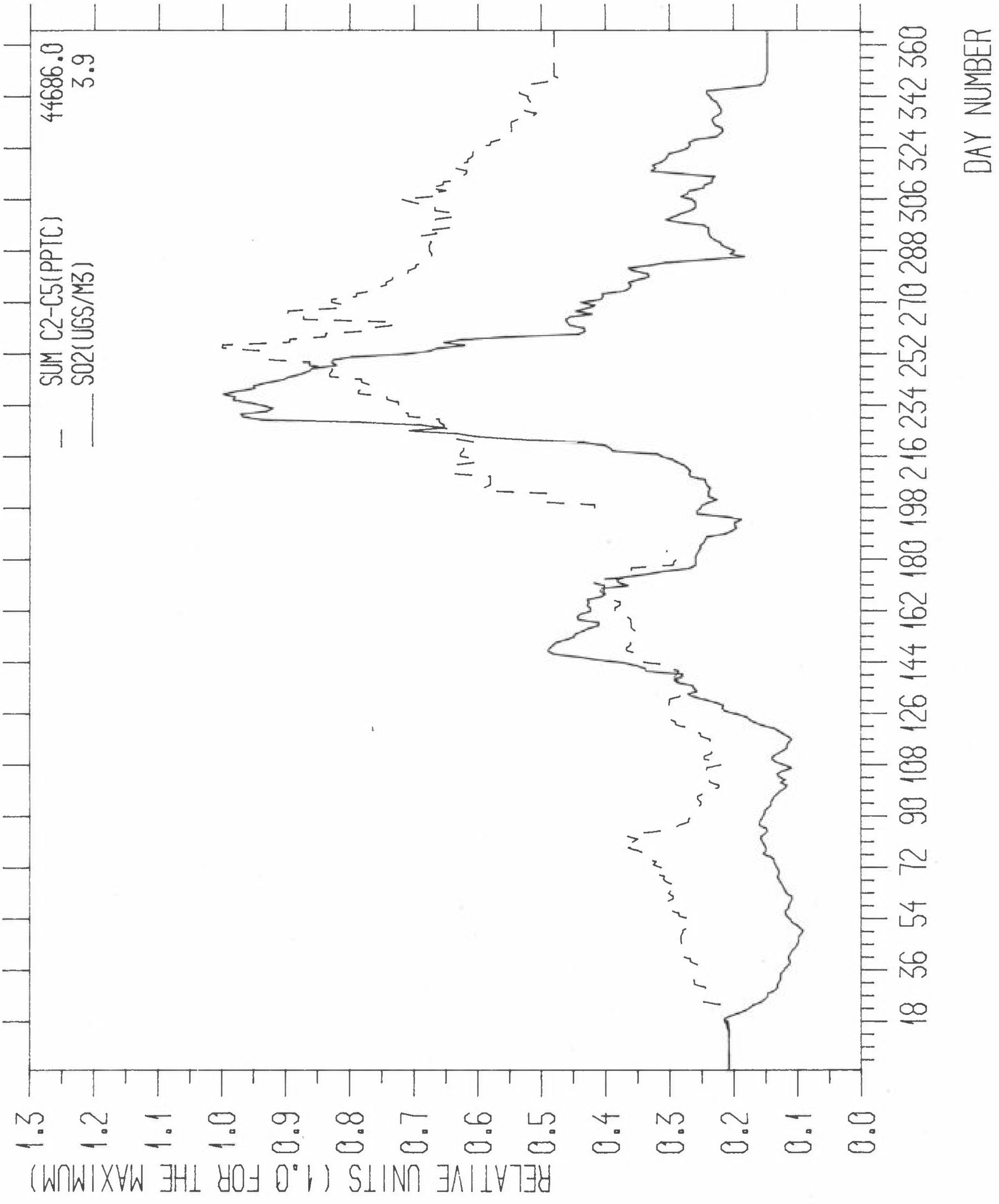
6d)


SUM C2-C5(PPTC) 44686.0
SO4 IN AIR(UGS/M3) 1.5
RELATIVE UNITS (1.0 FOR THE MAXIMUM)
0.0
0.1
0.2
0.3
0.4
0.5
0.6
0.7
0.8
0.9
1.0
1.1
1.2
1.3
18
36
54
72
90
108
126
144
162
180
198
216
234
252
270
288
306
324
342
360
DAY NUMBER

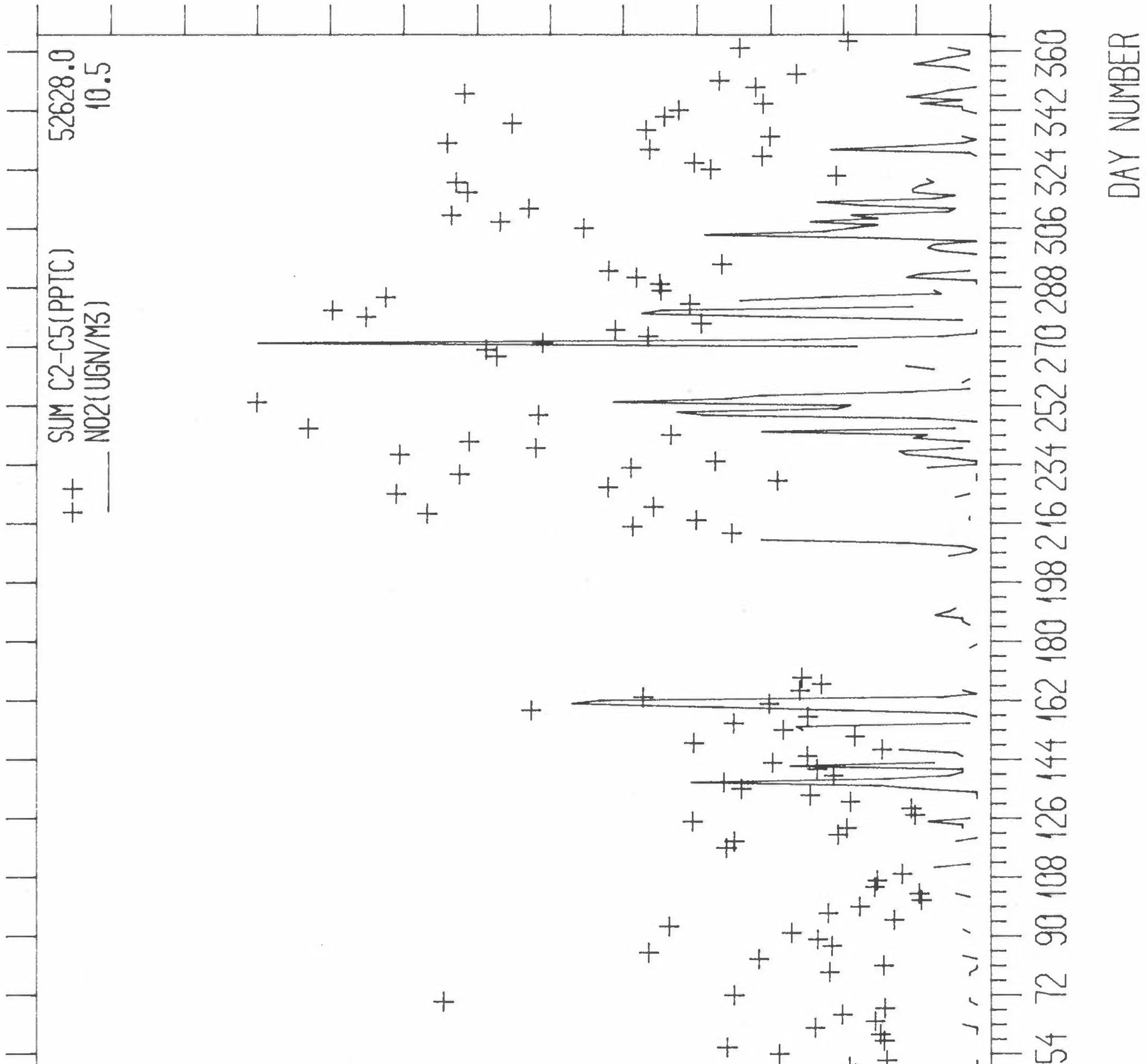
6e)


++ SUM C2-C5(PPTC) 52628.0
— SO2(UGS/M3) 14.6
DAY NUMBER
18
36
54
72
90
108
126
144
162
180
198
216
234
252
270
288
306
324
342
360
RELATIVE UNITS (1.0 FOR THE MAXIMUM)
0.0
0.1
0.2
0.3
0.4
0.5
0.6
0.7
0.8
0.9
1.0
1.1
1.2
1.3

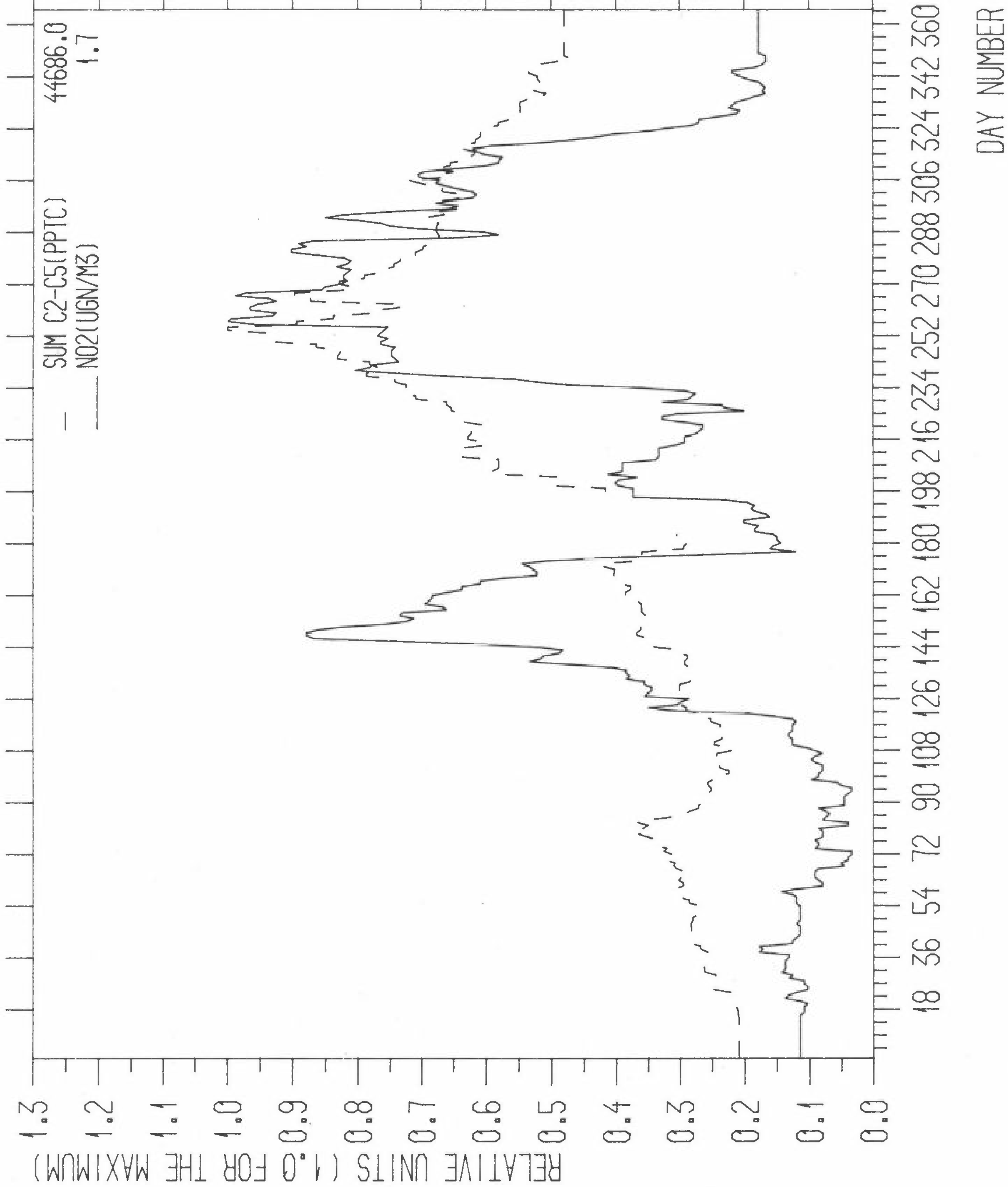
6f)


SUM C2-C5(PPTC) 44686.0
SO2(UGS/M3) 3.9
DAY NUMBER
18 36 54 72 90 108 126 144 162 180 198 216 234 252 270 288 306 324 342 360
RELATIVE UNITS (1.0 FOR THE MAXIMUM)
0.0 0.1 0.2 0.3 0.4 0.5 0.6 0.7 0.8 0.9 1.0 1.1 1.2 1.3

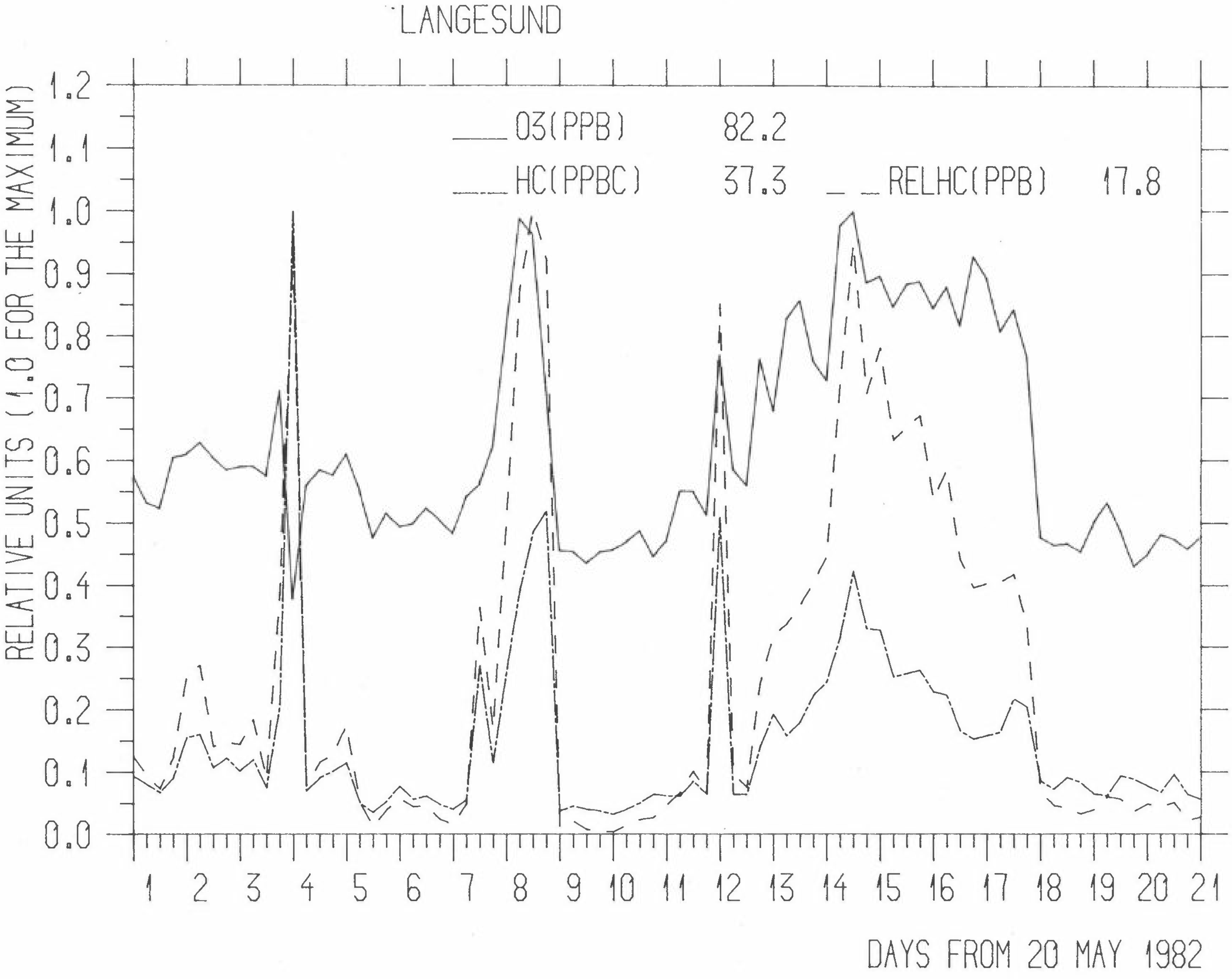
6g)


++ SUM C2-C5(PPTC) 52628.0
— NO2(UGN/M3) 10.5
DAY NUMBER
18 36 54 72 90 108 126 144 162 180 198 216 234 252 270 288 306 324 342 360
RELATIVE UNITS (1.0 FOR THE MAXIMUM)
0.0 0.1 0.2 0.3 0.4 0.5 0.6 0.7 0.8 0.9 1.0 1.1 1.2 1.3

6h)


SUM C2-C5(PPTC) 44686.0
NO2(UGN/M3) 1.7
DAY NUMBER
18
36
54
72
90
108
126
144
162
180
198
216
234
252
270
288
306
324
342
360
RELATIVE UNITS (1.0 FOR THE MAXIMUM)
0.0
0.1
0.2
0.3
0.4
0.5
0.6
0.7
0.8
0.9
1.0
1.1
1.2
1.3

7)


LANGESUND
O3(PPB) 82.2
HC(PPBC) 37.3
RELHC(PPB) 17.8
RELATIVE UNITS (1.0 FOR THE MAXIMUM)
0.0
0.1
0.2
0.3
0.4
0.5
0.6
0.7
0.8
0.9
1.0
1.1
1.2
1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16 17 18 19 20 21
DAYS FROM 20 MAY 1982

NILU

NORSK INSTITUTT FOR LUFTFORSKNING (NILU)
NORWEGIAN INSTITUTE FOR AIR RESEARCH
POSTBOKS 64, N-2001 LILLESTRØM

RAPPORTTYPE OPPDRAGSRAPPORT	RAPPORTNR. OR 4/89	ISBN-82-425-0004-5	
DATO JANUARY 1989	ANSV. SIGN. J. Schjoldager	ANT. SIDER 59	PRIS
TITTEL Hydrocarbon measurements at rural Birkenes, South Norway, May 1987-May 1988		PROSJEKTLEDER Ø. Hov	
		NILU PROSJEKT NR. O-1314	
FORFATTER(E) Ø. Hov, N. Schmidbauer og M. Oehme		TILGJENGELIGHET A	
		OPPDRAGSGIVERS REF.	

OPPDRAGSGIVER (NAVN OG ADRESSE)
Nordisk Ministerråd

3 STIKKORD (à maks. 20 anslag)
Hydrocarbons | Seasonal variation | Background atmosphere

REFERAT (maks. 300 anslag, 7 linjer)

TITLE

ABSTRACT (max. 300 characters, 7 lines)

Analysis of spot samples of air taken approx. every second day at a rural site in south Norway for one year showed that alkanes dominated in the samples. Ethane and propane made up about 50% of the total on a C-basis. The sum of C_2-C_5 hydrocarbons peaked at 52.6 ppbC in February 1988. The alkanes and acetylene had a distinct late winter peak, while the alkenes had a secondary summer maximum as well. The individual hydrocarbons are quite well correlated with NO_2 and SO_2 but not with O_3 or sulphate in air.

* Kategorier:	Åpen - kan bestilles fra NILU	A
	Må bestilles gjennom oppdragsgiver	B
	Kan ikke utleveres	C