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Emission estimates of C2-C5 hydrocarbons in the
Rijnmond area on the basis of ground level
measurements

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Summary

The Netherlands Ministry of Housing, Spatial Planning and Environment has commissioned a study to estimate, on the basis of an extensive series of measurements at ground level at Moerdijk, the emissions of C₂-C₅ hydrocarbons in the Dutch Rijnmond area.

This study was preceded by two earlier TNO-studies in which aircraft measurements were used to estimate emissions in the Rijnmond area.

The long-term version of the Netherlands National Model (a Gaussian Plume Model) was used to calculate the average wind rose at the measurement site Moerdijk (MC) from the collective and industrial emissions of the base year 1990. Taking into account the background concentrations in the upwind air, a contribution was calculated of the emissions from the Rijnmond area to the measured concentrations in the northwest quadrant at Moerdijk. This contribution was compared with the contribution shown by the measurements.

The study clearly showed that for distances over 20 km the calculated source contributions with the lowest wind speeds are very clearly too high. Therefore, it was decided to compare the calculated and measured contributions only in those situations where the wind velocity was higher than or equal to 3m/s.

The reactivity of the considered hydrocarbons and the consequent loss of mass between source and receptor do not play a role as long as short transport times are involved, except for propene. The loss of propene due to atmospheric reactions between the most important source areas and Moerdijk is around 30 %.

An important flaw of this study is the absence of sufficient data on concentrations in the upwind air, the air flowing from the North Sea, over the Rijnmond area in the direction of Moerdijk. This flaw applies specifically to those species which have both a small contribution from the Rijnmond area and whose background concentration cannot be clearly determined with the aid of the available measurement data. Ethene and propene are species for which this is a major problem.

The measurement data and the results of the calculations show that the ranking order of the nine C₂-C₅ hydrocarbons in the Emission Inventory based on the strength of the emissions in the Rijnmond area is different from the ranking order of the emissions derived from measurements. The ranking order according to a previous aircraft study agrees with the order found in this study.

The agreement between the emissions derived from ground level measurements in this study and registered emissions is good for the pentanes and the butanes. Propene emissions appear to be higher than those in the Emission Inventory. The uncertainty margins for the propene emission estimates are very high. The ethene

and acetylene emissions appear to be lower than the registered emissions. For ethane and propane higher emissions were found than in the Emission Inventory.

The emissions found in the aircraft study are systematically and significantly higher (a factor of about three) than the emissions derived in this study. A reason for such a large systematic difference between both methods is (as yet) unknown. Validation of the method by calculations with NO_x , using six RIVM (National Institute of Public Health and Environmental Protection) measuring stations around the Rijnmond area shows that this method gives substantial agreement between calculated and measured source contributions. The uncertainty margin of the calculations is about 30%.

The validation of the method of calculation with the aid of NO_x ground level measurements shows that the emissions derived from aircraft measurements are probably (much) too high. Reviewing the results of both studies, it becomes clear that the derived emissions of ethane and propane from the Rijnmond area are clearly higher than the registered emissions. Given the large uncertainty in the emission estimates of propene it is suggested that the propene emissions are possibly higher than those in the Emission Inventory. For the other species both studies do not give a clear indication that the emissions from the Rijnmond area are being either overestimated or underestimated.

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1. Preface

In 1989, by means of a limited number of aircraft measurements, emissions of hydrocarbons, nitrogen oxides and sulphur dioxide in the Dutch Rijnmond area were estimated (Roemer et al., 1991). These emission estimates give an idea of the emissions during a period of a few hours. Comparison with annually averaged emissions according to the Emission Inventory showed large differences, with the exception of SO₂ and acetylene. The estimates based on aircraft measurements showed much higher emission estimates than the annually averaged emissions according to the Emission Inventory. The large discrepancies are possibly caused because the comparison was made between annual averages and samples based on a few hours. Because few sources are active continuously throughout the year, the comparison with annually averaged emissions may give a distorted picture, especially for those species whose emission pattern can strongly vary over the day and/or the year. In a second study the information stored in the Emission Inventory on the variation of emissions with time in the Rijnmond area was used to focus the comparison as accurately as possible on the hours in which measurements were carried out (Berdowski et al., 1992). This study showed that by using this method of comparison the emission estimates based on aircraft measurements were no longer inconsistent with the registered emissions for benzene and xylene. For ethane, ethene and propene it was unlikely that the emissions calculated according to each method can be made to agree with one another. For propane, the butanes and pentanes there was insufficient data to enable any pronouncement to be made.

The emissions calculated from aircraft measurements were based on no more than a few measurements which were not necessarily representative for the annually averaged situation. This disadvantage does not occur with ground level measuring stations which carry out measurements on an hourly basis during a period of a few years. The TNO ground level measuring station at Moerdijk (Moerdijk MC) which measured C₂-C₅ hydrocarbons (ethane, ethene, acetylene, propane, propene, normal butane, isobutane, normal pentane and isopentane) on an hourly basis in the period 1981-1991, has been used in this study to estimate emissions from the Rijnmond area.

The emissions used are the emissions from three provinces; Zeeland, Noord-Brabant and Zuid-Holland for the base year 1990. The concentrations at the receptor point Moerdijk have been calculated with the Netherlands National Model, a Gaussian Plume Model (SDU, 1976, 1984). An important problem with this method and the measurement data available is the lack of measurements on the opposite side of the Rijnmond area. Estimates of the hydrocarbon levels in the up-wind air have been made on the basis of measurement data of an English North Sea measuring station, analyses of the adjacent 'clean' west sector at Moerdijk and with the aid of published background measurements above the North Sea and the Atlantic Ocean.

The findings concerning hydrocarbon emissions in the Rijnmond area do not stand in isolation. From other (foreign) research it also appears that hydrocarbon emissions could possibly be underestimated. As far as is known, these (American) studies are especially concerned with traffic. In this study a literature search was carried out to find as many publications as possible in which emissions based on atmospheric measurements are compared with emissions according to Emission Inventories.

This report is organized as follows. The most important results of the abovementioned literature search are dealt with in Chapter 2. Chapter 3 discusses the historical development of the emissions and hydrocarbon concentrations in the Rijnmond area since 1971. Estimates of the C₂-C₅ concentrations in the upwind air are given in Chapter 4. The core of this study, i.e. the evaluation of the emissions from the Rijnmond area with the aid of diffusion calculations and the measurements of hydrocarbons at Moerdijk are discussed in Chapter 5 (method) and Chapter 6 (results).

2 Survey of methods used to estimate atmospheric hydrocarbon emissions

Emission estimates of hydrocarbons in the Rijnmond area by means of aircraft measurements (Roemer *et al.*, 1993) were based on the difference between hydrocarbon fluxes downwind and upwind of the source area. The substantial discrepancy (a factor of 3) between the emissions calculated from the measurements and those registered raised the following questions: 1: What is the validity of estimates based on only a few measurements? 2: Can we use other methods of estimation? 3: What experience do other countries have with this kind of experiments? A limited literature search was carried out to find a (partial) answer to the last two questions. Although the literature search was limited, we feel that not much more is known in this field than what was found in this study, based on several discussions with experts in the Netherlands and abroad.

Outside the Netherlands (mainly in the USA) a few experiments and studies have been carried out with the aim of comparing hydrocarbon emissions (CO and NO_x) as known from the various Emission Registrations with the emissions that are necessary in order to explain the measured concentrations of these species in the ambient air.

We can distinguish various methods:

- the source reconciliation method;
- tunnel studies;
- atmospheric measurements with emphasis on VOS/NO_x and CO/NO_x ratios;
- balance studies with and without the aid of aircraft measurements;

These methods and the accompanying findings are discussed below. It should be noted that this classification is not entirely unequivocal. Some studies can be placed into more than one category. Nevertheless, this classification may be useful to distinguish the various studies.

2.1 Source Reconciliation Method

The source reconciliation method calculates on the basis of measured atmospheric (hydrocarbon) concentrations and hydrocarbon profiles from the source categories the amount that a specific source category contributes fractionally to the hydrocarbon concentrations (Mayrsohn and Crabtree, 1976).

In abovementioned article, which can be considered basic to the field and in which the composition of the air in Los Angeles was studied, six source categories were distinguished: (1) traffic combustion emissions, (2) complete evaporation of gasoline, (3) partial evaporation of gasoline, (4) commercial natural gas, (5) non-commercial natural gas and (6) LPG (liquefied petroleum gas). Obviously, the choice of the dominating source categories depends on the area; in Los Angeles

traffic is by far the major source. Other studies also take into consideration emissions from solvents or from refining. The number of individual hydrocarbons measured should be larger than the number of source categories.

The method used is the 'least-squares' method where the square of the difference between the calculated atmospheric concentration (by source profile and source contribution) and the measured atmospheric concentration is minimized. This method gives an understanding of the fractional contributions of the source categories to the actual concentrations, but says nothing about the emission in annual quantities by weight. The most significant findings of the five studies falling into this category are discussed below.

Mayrsohn and Crabtree (1976) analysed the hydrocarbon concentrations measured at three sites in Los Angeles in June and July of 1973 during three periods: at night (02:00–05:00h), during the morning peak traffic (06:00–09:00h) and in the early afternoon (12:00–14:00h). They found the following division of sources in Los Angeles: 47% traffic combustion emissions, 31% (partial) evaporation of gasoline, 8% commercial natural gas and 14% non-commercial natural gas. It is noted that this study does not take into consideration the reactivity of the species, nor the background concentrations. Due to the choice of species (low reactivity) and the site of the measurements (dominating influence of nearby sources) neither of these arguments is important. However, it is important that because species like toluene are absent certain categories (solvents) are not, or not properly taken into account, as a consequence of which the percentages mentioned should be regarded as upper limits.

As part of the Los Angeles Reactive Pollutant Program (LARPP) this method was applied to a large number of measurements which were carried out from helicopters above a specific area in Los Angeles (**Feigley and Jeffries, 1979**). Contrary to Mayrsohn and Crabtree (1976), who calculated the contribution of natural gas at 22% in total, Feigley and Jeffries found a contribution of no more than 7%. They attribute this to the fact that they included two additional species (hexane and methane minus background).

This method was applied to an inventory containing many more hydrocarbons, approximately 60 components in the C₂-C₁₀ series, for Sydney (**Nelson et al., 1983**). They made use of 137 samples, collected at three different sites in the city. After comparing this inventory with a much larger one, (Post, 1979) the inventory was considered representative of the composition of the air. The division of hydrocarbons over the source categories in Sydney was as follows: 36% traffic combustion emissions, 32% complete and partial evaporation of gasoline, 23% solvents, 4% natural gas leakage and 5% process emissions. The contribution of process emissions was treated as a residual term. If for the C₂-C₄ alkanes and olefins the other source categories did not make up the full load the remaining part was attributed to the process emissions category.

Two types of sensitivity calculation were carried as to 1) the uncertainty margins in the hydrocarbon measurements and in the category profiles and 2) the reactivity of the hydrocarbons, or to be more precise the individual difference in reactivity. From the first type of calculations, in which a Monte Carlo technique was used, it turned out that the division over the source categories was stable. The relative standard deviation of the source contributions ranged from 25% for full gasoline evaporation to approximately 10% for traffic combustion emissions.

The authors chose the ratio of m,p-xylene to ethylbenzene as measure for chemical activity because this ratio in the composition of emissions is more or less identical for all the considered source categories (according to the authors) and because m,p-xylene is broken down significantly faster in the atmosphere than ethylbenzene. Subsequently, the measurements, on the basis of this ratio, were divided into a number of classes. It turned out that the source division was not very sensitive to changes in the m,p-xylene/ethylbenzene ratio. It is not clear though, whether this ratio is actually a good measure for the reactivity of the atmosphere. The proximity of the sources and the fact that the measurements were made in the morning when the reactivity of the atmosphere is still relatively low give cause to suspect that uncertainties in the composition of the emissions can also have played a role.

The source reconciliation method was also applied to measuring results from an Atlanta study in 1990, in which hydrocarbons and CO were measured during two months at six sites in and in the vicinity of the city (Stevens *et al.*, 1993). The distribution of hydrocarbons over the various source categories as traffic, evaporation, solvents and biogenic agreed well with the distribution according to the emission registration of Georgia. Only the contribution of the biogenic emissions was underestimated in the source reconciliation method, possibly a consequence of not taking into account the reactivity of isoprene.

The source reconciliation method was applied to 192 samples taken between 300 and 1500 metres altitude during six flights above Tokyo on 16 and 17 July 1981 (Wadden *et al.*, 1986). Seventeen different hydrocarbons were measured, which were attributed to five categories: traffic combustion emissions (7%), gasoline evaporation (11%), refineries (26%), paint solvents (27%) and others or unaccounted for (29%). These findings are remarkable, not only because of the large discrepancy with the previously mentioned cities (Los Angeles and Sydney), but especially because of the discrepancy with the division according to the Emission Registration of Tokyo, for which the percentages on an annual basis are 27 (combustion emissions plus gasoline evaporation), 5 (refineries) and 37 (paint solvents). The authors put forward a number of reasons for the discrepancies. For some of the flights the tracks flown were not representative for the average emissions in Tokyo because they were either heavily influenced by one particular source (refinery) or because they were above the inversion layer (in almost a quarter of the cases (!)). Moreover, it is not clear whether the background

concentrations have been taken into account, which is especially important with aircraft measurements.

The last in the series is a study by Heyes and Williams (1993). They compared the composition of hydrocarbons as found in measurements in Harwell (approximately 487 measurements between 1986 and 1990), Great Dunfield (166 measurements between 1989 and 1991) and West Beckham (186 measurements between 1989 and 1991) with the composition as known in the Emissions Registration for Great Britain. Harwell lies northeast of London, while the two other stations are on the coast. Seventeen individual hydrocarbons were analysed. Five source categories were distinguished: traffic combustion emissions, gasoline evaporation, solvents, gas leakages and industrial combustion emissions.

It is noticeable in the results that nothing fell into the category of solvents. The authors put this down to the fact that species like octane and higher alkanes were not included. Species that were measured, like toluene indeed exist in large quantities in solvents, but so they do in traffic emissions. It is curious that in the Tokyo study (Wadden *et al.*, 1986), in which practically the same measured species were used as in Great Britain, emissions from solvents were especially prominent. Moreover, in both Emission Registrations about the same percentages are used for the contribution of emissions from solvents.

Furthermore, it is notable that the contribution of gasoline evaporation is much higher (42%) in Harwell than at the other two stations (8 and 19%). The authors attribute this to the disproportionately high concentrations hexane and butane in Harwell during a number of years.

In a second phase of this study a diffusion model was applied that had been used earlier for NO_x (Simpson *et al.*, 1990). Such a study is not directed solely at the fractional contributions of sources, but also attempts to analyse the absolute emission levels. In doing so, background concentrations from the Atlantic Ocean and the influence of emissions from Europe are taken into account. With some reservations the authors reach the conclusion that the results of this model suggest that the total mass of VOC-emissions in Great Britain is underestimated by 35% at most.

2.2 Studies in tunnels and along roads

Tunnel measurements in which the concentrations in the air are measured at both entrances of a tunnel (and sometimes halfway as well) are pre-eminently suited for calculating the emissions from vehicles under realistic driving conditions (in the tunnel). Extensive measurements have been done in a number of tunnels and along several roads in the United States. With respect to Europe there are studies from the Netherlands (Drechtunnel: Thijssen en den Tonkelaar, 1987), Belgium (De Leopold II tunnel in Brussels: Vanderstraeten *et al.*, 1991), Sweden (Klaratunnel in Stockholm: Johansson, Berges, 1994; Tingstadunnel in Göteborg: Barrefors and

Petterson, 1992), Switzerland (Gubristunnel near Zurich: Staehelin *et al.*, 1994), Austria (Tauernunnel: Gregori *et al.*, 1989) and Germany (the Elbe tunnel near Hamburg: Dannecker *et al.*, 1990).

A well-known study that drew a lot of attention was the Van Nuys tunnel study in 1987 in Los Angeles (Ingalls *et al.*, 1987). The NO_x emissions derived from the measurements

agreed well with those based on the emission model EMFAC7C, a model of the Californian Air Resources Board (CARB). On the other hand, the CO and hydrocarbon emissions derived from the measurements turned out to be, averaged over all the experiments, higher by a factor of 2.7 ± 0.8 and 4.0 ± 1.8 respectively than according to EMFAC7C. A survey of the results of this study and of previous American studies (tunnel studies as well as other studies) can be found in Pierson *et al.* (1990). This article has been used as a guide for the following survey.

The Van Nuys tunnel measurements showed:

- that the discrepancies were particularly large with high speeds (19 experiments); significantly smaller discrepancies occurred in the case of two experiments involving traffic jams, although in these cases the measurements were not unequivocal.
- using EMFAC7D hardly led to improvement in the equation.
- on the other hand, much better agreement was achieved when the EPA emission model MOBILE 4.1 was used (discrepancy factors were reduced to 1.9 for CO and 1.7 for hydrocarbons; however, the predicted NO_x emissions were approximately a factor of two higher than what was measured;
- as possible causes for the discrepancies can be put forward a) gasoline evaporation during the driving (running-loss evaporative emissions) although the indications for this are unclear, b) in reality the percentage of cars with high emissions was far higher due to bad maintenance or tinkering with the emission control system.

In 1991 and 1992 the US-EPA and Desert Research Institute carried out measurements in the Fort McHenry tunnel (Maryland) and the Tuscarora tunnel (Pennsylvania). The results of the experiments in the Fort McHenry tunnel showed that the CO, NMHC and NO_x emissions measured were higher than according to MOBILE 4.1 for light vehicles (Light Duty Vehicles; LDV), but that for heavy vehicles (HDV) there was good agreement (Cadle *et al.*, 1993). In comparison with MOBILE5 the LDV measured emission factors are in agreement for CO and NMHC, but now NO_x is being overestimated by 60% (Pierson *et al.*, 1994). In the Tuscarora tunnel, where vehicles maintain a constant speed (on a level road) good agreement was found for NO_x for HDV on comparison with MOBILE 4.1, but now it turned out that the measured CO and NMHC emissions were factors of 1.4 and 1.5 lower for LDV and factors of 1.4 and 1.6 for HDV (Pierson *et al.*, 1994). Application of MOBILE5 in all cases (3 species; LDV and HDV) resulted in a substantial overestimation by MOBILE5 of the emission factors measured. The

agreement between emissions measured and emissions according to a model (MOBILE 4.1) is (much) better for these tunnels than for the Van Nuys tunnel. Possible causes are: a more constant speed and better maintained cars in the previously mentioned tunnels and developments over the the last five years in the emission models (Pierson *et al.*, 1994). Where the CO/NO_x ratio and the NMHC/NO_x ratio are concerned the agreement between MOBILE 4.1 and the measurements is rather good. On the other hand, the ratios for abovementioned combinations in MOBILE5 are systematically lower than the measurements. An important finding from the studies in the Fort McHenry and Tuscarora tunnels is that upward slopes can lead to a factor of two increase in emission factors (expressed in g/km), but show no discrepancy if the emission factors are expressed in g/l fuel. Moreover, it was remarked that a substantial part of the emitted hydrocarbons, and consequently a substantial part of the capacity of exhaust gas to form ozone, were found in the heavier components, larger than C₁₀ (Pierson *et al.*, 1994).

Experiments in the Lincoln tunnel (New Jersey/New York) in 1970 and 1982 indicate that during this period the NMOC (Non-Methane Organic Compounds) traffic emissions decreased by a factor of 4, and that for acetylene a reduction of a factor of 6 had even been achieved (Lonneman *et al.*, 1974; Lonneman *et al.*, 1986). The average CO/NMOC/NO_x ratio on a mass basis measured 10.2/2.6/1 in 1970 and 6.5/1.8/1 in 1982.

CO emissions from cars (with spark injection, SI) and heavy truck traffic calculated from measurements in 1979 in the Allegheny Mountain Tunnel in Pennsylvania turned out to agree reasonably well (approximately 1 standard deviation lower) with emissions calculated from MOBILE1 and a factor of 2/3 too low when compared with MOBILE2 (Gorse and Norbeck, 1981). No corrections were applied for tail wind, slope and elevation of the road. Application of the first two corrections would bring the CO emissions in agreement with the measurements. The effect of the third correction is unclear.

Measurements in 1981 in the same tunnel showed identical results for CO. The calculated emissions of CO and hydrocarbons, after application of the three corrections, turned out to be in agreement with MOBILE2, as did the NO_x emissions from diesel traffic. However, the NO_x emission from SI-cars calculated from the measurements was a factor of 2 lower than the emission predicted on the basis of MOBILE4.

On the basis of measurements in 1976 and 1977 along four motorways in Texas, Bullin *et al.* (1980) reported very high emission factors for CO (Tab. 2.3). The value of these measurements is not undisputed (Sedefian *et al.*, 1981; Bullin and Polasek, 1981). Significantly lower CO emission factors, which were more in agreement with the tunnel measurements, were found in 1984, also on the basis of measurements along a motorway in Texas (Hlavinka and Bullin, 1988).

Zweidinger *et al.* (1988) measured SF₆ (as tracer), CO, NO_x and hydrocarbons along a motorway (near to traffic lights) in North Carolina in 1983. The emission factors on the basis of measurements were approximately 30–40% lower (CO and hydrocarbons) at low speeds (20 miles/hour) than those of MOBILE3, and for NO_x a factor of 2 lower than MOBILE3. At higher speeds (35 miles/hour) the emission factors derived from the measurements were higher than those in MOBILE3. For NO_x the discrepancy was a factor of 1.7, although due to the large variation in the NO_x measurements this discrepancy was not significant. However, for CO and hydrocarbons the discrepancies were significant, factors of 3 and 2 respectively higher than MOBILE3. The discrepancies could be caused by not taking into account the evaporation losses in MOBILE3 and also not taking into account emissions from heavy truck traffic and from cars without catalysts.

Less CO and hydrocarbons are emitted when driving is constant than when there is much acceleration and braking. Kennedy *et al.* (1975) measured the emissions from the exhausts of 45 trucks that drove a 9-mode FTP cyclus and a specific route on the road. Contrary to circumstances in practice the cyclus contains hardly any periods of acceleration or deceleration. The CO/HC/NO_x ratio changed from 13/1.2/1 during the FTP test to 21/2.2/1 on the road, in which case the CO and hydrocarbon emissions increased and those of NO_x decreased.

Remote sensing of CO in exhaust gasses in streets or along motorways has been applied at a number of places in the United States, viz. Denver (Bishop and Stedman, 1989; Stedman, 1989), Chicago (Stedman and Bishop, 1990), Ute Pass Colorado (Stedman and Bishop, 1990) and Los Angeles (Lawson *et al.*, 1990). An important finding which emerged from all the studies was that 8–10% of the cars were responsible for 50–55% of the CO traffic emissions. Although the older cars contributed more than the newer ones, it was notable that in this last category some cars were extremely polluting. Approximately 1% of the cars emitted more CO (on mol basis) than CO₂.

Many of the emission factors (MOBILE and EMFAC) make use of so-called test fleets of cars with the cooperation of volunteers. Research shows that precisely in these kinds of fleets the highest polluters are under-represented. Instead of 8–10% of the fleet, half the CO emission derives from 17–20% of the fleet.

Many of the highest emissions in Los Angeles came from cars that were found to be in order at their most recent (two-yearly) smog check or their I/M check (Inspection and Maintenance) (Lawson *et al.*, 1990). The CO and hydrocarbon emissions of these cars were much higher than the emissions reported during their most recent check. In almost half the cases their emission control systems had been tinkered with.

In 1986 and 1987 TNO carried out measurements in the Drecht tunnel (a motorway) near Dordrecht. The emission factors found for CO and NO_x from passenger cars and light truck traffic agreed well (within 10–20%) with those of the CBS (1985). Concerning heavy truck traffic there was agreement on CO, but for NO_x

the emission factor derived from the measurements was about half that of the CBS (Thijssse and den Tonkelaar, 1987).

In the period December 1988 up to and including February 1989, ten measuring campaigns were carried out during peak traffic in the Leopold II tunnel in Brussels (Vanderstraeten *et al.*, 1991). During the peak traffic period the time spent in the 3 kilometre tunnel can run up to 10–20 minutes due to traffic jams. The aim of the measurements was to form an impression of possible health effects. The NO₂/NO volumetric ratio, which comes to 0.04–0.08 in the case of traffic driving normally can increase to 0.12–0.18 for stationary traffic. Likewise, the CO/NO_x ratio can increase from approximately 10 up to 60 even.

The Elbe tunnel, a motorway tunnel near Hamburg, was the site of a study in the period of August 1988 up to and including January 1989 into the emissions of organic and non-organic gasses and aerosols from motor traffic (Dannecker *et al.*, 1990). The most significant gaseous components (sampled on filters) were benzene, ethylbenzene, the xylenes and some trimethylbenzenes, always in a fixed ratio. (Toluene and the most volatile hydrocarbons were not sampled.)

Most of the results of a series of measurements in the Klara tunnel had not yet been published at the time of writing (October 1994). The part which has been published shows that the CO/NO_x ratio calculated from the measurements was on mass basis approximately thirteen.

The Tingstad tunnel is a motorway tunnel near Gothenburg where measurements of hydrocarbons were carried out in 1991 and 1992 (Barrefors and Petersson, 1992). The highest concentrations of C₂-C₁₀ were measured when traffic jams slowed down traffic. Assuming a ventilation speed of 5 m/s due to the speed of the cars themselves, on the basis of the published measuring results over three days, an emission factor for the sum of C₂-C₁₀ for fast traffic (60–80 km/h) is calculated at between 0.6 and 1.7 g/km. For the two days when traffic jams occurred and the speed ranged from 0 to 70 km/h and between 0 and 40 km/h a higher emission factor was calculated, viz. 2.9 and 4.7 g/km respectively.

However, the assumption concerning the ventilation speed is probably not tenable in these two cases, because the vehicles through their movement contribute significantly to the ventilation in a tunnel. The contribution on the basis of mass of alkenes (C₂-C₆), alkanes (C₂-C₉) and aromatics (C₆-C₁₀) amounted to 14%, 32% and 49% respectively.

The results of the measurements in the Gubris tunnel near Zurich were not available at the time this was written.

The Tauern tunnel is a 7 kilometre motorway tunnel, about 80 km south of Salzburg. The average gradient of the tunnel is 1.5%. In September 1988 Vienna University organised extensive measurements in the tunnel with the aim of

characterizing the traffic emissions more accurately (Gregori *et al.*, 1989). Measurements were carried out on a Friday and Sunday in the tunnel section for ascending traffic. The emission factors calculated from the measurements were: 15.3 ± 2.6 g/km (CO), 2.3 ± 0.6 g/km (NO_x) and 2.0 ± 0.3 g/km (hydrocarbons). A comparison with emission factors 'registered' (BUA Bern, 1986) shows that there is very good agreement for hydrocarbons, that a slight overestimation (20%) occurs in the registration for NO_x , and that CO is underestimated (20 and 100%) in the registration. Grigori *et al.* (1989) attribute the discrepancies to the elevation of the road and argue that the emission factors mentioned are reasonably workable.

2.3 Atmospheric measurements at ground level

A number of studies has been carried out in which the VOS/ NO_x ratio in the atmosphere of cities was compared with those according to the Emission Registration. Most of the (known) measurements are from the United States. A survey of American studies in this field can be found in Pierson *et al.* (1990 and 1994). The general impression from these studies is that emissions of hydrocarbons in urban areas in the United States, in which traffic emissions play a major role, are substantially (factors of 2–4) underestimated in the Emission Registrations.

Typical VOS/ NO_x ratios found in many American cities are between 8 and 12 on ppmC/ppm basis (Westberg and Lamb, 1985; Lee *et al.*, 1988; Richter *et al.*, 1985; Baugues, 1986; Kuntasal and Chang, 1987; Morris, 1990; Fujita and Croes, 1990). The VOS/ NO_x ratio in the emissions in these cities is, according to the (local) emission registrations, between 2 and 5. However, there are problems involved in comparing VOS/ NO_x ratios in emission registrations and atmospheric measurements. One significant flaw of this comparison is that a substantial part of the NO_x emissions is emitted at a high altitude (100–200 metres or higher), whereas on the other hand the hydrocarbons are almost all emitted close to the ground. As it may be assumed that the NO_x emitted at high altitude has no influence on the NO_x concentrations in the city, this leads to a higher VOS/ NO_x ratio in the measurements than would be predicted on the basis of the registrations.

In addition matters like reactivity and interference of background air probably play a minor role in most cities. In large cities with high NO_x concentrations the concentrations of O_3 and OH are generally so low that within a period of a few hours only a very limited influence of chemical reactions on the concentrations can be expected. Only for the very reactive hydrocarbons (like isoprene) can the chemical reactivity lead to higher concentrations. For those cities in which biogenic emissions play a not insignificant part, atmospheric decomposition could (possibly) lead to an underestimation of the actual VOS/ NO_x ratio emitted.

Background air has a higher VOS/ NO_x ratio than urban air. Thus it is possible for the interference of background air to increase the VOS/ NO_x ratio in urban measurements. However, the concentrations of hydrocarbons and NO_x in back-

ground air are so much lower than those found at the centre of a (large) city that this will not be of much influence.

A recent survey of CO, NMHC and NO_x measurements in California suggests that, taking into account the considerations mentioned above, the CO/NO_x ratio and VOS/NO_x ratio in the atmosphere are factors of 1.5 and 2–2.5 respectively higher than the corresponding ratios as derived from the inventoried emissions (Pierson *et al.*, 1994). Because of the site and the time of the measurements the cause of the discrepancy must be found entirely in emissions from traffic.

Fujita (1993) investigated the trend of atmospheric concentrations in Los Angeles over the period 1976–1990 and compared this to the trend of the registered emissions. Trends of CO, NMHC and NO_x concentrations agree well, certainly for the summer measurements, with the corresponding emission trends. For reasons which are as yet unclear, the trend of the autumn measurements shows some discrepancies, possibly due to the fact that interference in the morning of accumulated air pollution is greater in the autumn than during the summer (Pierson *et al.*, 1994). Furthermore, it turns out that the atmospheric CO/NO_x and NMHC/NO_x ratios are factors of 1.5–2 and 1.7–3.4 respectively higher than the registered emission ratios and that these discrepancies have not changed much over the entire 1976–1990 period.

There are few known hydrocarbon measurements for major European cities, although CO and NO_x are measured in many cities. During the last few years in the Netherlands the RIVM has carried out CO and NO_x (and other) measurements at approximately 16 sites in Dutch towns. The RIVM distinguishes between street stations and urban background stations. The CO/NO_x ratio (on mass basis) varies between 7 (Vlaardingen and Amsterdam-North) and 13 (Haarlem). The average ratio is 8.5. The ratio seems to be increasing slowly from 8.3 in 1989 to 9.0 in 1992.

Similar CO/NO_x ratios were also found for Hamburg and London (Umweltbehörde, 1989; Derwent *et al.*, 1994). A CO/NO_x ratio of 8–9 agrees very well with that reported by the CBS for passenger cars in the built-up area (CBS, 1991). However, when the average composition of the urban traffic is studied the CO/NO_x ratio turns out to be considerably lower, approximately 4.5 (CBS, 1991). Possibly the contribution of trucks and busses, which has a lowering influence on the CO/NO_x ratio, is lower than average in the streets where the measurements took place. Hourly atmospheric measurements of CO, NO_x, SO₂, O₃, CO₂ and 28 hydrocarbons during a year (July 1991–July 1992) in the city centre of London were used to estimate the emissions from London (Derwent *et al.*, 1994). By means of the principal components analysis (PCA) the most important sources were identified, i.e. traffic for almost all hydrocarbons, and natural gas leakages for ethane and propane. Concentrations of SO₂ and trans-2-butene were correlated, which points to the possibility of this hydrocarbon being associated with industrial combustion processes.

Because of higher ethane concentrations in London as compared to those in Harwell, the authors estimate that approximately 1% of the natural gas in the distribution network is lost due to leakages.

With the aid of relatively simple distribution calculations and taking into consideration the traffic flow intensity in London, the emission factors for acetylene in the calculations were adapted in such a way that calculations and measurements matched one another as well as possible. For acetylene different emission factors were used for the morning and evening traffic peaks, namely 249 and 338 mg/km. This is a higher value than the 163 mg/km as determined in test measurements under urban conditions (Bailey *et al.*, 1990; Bailey and Parkes, 1993). The emission factor for CO based on measurements: 23.4–30.2 g/km agrees very well indeed with the value from measurements at the exhaust: 21.4 ± 10 g/km. This emission factor is close to the more recent American emission factors (derived from measurements) for slow driving traffic.

Comparison of the emission factors for traffic calculated from this study (in which emissions from the exhaust and through evaporation are accumulated) and the emission factors as determined from measurements at the exhaust (Bailey and Parkes, 1993; Bailey *et al.*, 1990) shows that the London study calculates higher emission factors for the butanes (a factor of 2), acetylene (1.5–2), and lower emission factors for ethene (0.7), toluene (0.5–0.4), xylenes (0.25) and ethylbenzene (0.3). The emission factors of the remaining 10 reported species were within limits. It is important to note that it is not clear how the 'registered' emission factors are compiled. It is possible that influences from findings from atmospheric measurements have been taken into account (Eggleston, 1993).

2.4 Aircraft measurements

Only one publication has been found in which aircraft measurements were used in a similar way as in the Rijnmond study (Roemer *et al.*, 1991; Roemer *et al.*, 1993) and in which an estimation of hydrocarbons is given as well. This concerns a series of measurement flights carried out by the KEMA above the Botlek area between 1975 and 1978 (van Duuren *et al.*, 1979; KEMA, 1982). These measurements will be discussed in chapter 3.

Potentially usable hydrocarbon measurements were carried out above London. Upwind and downwind masses of air were sampled (Penkett *et al.*, 1993). However, the flights had a purpose different from that of estimating emissions of hydrocarbons.

In order to follow the changes in emissions in the former GDR after the reunification the SANA project has been launched. One of the programmes concerns aircraft measurements of hydrocarbons (among other things) upwind and downwind of source areas. The results are as yet unknown.

Sexton and Westburg have carried out many measurements (hydrocarbons, NO_x, and O₃) in the vicinity of source areas. These concerned ground measurements as well as aircraft measurements, sometimes in conjunction. The emission from an oil refinery in Robinson, Illinois was studied in June and July 1977 (Sexton and Westberg, 1983). Approximately 80–95% of the NMHC emissions consisted of paraffins, aromatics (5–15%) and olefins (1–5%). The results agree with previous studies at other refineries (Westberg *et al.*, 1977; Sexton and Westberg, 1979). Estimates of emissions (in weight per unit of time) were not given.

A similar study was carried out in the vicinity of a large car respraying shop in Wisconsin in 1977 (Sexton and Westberg). The highest concentrations measured were successively of toluene, m,p-xylenes, o-xylene, ethylbenzene, methylpentanes and n-octane. The measured ratio of toluene and xylenes agrees well with the registered ratio. Indeed, half the registered emissions consist of oxygen-containing hydrocarbons, especially acetone, methanol and acetates.

Other studies refer to both large urban areas like Chicago and Milwaukee (Westberg *et al.*, 1981) and Houston (Sexton and Westberg, 1980) and smaller urban areas (Sexton, 1983). In all these studies the emphasis was on the ozone producing potential of the air parcels and not on the emissions themselves.

A discussion of the strategy of measurement and method of calculation used to estimate emissions with the aid of (aircraft) measurements upwind and downwind of urban areas is found in an article by Ching *et al.* (1987) and a presentation by Ching (1994).

2.5 Traffic Emission Factors

Emission factors for traffic can be derived from both tunnel studies and atmospheric measurements. It is interesting to compare these with the factors used by the Emission Registrations. At the same time it can be established whether there are differences between for instance the United States and Europe and which developments have occurred over the last 10–20 years. An important problem that occurs with this kind of comparisons is that sometimes information is lacking on the composition and speed of traffic. Also, it is often not clear whether the basis of comparison is the same: is the evaporation of hydrocarbons included, is it an average of the fleet of cars or only of passenger cars (gasoline), is it an average local journey, or only valid at one specific speed, have temperature effects and altitude effects been taken into account, etc.. The comparison has been divided into four classes: emission factors from the individual registrations (Table 2.1), measured and registered emission factors at low speed (Table 2.2) and at high speed (Table 2.3) and trends (Table 2.4).

On comparing the emission factors from the various emission models (Table 2.1) it is noticeable that the emission factors used in Switzerland for passenger traffic are

lower (CO and especially VOS) than those in the Netherlands, but in contrast those for NO_x are higher. In the Netherlands lower factors for all three species (groups of species) are used for truck traffic. From the American Emission models it emerges that emission factors for VOS and CO are higher (10–30%) at an altitude of 1700 metres than those at an altitude of 150 metres and that the emission factor for NO_x is somewhat lower (Black, 1989). It is not clear whether a similar aspect has been incorporated into the Swiss models.

In Table 2.3 it is noticeable that the emission factors based on measurements of CO, hydrocarbons and NO_x strongly differ from one another in three tunnel measurements. The order from high to low is as follows: Van Nuys tunnel, Fort McHenry tunnel and Tuscarora tunnel. In the case of the Van Nuys tunnel there was a substantial underestimation of the measured CO and VOS emission factors by EMFAC7C, later versions of the EMFAC7 series have been modified in such a way that there might even be overestimation instead of underestimation. For EMFAC7G (1995) a triplication of the hydrocarbon emissions and more than a doubling of the CO emissions apply in relation to EMFAC7D (1988); NO_x emissions have been raised by 30% (Fujita and Lawson, 1994). The same phenomenon, but less drastic is shown by the EPA models (compare: MOBILE4.1 and MOBILE5).

Comparisons of the measured emission factors with those in models (registered) do not show an unequivocal picture. The impression is that the current emission models are more in agreement with the measurements than those of a few years ago. There is a much clearer picture where trends are concerned (Table 2.4). On this point the estimates based on atmospheric measurements and the estimates of the emission registrations agree extraordinarily well, both in California and in the Netherlands. The NO_x trend during the past 10–15 years is downward (California) or absent (the Netherlands). The CO trend was the same in both areas (an approximate reduction of 40%), but hydrocarbons from traffic dropped far more in California (50%) than in the Netherlands (30%).

The developments in emission factors are very similar for the Netherlands and the United States. In the period 1975–1990 the emission factors for CO and hydrocarbons decreased by 80% and 70% respectively. For NO_x there was a reduction of 50% (United States) and 25% (the Netherlands) over this period. The increase in car traffic has meant that measures had little or no effect for NO_x, but this did not prevent an actual reduction in CO and hydrocarbons being achieved.

2.6 Conclusions

- The source reconciliation method shows that in American cities and in London, traffic is the dominant source of hydrocarbons. This method enables the calculation of a relative source contribution (in a percentage of the total amount), but not an absolute contribution (in tonnes per annum).

- Aircraft campaigns with the aim of estimating hydrocarbon emissions, have for so far known only been carried out in or in the vicinity of the Rijnmond area.
- A number of tunnel studies carried out in the 1980s showed significantly higher emission factors for CO and hydrocarbons than those according to the emission models. Modification of these emission models and a reduction of the actual traffic emissions per car have led to the emission factors of the emission models agreeing reasonably well with the emission factors calculated from some recent tunnel measurements.
- CO/NO_x and NMHC/NO_x ratios from measurements in American cities are significantly higher than those according to the emission registrations. The repeatedly made observation from measurements that 10% of the vehicles is responsible for 50% of the emissions could possibly be the reason. No studies have been found that have carried out similar analyses for European cities.
- There is very good agreement between trends based on measurements and trends according to emission models. This is the case for CO and hydrocarbons and for NO_x, and applies for the Netherlands as well as the United States.
- The emissions from traffic have been substantially reduced over the period 1975–1990 as far as CO and hydrocarbons are concerned. For NO_x the reduction is limited (United States) or even absent (the Netherlands).

Table 2.1: Overview emission factors from emission models at various velocities

Country	Year	Type	Speed (mi/h)	CO (g/mi)	VOC (g/mi)	NO _x (g/mi)	Ref
Switz./Austria	1985	PKW ¹⁾	38	9,4	1,4	3,2	a
			63	7,4	1,1	6,1	
			81	17,3	1,3	7,7	
		LKW ²⁾	38	6,2	4,3	22,4	
			63	8,8	4,2	39,4	
The Netherlands	1985	private cars	44	11,7	2,0	2,7	b
			63	14,7	2,2	4,7	
			75	20,2	2,4	6,6	
		truck	38	3,1	2,2	18,4	
			63	5,1	3,5	29,4	
The Netherlands	1990	private cars	44	6,6	1,3	2,2	b
			63	8,3	1,4	3,8	
			75	11,4	1,5	5,4	
		truck	38	2,7	1,8	16,5	
			63	4,5	2,8	26,4	
U.S.A.	1985	LDGV ³⁾	20	19,1	3,5	2,0	c
		HDDV ⁴⁾	20	12,4	4,6	20,5	

- a. BUA, 1986 ¹⁾ PKW Personen Kraft Wagen
b. CBS, 1991 ²⁾ LKW Last Kraft Wagen
c. # ³⁾ LDGV Light Duty Gasoline Vehicle
⁴⁾ HDDV Heavy Duty Diesel Vehicle

Table 2.2: Overview emission factors traffic from measurements and emission models under low speed conditions

Location	Year	Type	Speed (mi/h)	CO (g/mi)	VOC (g/mi)	NO _x (g/mi)	CO/VOC/NO _x (NO _x ≡1)	Ref
North Carolina highway Mobile 3	1983		20	21,4	2,7	1,8	12,0/1,5/1	a)
			21	29,7	3,6	3,1	9,6/1,2/1	
North Carolina highway Mobile 3			34	39,4	5,1	5,1	7,8/1,0/1	a)
			35	11,2	2,6	3,1	3,6/0,8/1	
Van Nuys tunnel, LA EMFAC 7C	1987		13	41	5	1,3	32,5/4,0/1	b)
				33,6	2,7	2,0	17,3/1,4/1	
Denver Interstate ramp	1989	LDV ¹⁾	25-30	15-35				c)
Chicago Interstate ramp	1989	LDV	27	20				d)
Los Angeles; street	1989		20	25				e)
UK urban (cold)					8,8			f)
UK urban (hot)					4,8			f)
UK suburban					2,8			f)
London	1991/2			37-48	>2,3	2,9-3,2		g)
The Netherlands, urban	1990			16	3,8	3,5		h)

- a) Zweidinger *et al.*, 1988 e) Lawson *et al.*, 1990 ¹⁾ LDV Light Duty Vehicle
b) Ingalls, 1989; Ingalls *et al.*, 1989 f) Eggleston, 1993
c) Bishops and Stedman, 1989 g) Derwent *et al.*, 1994
d) Stedman and Bishops, 1990 h) CBS, 1991

Table 2.3: Overview emission factors traffic based on ambient air measurements and from emission models under high speed conditions

Location	Year	Type	Speed (mi/h)	CO (g/mi)	VOC (g/mi)	NO _x (g/mi)	CO/VOC/NO _x (NO _x ≡1)	Ref
Lincoln Tunnel, NY	1970						10,2/2,6/1	a)
	1982						6,5/1,8/1	b)
Texas Interstate	may 1976		≥55	144				c)
	jan. 1977		≥55	44				c)
	aug. 1977		≥55	65				c)
	nov–dec 1977		≥55	119				c)
	nov–dec 1984		≥55	24				d)
Allegheny Tunnel, PA	summer 1979	LDV ¹⁾	55	–	0,8–1,6	–		e)
	summer 1979	LDV	55	16,7	–	–		f)
	summer 1981	LDV	55	14,3	1,6	≤1,9	>7/>0,8/1	g)
North Carolina highway	1983		41	34,9	4,7	4,6	7,6/1,0/1	h)
Van Nuystunnel, CA	1987		41	21	2,7	1,6	13,3/1,7/1	i)
EMFAC 7C			41	7,5	0,7	1,4	5,3/0,5/1	
Mobile 4			41	(11,1)	(1,6)	(3,2)	3,5/0,5/1	
Fort McHenry tunnel	1992	LDV	38–53	6,4	0,6	0,8	7,8/0,8/1	j)
Mobile 4.1		LDV		3,7	0,4	0,6	6,1/0,6/1	
Mobile 5		LDV		6,9	0,6	1,3	5,3/0,5/1	
Tuscarora tunnel	1992	LDV	50–60	4,9	0,3	0,4	12,7/0,8/1	j)
Mobile 4.1				7,1	0,5	0,6	12,0/0,8/1	
Mobile 5				12,5	0,8	1,6	7,8/0,5/1	
Fort McHenry tunnel	1992	HDV ²⁾	38–53	9,8	1,5	14,4	0,7/0,1/1	j)
Mobile 4.1				11,1	1,3	14,5	0,8/0,1/1	
Mobile 5				13,9	1,6	17,0	0,8/0,1/1	
Tuscarora tunnel	1992	HDV	50–60	6,0	0,7	19,5	0,3/0,04/1	j)
Mobile 4.1				8,5	1,1	19,2	0,4/0,06/1	
Mobile 5				9,8	1,3	22,4	0,4/0,06/1	
Drechtunnel, NL	1986/7	LDV	>55	7,8	–	4,5	1,7/–/1	k)
Drechtunnel, NL	1986/7	HDV	>55	8,0	–	15,8	0,5/–/1	k)
Tingstadtunnel, Sw	1991/2		40–50		1,0–2,7			l)
Klaratunnel, Sw	1992?						12,7/.../1	m)
Tauerntunnel, Austria	1988		40–45	24,5	3,2	3,7	6,6/0,9/1	n)
UK highway			56		1,1			o)
			70		(0,3–2,9)			
					1,0			
					(0,3–1,8)			

1) LDV Light Duty Vehicle

2) HDV Heavy Duty Vehicle

a) Lonneman *et al.*, 1974

b) Lonneman *et al.*, 1986

c) Bullin *et al.*, 1980

d) Hlavinka and Bullin, 1988

e) Hampton *et al.*, 1983

f) Gorse and Norbeck, 1981

g) Gorse, 1984

h) Zweidinger *et al.*, 1988

i) Ingalls, 1989

j) Pierson *et al.*, 1994

k) Thijse and Den Tonkelaar, 1987

l) Barrefors en Petersson, 1992

m) Johansson, 1994

n) Gregori *et al.*, 1984

o) Eggleston, 1993

Table 2.4: Overview of trends of ambient air concentrations, traffic emissions and emission factors. Base Year 1990 \equiv 100

Location and kind	Year	CO	VOC	NO _x
South Coast Air Basin CA				
• traffic emission	1990	100	100	100
	1985	125	150	120
	1980	155	210	125
	1976	170	240	120
• ambient air concentrations summer	1990	100	100	100
	1985	130	175	120
	1980	170	200	140
	1976	225	195	140
The Netherlands				
• traffic emission	1990	100	100	100
	1985	135	118	96
	1980	165	132	99
• ambient air concentration acetylene, Moerdijk	1991	–	100	–
	1981	–	140	–
U.S.A.				
average emission factors traffic	1990*	100	100	100
	1985	180	160	130
	1980	360	270	175
	1975	480	380	200
The Netherlands				
emission factors private cars highway	1990	100	100	100
	1985	180	160	120
	1980	245	190	140
	1975	435	380	135
	1970	550	470	125
The Netherlands				
emission factors private cars urban area	1990	100	100	100
	1985	170	160	130
	1980	235	205	150
	1975	410	340	140
	1970	520	430	130

3. Survey of hydrocarbon measurements in and around the Rijnmond area

Since 1971 a number of Dutch institutes have carried out measurements of hydrocarbons in and around the Rijnmond area. The most important findings from these measurements, especially those concerning emission estimates for the Rijnmond area, will be discussed individually for each institute. Finally, as far as is possible, the developments of hydrocarbon emissions in the Rijnmond area over the 1970s will be discussed.

3.1 KEMA

Between 1975 and 1978 the KEMA carried out sixteen flights around the Botlek area during which, among others, O₃, NO and NO_x were measured (van Duuren et al., 1979; KEMA, 1982). During five flights hydrocarbons were sampled as well. These samples were taken in such a way that average concentrations per track were obtained. Measurements were carried out at a number of altitudes between 150 and 520 metres and in some cases between 150 and 610 metres. A further distinction was made between an upwind track (track 1), and two downwind tracks (2 and 3) which were respectively just beyond the source area and at some distance from the source area (8-18 km). A survey of estimated emissions based on the measurements (supplied by the KEMA) shows that the emissions vary widely for four of the flights (Table 3.1).

In two cases negative emissions were found because the concentrations in the upwind air were higher than in the downwind air. The possible influx of air with high concentrations from above the inversion layer, into the mixed layer of the source area could explain this, according to the KEMA.

Taking into account that the Botlek area is significantly smaller than the entire Rijnmond area and that important sources of hydrocarbons exist west of the Botlek area as well, it should be noted that the estimated emissions from flight number 13 are rather high. The estimated emissions from flight number 14 on the other hand do not seem to disagree with the more recent TNO estimates. It is noted that there were about 13 years between the KEMA and TNO measurements, during which period major developments in the field of hydrocarbon emissions have taken place. The impression from the KEMA study is that determining emissions with the aid of aircraft measurements above a relatively small area surrounded by other source areas is a very difficult matter.

3.2 RIVM (National Institute of Public Health and the Environment)

Since a few years the RIVM has carried out measurements of hydrocarbons at a number of sites in the Netherlands. In the city centre of Rotterdam about 31 individual components are measured with a frequency of 11 samples a week. However, these concern the less volatile components C₆-C₁₆ amongst which benzene and toluene. No measurements of the very volatile components (C₂-C₅) in the Rijnmond area are carried out.

3.3 TNO (Netherlands Organization for Applied Scientific Research)

TNO has carried out hourly measurements of hydrocarbons (C₂-C₅) since July 1971 at the TNO premises at Delft. This series at Delft continued until, and included, 1977. The samples were analysed with the aid of the so-called direct injection method. This method has the disadvantage, especially in comparison with more recent methods, that the detection limits are relatively high, varying from 1 ppb for species like ethane and ethene to 4 ppb for the butanes and 5 ppb for the pentanes. As a result, especially the butanes and pentanes in the less polluted wind sectors were comparatively often measured below the detection limit.

The wind roses at Delft constructed on the basis of these measurements show that the highest concentrations of C₂-C₅ hydrocarbons at Delft are found when the wind comes from the Rijnmond area. In Chapter 3.5 the measurements from the 1970s at Delft will be discussed.

During the period 1982-1984 hydrocarbons were again measured at Delft, this time with the same method of analysis that is applied at Moerdijk. With this method the detection limits vary from 0.1 ppb to maximally 0.6 ppb.

Through the years TNO has operated three measuring stations in the vicinity of the Moerdijk industrial zone. Measuring point MA, to the east of the industrial zone and near Moerdijk village, was operational during the period 1975-1985.

Measuring point MB, at the industrial zone itself, was operational for a limited number of years. Measuring point MC is located to the west of the industrial zone near Klundert. Measurements were carried out here during the period 1981-1991. After 1991 the measuring programme was changed. Henceforth, only ethene, acetylene and propene are measured. In addition, daily averaged concentrations of C₆-C₁₆ hydrocarbons are measured at Moerdijk MC.

3.4 DCMR (Environmental Protection Agency Rijnmond)

The DCMR has been measuring C₂-C₅ hydrocarbons at two sites (Schiedam and Maassluis) since 1974. In 1976 a third measuring site was added, at Hoogvliet. The

method of analysis used is the same method TNO used during the 1970s at Delft. The drawback of a relatively high detection limit is less important in this case as the levels are much higher than at Delft (DCMR 1984). In 1987 the measurements were stopped.

According to an analysis by DCMR the levels at the Schiedam measuring station are strongly influenced by local traffic, whereas at the Maassluis measuring station the industrial emissions are the dominating factor.

3.5 Developments in hydrocarbon emissions in the Rijnmond area 1971-1984

In October 1970 the Rijnmond area was declared a Sanitation Area. In September 1971 the provisional Rijnmond Area Pollution Control Committee published an outline plan consisting of three parts: 1) the reduction of the concentrations of air polluting components under unfavourable conditions, 2) the reduction of the level of air pollution with respect to the components odour, oxidants and dust, the high-priority programme, and 3) the quality control of all polluting components, the so-called long-term programme (DCMR, 1973). In order to carry out the high-priority programme a study group was formed in November 1971 with the aim of, among other things, compiling an emission inventory of SO₂, NO_x and hydrocarbons. Two pollution controlling measures were taken. The first, published on 21 February 1974, concerned the reduction of hydrocarbon losses. The aim of the measure was to reduce the losses due to displacement or evaporation with tank storage by 30% by 1 July 1975 and by 50% by 1 January 1978. The second pollution controlling measure concerned the reduction of odour nuisance and probably had little effect on the emissions of the C₂-C₅ hydrocarbons (DCMR, 1984).

Emissions

In the period 1971-1984 three inventory cycles took place, namely, a survey in 1971-1972 by the aforementioned study group and two surveys by TNO, the first of which concerns the year 1974 (Report 2 Emission Registration) and the second concerning the year 1983 (Report 13 Emission Registration). A survey of the development in time of the registered emissions is given in table 3.2.

In the study by the study group four areas are distinguished, namely, the City of Rotterdam, Pernis, Botlek and Europoort; at that time there were no industrial installations on the Maasvlakte. The emissions are further subdivided into five categories: ballast emissions, evaporative emissions from tanks, emissions due to the filling up of cone-roof-tanks and emissions related to loading and cleaning tanks. These emissions are, in fact, involved with storage and transfer activities.

The information in the Emission Registration reports has been obtained from the categorie 'Industry' and subsequently subdivided by map squares of 5x5 km² (1974) or 20x20 km².

The comparison can only be indicative as it is for instance not clear whether the same definition of hydrocarbons has been applied, and because the categorie 'Industry' also comprises process emissions.

The proportion of emissions from storage and transfer activities in the total of industrial emissions in the Rijnmond area is estimated at 70% (DCMR, 1983). The hydrocarbon emissions from the Rijnmond area due to storage and transfer activities therefore seem to have decreased by about 45% over the period 1971-1984, at least according to the Inventory. (See Tab. 3.2: 44.2 kton/yr in 1971-1972 versus 24.2 kton/yr in 1983.) The question is whether this decrease of emissions is also found in the measurement data of DCMR and TNO.

DCMR Observations

The conclusion drawn by the DCMR, based on its measurement data (DCMR, 1984), is that the emissions due to displacement when tanks are filled and tank evaporation do not play an important role in the concentrations in Schiedam and Maassluis, so that the effect of the first pollution control measure on the concentrations of the lower hydrocarbons in Schiedam and Maassluis cannot be made visible amongst other interfering effects. Among interfering effects can be regarded, among other things, the influence from traffic.

A number of remarks can be made: In the first place, although the measuring point at Schiedam is strongly influenced by the local traffic, Maassluis is a measuring station with a dominant influence from industrial emissions, for most species, which, considering the measuring station's location, is to be expected.

Furthermore, it can be remarked that the abovementioned conclusion is based on an evaluation of monthly averaged figures. The course of the concentration at Maassluis as function of the wind rose shows that the concentrations of saturated hydrocarbons strongly decreased between 1974 and 1978, but that in 1980 the levels were again clearly higher (annual report DCMR 1980). As a cause for this increase the DCMR suggests an increase in the oil flow in Rotterdam as well as increased industrial activity. Moreover, it is notable in these wind roses that the decrease in concentrations over the period 1974-1978 does not only occur in the sectors Europoort and Botlek, but in most of the other wind direction sectors as well.

TNO Observations

The course of the concentration levels of hydrocarbons in Delft with wind from the Rijnmond-Rotterdam area over the period 1971-1984 is shown in figure 3.1. The pentanes are not shown because of the large number of missing measurements. The Rijnmond area is defined here by the wind direction sectors 151°-200°. This sector is rotated slightly to the east, as compared to its position on topographical grounds alone. However, the wind has a tendency to back 10°-20° over somewhat greater distances. If, however, the Rijnmond area were to be defined a little wider, say 171°-240°, the same picture would still emerge as in figure 3.1, although the concentration levels would then be somewhat lower. For all seven species the trend over the period 1971-1984 appears to be strongly decreasing (Table 3.3).

When only the period 1971-1977 is considered, it appears that there is a downward trend of 4-8% per year. When the years 1982-1984 are also included in the analysis the downward trend is reduced to about 4% per year, which over a period of 13 years still means an important reduction. Figure 3.1 clearly shows that from 1974 onward the levels are significantly lower than during the three preceding years.

Delft 1971-1984

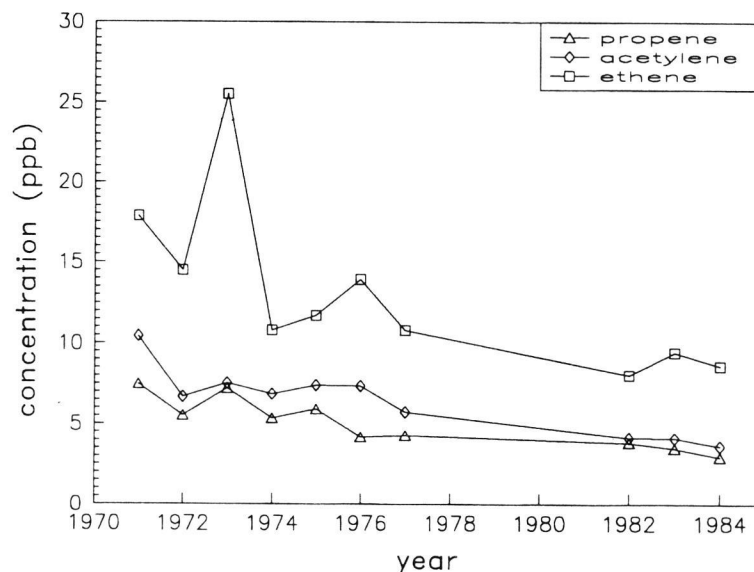


Figure 3.1a: Mixing ratios of ethene, acetylene and propene measured at Delft (Rijnmond sector 151°-200°) from 1971 to 1984.

Delft 1971-1984

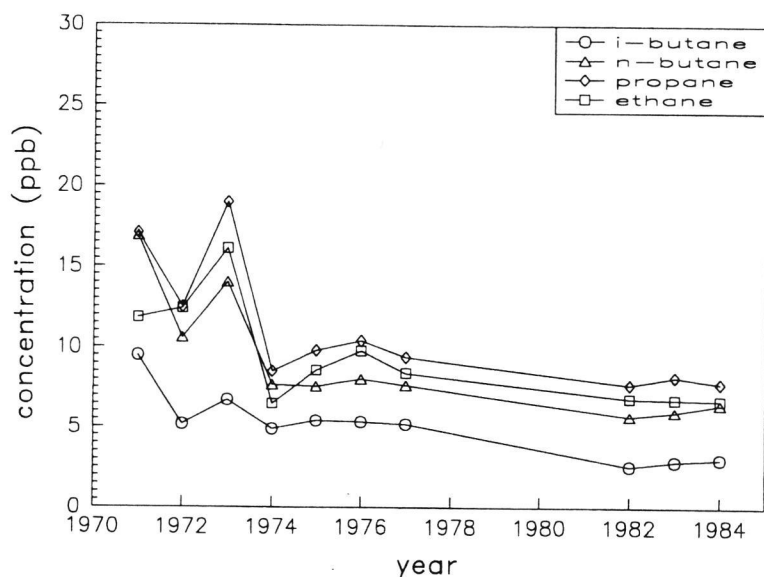


Figure 3.1b: Mixing ratios of ethane, propane, n-butane and i-butane measured at Delft (Rijnmond sector 151°-200°) from 1971 to 1984.

Before linking this trend to possible effects of the first Pollution Control Measure it is prudent to consider other possible influences, namely meteorological influ-

ences and the quality of the measurements. Variations in altitude of the mixing layer and wind velocity can have a great effect on the concentrations, also on annually averaged concentrations from a specific wind sector, especially when extremes occur during the winter months. The results of the measurements at Moerdijk show that fluctuations from year to year are in the order of 30%, but even a variation of 50-60% is not excluded. A study addressing the correlation between high concentrations and exceptional meteorological conditions falls outside the scope of this study. It is sufficient to note that the meteorological conditions are an important factor in the interpretation of the measurement figures.

The measurements in 1982-1984 were carried out with a different method than those in 1971-1977, with the important difference that the detection limit in the 1980s was substantially lower (roughly a factor of 10) than in the preceding period.

(Observations below the detection limit have been assumed in the calculations at a value equal to 2/3 of the detection limit.) The number of observations that, in the period 1972-1977, fell below the detection limit was 20-30% for propene and the butanes and was about 90% for the pentanes. However, the number of measurements below the detection limit is significantly lower in the Rijnmond sector, so that for the seven species considered in this study the change in detection limit has probably been of limited influence.

Further examination of the figures shows that a proportion of the measurements could be influenced by matters relating to the measuring technique. Some widely varying monthly averaged concentrations can hardly be explained in any other way. Although such phenomena are rare, their existence makes it impossible to disregard the possibility of specific averages being influenced by erroneous individual measurements which are now inconspicuously hidden amongst a series of correct measurements. In the 1982-1984 series in Delft, as well as in the Moerdijk series wide variations of this kind (on a monthly averaged basis) were not found. Another indication of the possibility of interference by inaccurate measurements is to be found in the trend of the concentrations in other wind direction sectors. Here also, the levels in 1971-1973 were high.

No trend in the emissions is known that could explain the course of the concentrations in the early 1970s. Quite to the contrary, for instance if these years are not taken into account, then the trend in the continental sector, which is strongly influenced by traffic, is more in line of expectations.

Thus, there are good reasons to be cautious in interpreting the measuring results from the period 1971-1977. It will be considered whether it is possible to rid these old data of measuring artefacts on semi-objective grounds. Although it is impossible to quantify trends at this time, it can nevertheless be observed that the figures from the Rijnmond area very strongly point in the direction of a substantial reduction during the 1970s. Attention can be drawn to the fact that the levels in the period 1982-1984 are clearly lower (25-40%) than those in the period 1974-1977, which themselves were lower than the levels of the first three years (1971-1973). It

cannot, at this moment, be substantiated that this reduction can be attributed to the first Pollution Control Measure, however, this does seem to be the most likely explanation.

Table 3.1: Emissions of hydrocarbons (ton/day) in the Botlek area according to KEMA measurements¹⁾ and in the Rijnmond area according to TNO measurements²⁾.

species	KEMA flight nr.				TNO 3 flights
	13	14	15	16	
	22-2-77	15-3-77	16-8-77	6-4-78	
ethaan	75-100	18-24	< 0	< 0	17-61
etheen	95-125	8-11	< 0	< 0	19
propaan	56-75	17-23	< 0	< 0	40-82
n-butaan	85-115	17-23	9-13	< 0	47-69

1) van Duuren *et al.*, 1979; KEMA, 1982

2) Roemer *et al.*, 1991

3) the data used are:

- . table 6 from ¹⁾, taking the difference between track 1 and 2
- . table 1 from ¹⁾; wind speed 6-8 m.s⁻¹, track length 11.5 km
- . height interval 370 m

Table 3.2: Overview of registered hydrocarbon emissions (kton/year) from the Rijnmond area.

	working group ¹⁾	Emission registration	
		first cycle	second cycle
	1971-1972	1974	1983
Europoort	8.2	18.2	
Botlek	10.8	11.4	
Pernis	25.2	24.5	
Total	44.2	54.1 ²⁾	34.6 ³⁾ (24.2) ⁴⁾

1) DCMR, 1973

2) The areas are defined as follows (report 2 Emission Registration)

Europoort : D8+E7

Botlek : F6

Pernis : G6

3) Total : C8+D7 (report 13 Emission Registration)

4) The estimated contribution of emissions by storage tanks is 70% (DCMR, 1983).

Table 3.3: Overview of trends (%/year) of hydrocarbons measured at Delft for the Rijnmond sector (15°C-200°), at the 95% confidence level.

species	period		
	1971-1977	1971-1977 + 1982-1984	1974-1977 + 1982-1984
ethane	-6.9 ± 9.3	-4.0 ± 2.9	-2.5 ± 3.5
ethene	-7.2 ± 10.3	-4.4 ± 3.2	-3.5 ± 2.6
acetylene	-4.4 ± 4.2	-3.7 ± 1.2	-5.6 ± 1.5
propane	-7.6 ± 7.1	-3.6 ± 2.4	-2.2 ± 1.8
propene	-6.4 ± 4.0	-3.9 ± 1.5	-4.1 ± 1.9
i-butane	-5.3 ± 5.4	-3.9 ± 1.7	-5.9 ± 2.0
n-butane	-8.3 ± 5.4	-3.6 ± 2.1	-2.6 ± 1.2

4. C₂-C₅ concentrations at the Moerdijk measuring stations

From 1975 until today, TNO has operated from one to three measuring stations in and/or around the Moerdijk industrial zone. The aim of these measurements, which were commissioned by the province of Noord-Brabant, was to make an estimate of the C₂-C₅ emissions from the industrial zone (Den Tonkelaar and Thijsse, 1986). The most suitable measuring station for this study is MC, the station on the west side of the industrial zone, near Klundert. Air parcels advected directly from the Rijnmond area to this measuring station are not significantly influenced by nearby sources. On the other hand, the measuring stations MB and MA, which are located in the zone and to the east of the zone respectively, are affected by emissions from the industrial complex. During the period 1981-1991, hourly averaged C₂-C₅ samples were continuously taken, analysed and processed at this measuring station (MC). The locally measured wind direction and wind velocity were included in the record. The detection limit of the hydrocarbons measured at Moerdijk is: 0.1 ppb for ethane, ethene, propane and propene, 0.2 ppb for acetylene and the butanes, and 0.6 ppb for the pentanes. When concentrations fell below the detection limit, substituted values have been used. A value of 2/3 of the detection limit was chosen for this. The concentrations in the upwind air are such that for the pentanes measurements below the detection limit occur very frequently, but this is very rarely the case for the other species.

4.1 Source contributions at Moerdijk

An analysis of the annually averaged wind rose at Moerdijk shows that the hydrocarbon levels in situ are characterised by the marine and continental background concentrations and, in addition, by contributions from three source areas nearby, namely, the Moerdijk industrial complex (40°-80°), Antwerp with its harbour area (160°-200°) and the Rijnmond area (290°-330°), see figure 4.1.

The concentrations from the Moerdijk industrial zone are very high for three species: ethene, acetylene and propene. Also for the other species high contributions are found, but in these cases the elevations with respect to their background levels are less than for the previously mentioned three species (Figure 4.2). The contribution from Antwerp (in the sense of an increase compared to the background level) is rather difficult to quantify because, seen from Moerdijk the harbour area of Antwerp, which is likely to be the major source area of the Antwerp emissions, is located precisely at the transit point between the continental background and the marine background.

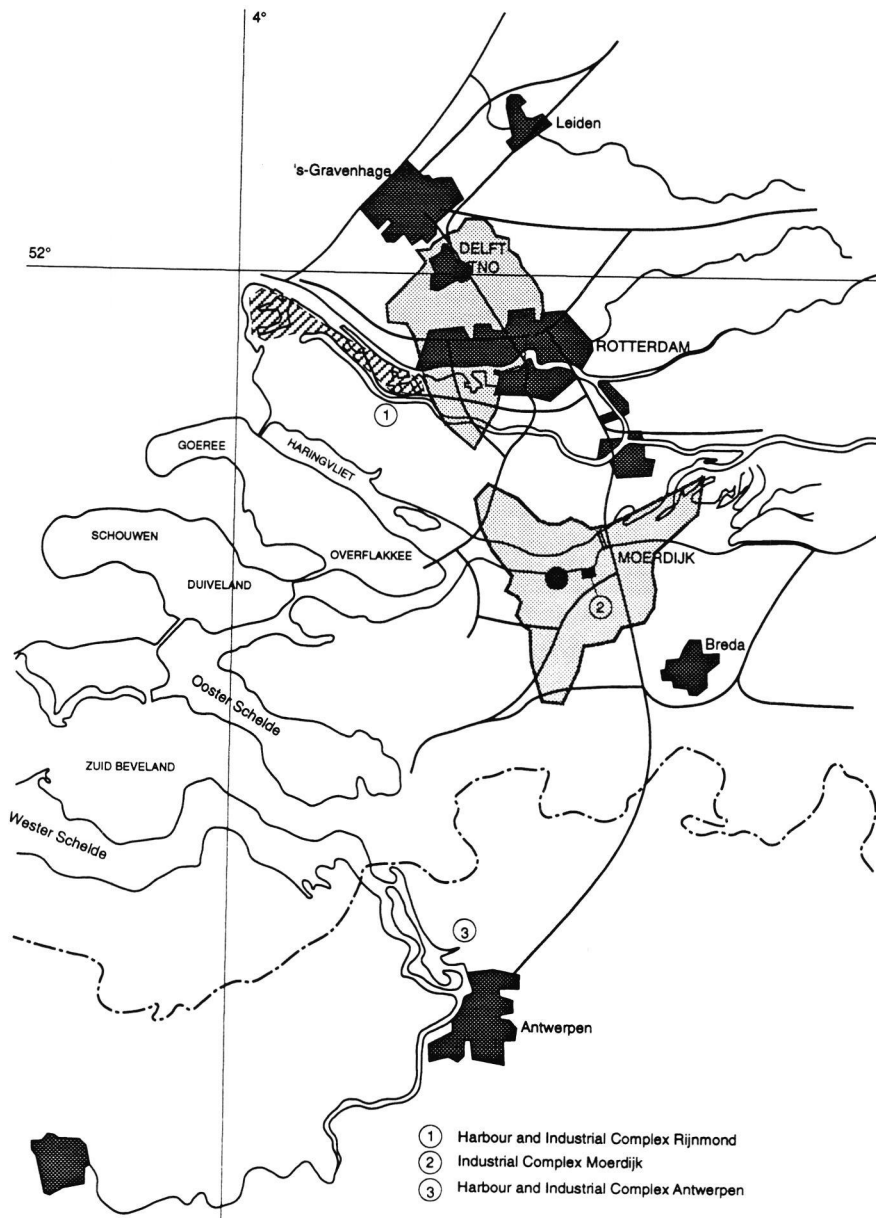


Figure 4.1: Averaged concentration of i-butane per wind sector of 10° at Delft (1982-1984) and Moerdijk (1981-1984).

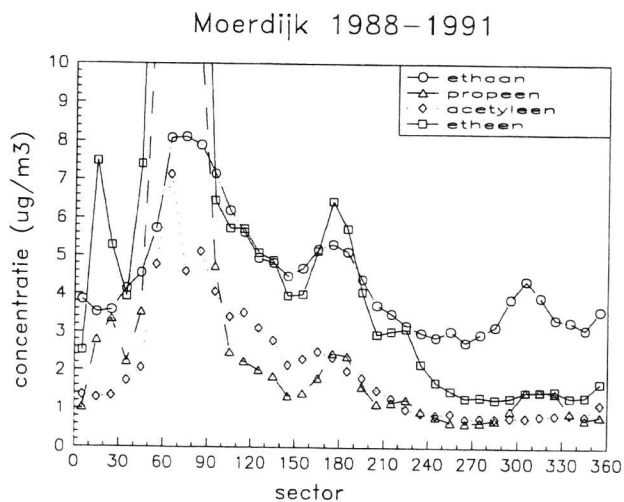


Figure 4.2a: Annual average wind roses (wind speed $\geq 3 \text{ m}\cdot\text{s}^{-1}$) of ethane, ethene, acetylene and propene at Moerdijk from 1988 to 1991. Rijnmondsector: 290°-330°.

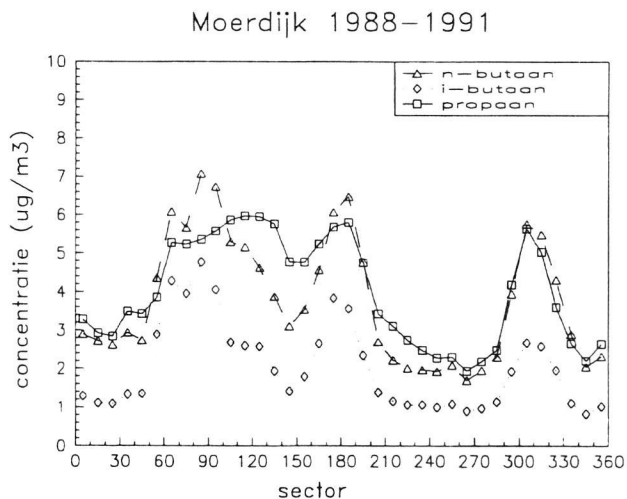


Figure 4.2b: Annual average wind roses (wind speed $\geq 3 \text{ m}\cdot\text{s}^{-1}$) of propane, n-butane and i-butane at Moerdijk from 1988 to 1991. Rijnmondsector: 290°-330°.

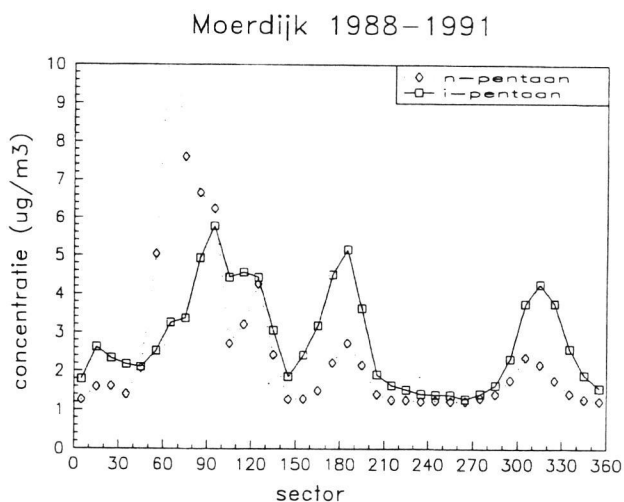


Figure 4.2c: Annual average wind roses (wind speed $\geq 3 \text{ m}\cdot\text{s}^{-1}$) of n-pentane and i-pentane at Moerdijk from 1988 to 1991. Rijnmondsector: 290°-330°.

Easier to quantify is the increase due to emissions from the Rijnmond area, because the lowest concentrations measured in Moerdijk occur in the adjacent clean west sector, and because the concentrations in the upwind air (the North Sea) are lower still. Figure 4.2 shows that the concentrations of the alkanes in the Rijnmond area are very clearly increased compared to the background level, that for propene an increase is also found, but that the concentrations of ethene and acetylene are not, or barely increased. This is a clear indication that the emissions of the alkanes, and specifically of propane, n-butane, i-butane and i-pentane are significantly higher than those of the unsaturated hydrocarbons. This impression is confirmed when the wind rose of the C₂-C₅ hydrocarbons measured at the TNO premises in Delft is also taken into consideration (Figure 4.1). These measurements, over the period 1982-1984, were carried out according to the same technique used at Moerdijk MC. The wind roses of ethene, acetylene and propene in Delft showed no increase compared to the continental background level. The wind roses of the alkanes do show such an increase, in addition to which two maxima attract notice: one in the southern direction and one to the southwest. The latter one points to the direction of the Europoort area, where large tank farms are located.

4.2 Trends 1981-1991

In the study of trends of the annually averaged concentrations five wind direction sectors have been distinguished, namely: the Moerdijk industrial zone, Rijnmond, Antwerp, "clean" and total, in which case all wind directions are included, except those directly originating from the industrial complex. The pentanes were not involved in this study because figures below the detection limit appear to be the dominating factor.

It turns out that the five sectors have not undergone the same developments over the 1980s (table 4.1). The annually averaged concentrations in the sector of the Moerdijk industrial zone vary very strongly from year to year, which results in large standard deviations of the calculated trends. Significant downward trends (within the 95% confidence interval) are found in this sector for ethene and propene. Ethane also shows a significantly downward trend, although this trend is less marked than that of ethene and propene.

Table 4.1: Trends of C₂-C₄ hydrocarbons at Moerdijk over the period 1981-1991. Uncertainty margins at 95% confidence level.

	Wind sectors				
	Moerdijk Industry (41°-80°)	Rijnmond (291°-330°)	Antwerpen (161°-200°)	clean	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

In the Rijnmond sector downward trends are found for all seven species in the range of 2.5 to 6 per cent annually, only the trends of propane and i-butane being not significant. The most remarkable trend is of ethene with an average reduction in annually averaged concentration (for this sector) of about 60% (Figure 4.3). For ethene this trend has been compared with developments in the ethene emissions from the Rijnmond area. In the second round of the Emission Registration (1981-1984) an industrial ethene emissions of 2.7 kton/year is given (VROM, 1990), whereas in the third round (1987) no more than 0.1 kton/year is registered as industrial ethene emission (Publication Series Emission Registration no. 1, 1990). The total ethene emission from the Rijnmond area decreased from 4.6 kton/year to 1.8 kton/year over this period, a reduction of 60 per cent, entirely in line with the developments in the ethene concentrations. According to the measurements, this change took place mainly, or possibly entirely, after 1985 (Figure 4.3).

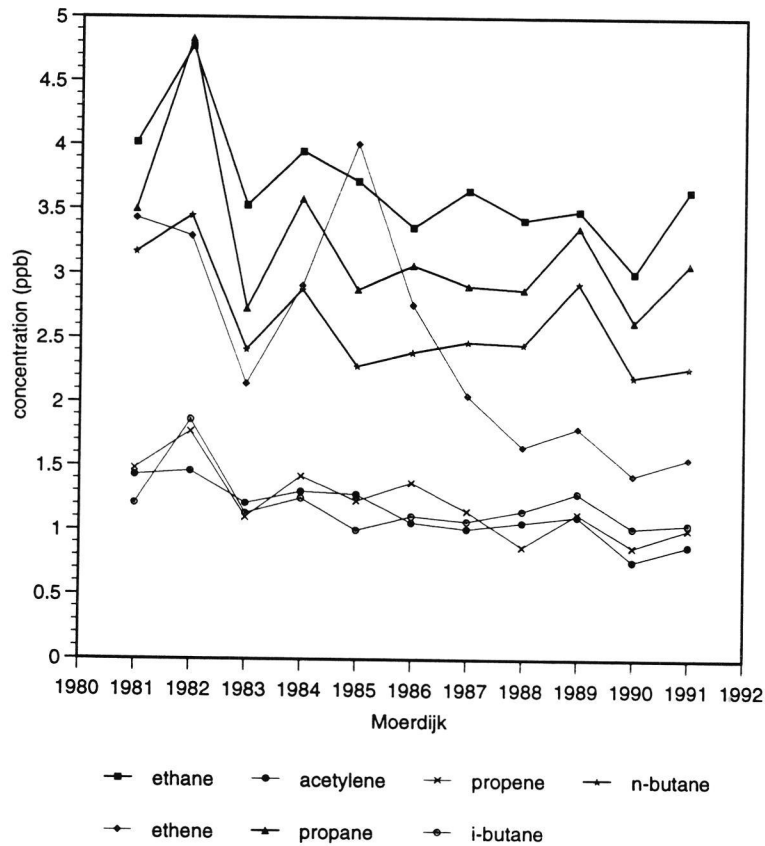


Figure 4.3: Trends of C₂-C₄ hydrocarbons at Moerdijk for the Rijnmond sector.

In the Antwerp sector the changes are much smaller than those in the Rijnmond area, and for butanes there is even an increase (not significant). Only acetylene shows a significantly downward trend. When all wind directions are taken into consideration, except for the Moerdijk sector, the trend of acetylene is the only significant one. In ten years the average concentration of acetylene has decreased about 30%. This agrees well with developments in the hydrocarbon emissions from traffic during the 1980s. Road traffic is by far the most important source of acetylene. Both in the Dutch and in the (West) German Emission Inventory the hydrocarbon emissions from traffic have been decreasing since 1975. This decrease was still small in the early 1980s, but becomes stronger after that time. The emissions in 1991 are 26 per cent lower than in 1981 according to the registrations, and when only petrol traffic is taken into account the reduction is even 30 per cent, which is again in excellent agreement with the atmospheric measurements.

4.3 Concentrations in the upwind air

Air parcels arriving at Moerdijk from the Rijnmond area are advected from the North Sea if straight trajectories were followed. The concentrations in the Rijnmond sector seen from Moerdijk are the sum of the concentrations in the up-

wind North Sea air and the contribution from the Rijnmond area. A correct budget is achieved when the concentrations in the upwind air are taken into account. Unfortunately there are no measurements available which can be used to determine these concentrations in the upwind air. The measuring station where C₂-C₅ hydrocarbons are measured and which would be most suitable for this study is the one at West Beckham in East Anglia (England). During two years, from April 1989 to March 1991, the University of East Anglia took samples with a frequency of twice a week, which were not only analysed for C₂-C₅ species, but for higher components as well. Unfortunately neither wind direction or wind velocity were measured.

To form an impression of the background concentrations estimates have been made in three different ways, namely: 1) by way of the adjacent clean west sector (from Moerdijk) with the condition of high wind velocity, 2) from the published measurement results in Norway and Scotland, and 3) through selecting the measurement data at West Beckham on a ranking order of the concentration levels.

West sector

The lowest concentrations at Moerdijk are usually measured in the west sector. The air then flows in from the Atlantic Ocean, picking up emissions from a part of England (e.g. London) and the Dutch province of Zeeland during the last part of its trajectory. In order to be able to minimize the influence of local emissions (0-100 km before arrival) it has been decided to calculate the average in this sector from only those measurements carried out with a wind velocity of more than 4m/s. Nevertheless, it can be said that in this way certain concentrations will show an overestimation of the actual concentrations above the North Sea because large source areas in England have been crossed. The concentrations found in this way should be regarded as an upper limit.

Penkett and Lightman have carried out twenty aircraft measurements before the coasts of England, Ireland and Scotland, during which very clean air from the Atlantic Ocean was sampled (Lightman et al., 1990; Penkett et al., 1993). The results of these measurements can be regarded as a lower limit, as it is unlikely that, on the average, air flowing in over the North Sea will have undergone no influence at all by emissions from England, Scotland or Northwestern Europe.

The wind rose at West Beckham can roughly be divided into three more or less equal sectors: wind from England and Scotland, wind from continental Europe, and wind from the North Sea, the Atlantic Ocean and Scandinavia. For most species the lowest concentrations are found in the North Sea sector. For three anthropogenic hydrocarbons, acetylene, benzene and toluene a ranking order has been established. Of the about 100 measuring results of West Beckham the average was taken of the lowest third of the measurements, as being typical North Sea background concentrations. For the concentrations so determined it made little difference (10-30%) which of the three species determined the ranking order.

A survey of the background concentrations is given in table 4.2. It turns out that the concentrations derived from the West Beckham measurements fall somewhere between the concentrations determined from the west sector and the concentrations found in the aircraft measurements. In the calculations the West Beckham data has been used. The two other estimates of background concentrations were used afterwards to indicate the limits of the emission estimate.

Table 4.2: Overview of background concentrations (ppt)

	A	B ₁	B ₂	C
ethane	2200	1900	2100	2100
ethene	1200	200	600	800
acetylene	750	500	600	600
propane	1100	600	900	850
propene	370	50	150	120
n-butane	750	250	800	800
i-butane	400	150	400	–
n-pentane	≤ 400	100	250	200
i-pentane	≤ 400	100	400	400

- A Based on observations at Moerdijk in the clean sector (241°-270°) and with wind speeds $\geq 4 \text{ m.s}^{-1}$
 B₁ Aircraft measurements above Scotland and Ireland (Lightmann *et al.*, 1990; Penkett *et al.*, 1993)
 B₂ Measurements at Birkenes, Norway for wind from the UK (Solberg *et al.*, 1994).
 C Based on measurements at West-Beckham

5. Description of the model and the calculations

The relationship between the concentrations of C₂-C₅ hydrocarbons measured at the measuring station MC at Moerdijk and the registered emissions of these species according to the Emission Inventory has been studied by means of a diffusion model. On the basis of the data from the Emission Inventory wind roses were calculated with the model for the Moerdijk receptor point, and these calculated wind roses have subsequently been compared with the annually averaged wind roses from the observations. Comparison of both wind roses gives an idea of how much the C₂-C₅ emissions in the area around Moerdijk contribute to the concentrations according to the Emission Inventory, and to what extent these agree with the concentration contributions derived from the measurements. Before being able to attribute meaning to the results of such a comparison, it is necessary to quantify the limitations and assumptions of the method, and express these in an uncertainty margin. In this study two paths were followed to form an idea of the uncertainty margins of the method. The method has been tested for nitrogen oxides (NO_x), the emissions of which are considered to be better known than those of hydrocarbons and of which far more measuring results are available. Furthermore, a number of sensitivity measurements have been carried out to quantify the influence of specific characteristics of the method.

Seen from Moerdijk, the Rijnmond area is located in north-northwestern direction. In comparing measured and calculated wind roses, only the northwest quadrant (270°-360°) has been taken into account. The concentrations in this sector are largely determined by the emissions from the northwest quadrant plus the so-called pre-loaded air, which comes from the North Sea and/or parts of Great Britain. An estimate of the pre-load was made on the basis of various measuring figures. The range in the estimates of the pre-load is part of the sensitivity analysis.

5.1 Emissions

The emission data used in the calculations are the collective and industrial emissions of the provinces Zuid-Holland, Noord-Brabant and Zeeland. The base year of the data is 1990.

Some of the emissions are registered under general terms like petrol or crude. The proportion of a specific hydrocarbon in this group is expressed by means of a so-called OM factor. The OM factors used are shown in table 5.1.

Table 5.1: OM-factors (%).

ER-code	Description	Ethane	Ethene	Acetylene	Propane	Propene	n-butane	i-butane	n-pentane	i-pentane
1030	HC saturated, C ₁ -C ₄	20.0			30.0		24.0	6.0		
1110	HC saturated, C ₄ -C ₁₀						8.0	2.0	10.0	10.0
1201	HC alif. mixture C ₂ -C ₁₀	2.0	1.0		5.0	1.0	25.0	10.0	20.0	8.0
1205	HC saturated								25.0	25.0
1208	HC alif. unsaturated					10.0				
1212	crude	8.0			20.0		35.0		20.0	
1214	petrol						22.0	5.0	15.0	15.0
1231	HC combustion nat. gas		10.0							
1232	HC combustion oil		11.0							
1233	HC combustion engines (petrol)	1.4	7.85	7.0	2.5	3.7	2.1	1.05	2.56	5.12
1236	HC combustion engines (LPG)	3.0	15.0	22.0	35.0	3.5				
1237	HC combustion engines (diesel)	0.5	11.0	3.0		8.0				
1238	HC combustion LPG		15.0							
1239	HC combustion other gases		10.0							
1241	HC jet engines		15.0							
1242	HC combustion engines unspecified		10.0							
1250	natural gas	5.0			0.9		0.04			
2931	species heated oil >500°C		5.0			5.0				

The industrial and collective emissions from the Rijnmond area, the area defined in this study as enclosed by the Amersfoort coordinates (445-430, 60-80 and 440-430; 80-100), the emissions from Dordrecht (430-420; 100-120) and the emissions from The Hague (460-445; 70-90), are shown in table 5.2. Compared with the emissions used in previous studies, the aircraft studies (Roemer et al., 1991; Berdowski et al., 1992), there are a number of small differences. The emissions of acetylene used in this study are somewhat lower than those in the previous two studies. On the other hand, the n-butane emissions turn out to be a little higher, as do also the emissions of the sum of the pentanes. Larger differences occur with the relationship of normal pentane and isopentane. Pentanes are partly registered as unspecified which makes a subdivision impossible. For this reason it is preferable to compare the registered emissions and the emissions derived from measurements for the sum of the pentanes.

Tabel 5.2: Registered emissions (ton/day) in the Rijnmond area, The Hague and Dordrecht.

species	R 91/282 ²⁾	R 92/024 ³⁾	this study
ethane	2.5	2.5	2.3
ethene	7.2	7.6	6.7
acetylene	5.5	6.6	4.6
propane	6.1	6.1	6.5
propene	4.4	4.4	3.6
n-butane	18.7	17.3	20.9
i-butane	6.2	6.0	6.2
n-pentane	7.6	10.4	14.5
i-pentane	15.2	11.4	10.6
sum pentanes	22.8	21.8	25.1

1) the areas are defined by the following map coordinates:

445–430; 60–80 + 440–430; 80–100 (Rijnmond)
 430–420; 100–120 (Dordrecht)
 460–445; 70–90 (The Hague)

2) R91/282: Roemer *et al.*, 1991

3) R92/024: Berdowski *et al.*, 1992

5.2 Model and definition model calculations

The model used is the long-term version of the Gaussian plume model (SDU, 1976; SDU, 1984). The climatology of Zestienhoven over the period 1988-1991 has been used in the calculation. A climatology consists of a frequency distribution of 12 wind direction sectors (of 30° wide), three classes of wind velocity and six classes of stability. Following a standard procedure, the model calculates long-term averaged (in this case annually averaged) concentration contributions by wind direction sector, from which an annual average follows. For the purpose of this study a calculation modulus has been written that constructs a wind rose on the basis of the concentration contributions of sources by wind direction sector. The wind rose is calculated on the basis of 5° sectors. This is subsequently processed into a moving average with a width of 35°, in order to account for the atmospheric diffusion.

The Gaussian plume model is a rather simple dispersion model that has proved its worth for various applications in the past. It is based on a number of assumptions which are important to know when assessing the results of the calculations. The validity of the model becomes doubtful for distances over more than 30-40 kilometres. The following should be noted:

- the coefficients of dispersion σ_y and σ_z for large distances are only known as extrapolated values (SDU, 1976). The assumption that the emitted species is transported to the receptor point in a straight line does not apply for longer dis-

tances. Also, for longer distances (i.e. longer transport times) the assumption of stationary and homogeneous turbulence no longer applies. Finally, over longer distances the change of wind direction with altitude is of importance.

- The wind velocity distribution is divided into three classes with typical wind velocities of 1.45 m/s, 4.0 m/s and 8.0 m/s respectively. With distances of 25 km or more, a constant flow from a specific direction of five hours or longer is assumed for the calculations in wind velocity class 1. In actual practice the flow will not be constant with very low wind velocities, it will more likely come from various wind directions.
- The velocity with which the emitted species is transported is equal to the wind velocity near the source. Over larger distances and when the species is distributed over the entire mixing layer, it is preferable to use an average wind velocity over the mixing layer.

A number of these characteristics will be further discussed in Chapter 6 (Results).

With the model the contribution from the hydrocarbon emissions in the three provinces at the northwest quadrant of the wind rose at Moerdijk is calculated. On comparison with wind roses based on measurements in this quadrant the concentration of the upwind air (North Sea/England) is subtracted so that the wind rose of the measurements represents the (estimated) contribution from the Rijnmond area. The concentration in the upwind air is based on three kinds of measurements: measurements carried out at West Beckham, on the English North Sea coast, aircraft measurements carried out above Scotland, and measurements at Moerdijk in the adjacent west sector, in the direction of England (see also Chapter 4). The average values obtained from these various measurement series vary fairly significantly for some species, which means that, when the emissions from the provinces are low, there can be considerable uncertainty concerning the estimated emissions.

In a first phase, calculations were made in which the species were assumed to be inert, i.e. chemically non-reactive and not sensitive to deposition. The importance of deposition is negligible for this group of hydrocarbons. The importance of chemistry is not negligible, especially not for the very reactive hydrocarbons like ethene and propene. In a second phase of calculations chemical reactivity was taken into account as well. For the hydrocarbons an atmospheric residence time has been defined which is inversely proportional to the product of the reaction constant for the reaction with the OH radical and the assumed OH concentration. For ethene and propene the reaction between these species and ozone has also been taken into account.

For OH an annually averaged concentration of $8 \cdot 10^5$ molec/cm³ was used and for ozone an annually averaged concentration of 25 ppb. The ozone value is based on measurements by the RIVM at Zierikzee and Westmaas, with selection of the Rijnmond sector. Because no measurements are carried out for OH, the value used of this radical is based on results from models. Comparisons between results from various models show that the calculated OH concentrations can differ a factor of two or more from each other. In air in which the NO_x concentration amounts to 10

ppb or more, the concentration of OH is suppressed. Consequently, the chosen value of $8 \cdot 10^5$ molec/cm³ is clearly lower than the average value based on continental diffusion models, in which the NO_x concentrations hardly ever reach such high values.

The values chosen for OH and ozone give a chemical loss rate for propene of about 10% per hour. Assuming a transport time of about 3 hours for an air parcel to cross the distance between the Rijnmond area and Moerdijk, this would mean that chemistry would be responsible for a substantial reduction of the propene concentrations. For the remaining species the average reduction due to chemistry is substantially smaller. However, for wind velocity class 1 (1.4 m/s) the importance of chemistry increases also for a number of other species because the transport time increases to 8-10 hours.

The following four types of calculation have been carried out with the model:

1. species treated as inert;
2. as 1, but with wind velocity classes 2 and 3 only;
3. as 2, and species treated as chemically reactive;
4. as 2, but with a certain diurnal variation of the emissions;

Three types of calculation have been carried out with a climatology from which wind velocity class 1 was left out. The reason for this is that the contribution by wind velocity class 1 receives undue weight in the calculation. It assumes a steady flow of air with an average wind velocity of 1.45 m/s during a period that, for the distance coastal-Rijnmond to Moerdijk, can take up to 8 hours. Analysis of the measurement data shows that with these kinds of low wind velocities the source contributions in the wind rose are far more difficult to recognize because the wind "is coming from all directions". When the concentrations measured at Moerdijk in the Rijnmond sector are averaged by wind velocity class (with a width of 1 m/s), the concentration for the higher velocities is inversely proportional to the wind velocity. On the average, the highest concentrations are measured at around 3 m/s. For even lower velocities the concentrations measured decrease again. On the other hand, the model assumes that the concentrations are inversely proportional to the wind velocity. The contribution of the lowest wind velocities to the concentrations calculated this way is much higher than is justified on the basis of the results of the measurements.

A better approach therefore is to leave out the lowest wind velocities. The comparison is then with wind roses in which only measurements have been selected with a wind velocity during the measurement of 3 m/s or more.

The fourth type of calculation was carried out to obtain some idea of the influence of the day-night pattern of the emissions on the concentrations calculated. In the first three types of calculation annually averaged emissions were used which were equally divided over day and night. Many source categories have a source pattern in which the majority of the emissions take place during the day. The characteris-

tics of the atmospheric dispersion are not identical during the day and during the night. In general the contribution of a specific amount of emitted species to the concentration at the receptor point will be higher at night than during the day. At night the stability of the atmosphere is often higher than during the day, which hampers the diffusion of the species and consequently keeps the plume "more concentrated".

Calculations have been made for wind velocity classes 2-3 alone, in which:

- traffic emissions during the day (06.00h-18.00h) were set at 75% of the twenty-four hour average, and
- the evaporative losses from storage tanks occur for 100% during the day. These emissions from storage tanks make up 28% of the ER-I registered emissions in the Oil industry (SBI code: 28) and 58% of the ER-I registered emissions from the Warehousing and storage activities (SBI code: 763). (Source: Emissies in Nederland-1992, Berdowski and Jonker, 1992.)

No division into seasons was made.

6. Results

The results of the calculations of type 2 and 4 (see Chapter 5) will be presented and discussed in this chapter. Type 1 shows unrealistically high contributions for low wind velocities. Type 3, in which the reactivity of the species is taken into account, shows substantial changes for propene only. This aspect will be discussed later.

The measurements and the calculations show that in the northwest quadrant (270°-360°) the lowest concentrations (or concentration contributions) occur in the western direction (270°). The maxima in the measurements are found at 315°, except for ethene and acetylene for which the maxima are more to the north (355°). The maxima in the calculations are 335°-340°, except for ethene and acetylene (350°-355°). Based on meteorological considerations, it is reasonable to assume that for longer distances the emitted species does not travel from source to receptor in a straight line, but along a somewhat curved trajectory. A displacement of 10°-20° in the wind rose is quite possible. The contributions measured will always be a little displaced in an anti-clockwise direction.

On comparing the "measured" wind roses with the calculated wind roses, the following procedure has been followed. Regarding the measurements (wind velocity larger than or equal to 3 m/s) the concentration increase has been plotted against the value at 270°. For the calculations (classes 2 and 3 only) two wind roses were made. Wind rose 1 gives the increase set against the contribution at 270°, in which case a fixed background concentration (column A in table 4.2) is assumed. Wind rose 2 gives the increase set against the contribution at 270° over the sector 270°-300° and the increase set against an other, lower background concentration (column C in table 4.2) over the sector 300°-355°. In this case it is assumed that the concentrations measured at West Beckham represent the background level between 300° and 355°. This second approach would appear to be the more plausible one, although disagreement is possible over the values used (e.g. when to change the background level). Integration of the surface below the curves between 270° and 355° produces the contribution from the Rijnmond area to the wind rose at Moerdijk (Table 6.1).

Table 6.1: Comparison between measured and calculated integrated contributions to the windrose at Moerdijk (270°-355°) for different backgrounds.

species	A observa- tions	B ¹⁾ calculations background 1	C ²⁾ calculations background 2	A/B	A/C	A/D ³⁾
ethane	67	17.5	10.9	3.8	6.1	6.1
ethene	8.8	50.0	25.8	0.18	0.34	0.64
acetylene	7.6	35.5	27.3	0.21	0.28	0.28
propane	125.7	50.0	25.8	2.5	4.9	4.2
propene	32.8	30.5	5.3	1.1	6.2	3.9
n-butane	151.5	172.5	172.5	0.9	0.9	0.9
i-butane	58.7	51.5	51.5	1.1	1.1	1.1
n-pentane	>34.8	119.5	87.8	>0.3	>0.4	>0.4
i-pentane	110.6	88.0	88.0	1.3	1.3	1.3
sum pen- tanes	>145.4	207.5	175.8	>0.7	>0.8	>0.8

- 1) Background 1: background based on concentrations measured in the adjacent clean west sector;
 2) Background 2: background based as ¹⁾ for 270°-300° and based on measurements at West Beckham for 300°-355°;
 3) Background 3: background based as ¹⁾ for 270°-300° and based on measurements at Birkenes (Norway) for the sector 300°-355° (column B2 in Table 4.1)

The concentrations of pentanes (especially n-pentane) measured at Moerdijk with wind from the west, are mostly below the detection limit of pentane (0.6 ppb). In such cases a value of two thirds of the detection limit (being 0.4 ppb) has been used (Roemer et al., 1995). This value is clearly higher than the background value of n-pentane derived from other measurements. Therefore, it is likely that the integrated contribution of n-pentane derived from measurements will be (somewhat) higher than the value tabulated in column A of table 6.1.

The ratio between the concentration contribution derived from the observations and the calculated concentration contribution based on the registered emissions, such as presented in Tab. 6.1, is for a given background concentration proportional to the ratio between the actual ambient emissions and the registered emissions from the Inventory.

The use of a different background level has evident consequences for some species (ethene and propene). For propene it makes just the difference between good agreement and very poor agreement. For species for which the contribution of the Rijnmond emissions to the concentrations at Moerdijk are apparently small, the emission estimates are very sensitive to the background level used. This is clearly a limitation of this method. For acetylene the contribution from the Rijnmond emissions is also small, but due to acetylene's longer atmospheric lifetime (a few weeks) the background concentrations are far less variable than those of ethene

and propene. Consequently, the estimates of the emissions are less sensitive to the background concentration used.

The calculations give the following picture: the emissions derived from measurements of

- ethane and propane are higher than the ER figures, those of
- acetylene and ethene are (much) lower than the ER figures, those of
- propene are very difficult to determine, and those of
- the remaining species agree reasonably well.

Chemical reactivity plays a major role for propene only. By taking this into account, the contribution of the Rijnmond area to the wind rose calculated works out 30% lower for propene than the value presented in table 6.1. The consequence of this is that the emissions of propene should be even higher in order to comply with the observed wind rose.

When instead of twenty-four-hourly averaged emissions, emissions are used for which, for certain source groups (see Chapter 5) a simple diurnal variation is applied, the calculated contributions of the Rijnmond area to the wind rose at Moerdijk become smaller. However, the difference with the calculations based on twenty-four-hourly averaged emissions is very limited. The relatively largest reductions are found for acetylene (-6%) and ethene (-5%), species for which traffic is the dominating source category in the Rijnmond area. For propane a reduction of 4% is found, for the remaining species reductions varied between 1% and 3%. The relatively small difference between both types of calculations can be understood from the fact that differences between daytime and nighttime dispersion are smallest precisely for wind from the sea. Application of the diurnal variation of the emissions is not of significant influence on the findings derived from table 6.1.

The results from table 6.1 give an impression of the relationship between emissions derived from measurements and registered emissions. However, the method itself (the use of the previously described model) exerts a specific influence, which has not yet been filtered out of the figures of table 6.1. In order to obtain an idea of the model's performance, validation calculations have been carried out with NO_x as test species. The emissions of NO_x in the Netherlands are reasonably well-known. The concentrations of NO_x in the Netherlands are also well-known, due to the network of RIVM measuring stations throughout the country. By analysing the measuring data of NO_x over the period 1988-1991 from six measuring stations around Rotterdam a picture was obtained of the contribution of the NO_x sources in the studied area to NO_x concentrations at the stations. This contribution was compared with the contribution calculated in the same way as for the hydrocarbons. By applying this method, omitting one of the six measuring stations, an uncertainty margin was calculated (Huygen, 1995). The most important finding is that the ratio of calculated contribution to measured contribution is 1.3 ± 0.4 . This minor underestimation of the measured contributions could be caused by a minor underestima-

tion of the actual NO_x emissions, as well as by a systematic underestimation of the concentrations by the model calculations. The figures in table 6.1 should be regarded in the light of the NO_x results. For instance, the ratio between calculated emissions and registered emissions is 1.3 for isopentane (last column table 6.1). Assuming the registered NO_x emissions correspond well with the "actual" NO_x emissions, the same can then be concluded for isopentane (based on the last column of table 6.1).

In how far is this method usable to determine emissions in a certain area more specifically? If the method implies estimating emissions on the basis of measuring results from various measuring stations around the studied area, then, based on calculations for NO_x , an uncertainty margin of 20-30% seems likely. At the same time, a slight tendency of the model towards underestimation of the concentrations measured cannot be ruled out. However, when there are fewer measuring data the reliability of the emission estimates becomes smaller. Based on the measuring data of mainly one measuring station, the method rapidly shows uncertainty margins of up to a factor of two. In general, the unreliability of the method will be large when the contribution from the emissions from the studied area to the concentration at the measuring point is small in respect to the (largely unknown) background concentration.

The ratio's between "measured" and "registered" emissions as presented in table 6.1 can be compared with those from the aircraft study (Berdowski et al., 1992), see table 6.2.

Table 6.2: Ratio between emissions derived from measurements and emissions according to the Inventory. Findings of this study as well as of the aircraft study.

species	this study ¹⁾			Berdowski et al., 1992 (R92/024) ²⁾	
	A/B	A/C	A/D	flight: 26-01-89	flight: 24-05-89
ethane	3.8	6.1	6.1	10.2	21.3
ethene	0.18	0.34	0.64	1.9R ³⁾	- 4)
acetylene	0.21	0.28	0.28	0.6	0.8R ³⁾
propane	2.5	4.9	4.2	6.2	12.8
propene	1.1	6.2	3.9	2.8	2.2R ³⁾
n-butane	0.9	0.9	0.9	2.9	3.6
i-butane	1.1	1.1	1.1	3.6	3.9
n-pentane	>0.3	>0.4	>0.4	3.5	2.6
i-pentane	1.3	1.3	1.3	2.4	3.5

1) See table 6.1;

2) The weighted emissions are used (Berdowski et al., 1992);

3) R: within the uncertainty margins of the measurements;

4) -: no measurements.

The aircraft measurements showed that the emissions of ethene, acetylene and sometimes propene agreed well with the ER figures, and that for the alkanes the emissions might possibly be (substantially) higher. From this study it emerges that the emissions derived from measurements of most of the alkanes agree reasonably well with those of the ER (with the exception of propane and, especially, ethane), but that the emissions of ethene and certainly acetylene are now much lower than those in the ER.

It could be said that the picture has changed totally, on the other hand the ranking order of species according to the strength of the emissions estimated from measurements, is almost identical for both this study and the aircraft study. And this ranking order is clearly very different from the one according to the ER. It is sufficient to compare the total emissions for the Rijnmond area (Table 5.2) with the concentration increases measured in the Rijnmond sector (Fig. 4.2). Figure 4.2 shows that the increase in concentration of propane is comparable to that of n-butane, while the registered emissions of propane are a factor of three lower. The registered ethane emission is, for example, lower than the registered acetylene emission, whereas on the other hand figure 4.2 shows a much higher contribution from ethane than from acetylene.

It is not clear why the emissions derived from aircraft measurements are significantly and systematically higher than those derived from ground level measurements. This difference amounts to a factor of about three for all species, except propene. A possibility could be a systematic overestimation in the aircraft study due to the taking of non-representative samples, which happened to be much too high for all four flights. Another possibility is that the calculations in this study systematically overestimate the observations because, for instance, in reality the plume from the Rijnmond area does not "completely touch" the measuring point at Moerdijk. However, this does not seem very probable. Such effects do exist, but not over distances of 20-40 km, and not to that extent that large systematic differences can be explained in this way.

On the basis of the findings with NO_x as test species for the model calculations, it seems as if the differences between the emissions derived from aircraft measurements and those based on ground level measurements are caused in the first place by a systematic overestimation of the emissions based on aircraft measurements.

On the basis of the findings from the aircraft studies together with the findings from the present study, it can be concluded that:

- the ranking order of hydrocarbons according to the strength of the registered Rijnmond emissions is definitely different from the ranking order based on emissions derived from measurements;
- the emissions derived from measurements of ethane and propane are clearly higher than the registered emissions;

- the propene emissions are possibly also higher than registered;
- for the remaining species it is not unequivocal whether the registered emissions are underestimated or overestimated.

7. Conclusions and recommendations

On the basis of the calculations and the comparison with measured data, the following conclusions are drawn:

- A method in which emissions of a source area are estimated with the aid of a Gaussian plume model on the basis of measurements from one ground level measuring station only, produces large uncertainties in the emission estimates.
- The estimated emissions are especially uncertain for those species for which both the contribution of the complex is limited in respect to the background level, and for which the average background level is difficult to determine.
- The method discussed in this study (based on one measuring station only) is suitable only for bringing to light large discrepancies (a factor of two or more) between registered and actual emissions.
- Application of this method using data from various measuring stations around the emission area, produces a substantial reduction of the uncertainty margins of the emission estimates as compared to the method with one measuring point only.
- The ranking order of the nine C₂-C₅ hydrocarbons on the basis of the strength of the emissions in the Rijnmond area according to the Emission Inventory is clearly different from the ranking order based on the emissions derived from measurements. The ranking order on the basis of ground level measurements agrees with the ranking order according to the aircraft measurements.
- Reasonable agreement was found between the emissions according to the Emission Inventory and the emissions derived from ground level measurements for the butanes and the pentanes. Substantial and significant underestimation of the emissions by the Emission Inventory was found for ethane and propane. The emissions in the Emission Inventory of ethene and acetylene are clearly overestimated in comparison with the measurements, those of propene possibly underestimated. The uncertainty margins of the calculations for propene are large (and unclear) to such an extent that it is difficult to indicate the significance of the discrepancies for these species.
- The results of the present study in combination with the aircraft study indicate an underestimation in the Emission Inventory of the emissions of ethane and propane from the Rijnmond area. For the other species there are no clear indications that the emissions from the Rijnmond area are being overestimated or underestimated.

The most important conclusions which can be drawn from the literature search are:

- Aircraft campaigns with the aim of estimating hydrocarbon emissions have, so far known, only been carried out in or around the Rijnmond area.
- There is very good agreement between trends based on measurements and those according to the emission models. This holds good for CO, hydrocarbons and NO_x, both in the Netherlands and in the United States.
- Atmospheric measurements and measurements in tunnels with the aim of estimating traffic emissions of hydrocarbons, CO and NO_x sometimes show substantial differences with the registered emissions. European studies, however, do not indicate a systematic underestimation of the traffic emissions by the Emission Inventory.

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Authorisation

Name and address of the sponsor

Ministry of VROM

Names and functions of the contributing personnel

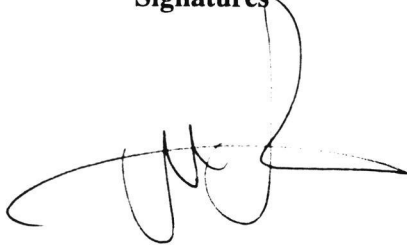
M.G.M. Roemer

Project leader

Period in which the research took place

January 1994 to March 1995

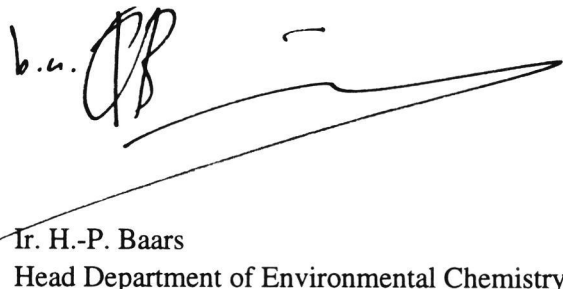
Signatures



M.G.M. Roemer
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