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Phone +31 15 69 69 00*TNO-report***C<sub>2</sub>-C<sub>5</sub> hydrocarbon measurements in  
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## **C<sub>2</sub>-C<sub>5</sub> HYDROCARBON MEASUREMENTS IN THE NETHERLANDS 1981-1991**

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**Abstract** - Measurements of C<sub>2</sub>-C<sub>5</sub> hydrocarbons on a hourly basis at the TNO site in Delft from 1982 to 1984 and at Moerdijk over the period 1981-1991 are presented. In combination with meteorological data (wind direction and wind speed) the Delft and Moerdijk series are evaluated to identify source categories, annual variations, background concentrations and trends. The C<sub>2</sub>-C<sub>5</sub> hydrocarbon concentrations at Delft and Moerdijk are determined mainly by emission characteristics and meteorological dispersion; the dominant sources are relatively nearby and atmospheric degradation is not of much importance. Under conditions of high wind speed the concentrations measured at Moerdijk in the marine sector are close to the Atlantic background concentrations in winter and somewhat above this in summer. The continental background concentrations are higher than the marine background concentrations by a factor of almost two. The annual variation of acetylene is more pronounced than that of the other hydrocarbons and most likely due to a different seasonal variation in acetylene emissions. The annual variation of propene is smoother, indicating stronger sources in summer than in winter. This feature of propene is observed in continental as well as in marine sectors.

The observations show that at Moerdijk C<sub>2</sub>-C<sub>4</sub> concentrations measured in the Rijnmond sector have decreased considerably since the early 1980s, corresponding with changes in emissions in that area. Averaged over all wind directions the trend of all species is downward, but for acetylene is the trend significant at a 95% confidence interval. The acetylene concentrations show an annual downward trend of 3 per cent during the 1980s, supporting

other estimates of decreasing hydrocarbon emissions from traffic over this period at the same rate.

Key word index: C<sub>2</sub>-C<sub>5</sub> hydrocarbons, trends, background concentrations, hydrocarbon ratios, annual variation

## 1. INTRODUCTION

Non-methane hydrocarbons (NMHCs) play an important role in the chemistry of the troposphere as precursors of ozone (O<sub>3</sub>) and peroxyacetylnitrate (PAN). Many model studies have indicated that ground level ozone concentrations, especially peak levels, in urbanized and semi-rural areas in Europe and the U.S. are sensitive to changes in anthropogenic emissions of non-methane hydrocarbons and nitrogen oxides (NO<sub>x</sub>) (Simpson, 1992; Builtjes, 1992; De Leeuw and Van Rheineck Leyssius, 1991; Sillman et al., 1990; Jacob et al., 1993).

The atmospheric residence time of NMHCs is determined by ambient concentrations of the hydroxyl radical (OH) and ozone and therefore depends on season and latitude. The lifetime varies from a few months (ethane) to a few hours or less for the most reactive components. Because of their relatively short residence time, concentrations of NMHCs in the free troposphere and in areas remote from sources are very low (Rudolph, 1988; Rudolph and Johnen, 1990; Greenberg and Zimmerman, 1984; Singh and Salas, 1982).

The contribution of NMHCs to the in-situ production of ozone in the free troposphere is small, the contribution of methane (CH<sub>4</sub>) and nitrogen oxides (NO<sub>x</sub>) being much more important. Since the ozone produced in the lowest kilometres of the atmosphere over Europe, the U.S. and other industrialized areas contributes significantly to the Northern Hemispheric ozone budget of the troposphere, NMHCs are nevertheless also important for ozone production at larger scale levels (Fishman et al., 1985; Vukovich et al., 1985; Roemer and

Van den Hout, 1992). In order to understand changes in the composition of the atmosphere that have occurred during the past several decades, it is therefore important also to study changes in NMHC concentrations and emissions.

This paper presents hourly measurements of C<sub>2</sub>-C<sub>5</sub> hydrocarbons at the TNO site in Delft (1982-1984) and at Moerdijk (1981-1991), both located in the western part of The Netherlands. By combining the data with meteorological data (wind speed and wind direction) and by comparing ratios of hydrocarbons it is possible to identify source areas and relatively clean sectors. The data are evaluated for possible trends.

In the 1970s (1971-1977) hourly C<sub>2</sub>-C<sub>5</sub> measurements were also performed at the TNO site in Delft (Guicherit et al., 1978). These measurements were using a different method (direct injection), resulting in much higher detection limits. A careful scrutiny of the data showed that although the main features of the measurements were consistent with the data obtained in the 1980s, the quality does not allow for a trend analysis for those species and in those wind sectors where the ambient concentrations are close to the detection limit.

## **2. EXPERIMENTAL DESCRIPTION**

Since the early 1970s monitoring techniques developed by TNO have been applied in several research projects and at several monitoring sites. By far the most extended series of measurements have been carried out at the TNO site in Delft and at Moerdijk.

### **2.1 Description of the sites**

The TNO monitoring site at Delft (52°00'N, 04°23'E) is located on the south-east side of Delft and south-west of the A13 highway from The Hague to Rotterdam. The site is not a typical town or traffic site, but neither it is not a rural site. It is best characterized as repre-

sentative of urban background concentrations in the industrialized western part of The Netherlands.

The monitoring site at Moerdijk (51°41'N, 04°32'E) is located about 2.5 km west-south-west of the Moerdijk industrial area. Apart from this industrial site there are no other relevant VOC sources in the surroundings of the monitoring station. For several years C<sub>2</sub>-C<sub>5</sub> measurements have been carried out there at more than one site, and a distinction can be made between the contribution of the nearby industrial site and more remote emissions.

The Delft data is combined with meteorological data (wind speed and wind direction) measured at Rotterdam airport, ten km south of the Delft monitoring site. At Moerdijk wind speed and wind direction are measured at the site itself.

## **2.2 C<sub>2</sub>-C<sub>5</sub> measurement**

The C<sub>2</sub>-C<sub>5</sub> hydrocarbons are measured on a one-hourly basis. The analytical part of the monitors consists of a gas chromatograph. Over the whole period the same, preconcentration technique was used. The system is described briefly below.

The air to be analyzed is drawn in through a so-called cold trap, consisting of a stainless steel loop submerged in liquid nitrogen. The VOCs in the air are thus concentrated in the loop. After one hour the carrier gas is led through the loop and the loop heated. In this way all the collected VOCs are transported to the gas chromatograph. During analysis of this sample the next one-hour-averaged sample (about 1 litre) is again collected in the cold trap. In order to prevent the loop becoming blocked with ice, the sample air must be dried. For this purpose a cartridge with Sicapent (P<sub>2</sub>O<sub>5</sub>) is placed in the sample line. The analytical conditions are:

Column : 20 cm \* 1/8 inch o.d. stainless steel packed with Porapak N (80-100 mesh) and 4 m \* 1/8 inch o.d. stainless steel packed with Alumina F-1 (60-80 mesh)

Column temperature : 130 °C

Detector : FID

Carrier gas : helium, 25 ml.min<sup>-1</sup>

Detection limits : 0.1 ppb (ethane, ethene, propane and propene)  
0.2 ppb (acetylene and butanes)  
0.6 ppb (pentanes)

The monitor was designed to operate unattended for a longer period of time. In practice the monitor had to be serviced once a week. The monitor is controlled by a computing integrator. Recalibration of the monitor is performed automatically and the chromatograms are integrated and processed at the site. The results of the analysis are stored on tape or disc.

The monitor was calibrated using commercially available calibration gases. The first calibration gas was an uncertified mixture obtained from Gardner and contained 20 ppb of the C<sub>2</sub>-C<sub>5</sub> hydrocarbons (no iso-pentane) in nitrogen. All calibration mixtures purchased later were compared with this first calibration gas and differences proved consistently to be ± 5% or less. The monitor was calibrated once a week.

### **2.3 Processing of measurements below the detection limit**

Concentrations of i-butane and especially the pentanes are relatively often below the limit of detection. In this study data below the detection limit have been set at two-thirds of the detection limit, this giving the best approximation of the true value (van de Wiel et al., 1988).

### 3. RESULTS OF C<sub>2</sub>-C<sub>5</sub> MEASUREMENTS

The large number of measurements at Delft and Moerdijk allows a number of cross sections to be made in the data set that still retain statistical significance. The theoretically maximum number of 8760 hourly average samples per year is never realized due to instrument failures for shorter or sometimes longer periods of time. The Delft series from 1982 to 1984 comprises approximately 5000-7500 samples per year and the Moerdijk series from 1981 to 1991 some 7000-8300 samples per year, all of which were analyzed and recorded in the database.

The Moerdijk data is divided into three time blocks: 1981-1984, 1985-1987 and 1988-1991. This is to obtain as much data as possible from the various cross sections but at the same time to avoid cross sections becoming perturbed by any trends that might have occurred over the ten-year period. In this paper the discussion is focused on 1) the 1982-1984 Delft period and the 1981-1984 Moerdijk period because these simultaneous measurements permit more powerful interpretation of the data, and 2) trends over the entire time span.

Most of the time the ambient concentrations of normal-pentane and isopentane appeared to be very close to and often below the detection limit (0.6 ppb). Pentane concentrations are therefore only presented in the first and second section.

#### 3.1 C<sub>2</sub>-C<sub>5</sub> concentrations as a function of wind direction

The wind roses of the hydrocarbons (for wind speeds larger than or equal to 1 m s<sup>-1</sup>) show very clearly the existence of nearby and more remote sources. As an example Fig. 1 shows the wind roses of acetylene and n-butane at Delft (1982-1984) and Moerdijk (1981-1984) projected onto the map of The Netherlands.

### 3.1.1 Delft

In Delft the lowest concentrations of all species are observed in the north sector ( $270^{\circ}$ - $090^{\circ}$ ), with concentrations in the north-west sector ( $270^{\circ}$ - $360^{\circ}$ ) somewhat lower than in the north-east sector ( $0^{\circ}$ - $90^{\circ}$ ) (Fig. 2). Wind in the north-west sector advects air from the North sea and the northern part of the United Kingdom. In the last 10-15 km before arriving at the receptor point the air parcels pick up emissions from The Hague (500,000 inhabitants) and Delft (90,000 inhabitants).

In the Delft data the wind roses of propane, n-butane, i-butane, n-pentane and i-pentane are very similar (Fig. 2). They all have a pronounced maximum at  $180^{\circ}$  and a secondary maximum at  $240^{\circ}$ . The maximum at  $180^{\circ}$  is caused by emissions from the petrochemical industries concentrated in a relatively small area 15 km south of the TNO site at Delft. The secondary maximum indicates emissions from storage tanks. Large tanker parks are located in the western part of the Rijnmond area, not far from the coast and about 15-25 km southwest of the Delft receptor point.

Although the primary and secondary maxima of ethane concentrations are in the same directions as those of the other alkanes, they are less pronounced. The atmospheric residence time of ethane is by far the highest of the  $C_2$ - $C_5$  hydrocarbons and the background concentration of ethane is therefore much higher than that of the other  $C_2$ - $C_5$  hydrocarbons. Ethane concentrations advected over the Atlantic Ocean at  $40^{\circ}$ - $60^{\circ}$ N range from 1 to 3 ppb (Rudolph and Ehhalt, 1981; Rudolph and Khedim, 1985; Tille et al., 1985; Lightman et al., 1990; Penkett et al., 1993). Concentrations of the other hydrocarbons measured simultaneously over the Atlantic Ocean are generally far below the 1 ppb level.

Ethene and propene concentrations peak in the east-south sector ( $100^{\circ}$  to  $210^{\circ}$ ) and are due to traffic as well as industrial emissions.

Industrial acetylene sources are known in the Netherlands Emission Inventory from only two locations in the western part of The Netherlands. The largest source is located in the Rijnmond area, south (180°) of the Delft monitoring site. The annual average contribution of this source to the acetylene concentrations in the south sector at Delft was about 1.5 ppb during the early 1980s. The second source is located in Moerdijk and does not contribute significantly to the acetylene concentrations at Delft.

Elevated acetylene concentrations are observed in the 90°-180° sector. Acetylene emissions are predominantly from traffic. The elevated concentrations in the south-east sector are due mainly to traffic emissions in continental Europe. The A13 highway from Rotterdam to The Hague, which passes the monitoring site a few hundred metres eastwards, does not show up distinctively in the data. The fact that the acetylene concentrations in the 30°-60° sector are so much lower than in the 100°-130° sector, even though the distance from the highway to the monitor is the same, indicates that the contribution of the highway is much smaller than contributions of more remote sources. Dispersion calculations indicate that the average contribution of the highway to the concentrations at the receptor point is about 0.6 ppb for acetylene.

### **3.1.2 Moerdijk**

The presence of the industrial site at Moerdijk only a few km eastward of the monitoring site is seen distinctively in the data of all species except i-pentane. Emissions of ethene and propene from the industrial site are particularly pronounced. The average 1981-1984 concentration in the wind sector straight from the Moerdijk sources is 46 ppb for ethene and 25 ppb for propene. The acetylene concentration in this sector, which is due almost entirely to the nearby industrial site, is also quite high. Emissions from the entire Moerdijk industrial site in the early 1980s have been calculated using three monitoring sites located east and west of the source area (den Tonkelaar and Thijssse, 1986). This study demonstrated that

peak concentrations in the 50°-70° sector were due almost entirely to emissions from the site itself and not from sources outside the area.

The wind roses at Moerdijk are characterized by relatively low concentrations in the south-west to north-east sector (230°-030°) and much higher concentrations from continental Europe (80°-210°). Superimposed on this pattern are the contributions of relatively nearby source areas (Fig.3). The elevated levels in the north-west sector (290°-330°) point to emissions from the Rijnmond area. Elevated levels in the south sector (170°-200°) are due probably to Antwerp and its port area.

The lowest concentrations at Moerdijk are found in the south-west-west sector (230°-270°). Air parcels in this sector have traveled over the Atlantic Ocean and picked up emissions from the southern part of the United Kingdom.

Excluding the Moerdijk industrial site sector, the highest acetylene concentrations are measured in the south-east sector (90°-150°) which is in agreement with the acetylene observations at Delft (1982-1984), although the latter levels are higher. The contribution of the industrial acetylene emissions in the Rijnmond area to the annual average concentration in the north-west sector was about 0.8 ppb during the early 1980s.

### **3.2 Contribution of source categories**

Since acetylene is emitted mainly by traffic, the ratio of other hydrocarbons to acetylene can be used to assess the contribution of nearby non-traffic emissions. The hydrocarbon-to-acetylene ratios for Delft are given in Fig. 4. In the Delft data the ratios (as an indicator of non-traffic emissions) are underestimated by about 40% in the south sector (180°) because of the industrial acetylene source in that direction. Fig. 4 shows very clearly the existence of non-traffic sources (industrial sources) south of Delft. The industrial emissions south of

Delft are concentrated in one direction (160°-210°) for ethene and propene, and in two directions (160°-200°; 220°-250°) for the alkanes.

The same Rijnmond area shows up in the acetylene ratios of the Moerdijk data, but now merged into one wind sector. The elevated acetylene ratios in this sector are consequently more pronounced for the alkanes than for the alkenes. The Antwerp sector is hardly visible in the acetylene ratios of the alkanes but is much better for ethene. Since information about possible industrial acetylene emissions in this area was not available, the acetylene ratios from this sector might not represent the traffic component only.

The acetylene ratios in sectors not directly dominated by industrial areas can be compared with acetylene ratios obtained in road test and tunnel studies (Tab. 1). The VOC composition of traffic emissions depends not only on the fuel used (petrol, LPG, diesel) but also on the motor speed (Eggleston, 1993). The exhaust of petrol-engined cars contains far more ethene and propene at high driving speeds than at low speeds. Petrol engine emissions measured in road tests under high speed conditions (Eggleston, 1993) are in good agreement with the results of a road tunnel study carried out in The Netherlands (Thijsse and den Tonkelaar, 1987). The left part of the Drecht highway tunnel, halfway between Rotterdam and Antwerp, is used by private cars and light vans only. The results resemble the road test emissions, except for propane. The propane to acetylene ratio found in the tunnel study is 10-20 times higher than that calculated from the road test emissions. A possible reason for this discrepancy may be that propane concentrations in the tunnel are determined by relatively high non-traffic sources such as diffusive losses from the natural gas distribution grid. The emission of propane by cars is very small.

The acetylene ratios calculated from the Delft and Moerdijk data in wind sectors not directly influenced by (large) industrial emissions are higher than the ratios from the road test, if it is assumed that the average traffic composition is equally represented by the six categories from Eggleston (1993) in Table 1. There is major uncertainty about the average

composition of traffic emissions. However, the difference between the ratios can be explained by other arguments. Industrial emissions from more remote sources are spread out over wide areas and are not detectable as such in the wind rose of the concentrations at the receptor points. At the time of arrival they are well mixed with traffic emissions, making the acetylene ratios in the data higher than would be expected on the basis of the composition of traffic emissions alone.

### 3.3 Annual variation

The highest monthly average concentrations in the clean sector ( $211^{\circ}$ - $290^{\circ}$ ;  $331^{\circ}$ - $010^{\circ}$ ), the sector not influenced by nearby sources, are generally observed in the winter months, the lowest in the summer months. Fig. 5 shows the annual variation at Moerdijk over the period 1981-1984. Due to meteorological conditions the monthly concentrations averaged over a few years may sometimes differ from this general pattern. At Moerdijk in the period 1981-1984 the September values of a number of species are enhanced compared to the August and October values. Very cold weather in January and February during three consecutive years (1985-1987) led to markedly higher concentrations during these months over this period than in November and December. In the period 1988-1991, however, the January and February concentrations were about equal to the November and December values.

The average winter (Nov.-Feb.) concentrations of  $C_2$ - $C_4$  species in the clean sector over the whole 1981-1991 period are 50-100% higher than the summer (May-Aug.) values, with two exceptions (Tab. 2). Propene concentrations do not vary much in the course of a year; the winter to summer ratio is 1.28. In contrast, the annual variation of acetylene is much higher, with a winter to summer ratio of 2.46 over the entire period. In this relatively clean sector at Moerdijk, if concentrations are determined by advection of clean Atlantic air, the

winter to summer ratio should depend on the reactivity of the species. Accordingly, propene should have the highest ratio and ethane the lowest. However, the ratios lie very close to one another, suggesting that the concentrations at Moerdijk are hardly influenced by chemical degradation.

The finding of low annual variation for propene and relatively high variation for acetylene is partly in line with results from a number of - but not all - other European sites. At Birkenes, located on the south coast of Norway, the winter (Dec.-Feb.) to summer (June-Aug.) ratio averaged over all nine C<sub>2</sub>-C<sub>5</sub> hydrocarbons for the period January 1988 - June 1993 is 2.5 (Solberg et al., 1993). The lowest ratio was found for propene (1.3), the highest for acetylene (4.2) and propane (3.7). The winter-to-summer ratios in Rörvik (Sweden) are considerably higher than in Birkenes, the highest ratios being found for acetylene (6.5) and propane (6.1). However, at Rörvik the ratio for propene was even somewhat above average. The annual variation of C<sub>2</sub>-C<sub>5</sub> hydrocarbons at other stations showed different behaviour (Eurotrac, 1993). The picture emerging from all available hydrocarbon measurements in Europe is not entirely clear. Sector analysis and data sets covering longer time periods could shed more light on the conditions determining the hydrocarbon concentrations in this part of Europe.

The seasonal variation has been examined in more detail by comparing winter (Nov.-Feb.) and summer (May-Aug.) concentrations in Delft (1982-1984) and Moerdijk (1981-1984) for all species as a function of wind direction. Fig. 6 shows the three-point running average (as a function of wind direction) of winter-to-summer ratios for the Moerdijk data. For all species the winter-to-summer ratio is significantly higher in the continental sector than that in the marine sector (240°-330°). This merely reflects the moderating influence of the sea. The atmospheric stability, temperature and consequently dispersion characteristics of marine air do not change much from winter to summer, whereas the seasonal change in the

atmospheric structure of continental air is rather large. The winter to summer ratio varies from 1.5-2.5 in the continental sector ( $0^{\circ}$ - $210^{\circ}$ ) to 0.8-1.4 in the marine sector.

The winter-to-summer ratios of propene and especially acetylene differ somewhat from those of the other components. For acetylene the ratio is generally higher in every direction than that of the other hydrocarbons. Even in the south-west direction, where the ratio of the other components is close to or even less than unity, the winter to summer ratio of acetylene is still 1.5. Since atmospheric chemistry can be ignored as an explanation for this behaviour, the most probable remaining cause must be an annual variation of the acetylene emissions, a variation different from that of the emissions of the other components.

The winter to summer ratio of propene is the lowest of all, for virtually all wind directions, although the difference from the ratios of the other components (except acetylene) is rather small. The ratio is close to unity in the marine sector ( $210^{\circ}$ - $330^{\circ}$ ) and up to 1.5-1.8 in the remaining sectors. Many authors have pointed out that surface waters might be a source of propene during the summer (Lightman et al., 1990; Rudolph and Johnen, 1990; Bonsang and Lambert (1985)), and the existence of nearby surface waters is often used to explain the winter to summer ratio of propene. However, Fig. 6 shows that in many continental directions, too, the winter to summer ratio of propene is lower than that of other hydrocarbons, demonstrating that other (continental) sources need to be taken into account.

The differences among the hydrocarbons in their winter-to-summer ratios is probably caused by differences in the seasonal behaviour of the emissions. A major proportion of the emissions in the Rijnmond area, especially for the alkanes, are from storage tanks. Evaporative losses from storage tanks are well-known seasonally dependent sources which are driven by the temperature variation over the day. There is consequently more evaporation in summer than in winter. The highest seasonal variation in emissions of this kind occurs by advection of continental air masses. The contribution of evaporative emissions to the concentrations at Delft and Moerdijk is seen in the south-west and north-west direction

respectively. As both these are marine sectors, however, these are unfavourable directions for expecting large seasonal variation. The winter-to-summer ratios at Moerdijk and Delft (Fig. 6) give no indication of large seasonally varying sources in the Rijnmond area. However, this does not of course exclude the existence of such a seasonally varying source under continental air flows.

### **3.4 Light alkanes and atmospheric chemistry**

The distribution patterns of all alkane concentrations are very similar (Fig. 2 and 3). The distribution of ethane as a function of wind direction is rather flat because of the much higher background concentration of this species. The distributions of concentrations of propane, n-butane, i-butane and i-pentane at Moerdijk and Delft have an almost constant ratio. Fig. 7 gives the ratio of n-butane, i-butane and i-pentane with respect to propane in the winter (Nov.-Feb.) and summer (May-Aug.) for the 1982-1984 Delft data. The n-butane to propane ratio is 0.7-0.8, the i-butane to propane ratio is 0.3-0.4 and the i-pentane to propane ratio is somewhat higher: 0.4-0.5. The largest variations in the ratios are observed in the south sector, the sector in which the concentrations are governed by the emissions in the Rijnmond area. Nevertheless, the variations are rather small, an order of magnitude smaller than the variations in the ratios with respect to acetylene (Fig. 4). This suggests that the alkanes are emitted in nearly fixed ratios and have largely the same sources. The ratio of the higher alkanes to propane is hardly affected by the season. The atmospheric residence time of propane is much longer than that of the butanes or pentanes, and if atmospheric degradation (initiated by the attack of OH on the alkanes) were of any importance it would show up in a larger ratio to propane in the winter than in the summer. Since this is not the case, it is concluded that the hydrocarbon concentrations are determined by sources so nearby that atmospheric chemistry can be neglected.

The conclusion derived in the previous paragraph was investigated in further detail by focusing on the 241°-270° sector, that least influenced by nearby sources. Air parcels arriving at Moerdijk in this wind sector are mainly of Atlantic origin and have picked up emissions from the southern part of the United Kingdom and, close to the receptor point, emissions from small local sources. The contribution of local sources westwards of the receptor point in The Netherlands is low. According to the Emission Inventory, the total VOC emission from this region in the 1980s was less than 250 ton/yr (Publikatiereeks Emissieregistratie No. 1, 1990). The total VOC emission from the U.K. in 1985 (based on CORINAIR data) was about 2300 kton/yr (Bultjes, 1992). Although for selected hydrocarbons the ratio of emissions between these two areas might possibly be different, the information from the Inventories suggests that the highest contribution in this wind sector comes from the United Kingdom, despite the difference in distance.

Following a method exploited by Rudolph and Johnen (1990) and by Parrish et al. (1992) (and references therein), the change in the concentration ratio  $r_{ij} \equiv C_i/C_j$  of hydrocarbons  $i$  and  $j$  by oxidation in a given air parcel as a function of time can be described by:

$$r_{ij} = r_{ij}^0 \exp(t \cdot [\text{OH}] \cdot (k_j - k_i)) \quad [1]$$

where  $r_{ij}^0$  is the initial concentration ratio,  $t$  is the travel time and  $k_i$  and  $k_j$  are the rate constants with respect to the reaction with OH. A second pair of hydrocarbons  $r_{kj} \equiv C_k/C_j$  can be used to remove the  $t \cdot \text{OH}$  term in equation [1]. A diagram of  $\ln r_{ij}$  versus  $\ln r_{kj}$  should theoretically give a straight line with a slope of

$$s = (k_j - k_i)/(k_j - k_k) \quad [2]$$

Assuming that the main sources are located in or nearby London, a distance of 400-500 km from the receptor point, the travel time is about 25-35 hours. In the summer (assuming an

average OH concentration of  $2 \cdot 10^6$  molecules  $\text{cm}^{-3}$ ) this travel time is long enough to allow for considerable removal of butane (40% lost by oxidation). The fraction of propane and ethane lost en route is smaller, 20% and 5% respectively. In the winter the OH concentrations are substantially lower (a concentration of  $5 \cdot 10^5$  molecules  $\text{cm}^{-3}$  was assumed), resulting in lower fractions oxidized on the way from source to receptor. For butane a loss of 10% was calculated. It is therefore to be expected that, if the assumptions are correct, this method will work properly for the summer situation only.

From the monitoring series for the entire 1981-1991 period those data were selected whereby the wind speed was  $3 \text{ m s}^{-1}$  or more, thus ensuring that the data were not influenced by nearby sources in other wind sectors under stagnant weather conditions. The summer subset (May-Aug.) as well as the winter subset (Nov.-Feb.) consists of about 2300 measurements.

Fig. 8 shows the natural logarithm of the propane to ethane ratio versus the natural logarithm of the n-butane to ethane ratio. A least squares fit gives a regression coefficient of 0.56 for the summer situation and 0.27 for the winter situation. The correlation in the winter is very poor, demonstrating that during the winter the oxidizing potential of the atmosphere is too low and the travel time from the major sources in this wind sector too short to allow chemical removal to put a clear mark on the concentrations at Moerdijk in this wind sector. In the summer the correlation is better but is still not very high. The slope of the least squares fit is  $1.3 \pm 0.1$  in the summer and  $1.0 \pm 0.1$  in the winter, a long way off from the theoretical slope of  $s = 2.4$  based on the rate constants given by Atkinson (1986).

McKeen and Liu (1993) have pointed out that mixing of air parcels with different background concentrations can result in  $\ln(\text{n-butane/ethane})$  to  $\ln(\text{propane/ethane})$  ratios substantially different from ratios based on purely photochemical considerations and air mass age. The slope of  $\ln(\text{n-butane/ethane})$  to  $\ln(\text{propane/ethane})$  ratios of background air measured in Point Arena, USA in 1985 was about 1.4 (Parrish et al., 1992). From measurements on the Atlantic Ocean a slope of 1.7 was derived (Rudolph and Johnen, 1990). These results

demonstrate that the effect of atmospheric degradation cannot be derived from the slope of the  $\ln(\text{n-butane/ethane})$  to  $\ln(\text{propane/ethane})$  ratios alone. However, the correlation of the  $\ln(\text{n-butane/ethane})$  to  $\ln(\text{propane/ethane})$  ratios in the aforementioned background studies was quite good (0.87 and 0.84 respectively), much better than the correlation found at Moerdijk, indicating the influence of other processes (emissions) not present during the measurements of background air. It is concluded that even in the cleanest sector at Moerdijk the influence of atmospheric degradation is too small to be visible in the data.

### **3.5 Background concentrations**

The measured hydrocarbon concentration in a given wind direction is the sum of contributions of nearby and more remote sources. Turbulence and dispersion increase as a function of wind speed. An increase in wind speed therefore reduces the contribution of the nearest sources, thereby bringing the concentrations at the receptor point closer to the background values.

For the Moerdijk site over the period 1981-1991 the relation between  $C_2$ - $C_4$  concentrations and wind speed was examined for two wind direction sectors: the marine sector ( $241^\circ$ - $270^\circ$ ), which on average is the sector with the lowest concentrations, and the  $101^\circ$ - $150^\circ$  sector, a continental sector in which the concentrations are hardly affected by nearby sources.

In the marine sector the highest concentrations are observed at wind speeds below  $1 \text{ m s}^{-1}$ . In stagnant conditions like this it is almost impossible to actually relate concentrations to sources and most probably the concentrations are affected by sources located in totally different directions. At higher wind speeds it is easier to define a wind direction and to attribute concentrations to source areas. The concentrations of all species gradually reach a

constant level at wind speeds above 6-7 m s<sup>-1</sup>, except in the case of ethene, the concentration of which keeps on decreasing (Fig. 9).

At increasing wind speeds the contribution of relatively nearby sources to the observed concentrations at the receptor point drops, while the relative influence of the remote background increases. The concentrations measured at Moerdijk at wind speeds higher than 10 m s<sup>-1</sup> (Tab. 3) were compared with the concentrations measured in air parcels arriving at the United Kingdom from the Atlantic Ocean (Lightman et al., 1990; Penkett et al., 1993). In the winter the measured concentrations at Moerdijk are close to the background values for ethane, acetylene, propane and the butanes. Ethene and propene concentrations are still considerably higher than the Atlantic background values. In the summer the measured concentrations at high wind speeds are somewhat higher than the Atlantic background concentrations and for ethene and propene much higher. The detection limit, which at Moerdijk is much higher than for the instruments used for the background measurements, cannot be of much significance since even at high wind speeds the concentrations of ethene and propene do not often fall below the detection limit (0.1 ppb). The reason that the wintertime values are closer to the Atlantic background concentrations than the summertime values is probably that during the winter atmospheric degradation has much less effect on the Atlantic background concentrations than during the summer. Atmospheric degradation is not of much importance for the Moerdijk data.

In the continental sector (101°-150°) the same feature is observed as in the marine sector: the highest concentration at the lowest wind speed and decreasing concentration with increasing wind speed. The number of observations in the high wind speed classes (> 7 m s<sup>-1</sup>) is low in this sector, much lower than in the 241°-270° sector. The standard deviation of the distribution of concentrations per wind class is much higher and consequently the high wind speed tail is not a smooth curve, as is the case in the marine sector, but instead ex-

hibits more fluctuations. The average concentrations at high wind speed are believed to represent continental background values. These continental background concentrations are considerably higher (by approximately a factor two) than the Atlantic background values.

### 3.6 Trends

The Moerdijk series was examined for trends. To relate long-term changes in concentrations to developments in emissions as far as possible, the Moerdijk time series was split into several wind sector subsets. The following wind sectors were examined: 1) the industrial site of Moerdijk (41°-80°), the Rijnmond area (291°-330°), the Antwerp area (161°-200°) and a clean sector (211°-290° + 331°-010°). Trends expressed in fractional changes (per cent per year) are with respect to the first year (1981).

In the Rijnmond sector a negative downward trend can be observed for all C<sub>2</sub>-C<sub>4</sub> species from 1981 to 1991 (Fig. 10). Except for propane and i-butane the trends are significant at the 2-sigma level (Tab. 4). Over this period ethene concentrations decreased at a rate of almost 6% per year. Although the interannual fluctuations are large, especially in the early 1980s, Fig. 10 suggests that ethene concentrations decreased after 1985/1986. This finding is in line with the fact that a large industrial ethene source disappeared during this period. According to the Emission Inventory between 1981 and 1984 the registered industrial ethene emission in the Rijnmond area was 2.7 kton/year (VROM, 1990), while in 1987 it was only 0.1 kton/year (Publikatiereeks Emissieregistratie No.1, 1990). The total ethene emission from this area decreased from 4.6 kton/year in 1983 to 1.8 kton/year in 1987.

Downward trends are seen in the Antwerp sector for the C<sub>2</sub>-C<sub>3</sub> species, but only for acetylene is this trend significant (-2.1% per year). The trends in this sector are considerably smaller than in the Rijnmond sector, indicating different developments in emissions. In

contrast to the other hydrocarbons the butane concentrations in the Antwerp sector increase, though not significantly. Fig. 11 shows almost identical interannual variations for the alkanes in the Antwerp sector. The variations of ethene and propene from one year to another do not match those of the alkanes. The concentrations of ethene and propene increase from 1984 to 1985, whereas they decrease for the other components.

In the clean sector the concentrations of all C<sub>2</sub>-C<sub>4</sub> hydrocarbons decreased. Significant downward trends of 2-4% per year are found for ethane, acetylene and propane (Tab. 4). The interannual variations are almost identical for the alkanes, while the fluctuations of ethene and propene sometimes differ from those of the alkanes (Fig. 12; see: 1984-1986)

Concentrations in the wind sector 41°-80° (the Moerdijk industrial site) vary considerably from one year to another. The largest interannual fluctuations are observed for acetylene. None of the species shows a positive trend. Significant negative trends are found for ethane, ethene and propene.

If all wind sectors are taken into account with the exception of the Moerdijk industrial sector, then only the trend of acetylene of -3.0% per year is significant, corresponding to a 30 per cent decrease over the whole period. This finding is in good agreement with the trend in VOC emissions by road traffic in The Netherlands according to the Emission Inventory (CBS, 1992) and with the VOC traffic emission trend in West Germany (Metz, 1993). The Inventory reports a gradual decrease of VOC traffic emissions since 1975. VOC emissions in 1991 were 26% lower than in 1981 and if only gasoline emissions are considered the drop in VOC emissions is 30 per cent over the 1981-1991 period. The development of VOC emissions from traffic in West Germany is similar: a slight increase during the 1970s and a marked decrease after 1985. VOC traffic emissions in 1991 were about 30% lower than in 1981.

## CONCLUSIONS

Two series of continuous one-hourly C<sub>2</sub>-C<sub>5</sub> hydrocarbon measurements in The Netherlands were studied. Pentane concentrations were often below the detection limit and therefore not included in most of this study.

From the wind roses of the observations at both sites (Delft, 1982-1984 and Moerdijk, 1981-1991) the presence of nearby sources is identified. Even in those wind directions not under the direct influence of nearby sources the concentrations at the receptor point are determined by emission and dispersion characteristics, not by atmospheric degradation.

The annual variation of the hydrocarbon concentrations is largely governed by annual variation of dispersion. The winter to summer ratio is close to unity in the marine sectors and about two in continental sectors. The winter to summer ratio of acetylene is considerably higher for virtually every wind direction than for the other hydrocarbons, a phenomenon most probably caused by a different seasonal variation of the emission. The winter to summer ratio of propene is somewhat lower than that of the other hydrocarbons, not only in the marine sectors but also in the continental sectors.

In wind sectors not under the direct influence of nearby sources the concentrations decrease as wind speed increases. At high wind speeds the concentrations of the species (except ethene) converge to a certain value, defined here as the background concentration. In the marine sector during the winter months the corresponding marine background concentrations are close to the concentrations observed at remote areas over the Atlantic Ocean. In the summer they are somewhat higher than the measurements over the Atlantic, especially for ethene and propene. In the continental sector the corresponding continental background concentrations are about a factor two higher than the marine background concentrations.

Downward trends over the period 1981-1991 were found for several source areas for most of the species. When averaged over all wind sectors, only the acetylene trend is significant at the 95% confidence interval. The annual decrease of 3 per cent in acetylene concentrations corresponds well with estimates from the Emission Inventories in The Netherlands

and West Germany of an approximately 30% decrease in VOC emissions by traffic over the same period.

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## FIGURE CAPTIONS

- Figure 1. Measured concentration of acetylene (a) and n-butane (b) as a function of wind direction averaged over the period 1982-1984 (Delft) or 1981-1984 (Moerdijk).
- Figure 2. Measured concentration of C<sub>2</sub>-C<sub>5</sub> hydrocarbons in Delft as a function of wind direction averaged over the period 1982-1984.
- a) ethane and n-pentane
  - b) ethene, acetylene and propene
  - c) propane, n-butane, i-butane and i-pentane
- Figure 3. Measured concentration of C<sub>2</sub>-C<sub>5</sub> hydrocarbons in Moerdijk as a function of wind direction averaged over the period 1981-1984.
- a) ethane and n-pentane
  - b) ethene, acetylene and propene
  - c) propane, n-butane, i-butane and i-pentane
- Figure 4. Ratio to acetylene of ethene and propene (a) and propane, n-butane, i-butane and i-pentane (b) as a function of wind direction at Delft (1982-1984).
- Figure 5. Annual variation of hydrocarbons measured at Moerdijk (1981-1984) in the clean sector (211°-290° + 331°-010°).
- a) ethane, ethene, acetylene and propene
  - b) propane, n-butane and i-butane

Figure 6. Three-point running average (0.25+0.50+0.25) of the winter to summer ratio of hydrocarbons measured at Moerdijk (1981-1984) as a function of wind direction.

a) ethane, ethene, acetylene and propene

b) propane, n-butane and i-butane

Figure 7. Ratio to propane of n-butane, i-butane and i-pentane as a function of wind direction at a) Delft (1982-1984) and b) Moerdijk (1981-1984).

Figure 8.  $\ln(\text{propane/ethane})$  versus  $\ln(\text{n-butane/ethane})$  at Moerdijk (1981-1991) in the  $241^\circ$ - $270^\circ$  wind sector for a) May-August and b) November-February.

Figure 9.  $C_2$ - $C_4$  hydrocarbon concentrations measured at Moerdijk (1981-1991) as a function of wind speed in the  $241^\circ$ - $270^\circ$  sector for a) May-August and b) November-February.

Figure 10. Trend in  $C_2$ - $C_4$  hydrocarbon concentrations measured at Moerdijk (1981-1991) in the Rijnmond sector ( $291^\circ$ - $330^\circ$ ).

Figure 11. Trend in  $C_2$ - $C_4$  hydrocarbon concentrations measured at Moerdijk (1981-1991) in the Antwerp sector ( $161^\circ$ - $200^\circ$ ).

Figure 12. Trend in  $C_2$ - $C_4$  hydrocarbon concentrations measured at Moerdijk (1981-1991) in the clean sector ( $211^\circ$ - $290^\circ$  +  $331^\circ$ - $010^\circ$ ).

## TABLES

Table 1 Acetylene ratios.

	Delft <sup>1)</sup> 1982- 1984	Moer- dijk <sup>2)</sup> 1981- 1984	Drecht- <sup>3)</sup> tunnel 1986	Road test emission <sup>4)</sup>					
				urban		sub- urban	rural	highway	
				cold	hot			90 km/h	113 km/h
C <sub>2</sub> H <sub>4</sub> /C <sub>2</sub> H <sub>2</sub>	1.2-1.5	1.4-1.7	2.0	0.5	0.9	1.1	1.3	1.8	1.9
C <sub>3</sub> H <sub>6</sub> /C <sub>2</sub> H <sub>2</sub>	0.8-1.0	1.0-1.2	0.5-1.0	0.02	0.03	0.03	0.06	0.08	0.03
C <sub>3</sub> H <sub>8</sub> /C <sub>2</sub> H <sub>2</sub>	0.4-0.5	0.5-0.6	0.6	0.17	0.3	0.4	0.48	0.7	0.6
iC <sub>4</sub> H <sub>10</sub> /C <sub>2</sub> H <sub>2</sub>	0.3-0.4	0.4-0.5	0.1-0.2	0.08	0.13	0.13	0.13	0.12	0.07
nC <sub>4</sub> H <sub>10</sub> /C <sub>2</sub> H <sub>2</sub>	0.7-0.9	0.6-0.8	0.4-0.6	0.21	0.29	0.31	0.30	0.23	0.17
iC <sub>5</sub> H <sub>12</sub> /C <sub>2</sub> H <sub>2</sub>	0.4-0.5	0.4-0.5	0.1-0.2	0.20	0.28	0.31	0.30	0.23	0.17
nC <sub>5</sub> H <sub>12</sub> /C <sub>2</sub> H <sub>2</sub>	0.2-0.3	0.3-0.4	0.1	0.11	0.16	0.18	0.20	0.14	0.11

1) 0°-120° + 270°-360°

2) 0°-30° + 90°-150°

3) tunnel study (Thijssen and den Tonkelaar, 1987)

4) from: Eggleston, 1993 (only petrol engined car exhaust)

Table 2 The winter (Nov.-Feb.) to summer (May-Aug.) ratio at Moerdijk in the clean sector (211°-290°, 331°-010°).

	1981-1984	1985-1987	1988-1991	1981-1991
ethane	1.49	1.93	1.71	1.66
ethene	1.46	1.57	1.56	1.49
acetylene	2.03	3.60	2.52	2.46
propane	1.52	2.44	1.96	1.85
propene	1.15	1.50	1.40	1.28
i-butane	1.23	2.10	1.59	1.52
n-butane	1.30	2.14	1.69	1.59

Table 3 Averaged concentration (ppb) at Moerdijk (1981-1991) at wind speeds  $\geq 10 \text{ m s}^{-1}$  in the sector  $241^\circ\text{-}270^\circ$  and in the sector  $101^\circ\text{-}150^\circ$ . The values are compared with Atlantic background concentrations

	November-February			May-August		
	Atlantic background <sup>1)</sup>	marine (241-270)	continental (101-150)	Atlantic background <sup>1)</sup>	marine (241-270)	continental (101-150)
ethane	2.0-2.5	2.50±0.07	3.6±0.3	1.0-1.5	1.84±0.15	2.4±0.4
ethene	0.2-0.3	1.16±0.08	2.9±0.6	0.1-0.3	1.26±0.16	2.0±0.5
acetylene	0.6-0.9	0.82±0.05	2.3±0.4	0.1-0.3	0.40±0.07	1.0±0.3
propane	0.7-1.3	1.26±0.05	2.2±0.2	0.1-0.3	0.60±0.07	1.0±0.3
propene	<0.1	0.40±0.03	0.8±0.1	<0.1	0.46±0.07	0.5±0.2
n-butane	0.3-0.5	0.69±0.05	1.2±0.2	0.05-0.15	0.37±0.07	0.6±0.2
i-butane	0.1-0.3	0.34±0.03	0.5±0.1	0.02-0.15	0.24±0.02	0.3±0.1
n-pentane	0.1-0.2	<D.L. <sup>2)</sup>	<D.L.	<0.05	<D.L.	<D.L.
i-pentane	0.05-0.2	<D.L.	0.6±0.2	<0.05	<D.L.	<D.L.

1) from: Lightman et al., 1990 and Penkett et al., 1993

2) D.L.: Detection Limit

Table 4 Trends (% per year) in C<sub>2</sub>-C<sub>4</sub> hydrocarbons in Moerdijk 1981-1991. Confidence interval at 2 $\sigma$ -level.

	Wind sectors				
	Moerdijk Industry (41°-80°)	Rijnmond (291°-330°)	Antwerp (161°-200°)	clean 211°-290° + 331°-010°	all, except (41°-80°)
ethane	-3.1±2.5	-2.3±1.7	-0.8±1.2	-2.0±1.1	-1.3±1.4
ethene	-5.1±3.3	-5.9±3.2	-1.7±2.5	-4.0±4.3	-2.7±2.9
acetylene	-12.4±20.3	-4.2±1.3	-2.1±1.5	-3.7±1.6	-3.0±1.8
propane	-3.5±7.6	-2.7±3.0	-0.9±1.6	-2.3±2.0	-1.2±2.1
propene	-7.1±5.9	-4.3±2.3	-1.6±2.6	-3.8±4.4	-2.9±3.1
i-butane	-0.6±14.0	-2.9±3.5	+1.3±2.1	-1.7±2.2	+0.8±3.1
n-butane	-2.3±6.4	-2.5±2.0	+1.0±2.1	-2.5±2.1	-0.6±2.2

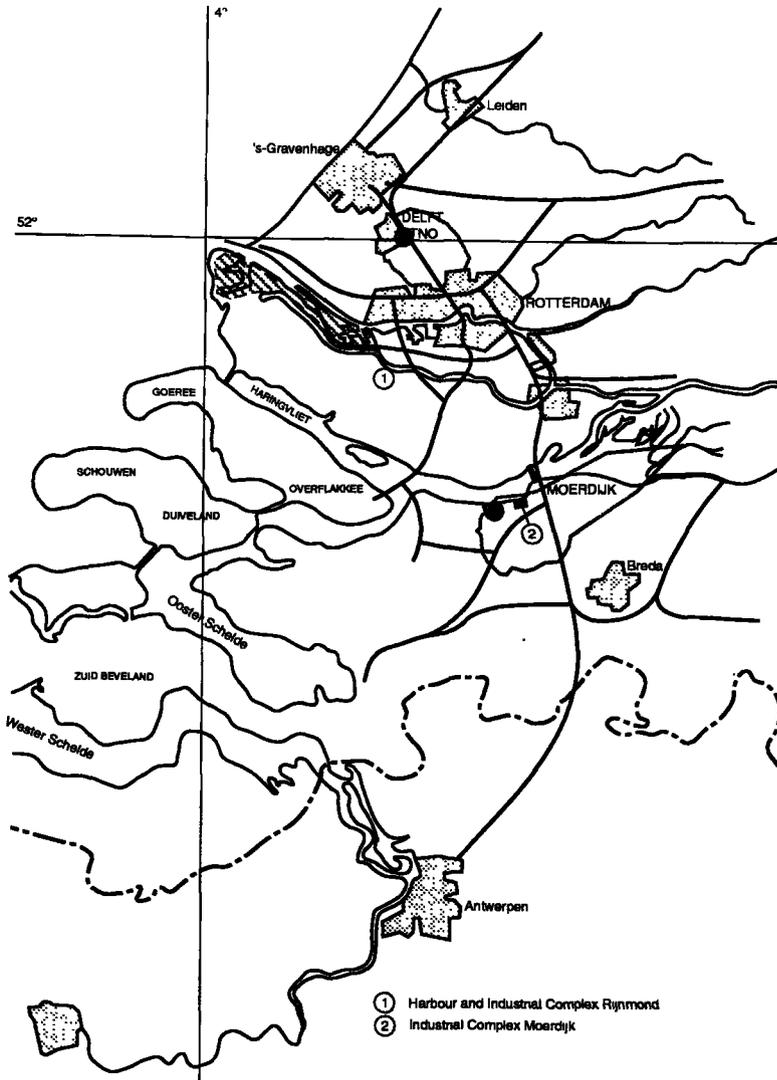
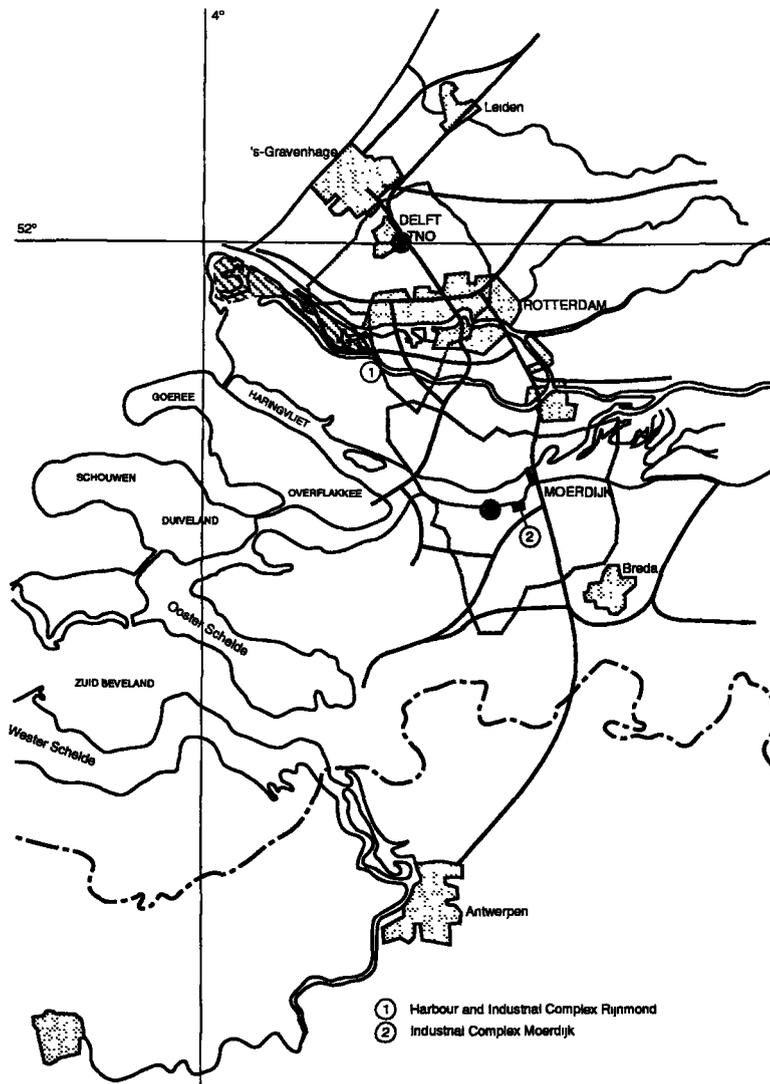
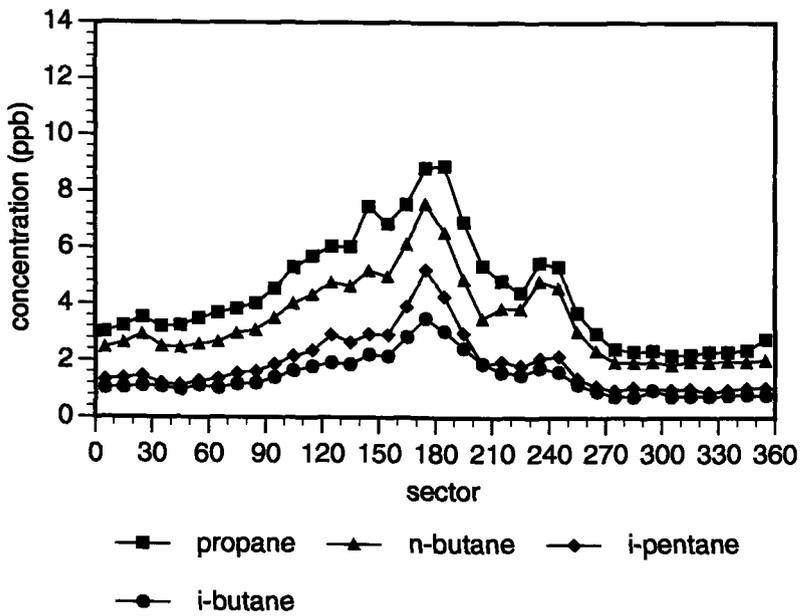
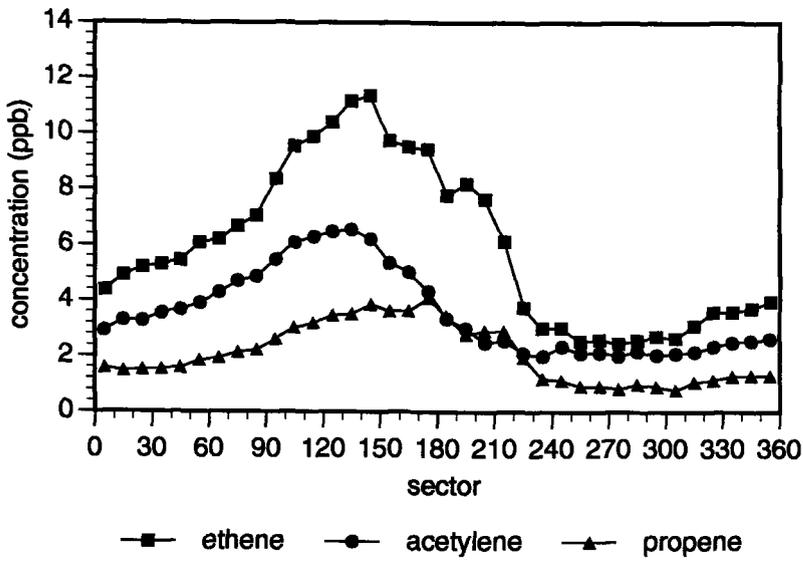
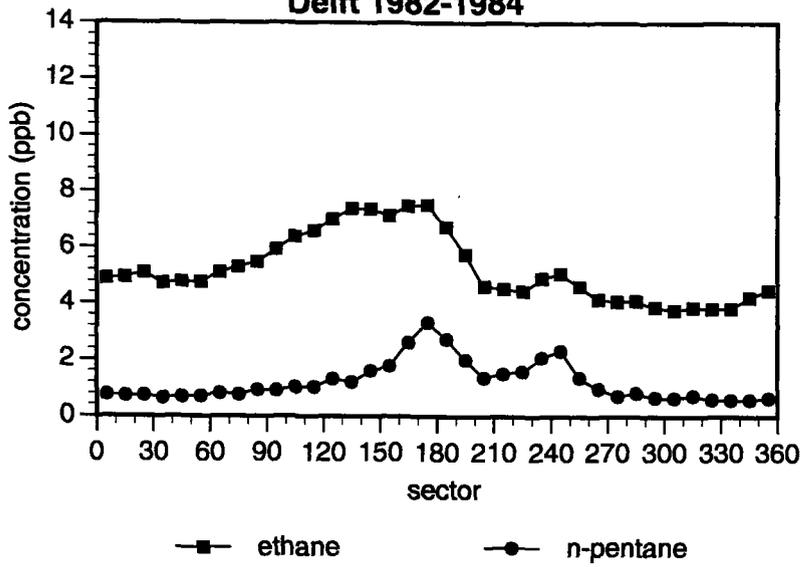


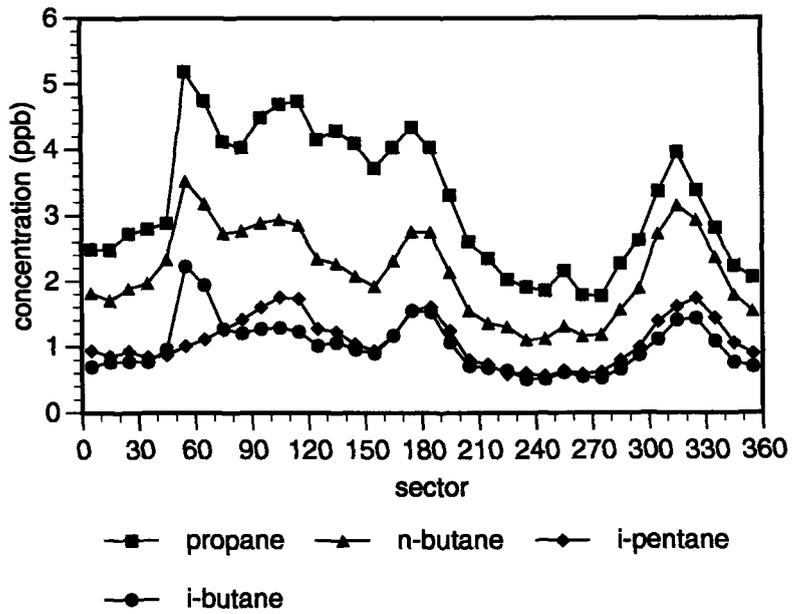
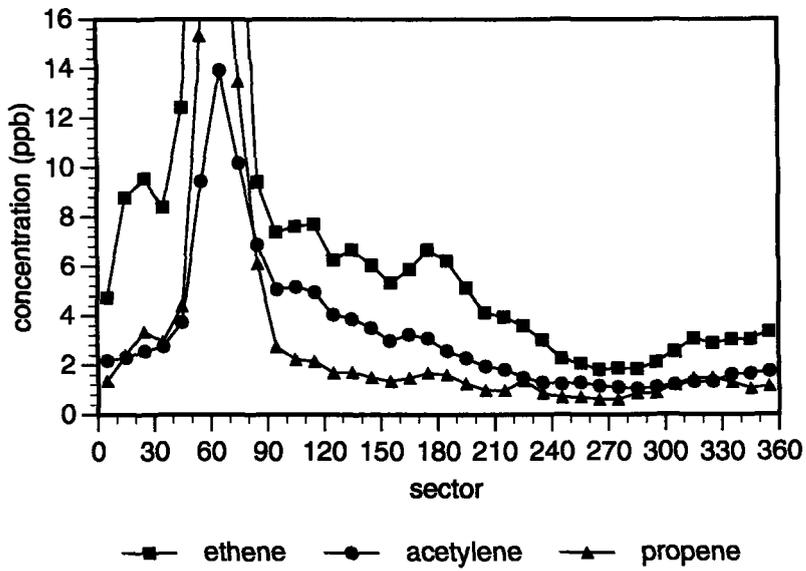
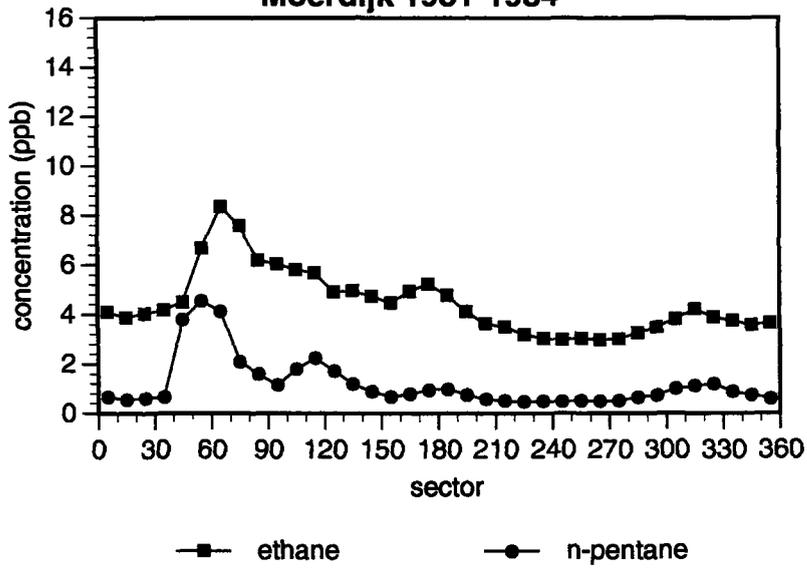
Fig 1a



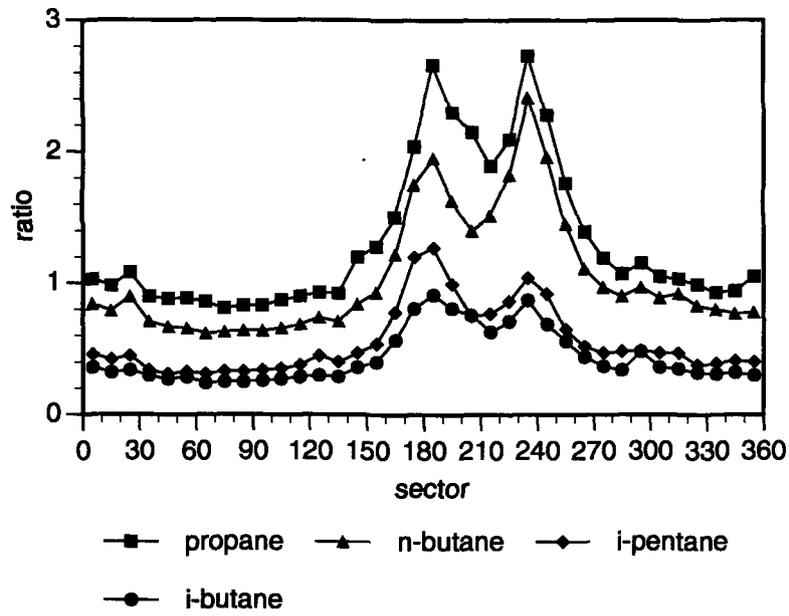
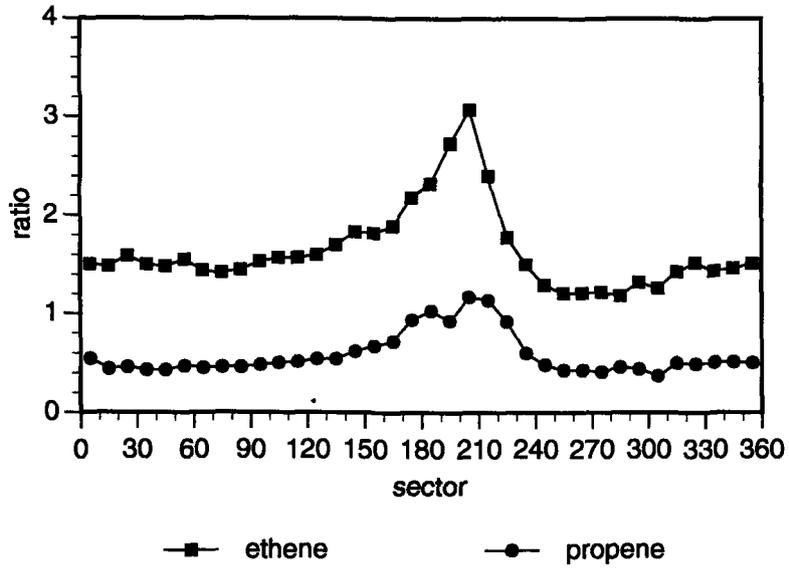
Delft 1982-1984



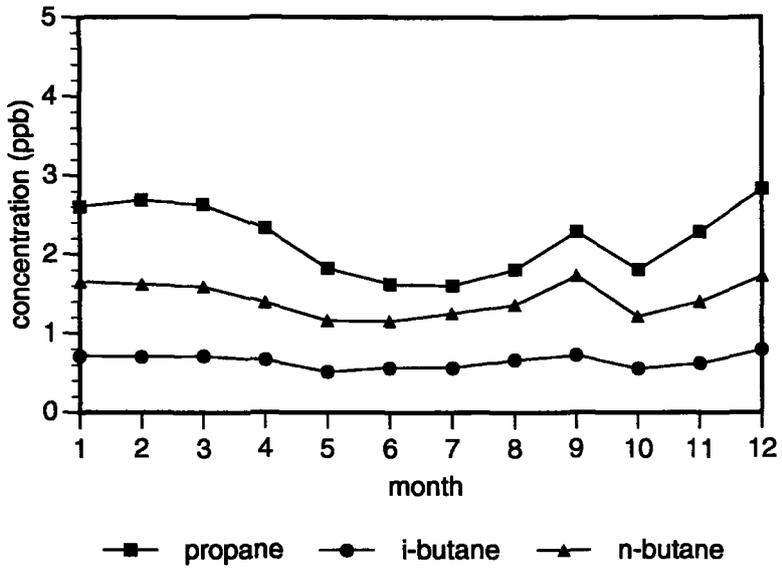
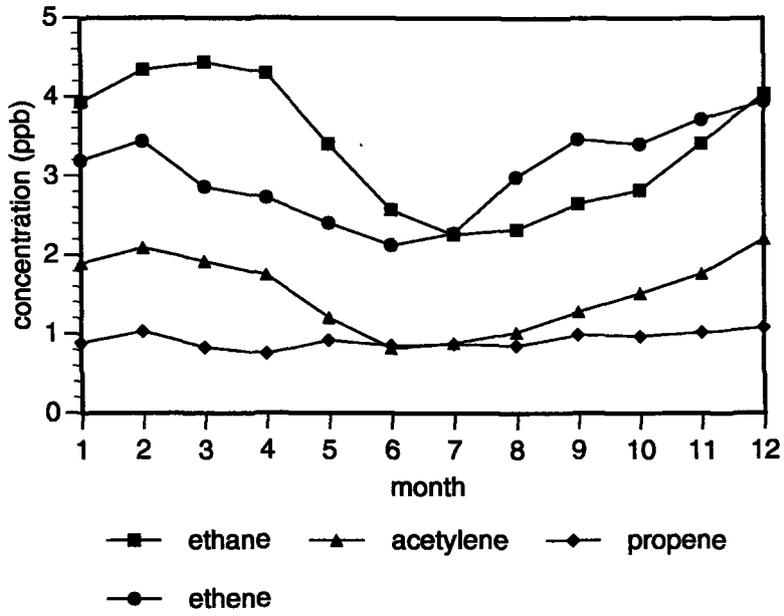
### Moerdijk 1981-1984



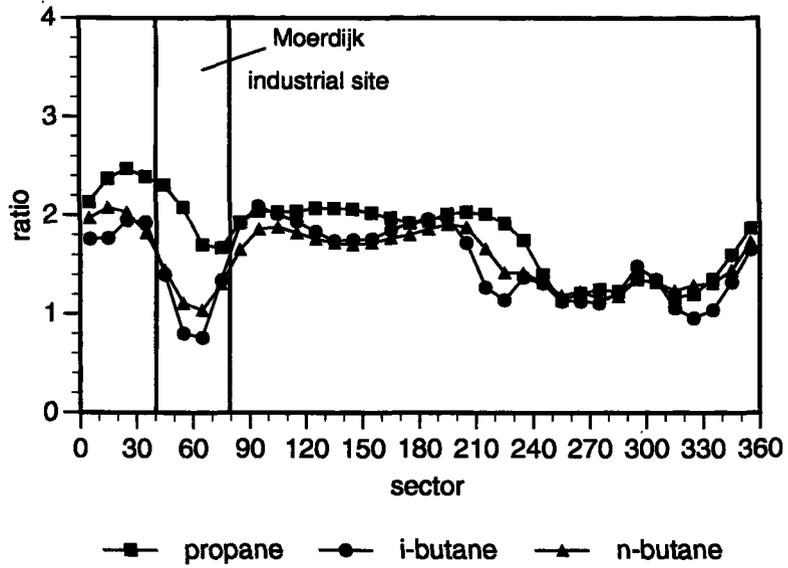
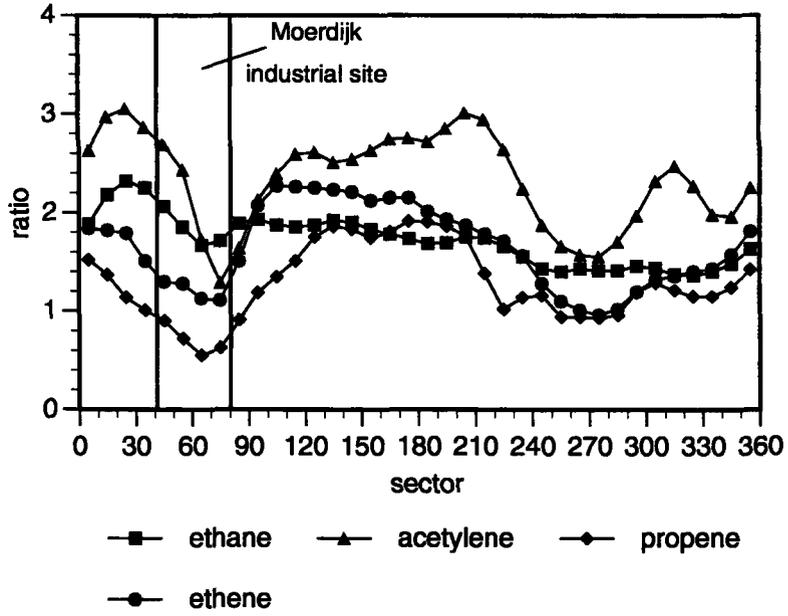
Delft 1982-1984, ratio acetylene



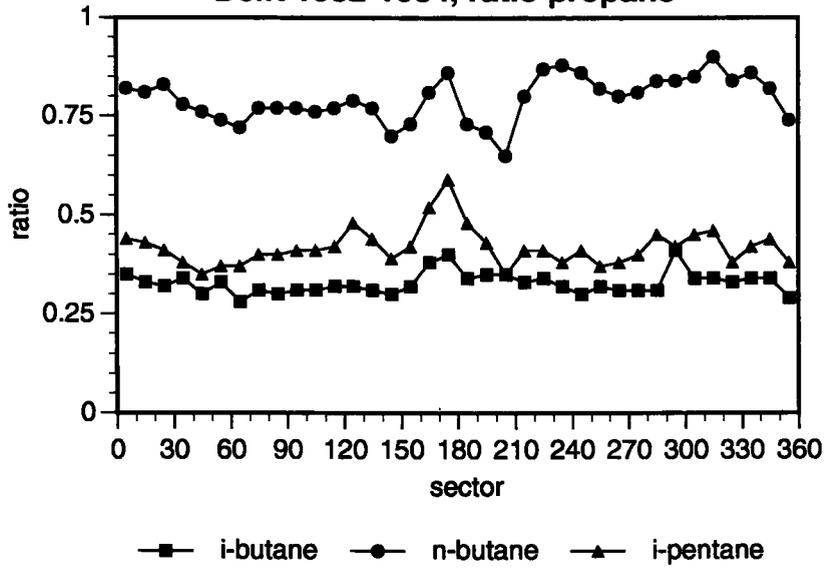
Moerdijk 1981-1984, annual variation,  
clean sector



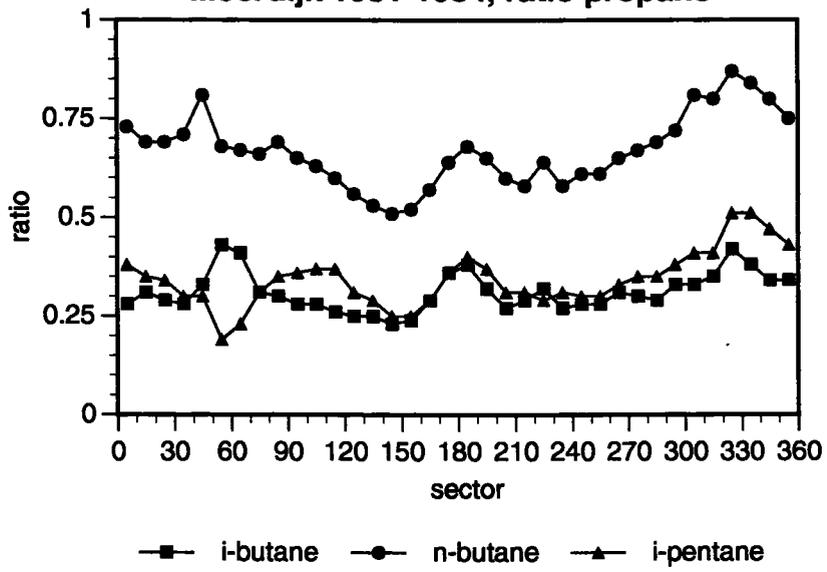
**Moerdijk 1981-1984  
winter-summer ratio**



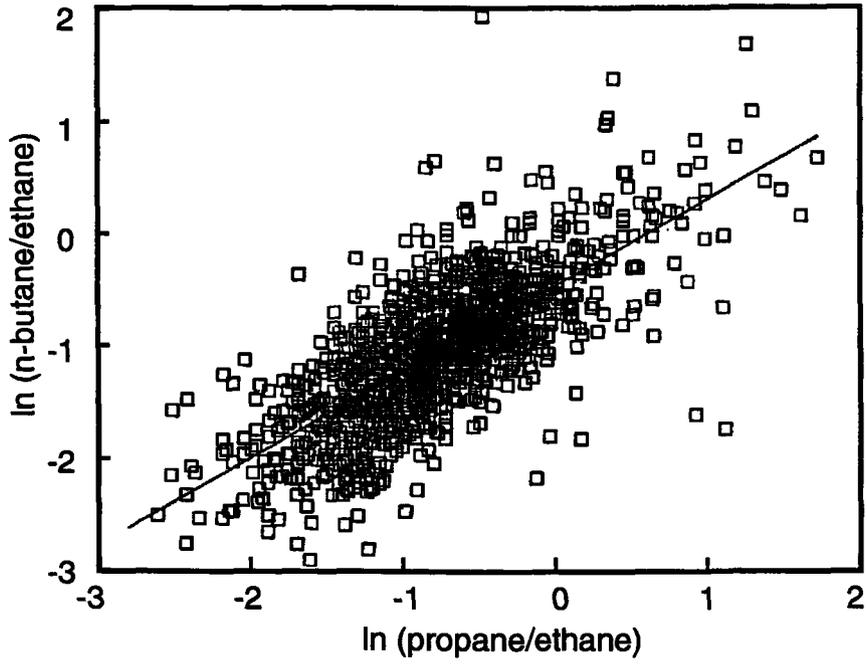
Delft 1982-1984, ratio propane



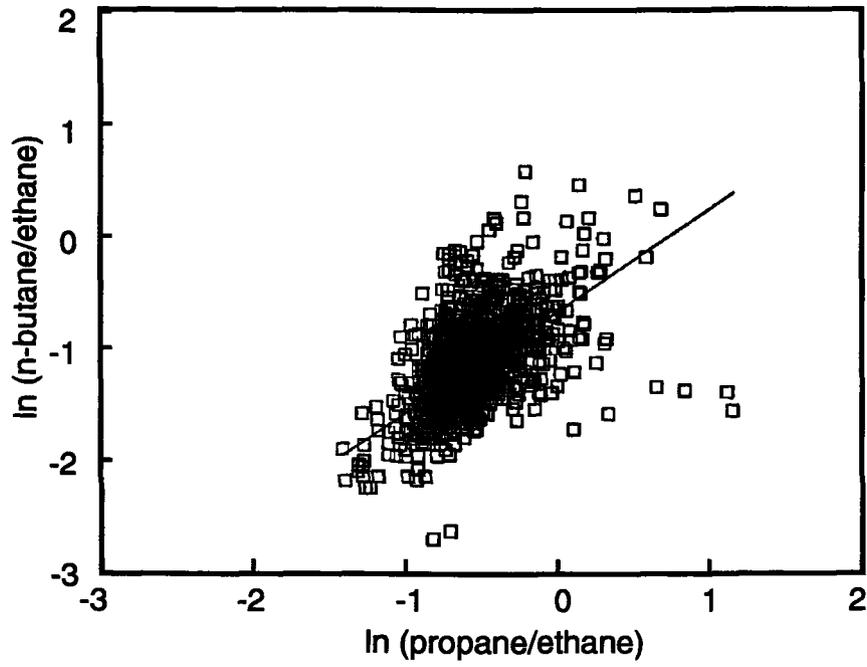
Moerdijk 1981-1984, ratio propane



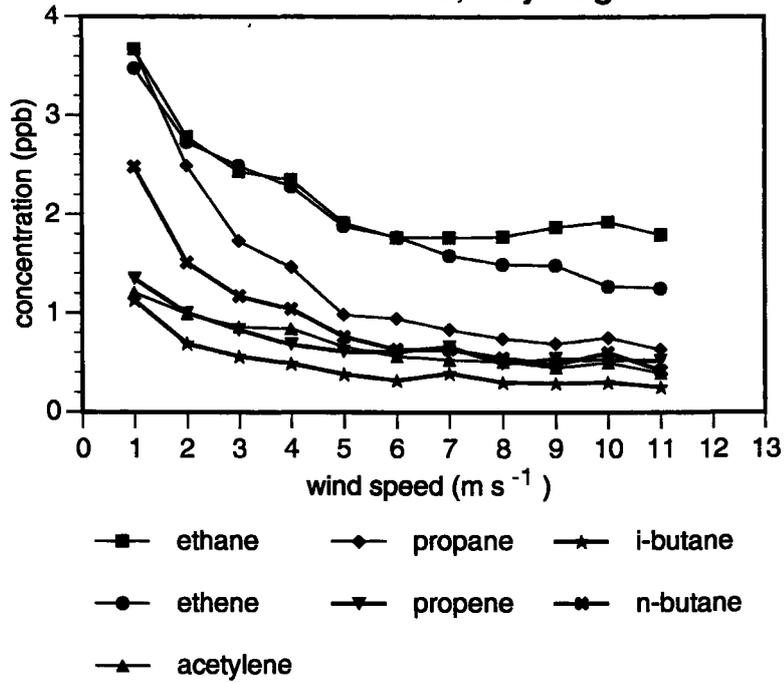
**Moerdijk 1981-1991, May-Aug.**



**Moerdijk 1981-1991, Nov.-Feb.**



**Moerdijk 1981-1991  
sector 241-270; May-Aug.**



**Moerdijk 1981-1991  
sector 241-270; Nov.-Feb.**

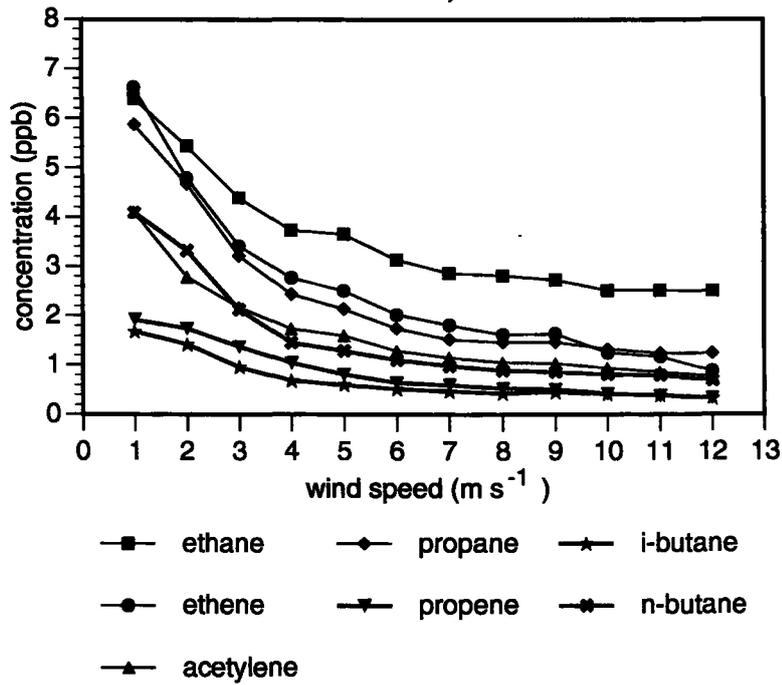
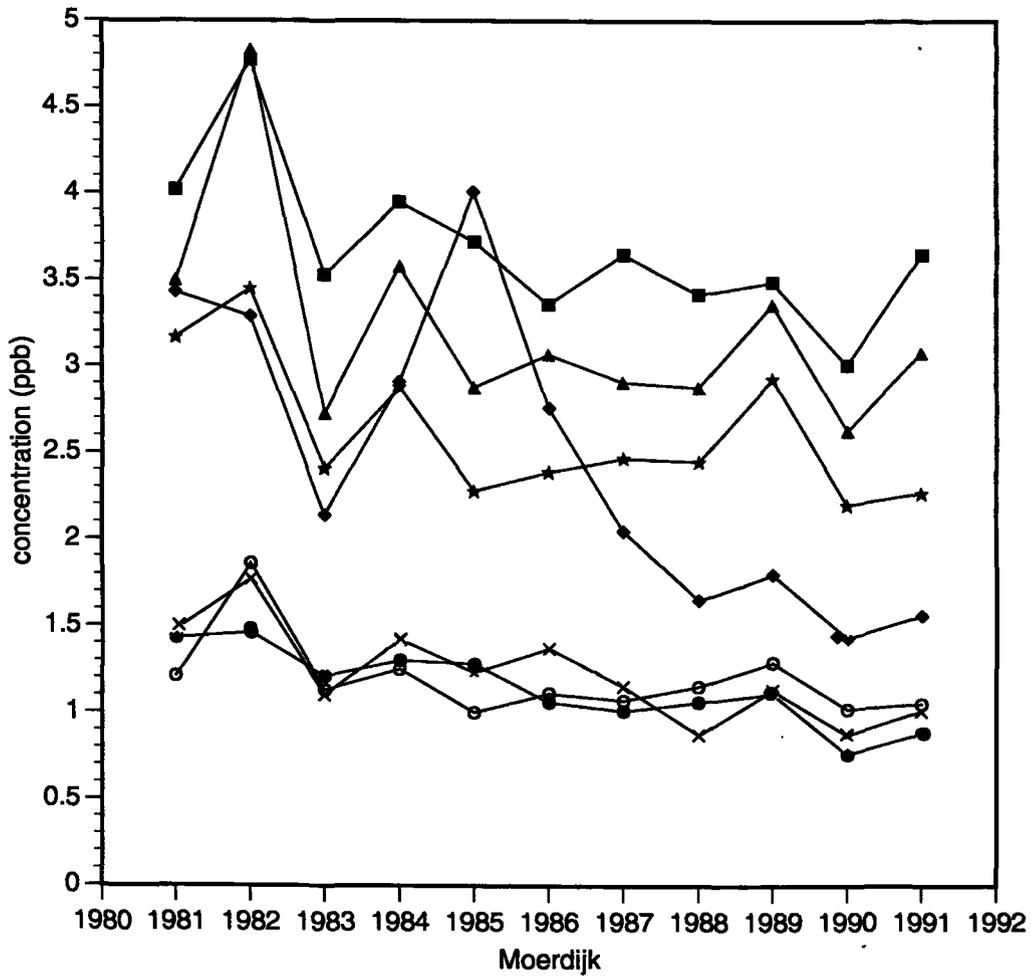
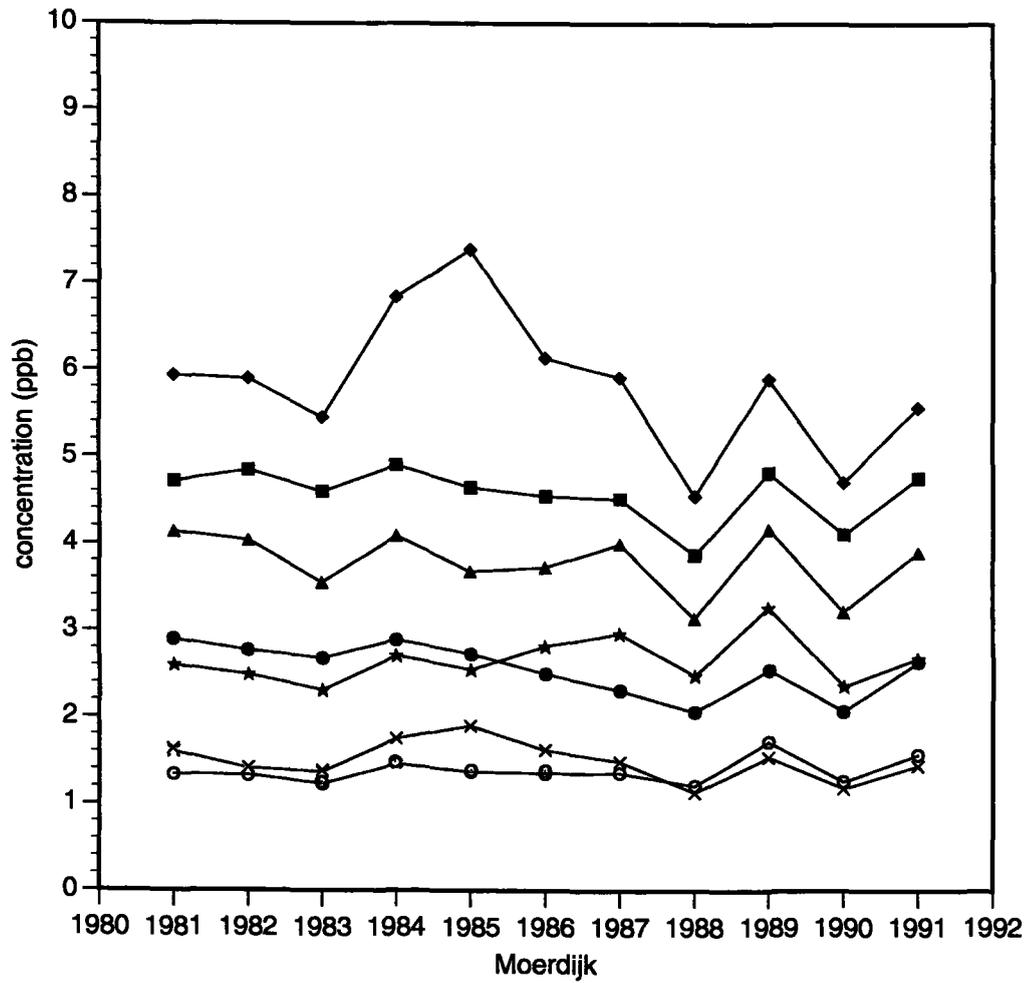


Fig. 5

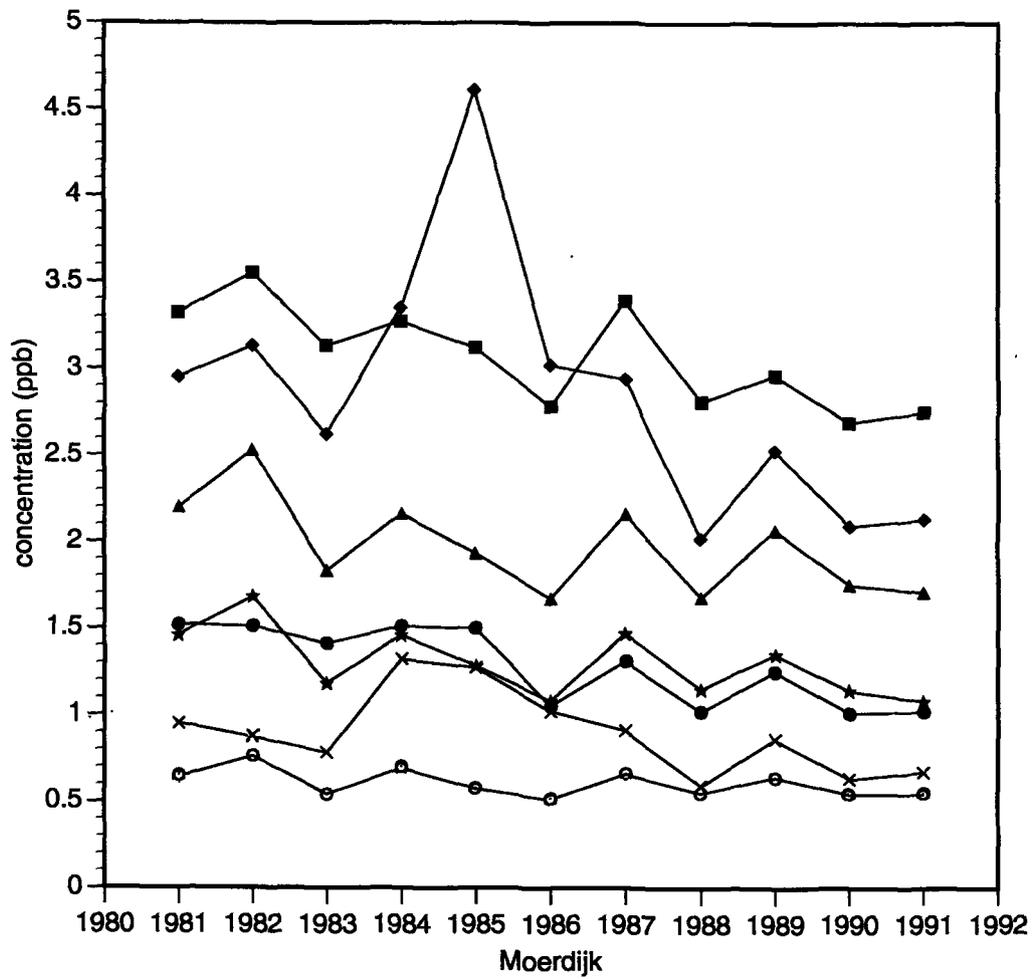


- |             |            |            |
|-------------|------------|------------|
| ■ ethane    | ▲ propane  | ★ n-butane |
| ◆ ethene    | × propene  |            |
| ● acetylene | ○ i-butane |            |

Handwritten marks at the bottom right corner of the page.



- |   |           |   |         |   |          |
|---|-----------|---|---------|---|----------|
| ■ | ethane    | ▲ | propane | ★ | n-butane |
| ◆ | ethene    | × | propene | ⊙ | i-butane |
| ● | acetylene |   |         |   |          |



- ethane
- ◆ ethene
- acetylene
- ▲ propane
- × propene
- ★ n-butane
- i-butane