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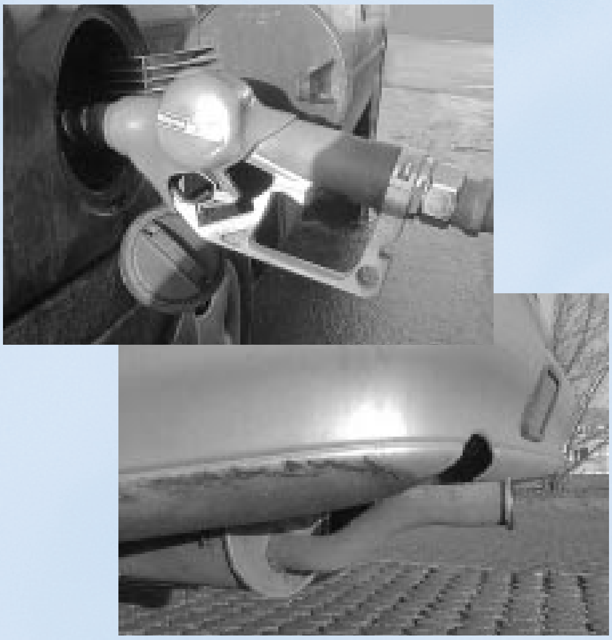
Benzene from traffic

Fuel content and ambient air concentrations

NERI Technical Report No. 309



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2000

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Data sheet

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Abstract:

The measurements of benzene showed very clear decreasing trends in the air concentrations and the emissions since 1994. At the same time the measurements of CO and NO_x also showed a decreasing trend, but not so strong as for benzene. The general decreasing trend is explained by the increasing number of petrol vehicles with three way catalysts, 60-70% in 1999. The very steep decreasing trend for benzene at the beginning of the period from 1994 was explained by the combination of more catalyst vehicles and reduced benzene content in Danish petrol. The total amount of aromatics in petrol, including toluene, increased only weakly. The analyses of air concentrations were confirmed by analyses of petrol sold in Denmark. The concentration of benzene at Jagtvej in Copenhagen is still in 1998 above the expected new EU limit value, 5 $\mu g/m^3$ as annual average. However, the reduced content of benzene in petrol from 1998 and the increasing number of vehicles with catalysts will probably lead to compliance with this limit value.

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Contents

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Preface

This report gives a summary of investigations of benzene and other aromatic compounds in air and petrol carried out since 1994. The investigations were carried out under different projects, i.e. the project "Air Pollution from Traffic in Urban Areas", conducted with support from the (Danish) National Environmental Research Programme 1992-1996 (SMP), the project "Traffic Surveillance Programme" funded by the Danish Ministry of Transportation and a project supported by the Danish Environmental Protection Agency.

Parts of the air quality measurements will from January 2000 continue under the National Air Quality Monitoring Programme (In Danish: Det Landsdækkende Luftkvalitetsmåleprogram, LMP) in accordance with the new EU directives on air quality.

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Summary

Many pollutants are of importance for assessing the adverse impact of the air pollution, e.g. NO_2, CO, lead, VOCs and particulate matter. Aromatic VOCs are of special great concern due to their adverse health impacts. Measurements of benzene, toluene and xylenes have been carried out in central Copenhagen since 1994. Hourly mean concentrations of benzene were observed to reach values of up to 20 ppb, which is critically high according to WHO's recommendations and the new EU limit values.

The emission of benzene is determined by petrol composition, driving conditions, composition of the car fleet and the percentage of catalytic converters. From year 2000 the content of benzene in petrol must be <1% in EU, a reduction from max. 5%.

Therefore it was decided to investigate this type of air pollution in more details, especially the relationship between the benzene content in petrol and the air concentration. This was supported by the Danish Environmental Protection Agency.

The following is a summary of the analysis of petrol sold in Denmark and the air quality measurements at two locations in Denmark, Jagtvej in Copenhagen and Albanigade in Odense. The objectives of the project were, to

- determine the benzene content in petrol and follow the changes in benzene content in petrol produced in Denmark,
- determine the air concentrations of benzene and other aromatic VOCs in Danish streets and determine the emissions from the Danish car fleet, and
- analyse the relationship between benzene content in fuel and air concentrations.

Crude petrol samples from the two Danish refineries, Shell in Fredericia and Statoil in Kalundborg, which deliver petrol to most of the petrol companies in Denmark West and East of the Great Belt respectively, have been analysed. Retail petrol from different petrol companies in Roskilde were also analysed. Samples were collected twice a year in the period August 1997 to July 1999. The results were also compared with earlier data. The benzene content was before 1995 approx. 3.5% for 95 RON. Statoil reduced the benzene content to approx. 2 % in 1995 and further to approx. 1 % in 1998. Shell reduced the benzene content from approx. 3.5% to approx. 1 % in 1998.

Air quality measurements of aromatic VOCs were started at Jagtvej in Copenhagen in 1994 and at Albanigade in Odense in 1997. The air concentration is a result of the emissions and the dispersion (meteorology). The air quality data were analysed using air quality models, i.e. Operational Street Pollution Model (OSPM). The method

used made it possible to remove the influence from the meteorology and determine the actual emissions.

The measurements of benzene showed very clear decreasing trends in the air concentrations and the emissions, especially at Jagtvej in Copenhagen, where long time series are available from 1994. At the same time the measurements of CO and NO_x also showed a decreasing trend, but not so strong as for benzene. The general decreasing trend is explained by the increasing number of petrol vehicles with three way catalysts, 60-70% in 1999. The very steep decreasing trend for benzene at the beginning of the period from 1994 was explained by the combination of more catalyst vehicles and reduced benzene content in Danish petrol. The total amount of aromatics in petrol, including toluene, increased only weakly.

The concentration of benzene at Jagtvej in Copenhagen was still in 1998 above the expected new EU limit value, 5 $\mu g/m^3$ as annual average. However, the reduced content of benzene in petrol from 1998 and increasing number of vehicles with catalysts will probably lead to compliance with this limit value.

The benzene contribution from diesel vehicles is small.

1 Introduction

Background

In most European cities emission from road traffic has become the most important source of local air pollution. Monitoring programmes are in operation in most larger European cities with the aim to follow the development in local air quality and to study the impact of various pollution regulations. The Danish Urban Air Quality Monitoring Programme (LMP) (Kemp and Palmgren, 1999) has been established to provide data for these purposes. As a part of the project on "Air Pollution from Traffic in Urban Areas", conducted with support from the (Danish) National Environmental Research Programme 1992-1996 (SMP) and the project "Traffic Surveillance Programme" funded by the Danish Ministry of Transportation, additional meteorological and air pollution measurements and automatic traffic counts were established in the street of Jagtvej in Copenhagen, close to the permanent LMP pollution measuring station.

Health impacts

Many pollutants are of importance for assessing the adverse impact of air pollution, e.g. NO_2, CO, lead, VOCs and particulate matter. Aromatic VOCs, e.g. benzene, toluene, ethylbenzene and xylenes (BTX), are of great concern due to their adverse health impacts (Field et al., 1992; Finlayson-Pitts and Pitts, 1993; Victorin, 1993). Measurements of BTX have been carried out in central Copenhagen since 1994. Significant correlation was observed between VOCs and CO concentrations, indicating that the petrol fuelled vehicles are the major sources of VOC air pollution in central Copenhagen. Hourly mean concentrations of benzene were observed to reach values of up to 20 ppb, which is critically high according to WHO's recommendations and the new EU limit values (Hansen and Palmgren, 1995) .

Benzene emission

The emission of benzene from traffic is determined by petrol composition, driving conditions, composition of the car fleet and the percentage of catalytic converters. From year 2000 the content of benzene in petrol must be <1% in EU, a reduction from previous max. value of 5%. Studies have shown that the emission of benzene from petrol-fuelled vehicles depend not only on the benzene content in petrol, but also on the total content of aromatics (Concawe, 1996).

This project

Therefore it was decided to investigate this type of air pollution in more details, especially the relationship between the content of benzene in petrol and the concentration in air. This study was supported by the Danish Environmental Protection Agency.

Benzene in fuel and air

The assessment of emission factors of pollutants are normally based on dynamometer studies with different driving cycles. While dynamometer cycles are essential to establish uniform emission standards for regulatory purposes and for testing of new technologies, they do not necessarily reflect the real on-road driving conditions and the level of maintenance of the actual vehicle fleet. Thus, there is a need for on-road emission estimates of air pollutants from the actual fleet. Such measurements are often performed in road-tunnels (Cadle et al., 1997), but they do not always represent typical urban traffic conditions. Such measurements also often require special measuring campaigns.

Inverse modelling

The relationship between emissions and pollution concentrations can be established by means of an air quality model describing the governing physical and chemical processes. The opposite procedure (an inverse method) can be formulated as: Having air pollution measurements, emissions from traffic can be calculated applying the relationships described by an air quality model. Application of such a procedure using measurements from the extensive monitoring site at Jagtvej and the Operational Street Pollution Model (OSPM) (Berkowicz et al. 1997) is presented here. A somewhat simpler version of the method has previously been applied for estimation of benzene emission factors of the Danish car fleet (Palmgren et al. 1995).

Aims

The report presents a summary of the analysis of petrol sold in Denmark and the air quality measurements at two locations in Denmark, Jagtvej in Copenhagen and Albanigade in Odense. The objectives of the project were, to

- determine the content of benzene in petrol produced and sold in Denmark and record the changes in benzene content,

- monitor the air concentrations of benzene and other aromatic VOCs in streets with dense traffic in Danish towns and determine the emissions from the Danish car fleet, and

- analyse and describe the relationship between the content of benzene in fuel and the benzene concentration in air.

2 Analysis of petrol

Aromatics in petrol

All samples of crude petrol of different qualities (i.e. 92 RON, 95 RON and 98 RON) and of unleaded retail petrol of the same three qualities from five major companies in Denmark were analysed by gas chromatography (GC) for the content of benzene and C7+C8 aromatics (BTX) quantified. Relative concentrations were then derived on a weight/weight (% w/w) basis as presented in the following sections. Reported values are slightly different from those typically reported on a volume/volume (% v/v) basis.

2.1 Method of analysis

GC/MS analysis

Benzene and other monoaromatics in petrol are usually analysed and quantified by gas chromatography (GC), as described in Kumar et al. (1986), ASTM Method D5580 (1994) and Martinez et al. (1996), or by gas chromatography mass-spectrometry (Mathiesen and Lubeck, 1998). Petrol contains hundreds of compounds, and co-elution of specific compounds is often observed unless special care is taken, e.g. by employing GC columns with enhanced separating capability (special PONA columns). This, however, does not entirely preclude co-elution, e.g. of benzene and methylcyclopentene present in cat-cracked products. Therefore, analyses of aromatics in petrol are often performed using relatively polar columns that has the resolution power necessary to separate aromatics from other groups of compounds (like paraffins, naphthenes and olefins).

Column type

In this project petrol analyses have been carried using a polar column of the type TCEP (1,2,3-tris-(2-cyano-ethoxy)-propane) by which benzene is retained till after the elution of undecane (C11-paraffin). Hence, practically all compounds eluting after benzene were aromatics and co-elution of olefins and aromatics avoided. At the same time a good separation of C7+C8 monoaromatics like benzene, toluene, ethylbenzene and xylenes (BTX) was achieved.

2.2 Sampling of petrol

Crude petrol

Crude petrol of three different qualities, 92 RON, 95 RON and 98 RON, for this project was sampled and delivered by the two refineries in operation in Denmark, Statoil in Kalundborg (East Denmark) and Shell in Fredericia (West Denmark). Sampling of crude petrol from Statoil was performed at the terminal close to Copenhagen (Hedehusene), which has a direct pipeline from the refinery in Kalundborg.

Sampling

Crude petrol was sampled in 1 L alumina bottles delivered by NERI to the refinery/terminal, and after sampling the bottles were returned to NERI. Sampling bottles were filled to the top to prevent extensive generation of headspace gases. During the project sampling of crude petrol took place during the following periods: August/September 1997, May/June 1998, August/September 1998, November/December 1998, February/March 1999 and June/July 1999, see also figure 7, chapter 3.

Retail petrol

Samples of retail petrol of the same three qualities as for crude petrol (i.e. 92 RON, 95 RON and 98 RON) were collected at five different petrol stations in Roskilde, Statoil, Shell, Q8, Hydro/Texaco and DK Benzin, during the following five periods: May/June 1998, August/September 1998, November/December 1998, February/March 1999 and June/July 1999. Before the actual sampling took place approx. 0,5 L was pumped to a waste container. Then the samples were collected in 1 L alumina bottles by continuing pumping. To reduce evaporation during sampling the piston was put as deeply into the bottle as possible. Again bottles were filled to the top to prevent generation of headspace gases and closed tightly. After collection all samples were sent to NERI where they immediately were cooled to and kept at -18°C until the time of analysis.

2.3 Sample preparation and analysis

Preparation

The content of benzene and C7+C8 monoaromatics (i.e. BTX) in collected petrol samples were quantified by gas chromatography (GC) using a combination of internal and external standards. First the GC system was calibrated by determining response factors for benzene, toluene and xylene using an internal standard (2-fluoro-toluene or 1,3-dichloro-benzene). Next petrol samples diluted in pentane containing the internal standard were analysed and the content of benzene, toluene, ethylbenzene and xylenes quantified on basis of the appropriate response factors, i.e. benzene (benzene), toluene (toluene), ethylbenzene and xylenes (xylene).

GC/FID analysis

All samples were analysed on a HP 5890 GC comprising a flame ionisation detector (FID) and a HP autosampler in the splitless mode using a 60 m * 0,25 mm ID * 0,40 µm TCEP fused silica capillary column with helium (He) as carrier gas (150 kPa) and temperature programming from 35°C to 130°C.

Standards

All calibration standards and diluted petrol samples were analysed in dublicates or triplicates, and between different sets and different petrol qualities blank and quality control (QC) samples (BTX) were analysed. Calibration curves generally had correlation's coefficients (r^2) better than 0,999 just as QC samples had relative deviations from nominal values of less than 10%. Relative standard deviations between doublicates/triplicates were also generally below 10% and hence the overall uncertainty of estimation less than 10%.

2.4 Results of crude petrol

Collection of samples

Samples of crude petrol from both the Statoil and Shell refineries were collected during six different periods (summer and winter) from September 1997 to July 1999, thus also covering minor variations in composition due to seasonal adjustments of vapour pressure.

Benzene in crude petrol

The benzene content in crude petrol from the Statoil and Shell refineries are shown in Figure 1 and 2, respectively. Generally, the benzene content in all three examined qualities of crude petrol from both refineries was reduced during the period covered. For Statoil crudes the content was reduced from about 2% in 1997 to 1% in 1999, while for Shell products the reduction was more substantial by going from about 4% in 1997 to 1% in 1999.

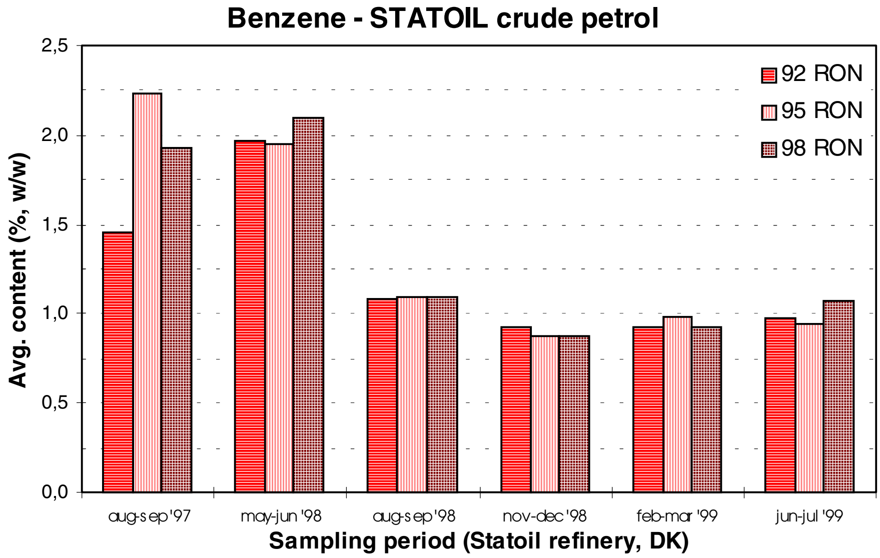

Figure 1 Average benzene content (%, w/w) in crude petrol from the Statoil refinery, DK, sampled and analysed in 1997-1999.

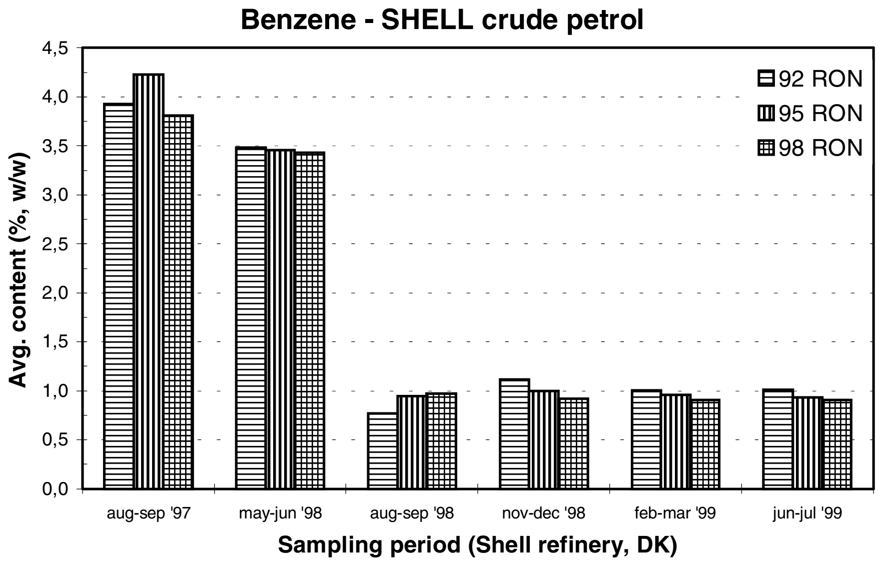

Figure 2 Average benzene content (%, w/w) in crude petrol from the Shell refinery, DK, sampled and analysed in 1997-1999.

C7+C8 aromatics in crude petrol

Besides the determination of benzene the content of C7+C8 mono-aromatic compounds (i.e. sum of toluene, ethylbenzene and xylenes) has also been quantified as shown in Figure 3 and 4 for the Statoil and Shell crude petrols, respectively. Generally, the average content of aromatics in both Statoil and Shell crude petrol has remained relatively constant during the project period, although some variations with a slightly decreasing tendency may be observed. For both brands of crude petrol the aromatics content can be observed to increase with octane number, this trend being more pronounced for the Statoil products. However, the sum of aromatics (i.e. BTX) is generally higher in the Shell products compared to Statoil products, about 35% vs. 30%.

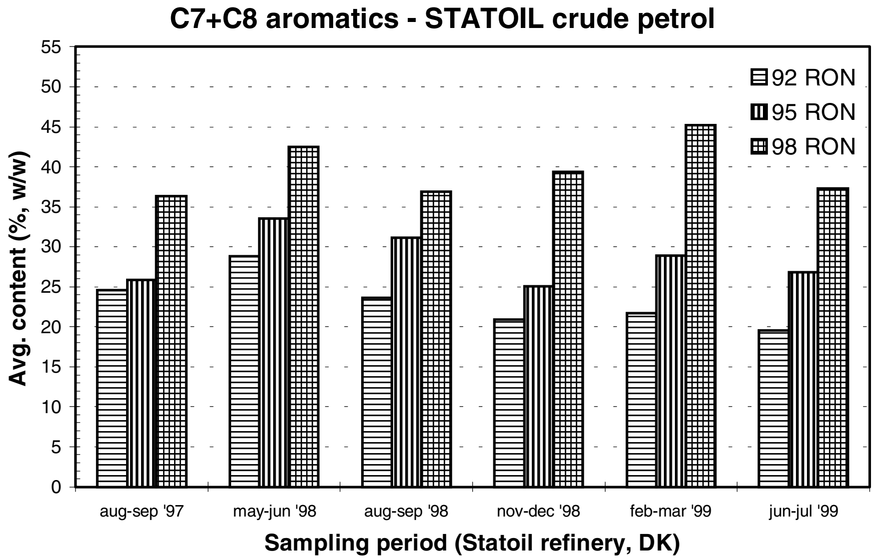

Figure 3 Average content (%, w/w) of C7+C8 aromatics in crude petrol from the Statoil refinery, DK, sampled and analysed in 1997-1999.

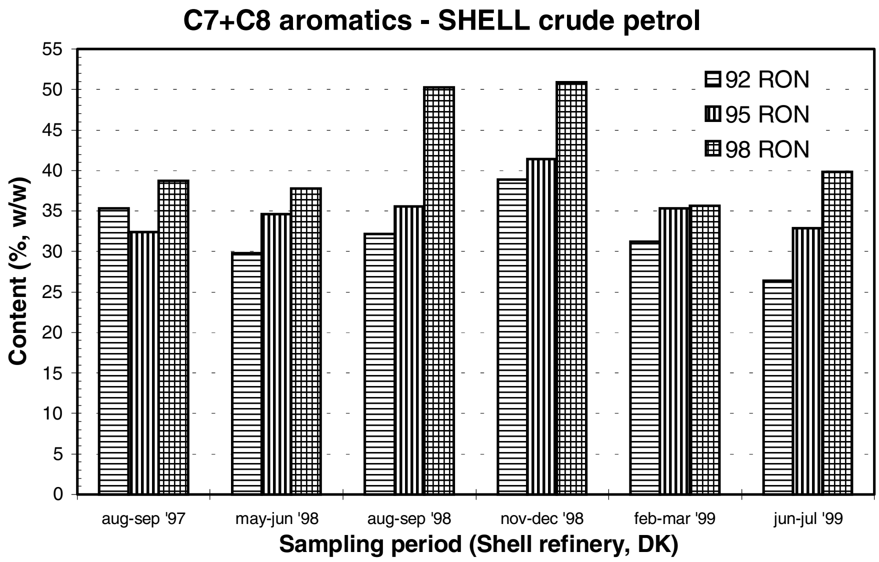

Figure 4 Average content (%, w/w) of C7+C8 aromatics in crude petrol from the Shell refinery, DK, sampled and analysed in 1997-1999.

2.5 Results of retail petrol analyses

Collection of samples

As for crude petrol samples of retail petrol of the same three qualities as for crude petrol were collected from five different companies (petrol stations) in Roskilde, Denmark, and analysed for the content of benzene and other C7+C8 monoaromatic compounds (i.e. BTX). Figure 5 and 6 show the average (for all companies) content of benzene and C7+C8 aromatics, respectively.

Benzene in retail petrol

Figure 5 shows that the average content of benzene in retail petrol (from five petrol stations) for all three qualities has been reduced from about 2% in 1998 to about 1% in 1999. As for crude petrol this reduction took place during the summer of 1998, and this overall trend is observed for all three qualities (i.e. 92, 95 and 98 RON) examined. After the reduction the content was observed to remain constant at 1%.

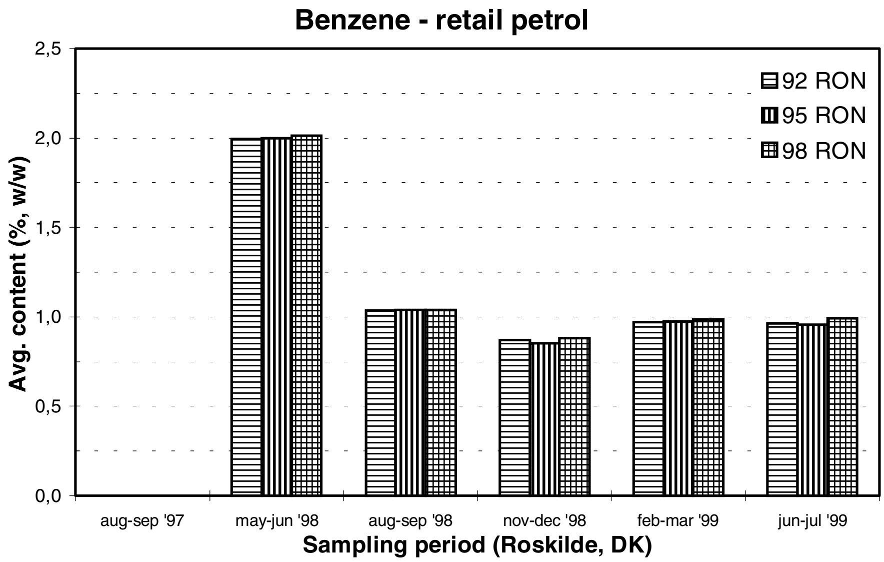

Figure 5 Average content of benzene in retail petrol from five different petrol stations in Roskilde, DK, sampled and analysed in 1998-1999

C7+C8 aromatics in retail petrol

Figure 6 presents the average content of C7+C8 aromatics in retail petrol from the same five petrol stations in Roskilde. As for the crude petrol the content is observed to increase with increasing octane number, but with less variation. During the period covered a small decrease in the BTX content from about 32% in 1998 to about 28% in 1999 (average for all three qualities) could be observed. This is similar to the trend that was observed for crude petrol from both the Statoil and Shell refineries.

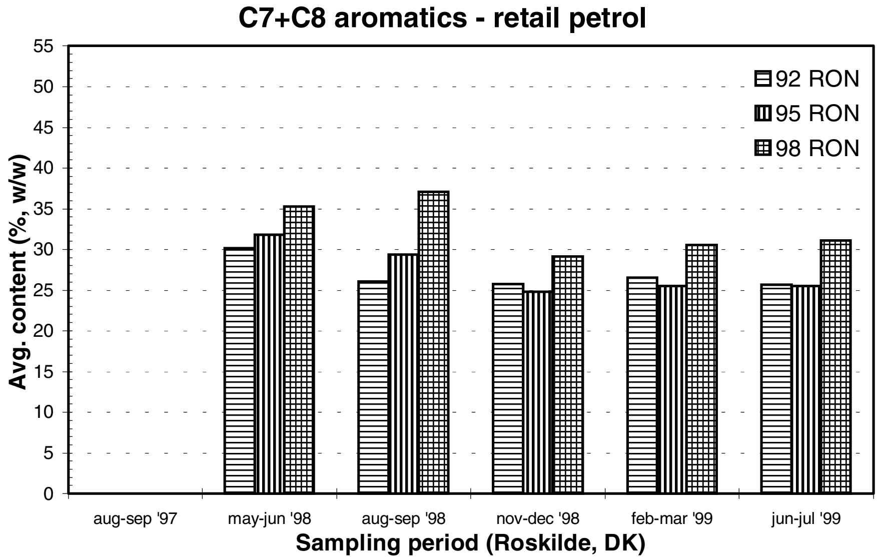

Figure 6 Average content of C7+C8 in retail petrol from five different petrol stations in Roskilde, DK, sampled and analysed during 1998-1999

Individual petrol stations

Appendix A gives the average results of both the benzene and C7+C8 aromatics content in retail petrol from each of the five petrol stations in Roskilde, i.e. Statoil (Figure A1 and A2), Shell (Figure A3 and A4), Q8 (Figure A5 and A6), Hydro/Texaco (Figure A7 and A8) and DK Benzin (Figure A9 and A10), from where retail samples have been collected during the five periods from 1998 to 1999.

3 Air quality measurements

Air quality data

Air quality data are available for Jagtvej in Copenhagen and Albanigade in Odense.

An overview of the available data is shown in figure 7.

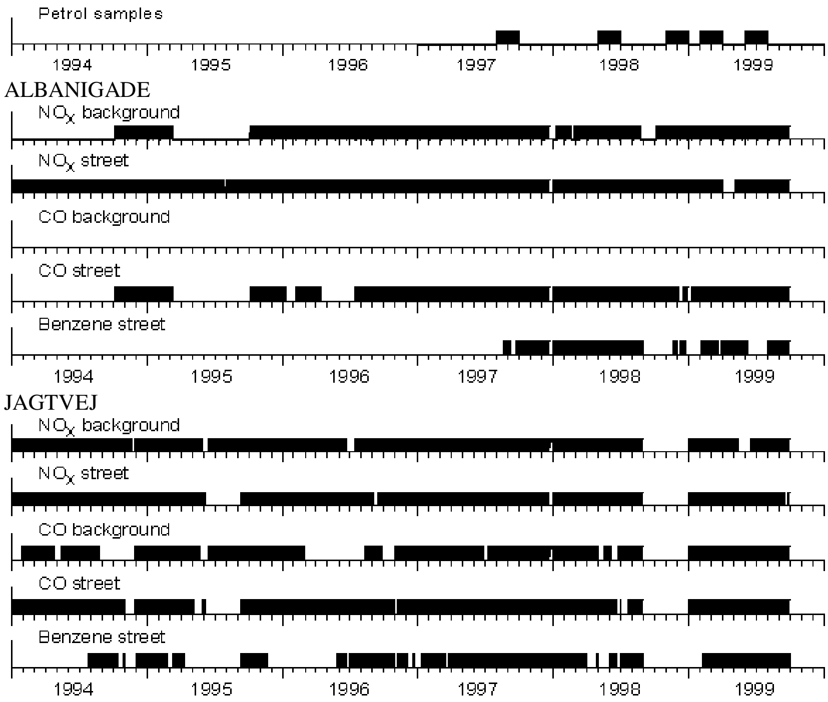

Figure 7 At the top are shown periods of available data on analyses of BTX in petrol from Statoil's refineri, Shell's refineri and petrol stations in Roskilde. Below are shown periods of available data on air quality (CO, NO_x and BTX) from Odense (Albanigade and urban background) and Copenhagen (Jagtvej and urban background).

3.1 Air quality

Concentration levels

Table 1 gives an overview of the measured concentrations of benzene and toluene at Jagtvej in Copenhagen and Albanigade in Odense. The EU limit value for benzene will probably be 5 $\mu g/m^3$ as an annual average, which means that this value was exceeded in 1998 at Jagtvej and close to be exceeded at Albanigade.

Table 1 Statistical parameters based on hourly results for benzene and toluene in 1998 measured at Copenhagen/1257 and Odense/9155. All values are given in µg/m^3. The values from Odense/9155 are based on only 8 months results. Lifetime risk and guideline value are from WHO, 1997. The 7 days maximum is calculated as a moving average based on 24 hour averages, (Kemp and Palmgren, 1999).

Specie	Station	Average	Median (hour)	98-perc. (hour)	99.9 perc. (hour)	Max 7 days	Lifetime risk at 1 µg/m^3	Guideline for 7 days average
Benzene	Copenhagen/1257	7.0	5.3	21	41	-	4.4 - 7.5 ,10^{-6}	-
	Odense/9155	4.8	2.8	20	43			
Toluene	Copenhagen/1257	23	17	80	158	47	-	260
	Odense/9155	16	9.3	75	150	34		

Correlation CO:BTX

The aromatic compounds showed year by year a very high correlation with CO (e.g. between benzene and CO in 1996, Figure 8), indicating that they were emitted from petrol fuelled vehicles. This was expected since the contribution of CO from diesel vehicles was relatively low at Jagtvej and the emission of aromatic VOCs from diesel fuelled vehicles were expected to be unimportant. The main emission of aromatic compounds from diesel vehicles is expected to be heavier hydrocarbons and PAHs.

Urban background

Because benzene was measured at the street only, the urban background concentrations was estimated by the measured urban background concentration of CO. The experimentally determined benzene/CO ratio was used to estimate the benzene concentration at the urban background location. Different ratios have been used for the periods depending on the benzene content in petrol, see chapter 4.

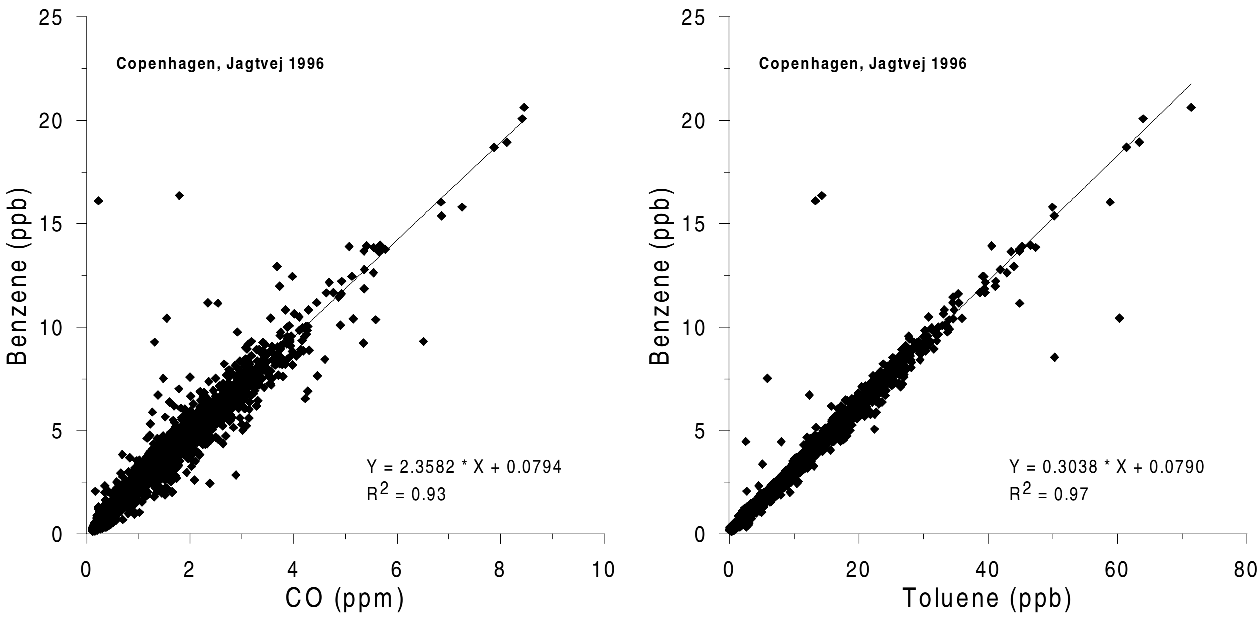

Figure 8 The concentrations of benzene versus CO and the concentrations of benzene versus toluene measured as 1 h averages at Jagtvej in Copenhagen, May-December 1996.

3.2 Air quality measurement programme

Air quality monitoring

Traditional measurements of nitrogen oxides (NO_x), O_3, CO, and SO_2 were performed continuously as ½ hour averages at two sites in central Copenhagen as part of the National Urban Air Quality Monitoring Programme (LMP) (Kemp and Palmgren, 1999). One site, which was established in 1987, is at kerb side about 3 m above ground at the street of Jagtvej; which is a relatively narrow two-lane street (street canyon) with approx. 22,000 vehicles/day of which 6-8% is heavy diesel traffic. The other site, which was established in 1991, is at the roof of a Copenhagen University building (H.C. Ørsted Institute) approx. 20 m above street level and a few hundred meters NE of Jagtvej. This rooftop monitoring site was chosen to provide information on the urban background concentrations in central Copenhagen. At this monitoring site meteorological data from a 10 m mast on top of the building also provided the necessary meteorological data, of which the most important for this purpose are wind speed and direction. The same type of monitoring was routinely carried out at Albanigade in Odense, a street with 1-2 storey houses at both sides. The traffic density here is approximately 20,000 vehicles/day of which 10-12 % is diesel vehicles.

BTX measurements

Continuous monitoring of benzene, toluene, ethylbenzene and xylene was performed by an automatic gas chromatograph (BTX-monitor, Chrompack). The monitor analysed 20-minutes samples every half hour. One hour averages were estimated by two 20 minutes averages per hour. Every fifth day a span gas was added to the monitor to control the stability. It always took place during night time. The uncertainty of the gas concentration was 10% and the uncertainty of the gas supply was estimated to 10%. The general absolute uncertainty is thus estimated to be less than 30%. However, the stability of the instrument probably was better, which means that the trends are estimated much better. These measurements were initiated in 1994 in Copenhagen and in 1997 in Odense. They were performed at the street sites only, Jagtvej and Albanigade.

Traffic statistics

Automatic traffic counts have been carried out by the Danish Road Directorate in 1994/95 at Jagtvej, classified in light and heavy vehicles as 1 hour averages. Supplementary manual traffic counts provided additional split-up of traffic in four vehicle categories: passenger cars, vans, trucks and buses; these data are discussed more in chapter 4. The passenger cars dominate the traffic with a diurnal variation obviously different from the other vehicle categories (Figure 9). At Albanigade there was relatively more diesel traffic than at Jagtvej.

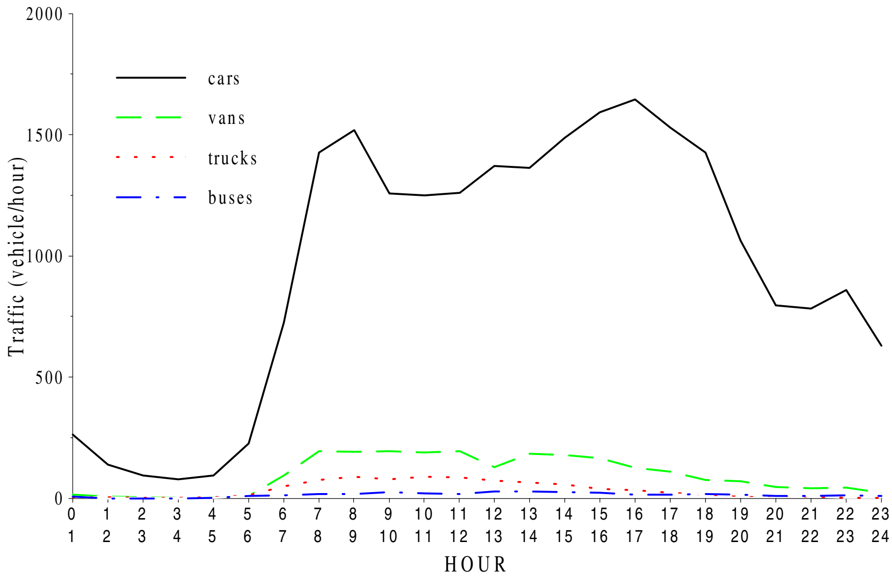

Figure 9 Average working days diurnal variation of traffic in Jagtvej.

3.3 Data analysis

Modelling

Atmospheric pollution dispersion models are usually used for calculation of air quality based on known theoretical relationships between emissions, meteorology and air concentrations. On the other hand, combining model calculations with ambient pollution measurements allows in-situ estimations of emissions.

Considering dispersion in streets of non-reactive or only slowly reactive car exhaust gases, the chemical transformations can be disregarded, and we formulate the problem in the following way,

$$C = F(\text{meteorology})\ Q + C_{background} \quad (1)$$

where C is the concentration of a particular pollutant in the street, Q is the emission of pollutants from the traffic in the street and F(meteorology) is a function describing dispersion processes. $C_{background}$ is the contribution to pollution concentrations in the street from all other sources than the traffic in the street.

Operational Street Pollution Model

The dispersion function F(meteorology) is calculated using a street pollution model, in our case, the Operational Street Pollution Model (OSPM). OSPM describes the dispersion in a street canyon based on meteorological parameters, mainly wind speed and direction above roof tops. In comprehensive tests on measurements from a number of monitoring sites, OSPM has shown to give a satisfactory description of the air pollutant dispersion in urban streets (Berkowicz et al., 1996).

Inverse calculations

The inverse of Equation (1) can be used for calculations of the hourly emissions from the traffic, provided that both street and background concentrations are available on an hourly basis.

$$Q_h = (C_h - C_{h,background})/F(\text{meteorology}) \quad (2)$$

The index h refers to a particular hour of the day.

Data treatment

Using different regression methods, Equation (2) has been applied to compute emissions from traffic hour by hour, when street and urban background concentrations are known. Modelling and measuring errors as well as unusual traffic and dispersion conditions can lead to "outliers" in the relationship C_h-$C_{h,background}$ / F_h(meteorology). These outliers were removed using the method described in Rousseeuw and Leroy, (1987). The average hourly emission, Q_h, is consequently calculated as the slope of the best-fit-line to the relationship C_h-$C_{h,background}$ / F_h(meteorology). This is illustrated in Figure 10, where scatter plots of the measured concentrations of benzene versus the model function F_h(meteorology) is shown for hours 7 to 10. The function F_h(meteorology) here corresponds to concentrations calculated by OSPM, but with a unit emission. Both the filtered data as well as "outliers" are shown in Figure 10. The number of "outliers" is normally not larger than a few percent and has small influence on the estimated emissions.

The accuracy increases with increasing number of observations. Taking only working days into account, time series covering 1 year results in about 250 data points for each hour.

Vehicle categories

When detailed traffic counts for various vehicle categories are available, it is possible to determine the total emissions and the emission factors for each category. For a specific hour, h, the total emission can be expressed as

$$Q_h = \sum_k N_{k,h} \times q_k \tag{3}$$

where $N_{k,h}$ and q_k are the traffic flow and emission factor for the k'th vehicle category, respectively. The equation forms for each hour of the day a system of 24 equations with the emission factors as the unknown variables.

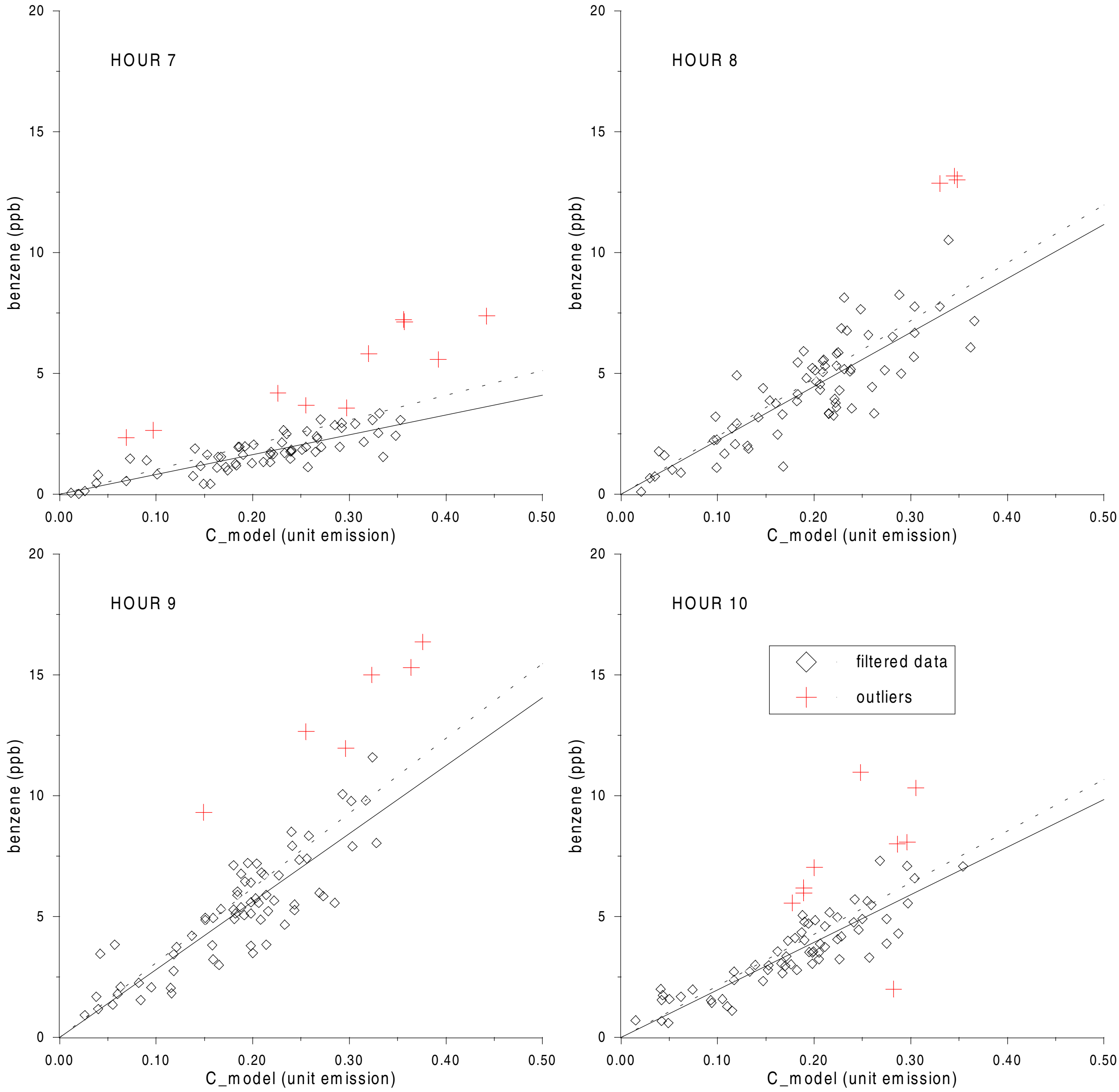

Figure 10 The procedure used for estimation of the emissions from traffic from the regression analyses is illustrated for benzene measurements in 1996 for hours 7 - 10 (ending hour). Regression lines obtained using all data are shown by dashed lines, while the regression lines for the filtered data are shown by solid lines.

4 Discussion

4.1 Petrol supply in Denmark

Major suppliers

The major supply of petrol in Denmark originates from the two refineries in operation in Denmark, Statoil in Kalundborg and Shell in Fredericia. Both companies have all their crude oil stock from the North Sea area; Shell from the Danish sector, and Statoil from both the Danish and Norwegian sector. Although the production of crude petrol from both refineries are based on similar North Sea feedstocks some variation in products may be expected due to differences in production design and operation (e.g. cracking and reformation).

Retail petrol

When it comes to retail petrol it is important to realise that retail petrol sold from petrol stations in the eastern part of Denmark (east of the Great Belt) to a major part is based on crude petrol from the Statoil refinery in Kalundborg. Besides Statoil itself, major companies like Shell and Hydro/Texaco presumably are supplied from the Statoil refinery. In the western part of Denmark (west of the Great belt) this situation is reversed as major companies like Statoil and Hydro/Texaco probably both get their supply of crude petrol from the Shell refinery. Q8 and "DK Benzin", on the other hand, are supposed to get most of their petrol from imported supplies.

Earlier studies of aromatics in petrol

Prior to the campaigns on studies of aromatics in petrol reported here NERI also did two similar campaigns in 1989-1990. The results of these two studies are shown in Figure 11 below (Iversen, 1999).

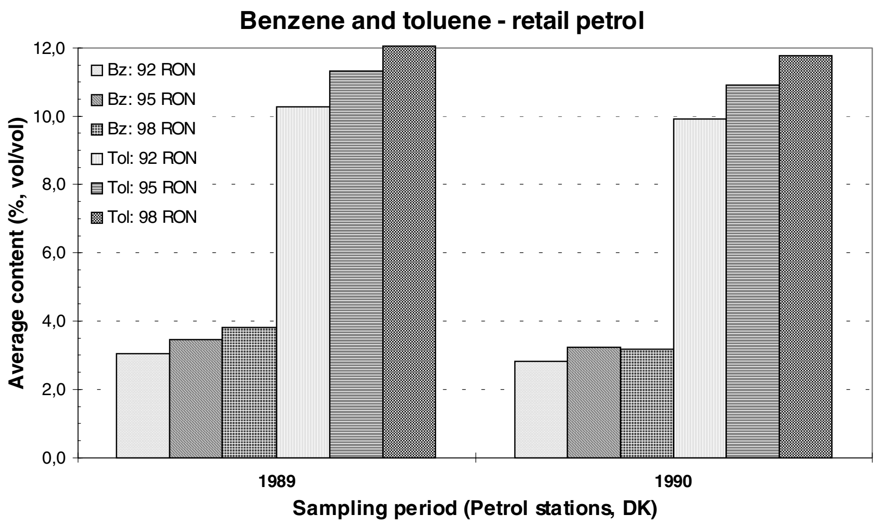

Figure 11 Average content of benzene and toluene in 92, 95 and 98 RON retail petrol from 10 different petrol stations in east Denmark sampled and analysed during two campaigns in 1989-1990.

The average benzene content in retail petrol from 10 different petrol stations in east Denmark was 3-4% (vol./vol.) in all three qualities. For 92 RON and 95 RON qualities the data are from retail, unleaded petrol while for 98 RON the data are from both leaded and unleaded samples. For toluene the content is 10-12% (vol./vol.), lowest for 92 RON and highest for 98 RON, and the same for both periods.

4.2 Crude petrol

Benzene in crude petrol

In this study the samples of crude petrol were obtained directly from the Statoil and Shell refineries. Both companies reduced the content of benzene to about 1% during the summer of 1998. Statoil reduced benzene content from about 2% in 1995, whereas Shell reduced from about 4% in 1998. These reductions took place at the same time for all three qualities (92, 95 and 98 RON) at the two refineries, respectively.

Aromatics in crude petrol

Simultaneously, the content of C7+C8 aromatics (i.e. toluene, ethylbenzene and xylenes) showed some variations from period to period and between qualities. While the contents in the 92 RON quality from both refineries were observed to decrease slightly from 1997 to 1999, no similar trends were observed for the 95 RON and 98 RON qualities. The aromatics content generally increased with increasing octane number, and although some variations in the content of both the RON 95 and 98 RON qualities remained almost constant. Generally, the C7+C8 aromatics contents in all three qualities were higher in the Shell than the Statoil products, despite products from both refineries are based on North Sea crude oil feedstocks. Differences in operating designs and processing are supposed to cause this difference in composition.

4.3 Retail petrol

Benzene in retail petrol

As was mentioned above Statoil supplies crude petrol for both Shell and Hydro/Texaco petrol stations east of the Great Belt. The benzene content in retail petrol from petrol stations in Roskilde closely related to the content in Statoil crude petrol. The reduction from about 2% to 1% during the summer of 1998 was observed for all three qualities. The benzene content in retail petrol seems to have been reduced also prior to 1997. The data presented in Figure 11 from two campaigns in show that it was higher (3-4%) in 1989-1990.

Aromatics in retail petrol

The changes of the aromatics content were different. For the Statoil crude petrol the aromatics content increased with octane number, but while the content in 92 RON seemed to decrease slightly, it remained more or less constant in 95 RON and 98 RON. This is not the same in the retail products, where the aromatics content is constant and almost the same in all three qualities except for the 98 RON quality, which is slightly higher. The average values presented here contains contributions from companies not getting supplies from Statoil, which affects the correlation to the Statoil crude products. Another factor, which must be considered is, that not all companies and petrol stations sell three different qualities all the time. 95 RON is often sold as 92 RON, and depending on actual supplies the same quality could possibly also be sold as both 92 RON, 95 RON and 98 RON for a limited time interval. This will also diminish the variation in aromatics content between the different qualities as shown in figure 4 and 6, chapter 2.

Other petrol suppliers

In Appendix A, Figure A1-A10 data on the content of benzene and C7+C8 aromatics in retail petrol from all five petrol stations in Roskilde are presented for the five periods, where samples were collected and analysed. These figures show that - for the five companies included in this study - the lowest overall BTX content was found in all three qualities from DK Benzin, whereas Statoil and Shell were very similar and had the highest content. Q8 and Hydro/Texaco - also being quite similar - had the highest content in 92 RON, but it was close to Statoil and Shell with respect to 95 RON and lower than these two companies with respect to 98 RON.

Toluene

Data from the two campaigns in 1989-1990 (Figure 11) show that the average toluene content was about 10-12% (vol./vol.), 98 RON being highest, in retail petrol from 10 different petrol stations in east Denmark. The average toluene content in samples of retail petrol from five different petrol stations in Roskilde analysed in this study (data not reported) increased compared to the first study, in particular for the 98 RON quality. The average contents are 12,7%, 12,9% and 15,9% for 92 RON, 95 RON and 98 RON, respectively. The higher toluene (and possibly also C8 aromatics) content in actual (1999) retail petrol may have been introduced in order to compensate for the reduced benzene content to maintain the required octane number.

Influence of analytical methodology

The results for the benzene content in crude petrol obtained in this project seem to be overestimated by 0,10-0,15% (absolute) compared to values for crude petrol provided by the Statoil and Shell refineries. There may be several reasons for that, but differences in analytical methodology (e.g. sampling, instrumentation, calibration) are probably the most significant. However, the purpose of this project has not been to control the benzene content to any exact value in neither crude nor retail petrol, but to study the trend for the reduction of benzene in petrol in relation to the new EU regulation of max. 1%, and demonstrate a probable corresponding decrease in the emission of benzene from traffic. Therefore, results presented in this study have only been subjected to *internal* quality control and no attempts have been devoted to *intercompare* accurately the methodology applied and results obtained with those from the refineries or elsewhere.

Reduced benzene in petrol

In conclusion this study has documented that the reduction in benzene content in retail petrol to about 1% as announced by all companies was introduced during the summer and second part of 1998. Since then the average content has remained constant at 1%. The analyses the content of C7+C8 aromatics have shown greater variations not only from company to company and from quality to quality but also from period to period. Overall, however, the average content of BTX in retail petrol showed a slightly decreasing trend during the period covered, while it seems to be slightly higher than in earlier campaigns in 1989-1990.

4.4 Trends of aromatics (BTX) in air

BTX in air

The available data on BTX from the two measurement sites have been analysed, especially for estimation of the trends. In order to remove the influence from the different meteorological conditions (dispersion) from year to year the method - inverse modelling - described in chapter 3 has been used. It has been assumed that the traffic was constant during the project period. This might not be true, but data were not available due to technical problems with the automatic traffic counters operated by the Road Directorate.

Trends at Jagtvej in Copenhagen

Calculating the diurnal emission profiles for several years provides estimation of the trends in the traffic contribution to air pollution. Concentrations depend on both emissions and meteorology, whereas the trend analysis of emissions is independent of the inter-annual variations in the meteorological conditions. Trend analysis of the average diurnal NO_x, CO emissions were performed for the years 1993-1999 and the benzene emissions for 1994-1999 at Jagtvej using the Filtered Least Square Method with zero intercept (cf. chapter 3.3). Results are shown in Figure 12 together with the measured annual average concentrations, where the background contribution was subtracted. Only weekdays were used for this analysis. The calculated emissions and measured concentrations show a similar long-term trend, but the inter-annual variation is different, illustrating the influence of meteorology on air pollution levels. It has to be taken into account that data are not available for complete calendar years all the years (see Figure 7, chapter 3), which means that not all annual averages are "true" averages.

CO and NO_x at Jagtvej

The emissions of NO_x and CO showed distinct decreasing trend, which mainly is due to increasing fraction of vehicles equipped with catalysts (approx. 60% in 1998).

Benzene at Jagtvej

The benzene concentration and emission decreased significantly at Jagtvej by a factor of 5. The most steep decrease was observed from 1994 to 1997. During the year 1997 to 1999 a weak decreasing trend was still observed for the emission. The concentration did not show a similar decreasing trend, probably due to bad dispersion and/or increasing traffic.

Trends at Albanigade in Odense

The trends at the monitoring station at Albanigade in Odense were similar, Figure 13, but the analysis was not so complete because data on BTX only were available from 1997-99

CO and NO_x at Albanigade

The emission of NO_x showed weak decreasing trends during the year 1997-1999. The CO emission is nearly constant.

Benzene at Albanigade

The emission and the concentration of benzene decreased slightly during the year 1997-1999. However, it must be realised that data are not available for complete calendar year, see Figure 7, chapter 3.

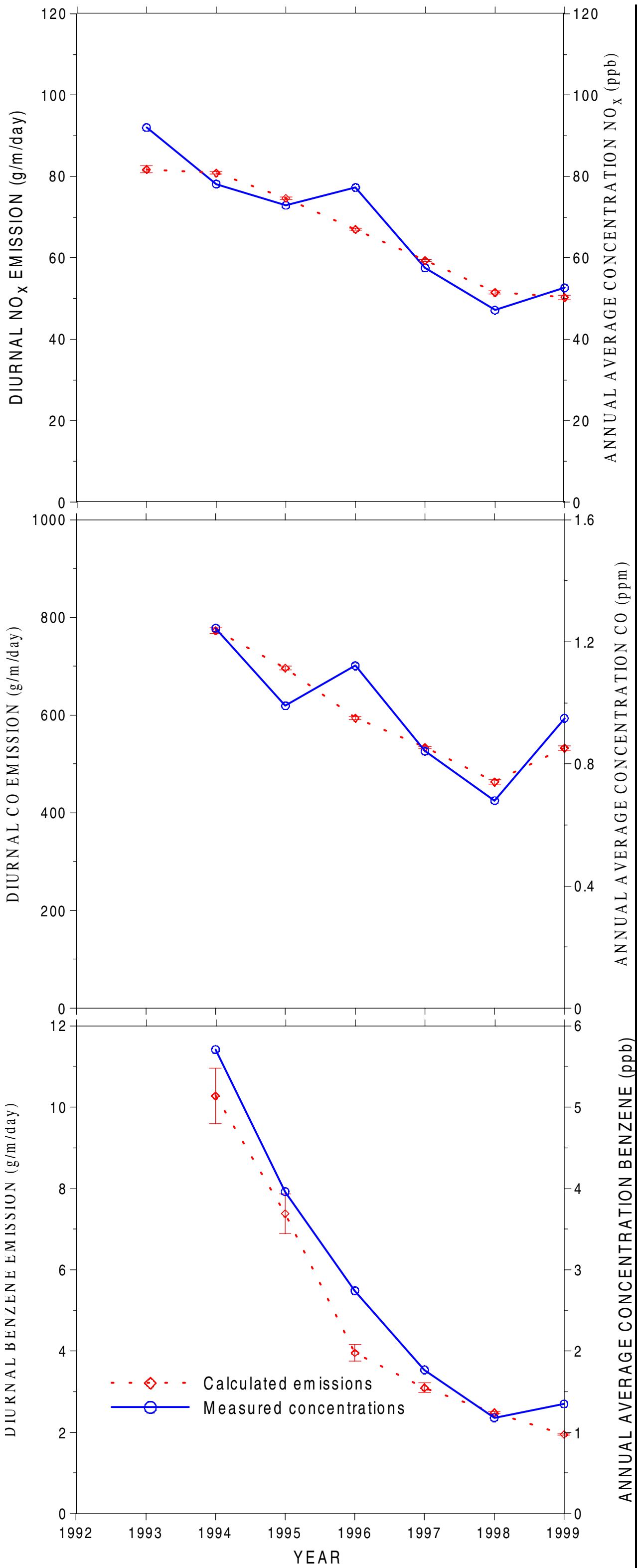

Figure 12 Trends of annual averages of NOx, CO and benzene concentrations and calculated traffic emissions in Copenhagen (street canyon, Jagtvej).

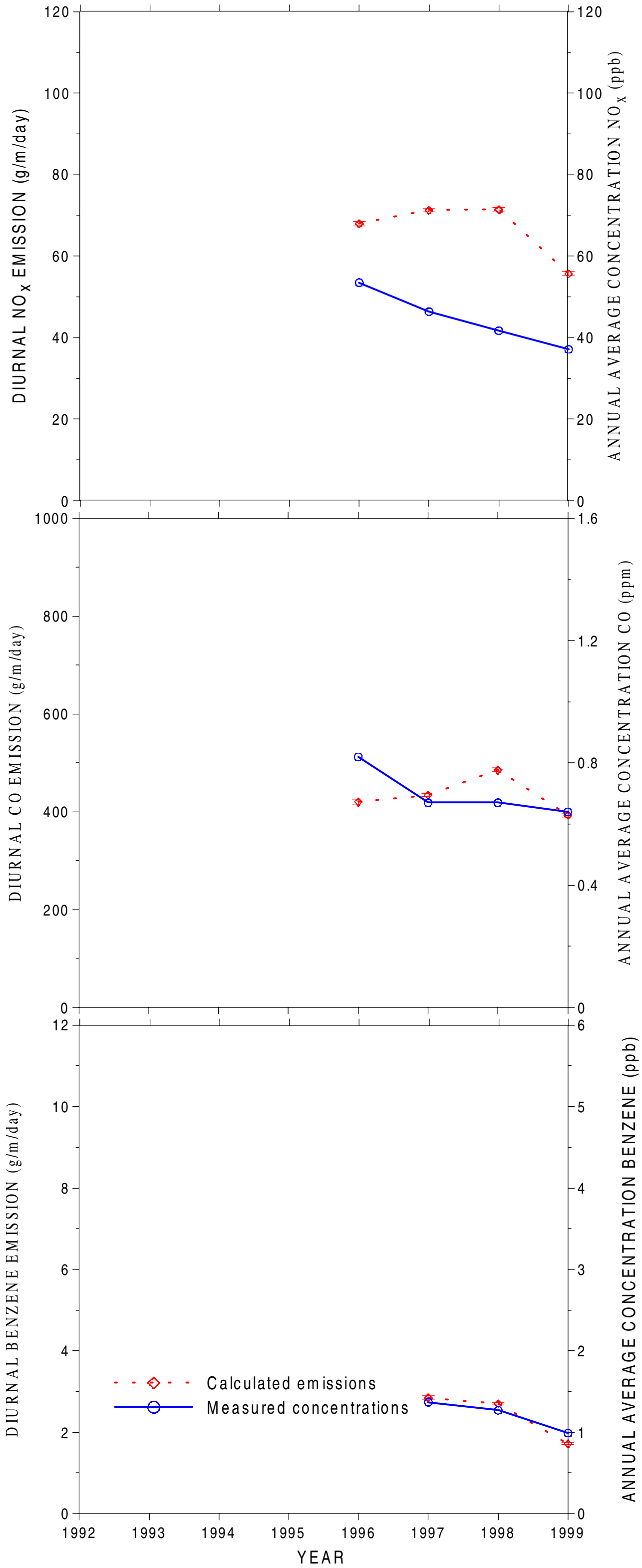

Figure 13 Trends of annual averages of NOx, CO and benzene concentrations and calculated traffic emissions in Odense (street canyon, Albanigade)

Comparison with benzene in petrol

The benzene content in the major part of petrol sold east of the Great Belt (from Statoil), e.g. in Copenhagen was reduced from approx. 3.5% in 1994 to approx. 2 % by the end of 1995; in July 1998 the benzene content was reduced to approx. 1%. The benzene content in the major part of petrol sold west of the Great Belt (from Shell), e.g. in Odense was approx. 3.5% until July 1998 and then reduced to approx. 1%. The content of other aromatic compounds in petrol was mainly unchanged. The reduction in benzene concentrations in air was mainly caused by the reduced benzene content in petrol and the increasing number of cars with three way catalysts. The fraction of cars with catalysts was in 1999 60-70% depending on the location. It is assumed that the highest fraction is present at the most busy streets, where the newest part of the car fleet operates.

Benzene: CO ratio

Another aspect of this reduction on the pollution composition is illustrated in Figure 14; it shows the annual averages of the ratios between benzene and CO (ppb/ppm), estimated as the slopes of the linear regression lines. A clear reduction of the benzene/CO ratio was observed between 1995 and 1996 for Jagtvej and another decrease at both sites during 1998, when both refineries reduced their content of benzene in petrol to 1%. In Copenhagen the ratio between benzene (ppb) and CO (ppm) was 4.3 in 1994 -95. In the period 1996 - 97 the ratio was 2.4. The reduction in this ratio corresponds to the relative reduction in the benzene content of approx. 40%. A similar analysis of data from a street in London (Marylebone Road, http://www.aeat.co.uk/netcen/aqarchive/my1.html) shows a ratio between benzene and CO of approx. 1.4. This is significantly lower than that derived from the Danish data, indicating different fuel qualities. The toluene/CO ratio did not change so drastically (Palmgren et al., 1999), which shows that benzene was removed specifically. A small year-to-year decrease of the toluene/CO ratio in the period 1994-1999 can be explained by reduced evaporation losses from newer cars with direct injection engines.

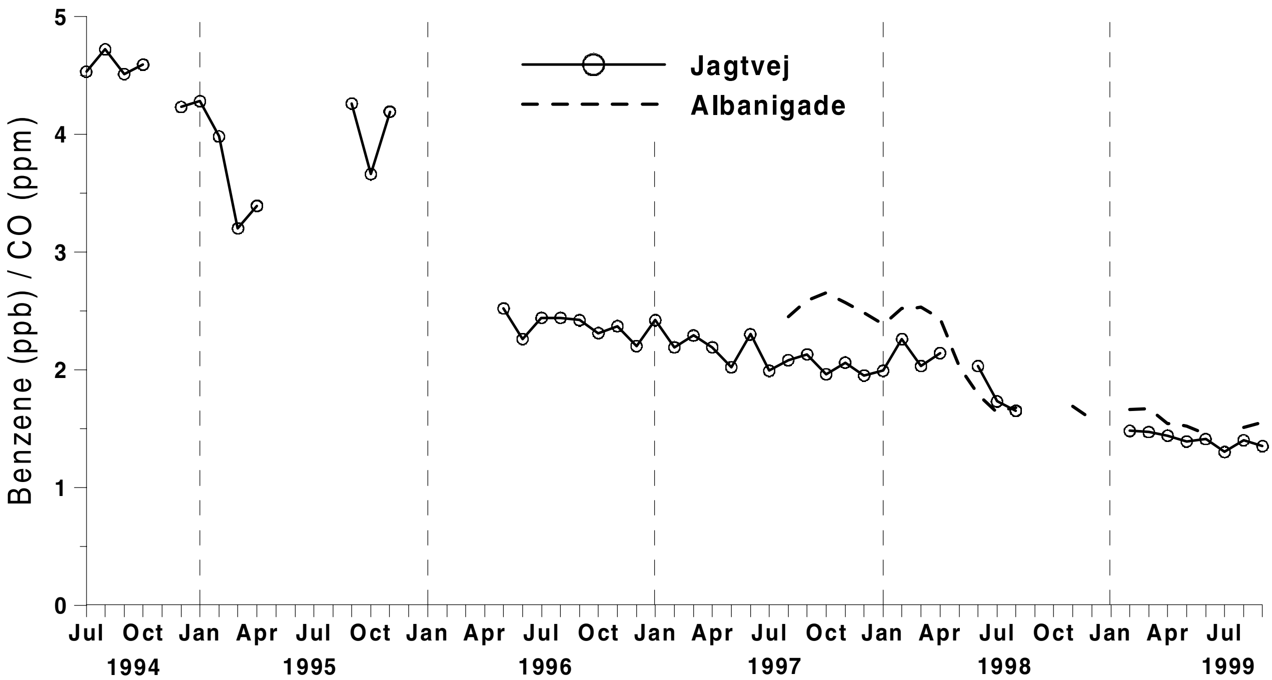

Figure 14 Monthly ratios benzene/CO (ppb/ppm), determined as the slopes of the linear regression lines.

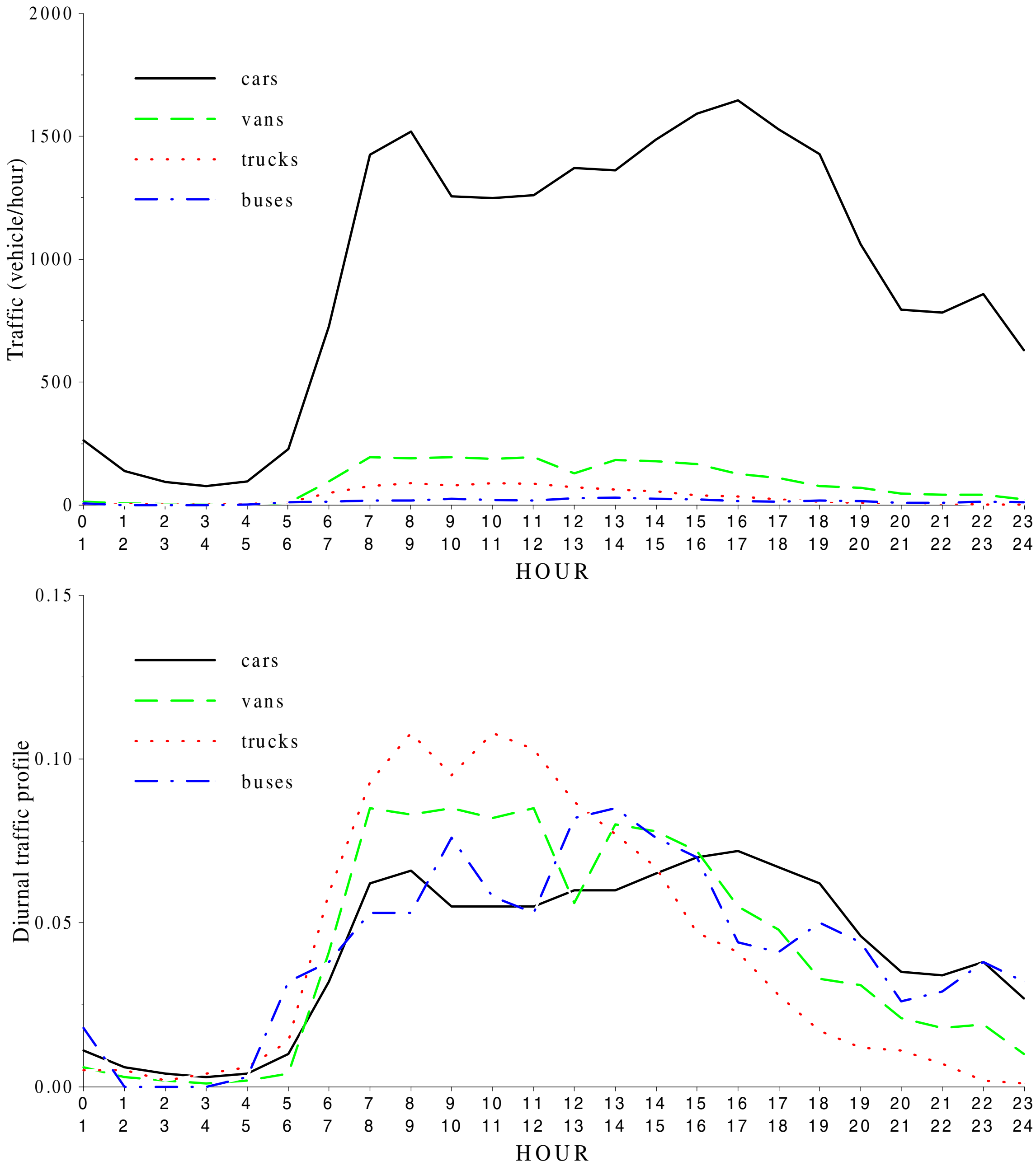

Figure 17 Average working days diurnal variation of traffic at Jagtvej; a) traffic flow, b) diurnal profile.

Benzene from other aromatic VOCs

A benzene contribution from the other aromatic VOCs could not be identified, and conversion of these species into benzene does not represent an important source at the moment compared to the contribution from the benzene in petrol.

Vehicle categories

Automatic traffic counts have been carried out at Jagtvej by the Danish Road Directorate in 1994/95 and classified in light and heavy vehicles as 1 hour averages. Supplementary manual traffic counts provided additional split-up of traffic in four vehicle categories: passenger cars, vans, trucks and buses. The passenger cars dominate the traffic with a diurnal variation significantly different from the other vehicle categories (Figure 15). This analysis was only carried out at Jagtvej.

The emissions from different vehicle categories were estimated by expression (3) in chapter 3. In order to make the system better defined, trucks and buses are treated jointly in the case of NO_x emissions and all diesel vehicles (incl. vans) are treated jointly for estimation of CO and benzene emissions.

Analysis in 1994/95

Because the traffic counts were available only from the 1994/95 period and the traffic may have changed since, the results obtained for the emission profile for the year 1994 were used as a basic profile. The emissions calculated for the other years were decomposed in a part proportional to 1994 and a residual. The least square estimations were made separately for each decomposed part of the total emission profile for each year except 1994. The least square solutions for the residuals were subtracted from the solutions obtained for the "proportional part" of the profiles.

Emission factors

The estimated emission factors are shown in Table 2. Because the contribution from diesel vehicles (the category "other vehicles") to CO and benzene emissions is small, the uncertainties of the estimations are very high. This analysis has not been repeated due to lack of accurate traffic data.

Table 2 Estimated emission factors (g/km) for the different vehicle categories. Vans, buses and trucks are included in one category for benzene and CO.

	NO_x			Benzene		CO	
Year	Cars	Vans	Trucks and buses	Cars	Other vehicles	Cars	Other vehicles
1993	1.6 ± 0.2	5.4 ± 4.5	20.7 ± 5.4	-	-	-	-
1994	1.8 ± 0.1	3.9 ± 2.5	18.0 ± 3.0	0.38 ± 0.04	0.10 ± 0.21	25.2 ± 1.1	11.2 ± 6
1995	1.5 ± 0.2	3.8 ± 3.3	18.0 ± 4.0	0.27 ± 0.03	0.09 ± 0.15	22.9 ± 1.0	12.7 ± 6
1996	1.2 ± 0.1	3.9 ± 2.6	18.6 ± 3.2	0.15 ± 0.01	0.04 ± 0.07	19.4 ± 0.8	10.8 ± 5
1997	0.9 ± 0.1	6.3 ± 2.5	12.5 ± 3.0	0.11 ± 0.01	0.05 ±0.05	17.3 ± 0,7	9.6 ± 4

The benzene emission factor for cars has been reduced to more than 1/3 or by approx. 70% from 1994 to 1997. This is more than the reduction of benzene in petrol from approx. 3,5% to 2% in the same period. The additional reduction of the benzene emission factor can be explained by the increasing number of cars equipped with catalysts.

5 Conclusions

Benzene in petrol

The reductions of the benzene content in crude and retail petrol have been documented by direct analysis of samples from the petrol terminals of the two Danish refineries, Statoil in Kalundborg and Shell in Fredericia. The benzene content was reduced from approx. 3.5 % to approx. 1 % at both refineries. Statoil reduced the benzene content to 2% already in 1995, but both refineries reduced the benzene content to 1 % during the summer 1998. the total content of aromatic VOC's was not changed significantly in this period.

Benzene emissions

The decreasing emissions and air concentrations of CO and NO_x were a consequence of the increasing number of petrol cars with three-way catalysts, which is 60-70% in 1999. The emissions and air concentrations of benzene were reduced much more, corresponding to the above reductions in benzene content in petrol sold in Denmark. The influence of other aromatic compounds in petrol could not be detected and is probably not important. The benzene concentrations in urban air are expected to decrease further the coming years corresponding to the increasing number of cars with catalysts.

Acknowledgement

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Dansk resumé - Danish summary

Benzene from traffic

Faglig rapport fra DMU nr. 309

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De negative effekter af luftforurening skyldes mange forskellige stoffer, fx NO_2, CO, bly, flygtige organiske forbindelser (VOC) og partikler. Aromatiske flygtige organiske forbindelser giver anledning til særlig bekymring på grund af deres negative helbredseffekter. Målinger af benzen, toluen og xylener er blevet udført i København siden 1994. Time-middelværdier af benzen på op til 20 $\mu g/m^3$ er blevet målt, hvilket er kritisk højt i forhold til WHO's anbefalinger og de nye EU grænseværdier.

Emissionen af benzen bestemmes af benzinens sammensætning, kørselsbetingelserne, sammensætningen af bilparken og procenten af biler med trevejskatalysatorer.

Det blev derfor besluttet, at undersøge denne type af forurening i detaljer, specielt sammenhængen mellem benzenindholdet i motorbenzin og koncentrationen i udeluft. Dette er gennemført med støtte fra Miljøstyrelsen.

Det følgende er et resumé af analyser af benzin solgt i Danmark og luftkvalitetsmålinger fra to lokaliteter i Danmark, Jagtvej i København og Albanigade i Odense. Formålet med projektet har været, at

- bestemme benzenindholdet i benzin og følge ændringerne i benzenindholdet i benzin produceret i Danmark,
- bestemme koncentrationen af benzen og andre flygtige aromatiske forbindelser i udeluft i danske bygader og bestemme emissionen fra den danske bilpark, og
- analysere sammenhængen mellem benzenindholdet i brændstof og koncentrationen i udeluft.

Råbenzin fra de to danske raffinaderier, Shell i Fredericia og Statoil i Kalundborg, som leverer benzin til de fleste benzin selskaber i Danmark, henholdsvis vest og øst for Storebælt, er blevet analyseret. Standerbenzin fra forskellige benzinselskaber fra servicestationer i Roskilde er ligeledes blevet analyseret. Indsamling og analyse er sket to gange om året i perioden august 1997 til juli 1999. Data er desuden

blevet sammenlignet med tidligere data. Benzin (95 oktan) produceret før 1995 indeholdt ca. 3,5% benzen. Statoil reducerede benzenindholdet til ca. 2% i 1995, og yderligere til ca. 1% i 1998. Shell reducerede benzenindholdet fra ca. 3,5% til ca. 1% i 1998.

Luftkvalitetsmålinger af flygtige aromatiske forbindelser startede på Jagtvej i København i 1994 og på Albanigade i Odense i 1997. Koncentrationen i luften er et resultat af emissionen og spredning (meteorologi). Luftkvalitetsdata blev analyseret ved hjælp af en luftkvalitetsmodel, i.e. Operational Street Pollution Model (OSPM). Modellen har gjort det muligt at eliminere meteorologiens indflydelse og dermed bestemme den faktiske emission.

Målingerne af benzen har vist en meget klar faldende koncentration i luft og i emissionen, specielt på Jagtvej i København, hvorfra vi har data tilbage til 1994. Samtidig viser målingerne af CO og NO_x også en klart faldende tendens, men ikke så kraftigt som for benzen. Den generelt faldende tendens skyldes den stigende andel af biler med katalysatorer, 60-70% in 1999. Det meget kraftige fald for benzen i begyndelsen af perioden kan forklares med kombinationen af flere katalysatorbiler og det reducerede benzenindhold i benzin solgt i Danmark.

Koncentrationen af benzen i luften på Jagtvej i København var dog stadig i 1998 over den foreslåede nye EU grænseværdi på 5 $\mu g/m^3$ som årsmiddelværdi. Imidlertid forventes det, at det reducerede benzenindhold fra midten af 1998 og det stigende antal biler med katalysatorer vil føre til at Danmark kan overholde denne grænseværdi i fremtiden.

Benzenbidraget fra dieselbiler er ubetydeligt.

Appendix A

Aromatics (BTX) content in unleaded retail petrol during 1998-1999.

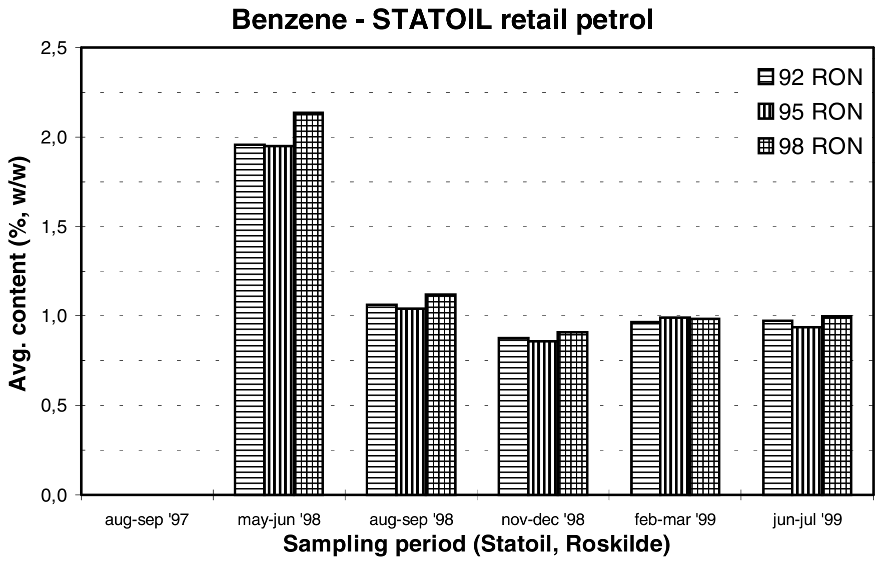

Figure A1 Average benzene content in retail petrol from Statoil, Roskilde, sampled and analysed during five different periods in 1998-1999.

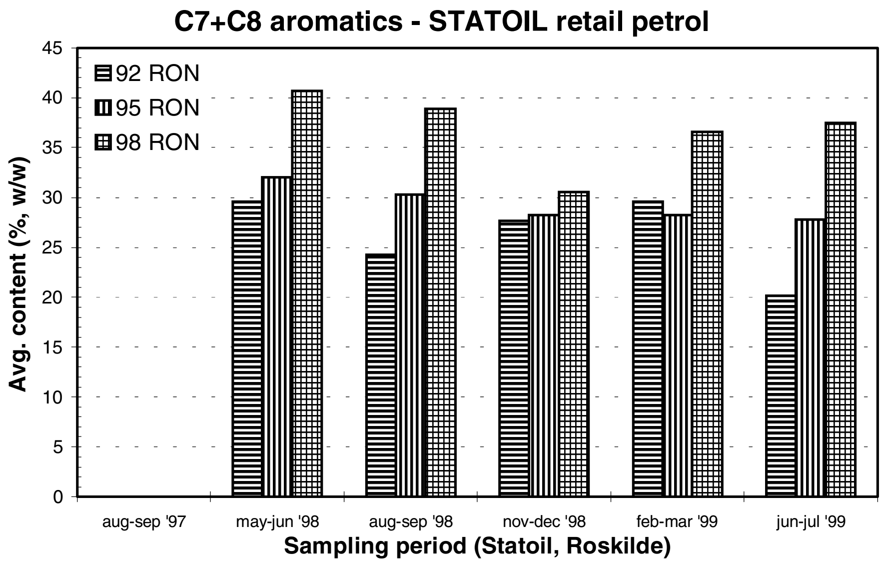

Figure A2 Average C7+C8 aromatics content in retail petrol from Statoil, Roskilde, sampled and analysed during five different periods in 1998-1999.

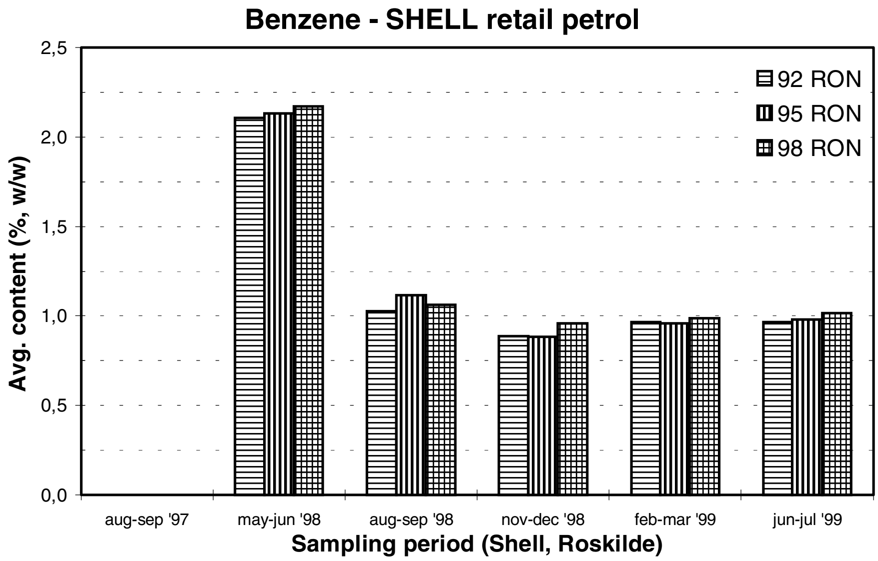

Figure A3 Average benzene content in retail petrol from Shell, Roskilde, sampled and analysed during five different periods in 1998-1999.

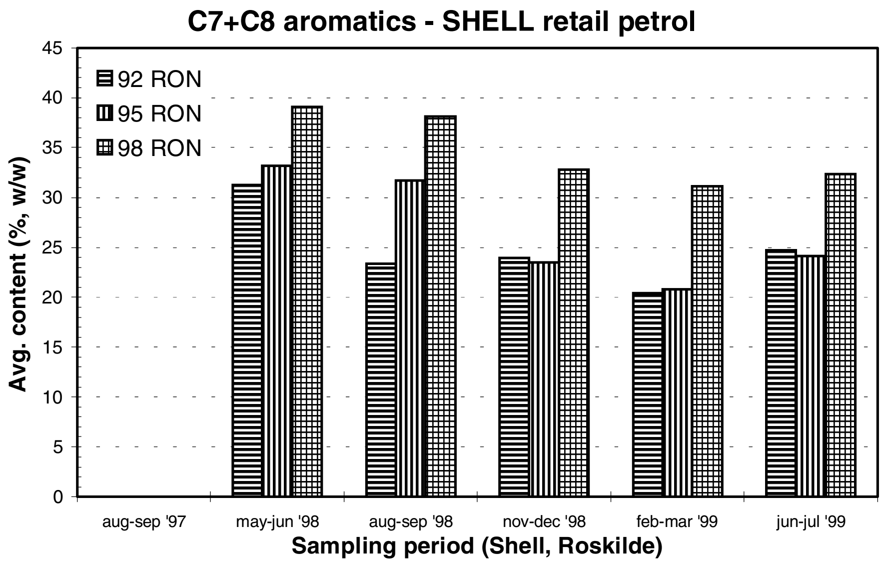

Figure A4 Average C7+C8 aromatics content in retail petrol from Shell, Roskilde, sampled and analysed during five different periods in 1998-1999.

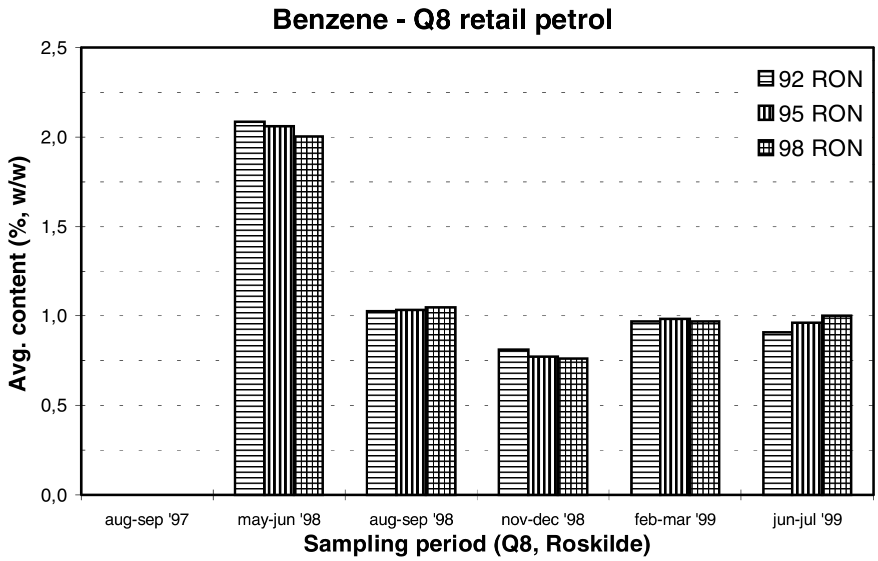

Figure A5 Average benzene content in retail petrol from Q8, Roskilde, sampled and analysed during five different periods in 1998-1999.

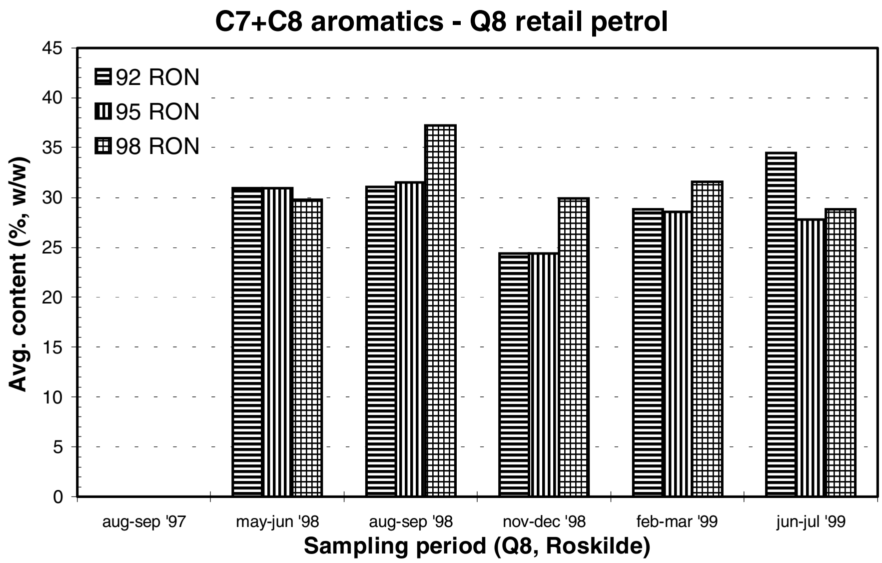

Figure A6 Average C7+C8 aromatics content in retail petrol from Q8, Roskilde, sampled and analysed during five different periods in 1998-1999.

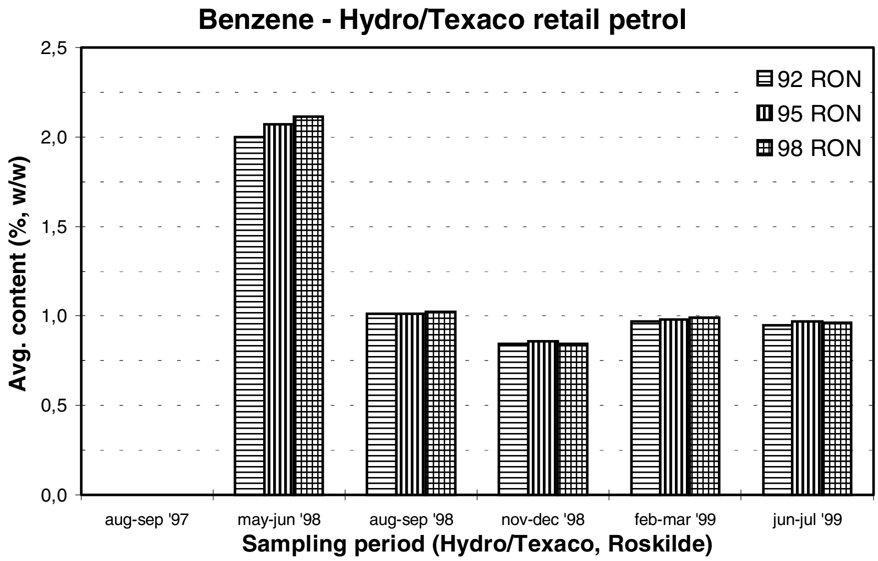

Figure A7 Average benzene content in retail petrol from Hydro/Texaco, Roskilde, sampled and analysed during five different periods in 1998-1999.

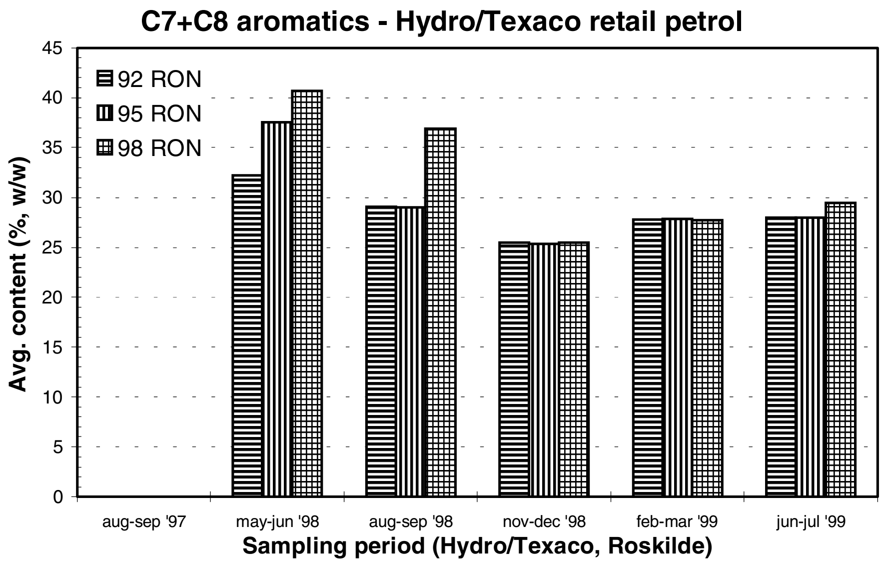

Figure A8 Average C7+C8 aromatics content in retail petrol from Hydro/Texaco, Roskilde, sampled and analysed during five different periods in 1998-1999.

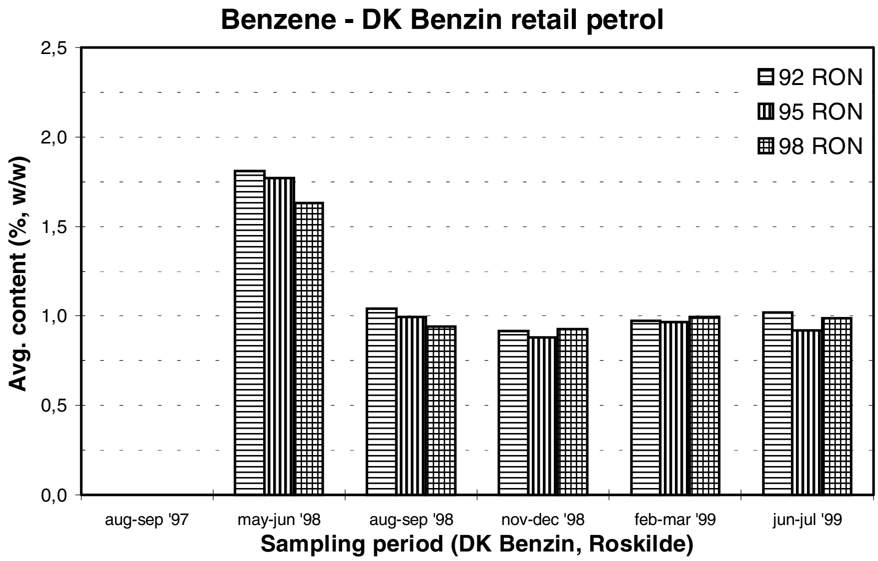

Figure A9 Average benzene content in retail petrol from DK Benzin, Roskilde, sampled and analysed during five different periods in 1998-1999.

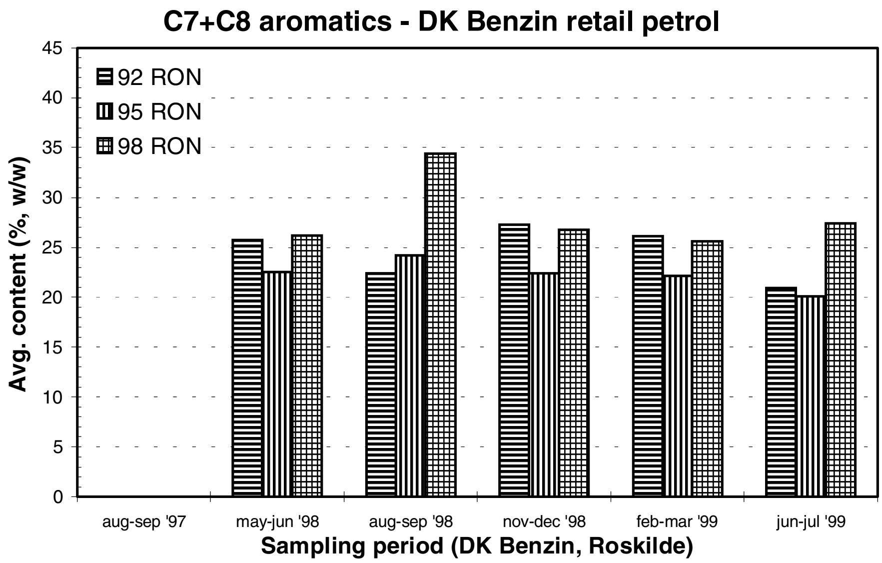

Figure A10 Average C7+C8 aromatics content in retail petrol from DK Benzin, Roskilde, sampled and analysed during five different periods in 1998-1999.

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The measurements of benzene showed very clear decreasing trends in the air concentrations and the emissions since 1994. At the same time the measurements of CO and NO_x also showed a decreasing trend, but not so strong as for benzene. The general decreasing trend is explained by the increasing number of petrol vehicles with three way catalysts, 60-70% in 1999. The very steep decreasing trend for benzene at the beginning of the period from 1994 was explained by the combination of more catalyst vehicles and reduced benzene content in Danish petrol. The total amount of aromatics in petrol, including toluene, increased only weakly. The analyses of air concentrations were confirmed by analyses of petrol sold in Denmark.

The concentration of benzene at Jagtvej in Copenhagen is still in 1998 above the expected new EU limit value, 5 $\mu g/m^3$ as annual average. However, the reduced content of benzene in petrol from 1998 and the increasing number of vehicles with catalysts will probably lead to compliance with this limit value.

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