# Atmospheric PAH in Denmark

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# Data sheet

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# Foreword

For many years it has been well known, that the group of Polycyclic Aromatic Hydrocarbons (PAH) contain several components with mutagenic or carcinogenic effects Nevertheless no systematic measurements of the level of PAH have been made in Denmark until now.

The emission of PAH originates from several sources, but it seems generally accepted, that the main contribution is due to traffic. In order to establish a background for an evaluation of the effect of the severe emission standards for motor vehicles, which will be introduced during the nineties - both for petrol and diesel driven motor vehicles - the Danish Environmental Protection Agency (DEPA) decided to support a project with the following main purposes:

1. Determination of the PAH level at different locations in Denmark.
2. Evaluation of the traffic contribution to PAH emission, including a split between petrol and diesel driven vehicles.
3. Evaluation of the health effects of PAH and other POM (polycyclic organic matter).

The superior project management has been taken care of by Department of Environmental Science and Technology, Risø National Laboratory (Risø), but several institutes have contributed to the project. Main contributions have been produced by National Environmental Research Institute (NERI), Institute of Toxicology (IT), Local Agency of Environmental Protection, Municipality of Copenhagen (CEPA) and dk-Teknik (dkt).

The project has been followed by a steering group with the following members:

DEPA: Erik Iversen (chairman)
Erik Rasmussen
Anders Carlsen
Risø: Torben Nielsen (project manager)
NERI: Mette Poulsen
Lone Grundahl (part of time)
Finn Palmgren (part of time)
IT: John Chr. Larsen
Preben Aagaard Nielsen (part of time)
CEPA: Jan Tønnesen
Raymond Skaarup
dkt: Allan Bang Jensen

The main results from the project is published in a report from the Danish Environmental Protection Agency:

Traffic PAH and other mutagens in air in Denmark (*Nielsen et al., 1995).* Details from the project are reported in 3 reports from the contracting institutes:

1. Traffic PAH and Other Air Pollutants in the Center of a Large City (*Nielsen et al., 1995).*
2. Atmospheric PAH in Denmark (*Poulsen et al., 1995*).
3. Mutagenic activity in the centre of Copenhagen (*Poulsen, Nielsen, 1995).*

The results from the project will contribute to the discussions about the need for specific actions against emissions of PAH and other mutagens from motor vehicles.

# Summary

*Objectives*

The objectives of the present project are:

1. To determine the PAH concentration levels and trends at different part of Denmark at existing monitoring stations,
2. To relate the measured values to the WHO limit values,
3. To make rough estimates of the contribution from different types of sources in Denmark and in our neighbour countries.

*Stations and components*

The stations in the urban areas were located in Copenhagen, Aalborg and Odense, and in the rural areas on Anholt and in Lille Valby. The samples were analyzed for 8 PAH: fluoranthene, pyrene, benzo(e)pyrene, benzo(a)pyrene, indeno(1,2,3-cd)pyrene, benzo(ghi)-perylene and the sum of benzo(b)-, benzo(j)- and benzo(k)fluoranthene. Because the stations were either identical with or placed nearby stations in other monitoring programmes inorganic components were measured at the same localities as PAH.

*Sampling and analysis methods*

The samples were collected by a filter pack sampler developed at the National Environmental Research Institute. The sampling volume was 58 $m^3$/day and the flow through each filter was 0.5 m/sec. The particulate matter was collected on a cellulose nitrate/acetate membrane filter. Before the analysis for PAH the filters were accumulated to monthly samples. The analysis consisted of a Soxhlet extraction in toluene, a clean up procedure on silica and determination on a gaschromatograph combined with a mass spectrometer. The recoveries of artificial samples spiked with the individual analyses were 75-96%. The recoveries of the deuterated internal standards were 86-98%, and for the standard reference material 53-91%. The detection limits for the individual PAH were 0.0030-0.037 ng/$m^3$.

*Results*

The concentrations of the PAH variate from place to place and exhibit seasonal fluctuations. The range of the concentrations for all stations are given in *Table 1*.

*Table 1*. The PAH concentrations in ng/$m^3$ for all stations from March 1992 to February 1994.

| PAH | Summer ng/$m^3$ | Winter ng/$m^3$ |
|---|---|---|
| Fluoranthene | 0.1 - 1.6 | 0.3 - 7.4 |
| Pyrene | 0.1 - 1.4 | 0.1 - 8.2 |
| Benzo(b+j+k)fluoranthene | 0.07 - 2.6 | 0.2 - 7.3 |
| Benzo(e)pyrene | 0.02 - 1.9 | 0.1 - 3.9 |
| Benzo(a)pyrene | 0.01 - 0.6 | 0.14 - 3.2 |
| Indeno(1,2,3-cd)pyrene | 0.01 - 1.1 | 0.04 - 4.4 |
| Benzo(ghi)perylene | 0.01 - 2.8 | 0.03 - 9.2 |

*Method evaluation*

A parallel sampling of the PAH were performed at the station Lille Valby in order to examine whether any losses of PAH occurred during sample treatment of the filter. The correlation analysis showed some variation in the concentration of PAH, but the difference was not significant at a 95%-level.

*PAH levels compared with other investigations*

The levels detected in this investigation were lower than in earlier investigations both in Denmark and in other countries, but comparable with investigations made in the nineties in other countries. This is properly due to reduced emission of pollutants.

*PAH levels in urban and rural location*

The concentrations in urban areas were 3-25 times higher than at the rural area Anholt/6008. In summer periods the differences were lager than in winter periods. *Table 2* shows these ratios for both summer and winter periods.

*Table 2*.The range of the ratios between urban areas and the rural area Anholt/6008, summer and winter periods.

| PAH | Summer | Winter |
|---|---|---|
| Fluoranthene | 4 - 6 | 3 - 5 |
| Pyrene | 4 - 8 | 5 - 10 |
| Benzo(b+j+k)fluoranthene | 8 - 18 | 3 - 6 |
| Benzo(e)pyrene | 7 - 22 | 5 - 8 |
| Benzo(a)pyrene | 7 - 21 | 4 - 8 |
| Indeno(1,2,3-cd)pyrene | 7 - 21 | 4 - 8 |
| Benzo(ghi)perylene | 16 - 63 | 9 - 20 |

*Seasonal variation of PAH levels*

The concentrations in the urban areas in winter periods were 2-7 times higher than the concentrations in the summer periods. In the rural areas differences between winter and summer periods were lager than for the urban areas. *Table 3* shows the ratios between the concentration in winter and summer periods, both in urban and rural areas.

*Table 3*. The range of the ratios between the concentration in winter and summer periods at both urban and rural areas.

| PAH | Urban | Rural |
|---|---|---|
| Fluoranthene | 4 - 5 | 5 - 6 |
| Pyrene | 4 - 7 | 4 - 8 |
| Benzo(b+j+k)fluoranthene | 3 - 5 | 9 - 12 |
| Benzo(e)pyrene | 2 - 5 | 6 - 9 |
| Benzo(a)pyrene | 4 - 7 | 12 - 20 |
| Indeno(1,2,3-cd)pyrene | 3 - 6 | 8 - 12 |
| Benzo(ghi)perylene | 2 - 6 | 8 - 12 |

*PAH profile in urban and rural location*

The PAH profile were normalized to benzo(e)pyrene. The PAH profiles in the urban areas were the same during summer and winter. They were different in the rural areas, especially with respect to benzo(ghi)perylene, which had a lower ratio.

*Seasonal variation of PAH profiles*

In urban areas the ratios for fluoranthene and pyrene were lower in summer periods compared with winter periods. This is in accordance with the gas-particle phase distribution. In the rural area the ratios were higher in summer periods compared with winter periods. The ratios for benzo(b+j+k)fluoranthene in the urban areas were the same in summer and winter periods, but in the rural areas the ratio was higher in the winter periods. The ratio for indeno(1,2,-3-cd)pyrene were the same for the urban and the rural areas, but the ratios during summer were lower. The ratios for benzo(ghi)perylene were higher for urban areas than for rural areas and there were no differences between the summer and the winter periods.

*Correlations between PAH and inorganic components*

The correlation or covariation between the PAH and other components can give some indications about the origin of the PAH. Many inorganic components show a clear seasonal variation with high concentrations in winter and low concentrations in summer. Good correlations were generally observed between inorganic pollutants from the same source. The correlation between sulphate (indicator for long transport) and the PAH was weak at all locations. No significant correlations have been observed between the measured PAH and the soil dust, indicating that the PAH were not connected to the coarse particles. The correlation between the measured PAH and $SO_2$ (indicator for combustion of coal and oil) were good, but due to the monthly time resolution it is unpossible to estimate the contribution from these sources. Because the use of wood for house heating correlates strongly with the use of coal and oil, the correlation could indicate contribution of PAH from wood burning. No correlations were observed between the measured PAH and vanadium from heavy fuel oil. The correlation between the lead concentration, adjusted for the significant negative trend, and the PAH indicate a contribution from petrol driven cars at all urban station. In all cases the correlation is not a clear proof for the origin of the PAH, because the correlation or a part of it could be due to a common third factor, e.g. the dispersion fluctuation.

*Estimates of PAH contribution from different sources*

Data of PAH emissions from Denmark are not available, but it is commonly indicated that the traffic exhaust and house heating are the main sources to the PAH pollution of the urban air. A ratio between indeno(1,2,3-cd)pyrene and benzo(ghi)perylene should be 0.37 for the PAH profile of traffic exhaust and 0.90 for domestic heating. The ratios for the two stations in Copenhagen had an average ratio at 0.46-0.48, 12-14% higher in winter than in summer periods. The average ratios for the other urban areas were 0.57-0.58, 23-43% higher in winter periods than in summer periods. This indicates a high contribution from the traffic to the PAH pollution at the two Copenhagen sites, whereas the contribution from house heating were higher at the other urban areas. At the rural sites the ratios were higher than 0.90 both summer and winter indicating that the ratio-source relation can only be used close to the sources.

*PAH compared to limit values*

It can be estimated that the average concentration of benzo(a)pyrene equivalents in the urban sites were higher than 1 ng/m$^3$. According to WHO's guideline, 9 out of 100.000 people exposed to 1 ng/m$^3$ over a lifetime would be at risk of developing cancer. At the rural sites the concentrations were significantly lower.

# 1 Introduction

Polycyclic Aromatic Hydrocarbons (PAH) on airborne particles are of great concern due to the carcinogenic nature of several of these components and their presence in respirable particles. In addition, the deposition to water and soil surfaces may lead to an impact on the environment.

*Background*

No systematic measurements of PAH in air have earlier been carried out in Denmark; only a few short campaigns have been performed. On the basis of measurements of other air pollutants and on emission factors from the literature, it is anticipated that the main contribution of PAH from national sources originates from the road traffic. From October 1990 three-way-catalysts have been installed in all new petrol driven cars, and stronger emission limits will be introduced for light and heavy diesel cars and trucks in the near future. Also some industrial plants, residential heating, incineration of waste, burning of wood and waste in wood stoves may contribute to the air pollution with PAH. Since Denmark is located in a region, where long range transport of air pollutants occur from our neighbouring countries East, South and West of Denmark, the contribution from foreign sources may be important.

*Spacial distribution and speciation*

In order to determine the level during introduction of the above mentioned measures and to follow the development, systematic and representative measurements of the PAH-pollution in Denmark has been initiated by the present project. The measurements must give information about the spacial distribution and the origin of the PAH pollution. Consequently, the measurements must be carried out at different positions and in different types of areas (rural and urban) and the PAH must be speciated and related to other air pollution measurements in order to determine the origins. In order to investigate the trend the measurements has to be repeated during a number of years.

*National Air Quality Monitoring Programme*

Because the PAH measurements are very time and labour comsuming, the most efficient way to obtain the above evaluations is to link the PAH measurement programme to running programmes i.e. the Danish Air Quality Monitoring Programme in urban areas (*Palmgren Jensen et al., 1991*) and the Background Air Monitoring Programme (*Hovmand et al., 1993*). The PAH samples were collected at selected monitoring sites in these programmes.

*Present report*

The present report comprises 2 years measurements carried out in 1992-94. A later phase has been scheduled to 1994-96.

*Other investigations*

Parallel to this measurement programme a project for determination of the contribution from traffic and a project for assessment of the health effects have been carried out (*Nielsen et al., 1995*).

*Objectives*

The objectives of the present project are:

1. To determine the PAH concentration levels and trends in different parts of Denmark at existing monitoring stations,
2. To relate the measured values to the WHO limit values and other relevant limit values,
3. To make rough estimates of the contributions from different types of sources in Denmark and in our neighbouring countries.

# 2 The monitoring programme

Since the beginning of 1992 samples for determination of PAH have been collected at 7 localities in Denmark, 5 localities in urban areas and 2 in rural areas. Six of the localities were identical to the localities in the Danish Air Quality Monitoring Programme (*Palmgren Jensen et al., 1991, Kemp et al., 1994*). One was identical to a locality in the Background Air Monitoring Programme (*Hovmand et al., 1993*). Relevant results from the existing stations are available in this report.

## 2.1 Stations

The stations in the urban areas were located in Copenhagen, Odense and Aalborg, and the stations in the rural areas on Anholt and in Lille Valby. The localities are shown in *Figure 2.1.*

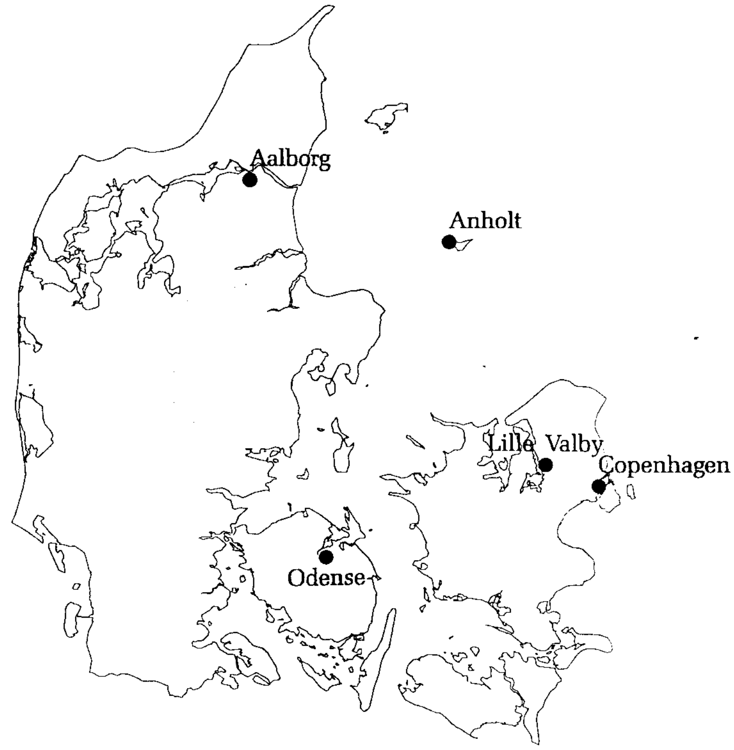

*Figure 2.1.* The localities used in the PAH measurement programme.

*Urban areas*

All the stations in the urban areas are identical to the stations in the Danish Air Quality Monitoring Programme. In Copenhagen the two stations were placed in the centre of the city, one at H.C. Andersens Boulevard (Copenhagen/1103) and the other at Jagtvej (Copenhagen/1257). Two stations were also used in Odense. One was placed at Albanigade (Odense/9155) which is in the centre of the city, while the other one was placed at Ringstedvejen (Odense/9154) close to the crossing between two big roads with a high traffic intensity.

The traffic intensity is given in *Table 2.1*. At Aalborg one station was used. This station was placed at Vesterbro (Aalborg/8151) in the centre of the city at the ramp of the bridge across the Liimfiord.

*Rural areas*

In the rural areas a station was situated at the west coast of Anholt. Anholt is an island in the middle of Kattegat more than 40 km from the coast. The station (Anholt/6008) was placed at the same location as the station (Anholt/6001) in the Background Air Monitoring Programme. It was necessary to set up an extra station for the PAH determination because the filter material from the existing station was used for other analyses.

The other rural station was at Lille Valby. Lille Valby is a small village about 25 km west of the centre of Copenhagen and about 6 km north of Roskilde. A main road passes about 1,5 km west of the station, and there are no other industrial or traffic activities in the areas.

Two stations were placed at Lille Valby. One station (Lille Valby/2090) was identical to the station in the Danish Air Quality Monitoring Programme and the other (Lille Valby/2098) was established for a parallel determination of PAH to verify whether different handling of the filters had any influence on the results of PAH.

*Description*

At most of the stations the different types of instruments were installed in a hut. The air intake of the instrument measuring PAH were placed on the roof of the hut, about 3 meters above the ground. In the remaining stations the sampler for PAH was installed in open air. The intake at all locations were placed approximately 3 meters above the ground. The stations in the cities were all located directly at kerbsides with heavy traffic passing a few metres from the stations, and the intakes were placed above the pavement. The stations in the rural areas were placed far from roads.

## 2.2 Components

*PAH*

No international recommendation have been made for sampling of PAH. WHO published a drinking-water standard in 1970 and 1971 based on a limit for the sum of six PAH *(WHO, 1984)*. It was decided in this program to measure these six, i.e. fluoranthene, the sum of benzo(b)-, benzo(j) and benzo(k)fluoranthene, benzo(a)pyrene, indeno(1,2,3-cd)pyrene and benzo(ghi)perylene. In addition it was decided to measure pyrene and benzo(e)pyrene. Pyrene together with fluoranthene may be an indicator for traffic pollution. Benzo(e)pyrene was included because it is formed in comparable amount as benzo(a)pyrene, but it is more stable than benzo(a)-

pyrene.

*Inorganic components*

As mentioned above all the stations in the PAH monitoring programme were either identical with or placed nearby stations in other monitoring programmes. Different inorganic components were therefore measured at the same localities as the PAH. In *Table 2.1* is indicated the localities and stations used in the PAH-monitoring programme. For each station the intensity of traffic passing the station is listed, as well as the measured components. The method for sampling and analysis of PAH is described in section 3, and the methods for the other components are described in *Hovmand et al.*, (1993).

*Table 2.1.* The localities, the station numbers, the traffic intensity per day and the measured components. TSP is the total suspended particulate matter.

| Locality | Station number | Traffic intensity | 24 hours sampling | Continuous sampling |
|---|---|---|---|---|
| Copenhagen, H.C. Andersens Boulevard | 1103 | 60.000 | PAH, TSP, elements | $SO_2$, NO, $NO_2$ |
| Copenhagen, Jagtvej | 1257 | 22.000 | PAH, TSP, elements, $SO_2$ | $SO_2$, NO, $NO_2$ |
| Aalborg, Vesterbro | 8151 | 28.500 | PAH, TSP, elements, $SO_2$ | $SO_2$, NO, $NO_2$ |
| Odense, Albanigade | 9155 | 19.500 | PAH, TSP, elements, $SO_2$ | $SO_2$, NO, $NO_2$ |
| Odense, Ringvejen | 9154 | 20.500* | PAH, TSP, elements, $SO_2$ | |
| Lille Valby | 2098 | - | PAH | |
| Lille Valby | 2090 | - | PAH, elements, $SO_2$ | $SO_2$, NO, $NO_2$ |
| Anholt | 6008 | - | PAH | |
| Anholt | 6001 | - | elements, $SO_2$, $SO_4^{2-}$, $NH_3$, $NH_4^+$, ($NO_3^-$+$HNO_3$) | |

* The traffic intensity at the crossing street, Hjallesevej, was 14.000 cars per day.

# 3 Sampling and analysis

It was decided in this project, as far as possible, to use existing monitoring stations and sampling methods. The sampling method used in the two mentioned monitoring programmes is the so called "filter pack method" by which air is sucked through different kind of filters mounted in series in a single filter holder.

## 3.1 Sampling method

*Sampler*

The sampler for the filter holders was developed at the National Environmental Research Institute (NERI). It is build with room for eight filter holders. The filter holders are mounted above the sampler shelter with downward pointing open inlets (*Figure 3.1*). The air is sucked through each filter holder during 24 hours. With eight filter holders, the change of filter holders have to be done only once a week.

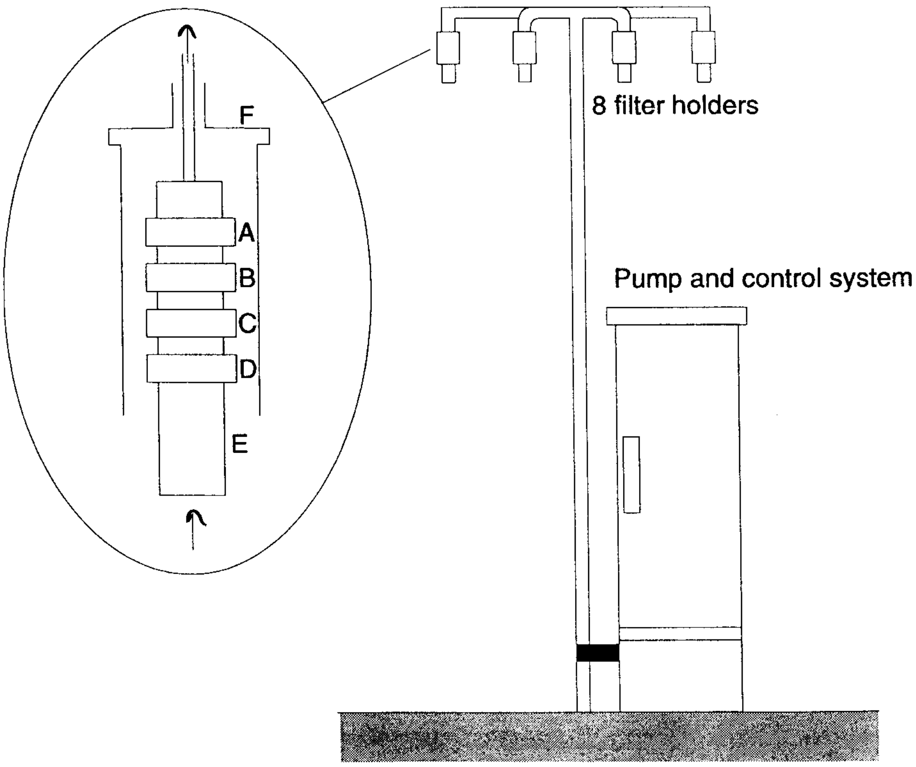

*Figure 3.1.* A sampler and a filter holder. A, B, C are filters impregnated in different ways for sampling ammonia, sulphur dioxide and nitric acid. In the PAH measurement programme this filter holder was used at Anholt/6001, while the filter holders at the other stations only contained 1 impregnated filter for sampling $SO_2$. D is the filter for sampling PAH, and the inorganic particulate matter. E is a PVC inlet and F a rain shield.

The sampling volume was 58 $m^3$/24 hour, the flow through each filter was 40 l/min and the air speed was 0.5 m/sec. at the inlet. The flow was controlled by a mass flowmeter in connection with a motor driven valve, which kept the flow constant through the filters within ± 0.5 l/min. The actual flow was, recorded on paper tape for control and the integrated volume was recorded by a counter. The volume was measured within ± 5% as a standard volume at 0°C and 760 mm Hg. The samplers were inspected and the volume calibrations were checked with intervals of one to two months.

*Filter holder*

PAH on particulate matter was collected together with inorganic particles on cellulose nitrate/acetate membrane filters (Millipore type RA, pore size 1.2 µm). After exposure the filters were treated in the laboratory in different ways, as described below. The exposed areas of the filters were 40 mm in diameter. The particle size cut off of the inlet depends on the surrounding wind speed (*Barrett, 1984*), but it corresponds in average to an aerodynamical diameter of around 20 µm. In this investigation the filter holders shown in *Figure 3.1* was used at Anholt/6001, while the filter holders at the other stations only contained one impregnated filter for sampling $SO_2$. The impregnated filters were cellulose fibre filter (Whatman 41) impregnated with a solution of 2N KOH with 5% glycerol. The $SO_2$ in the air was collected as $SO_3^{2-}$ on the impregnated filters with a collection efficiency of almost 100% under the conditions ($SO_2$-concentrations and humidity) occurring in Denmark (*Keiding, Hansen, 1983*). The filter holders for two weeks sampling were send to the stations in boxes made of wood. In the two monitoring programmes mentioned above all components from the filter packs were determined on a 24 hours basis. It was decided to determine the concentrations of PAH only as a monthly average value. Therefore the samples (the membrane filters) from one month were pooled into a monthly "sample".

*Membrane filters*

The membrane filters were used for the determination of PAH, TSP (total suspended particulate matter) and for determination of all elements with atomic numbers greater than 13 (Al). The amounts of TSP were determined by weighing. The weighing was performed in an air conditioned room with a relative humidity of 52 ± 2% and a temperature of 23 ± 0.5°C (*Miljøministeriet, 1986*). The weight of the particles was determined as the difference between the filters weight before and after exposure. The unexposed filters were kept for at least 2 days and the exposed filters for at least 7 days for conditioning prior to the weighing. After the weighing a cut out with a diameter of 20 mm disk was made. This cut out was used for the determination of the elemental composition in the aerosol samples by means of PIXE (Proton Induced X-ray Spectroscopy) (*Johanson, Campell, 1988*). The remaining part of the filter was used for the determination of PAH.

*Storage*

The procedure for handling the filter pack means that all filter samples were from 3 to 17 days old before they were received at the laboratory. Subsequently the filters from all stations except from Lille Valby/2098 and Anholt/6008 have to be conditioned and weighed. Thus the filters could be up to about 30 days old before they were stored in a dark and cool place (4-8°C). Filters from Lille Valby/2098 and Anholt/6008, which were only collected for the determination of PAH, were from 3 to 10 days old before they were stored dark and cold. When all the filters from a whole month were collected, the filters were pooled and stored in brown glass containers at freezing temperature until the analysis for PAH could be made.

## 3.2 Analysis of PAH

*Extraction*

The samples were Soxhlet extracted in toluene for 24 hours. The filters were placed on pre-extracted glass wool directly in the Soxhlet. Deuterated PAH (fluoranthene-d10, benzo(a)pyrene-d12 and indeno(1,2,3-cd)pyrene-d12) were added as internal standards and 300 ml toluene as solvent. The internal standards (only samples from the second year) were used for calculation of the recovery for each component in every sample, where they were added. The samples were extracted for 24 hours. The volume of the extracts were then reduced to ~ 1 ml using a rotary evaporator.

*Clean-up*

In order to clean up the samples, the extracts were transferred to a glass column with 6 g silica and 1 cm of sodium sulphate. The sodium sulphate served to remove any moisture. After conditioning with 25 ml n-hexane, the columns were eluted with 25 ml n-hexane and afterwards with 15 ml dichloromethane. The dichloromethane fractions were then concentrated to dryness under $N_2$ and redissolved in 1.00 ml of hexane with injection standards (pyrene-d12, benzo(b)fluoranthene-d10, benzo(k)fluoranthene-d12, benzo(e)-pyrene-d12, benzo(ghi)perylene-d12, 1,1-binaphthyl and squalane). The injection standards were used for compensation or the variation in response between the GC-analysis.

*GC-FID*

Aliquot of 1.0 µL of the extracts were analyzed by gaschromatography with Flame Ionisation Detector (GC-FID). The capillary column in the GC-FID was a 25 m × 0.2 µm i.d. fused silica coated with a 0.11 µm 5% cross-linked phenyl methyl silicone (HP Ultra 2). Helium was used as the carrier gas and the column were temperature programmed from an initial temperature of 60°C, held for 1 min, then increased to 310°C at a rate of 10°C /min and held for 30 min. The GC-FID chromatograms show a "fingerprint" of the samples, but are not suitable for quantification due to interfering substances.

*GC/MS*

Aliquot of 1.0 µL were also analyzed by chromatography connected to a INCOS 50 Mass Chromatograph (GC/MS). The capillary column in the GC/MS was also a HP Ultra 2. Helium was used as the carrier gas and the column were temperature programmed from an initial temperature of 60°C, held for 1 min, then increased to 290°C at a rate of 10°C /min and held for 10 min. The capillary column was interfaced directly to the ion source of a quadropole mass spectrometer. The mass spectrometer was operated under electron impact ionization (70 eV) conditions in the selected ion monitoring mode. The quantification was carried out by the MS analysis. Response factors for the individual analyses, relative to the deuterated injection standards, were determined from a gravimetrically prepared solution of the analyses and the injection standards.

*Quality Control*

Quality control was accomplished by the following procedure. Along with every extracting batch of six extraction one was either a blank sample, an artificial sample or reference standard. The blank samples were 25 unused filters. The artificial samples were 25 unused filters spiked with one of three different standard solutions containing the individual analyses. The range of the PAH concentrations in the spike solutions were 3.985-15.50 µg, 0.787-3.101 µg or 0.3985-1.550 µg. Both the blanks and the artificial samples were treated in the same manner as the real samples. The reference standard were SMR 1649, Urban Dust from NIST (*National Institute of Standards and Technology, 1992*). 1 g of the reference standard were weighed out and analyzed exactly like the real samples. The artificial samples and the Standard Reference Material were used for calculation of recoveries (See *Table 3.1, 3.2, 3.3* and *3.5*) In addition recoveries were determined by adding deuterated internal standards, added before the extraction (for the second years sample only) (See *Table 3.4).*

*Recovery*

The recovery were calculated as the relatively recovery in % of the spiked or certified values (see *Table 3.1, 3.2, 3.3, 3.4 and 3.5*).

*Confidence interval*

In order to evaluate the uncertainty of the analysis, two confidence intervals (in %) for each spike level were calculated. The first refers to the interval valid for the number of measurements carried out at the particular spike level. This interval is calculated by:

$$\frac{t_{97.5}(n-1)\times \text{standard deviation}}{\sqrt{n}}$$

where n are the number of measurements and $t_{97.5}(n-1)$ the 97.5% fractile of the Student t-distribution. The second confidence interval refers to the interval valid, if only a single measurement is made, for instead, if it is only possible to make 1 analysis per sample (as in this investigation). In this case n=1 whereas $t_{97.5}(n-1)$ and the standard deviation are the same as in the fist confidence interval. The two confidence intervals were calculated for the artificial samples (at all 3 concentration levels), the Standard Reference Material and for the deuterated internal standards (see *Tables 3.1, 3.2, 3.3, 3.4 and 3.5*).

*Table 3.1.* Spiked amount of PAH, recovery in %, standard deviation and confidence intervals for 5 and 1 measurements of artificial samples spiked with the individual analyses (3.985-15.50µg).

| Components | µg spiked PAH | Recovery | Standard deviation | Confidence intervals [1] n=5 measurements | Confidence intervals [1] single measurement |
|---|---|---|---|---|---|
| Fluoranthene | 3.985 | 81% | 6% | 7% | 17% |
| Pyrene | 4.172 | 81% | 4% | 5% | 12% |
| Benzo(b+k)fluoranthene | 15.50 | 79% | 2% | 2% | 5% |
| Benzo(e)pyrene | 8.429 | 78% | 3% | 4% | 9% |
| Benzo(a)pyrene | 8.512 | 75% | 7% | 8% | 18% |
| Indeno(1,2,3-cd)pyrene | 7.562 | 93% | 4% | 5% | 12% |
| Benzo(ghi)perylene | 10.25 | 84% | 3% | 4% | 8% |

[1] $t_{97.5}(n-1) = 2.78$

*Table 3.2.* Spiked amount of PAH, recovery in %, standard deviation and confidence intervals for 6 and 1 measurements of artificial samples spiked with the individual analyses (0.787-3.101µg).

| Components | µg spiked PAH | Recovery | Standard deviation | Confidence intervals [1] n=6 measurements | Confidence intervals [1] single measurement |
|---|---|---|---|---|---|
| Fluoranthene | 0.787 | 96% | 4% | 4% | 10% |
| Pyrene | 0.834 | 96% | 7% | 7% | 17% |
| Benzo(b+k)fluoranthene | 3.101 | 92% | 1% | 1% | 4% |
| Benzo(e)pyrene | 1.686 | 85% | 7% | 8% | 19% |
| Benzo(a)pyrene [2] | 1.702 | 52% | 21% | 22% | 53% |
| Indeno(1,2,3-cd)pyrene | 1.512 | 85% | 6% | 6% | 15% |
| Benzo(ghi)perylene | 2.050 | 83% | 7% | 7% | 17% |

[1] $t_{97.5}(n-1) = 2.57$

[2] See page 23

*Table 3.3.* Spiked amount of PAH, recovery in %, standard deviation and confidence intervals for 6 and 1 measurements of artificial samples spiked with the individual analyses (0.398-1.550µg).

| Components | µg spiked PAH | Recovery | Standard deviation | Confidence intervals [1] | |
|---|---|---|---|---|---|
| | | | | n=6 measurements | single measurement |
| Fluoranthene | 0.3985 | 85% | 3% | 3% | 7% |
| Pyrene | 0.4172 | 76% | 4% | 4% | 9% |
| Benzo(b+k)fluoranthene | 1.550 | 76% | 4% | 5% | 12% |
| Benzo(e)pyrene | 0.8429 | 76% | 4% | 4% | 10% |
| Benzo(a)pyrene [2] | 0.8512 | 68% | 25% | 26% | 63% |
| Indeno(1,2,3-cd)pyrene | 0.7562 | 69% | 8% | 5% | 21% |
| Benzo(ghi)perylene | 1.025 | 73% | 6% | 6% | 15% |

[1] $t_{97.5}(n-1) = 2.57$

[2] See page 23

*Deuterated standard*

The recoveries calculated from the deuterated internal standards are shown in *Table 3.4*. The confidence intervals were calculated in the same manner as described above. The number of replicates are 110, because the internal standards are added to all samples including the artificial samples and Standard Reference Material.

*Table 3.4.* Spiked amount of deuterated PAH, recovery in %, standard deviation and confidence intervals for 110 and 1 measurements of artificial samples spiked with the deuterated fluoranthene, benzo(a)pyrene and indeno(1,2,3-cd)pyrene (4.75-6.53µg).

| Components | µg spiked PAH | Recovery | Standard deviation | Confidence intervals [1] | |
|---|---|---|---|---|---|
| | | | | n=110 measurements | single measurement |
| Fluoranthene-d10 | 6.53 | 98% | 6% | 1% | 10% |
| Benzo(a)pyrene-d12 [2] | 4.75 | 54% | 28% | 4% | 47% |
| Indeno(1,2,3-cd)pyrene-d12 | 4.75 | 86% | 14% | 2% | 23% |

[1] $t_{97.5}(n-1) = 1.66$

[2] See page 23

*Standard Reference Material*

The results obtained from analyzing the standard reference material SMR 1649, Urban Dust from NIST are shown in *Table 3.5*. The recoveries are given in both µg/g as well as in %. The confidence intervals were calculated as described above.

*Table 3.5.* Recovery, recovery in µg/g and %, standard deviation and confidence intervals for 6 and 1 measurements of the Standard Reference Material, SMR 1649, Urban Dust.

| Components | Values µg/g | Recovery µg/g | Recovery % | Standard deviation | Confidence intervals [1] n=6 measurements | Confidence intervals [1] single measurement |
|---|---|---|---|---|---|---|
| Fluoranthene | 7.10[3] | 4.40 | 62% | 15% | 16% | 40% |
| Pyrene | 7.20 | 3.84 | 53% | 14% | 14% | 35% |
| Benzo(b+k)fluoranthene | 8.20 | 7.49 | 91% | 11% | 11% | 27% |
| Benzo(e)pyrene | 3.30 | 2.66 | 80% | 12% | 13% | 31% |
| Benzo(a)pyrene [2] | 2.90[3] | 1.92 | 66% | 11% | 12% | 29% |
| Indeno(1,2,3-cd)pyrene | 3.3[3] | 2.57 | 78% | 13% | 14% | 33% |
| Benzo(ghi)perylene | 4.5[3] | 3.58 | 79% | 23% | 24% | 58% |

[1] $t_{97.5}(n-1) = 2.57$
[2] See page 23
[3] Certified values

*Benzo(a)pyrene*

Benzo(a)pyrene is very easily fotooxidized. Consequently, in order to minimized the radiation, the samples were analyzed in a laboratory where the windows, the exhaust cabinets and the lamp were covered with coloured glass. The glassware made of brown glass or wrapped in alumina foil. In spite of this, the results for the deuterated benzo(a)pyrene added to the samples before the extraction, showed that the recoveries for benzo(a)pyrene in 40% of the samples were below 50%. Due to this observation it was decided to withdraw the results for the samples from the first year (March 1992-February 1993) and for samples with recovery for benzo(a)pyrene recovery below 10% from the second year. The rest of the results has been corrected proportional to the recovery for each sample.

*Detection limit*

The detection limits in ng/m$^3$ (see *Table 3.6*) were calculated as 3 times the concentration of the individual compound in the blank sample or if no peaks were detected, as 3 times the noise measured at the retention time of the individual compound.

*Table 3.6.* Detection limits for the individual PAH.

| PAH | Detection limit ng/m$^3$ |
|---|---|
| Fluoranthene | 0,032 |
| Pyrene | 0,037 |
| Benzo(b+j+k)fluoranthene | 0,0079 |
| Benzo(e)pyrene | 0,0047 |
| Benzo(a)pyrene | 0,0030 |
| Indeno(1,2,3-cd)pyrene | 0,0074 |
| Benzo(ghi)perylene | 0,0087 |

*Accuracy*

Because the Standard Reference Material was very similar to the samples, it was decided to use the accuracy found by analysis of the Standard Reference Material, as the accuracy for the analytical procedure. The size of the confidence intervals is (as described before) due to the fact that it is only possible to make a single measurement of the real samples because only one sample was collected for each month at each station.

## 3.3 Choice of methods

*Sampling method*

Measurements of trace elements has been a part of the monitoring programme for several years. For economical and man power saving reasons it was decided to use the samples already collected for monitoring of elements. The remaining part of the filters after the element analysis was used for analysis of PAH. Because the procedure for determination of total suspended particulate matter requires the filters to be kept at room temperature for one week to equilibrate before weighing, it was decided to investigate the effect of this sample treatment on the reliability of PAH determination. For that purpose parallel sampling especially for PAH was carried out at the Lille Valby station.

*Analytical method*

The literature describes a variety of different methods for analysis of PAH in environmental samples. The combinations of extraction techniques, solvent or solvent mixture and environmental matrixes are innumerable and no definite method has been recommended. In this study we have chosen Soxhlet extraction using toluene as solvent and a silicagel clean up, because it yielded satisfactory recoveries for the Standard Reference Material Urban Dust, SRM 1649 from NIST (*National Institute of Standards and Technology, 1992*). Due to interfering substances the quantification was carried out by using gaschromatography connected with a mass spectrometer instead of a flame ionisation detector.

# 4 Results

*Summer and winter periods*

In the following a summery is given of the data, i e. the range of levels of every measured PAH at the 7 stations and the PAH profile at every station. The data showed that the concentration of PAH in air (particulate matter) exhibited large differences from place to place and large seasonal fluctuations. On basis of the data the summer period was defined as the months with the obviously lowest concentrations, i.e. May, June, July and August. The winter period was defined as the months with the highest concentrations, i.e. October, November, December, January and February.

*General*

The seasonal fluctuation at all stations were very similar.
December 1993 and January 1994 showed a decline for all compounds and all stations compared to November 1993 and February 1994. Also in January 1993 the concentrations were lower than in December 1992 and February 1993. The levels for all compound were higher in the first period (March 1992 and February 1993) than in the second period.

*Benzo(b+j+k)fluoranthene*

It should be noted that the relatively high concentration of benzo-(b+j+k)fluoranthene in PAH profiles in section 4.2 were due to the occurrence of 2 or 3 individual isomers, which in this study has been measured as a sum.

## 4.1 PAH levels

*Fluoranthene*

The highest concentration levels of fluoranthene were measured in the winter period 1992-93. This level was 25-50% higher than in the winter period 1993-94. The winter concentrations were 6-8 times higher than the summer concentrations The summer concentrations were at the same level for both periods.. The levels for urban areas were 2-8 times higher than for the rural areas, with Odense/9155 as the least polluted urban station. Maximum values were measured at Aalborg/8151 in December 1992 and January 1993. See *Figure 4.1* and *Table 4.1.*

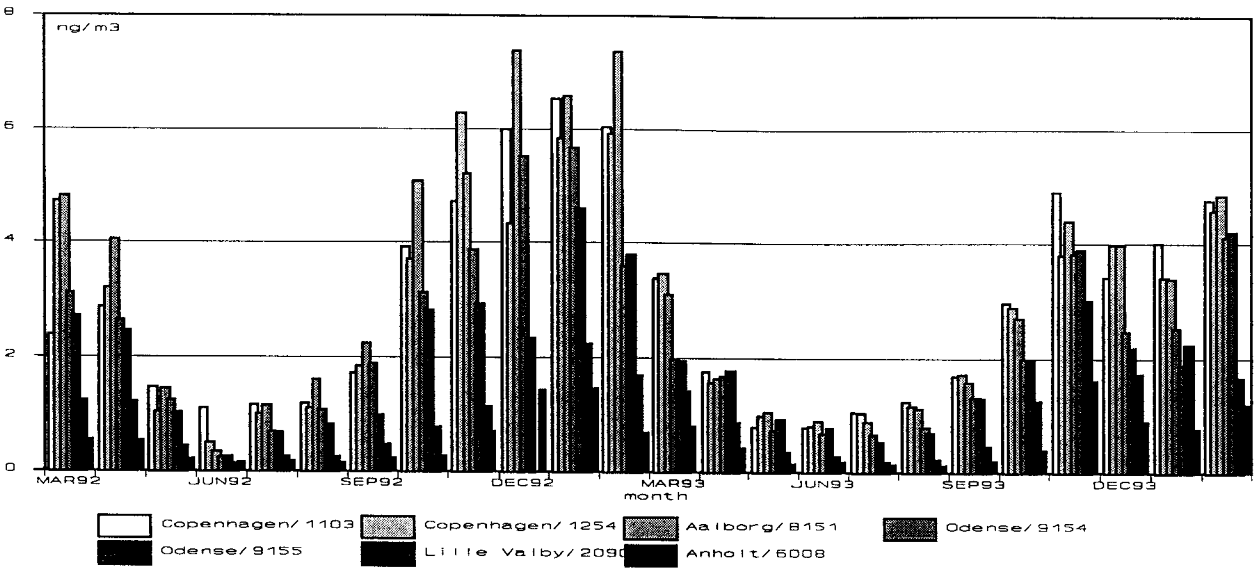

*Figure 4.1.* Monthly average concentration of fluoranthene for each station from March 1992 to February 1994 (ng/m$^3$).

*Table 4.1.* The range of the fluoranthene concentrations in ng/m$^3$ measured in summer and winter periods at different stations.

| Station | Summer (ng/m$^3$) | Winter (ng/m$^3$) |
|---|---|---|
| All stations | 0.1 - 1.6 | 0.3 - 7.4 |
| Copenhagen/1103 | 0.8 - 1.5 | 3.0 - 6.5 |
| Copenhagen/1257 | 0.5 - 1.2 | 2.9 - 6.3 |
| Aalborg/8151 | 0.4 - 1.6 | 2.7 - 7.4 |
| Odense/9154 | 0.3 - 1.1 | 2.0 - 5.7 |
| Odense/9155 | 0.3 - 1.0 | 1.9 - 4.6 |
| Lille Valby/2090 | 0.1 - 0.4 | 0.8 - 3.0 |
| Anholt/6008 | 0.15 - 0.24 | 0.3 - 1.5 |

### *Pyrene*

The highest concentration levels of pyrene were measured in the winter period 1992-93. This level was 25-50% higher than in the winter period 1993-94. The winter levels were 6-8 times higher than the summer levels. The summer concentrations were at the same level for both periods. The levels for urban areas were 2-8 times higher than for the rural areas, with Odense/9155 as the least polluted urban station. Maximum values were measured at Aalborg/8151 in December 1992 and January 1993. See *Figure 4.2* and *Table 4.2.*

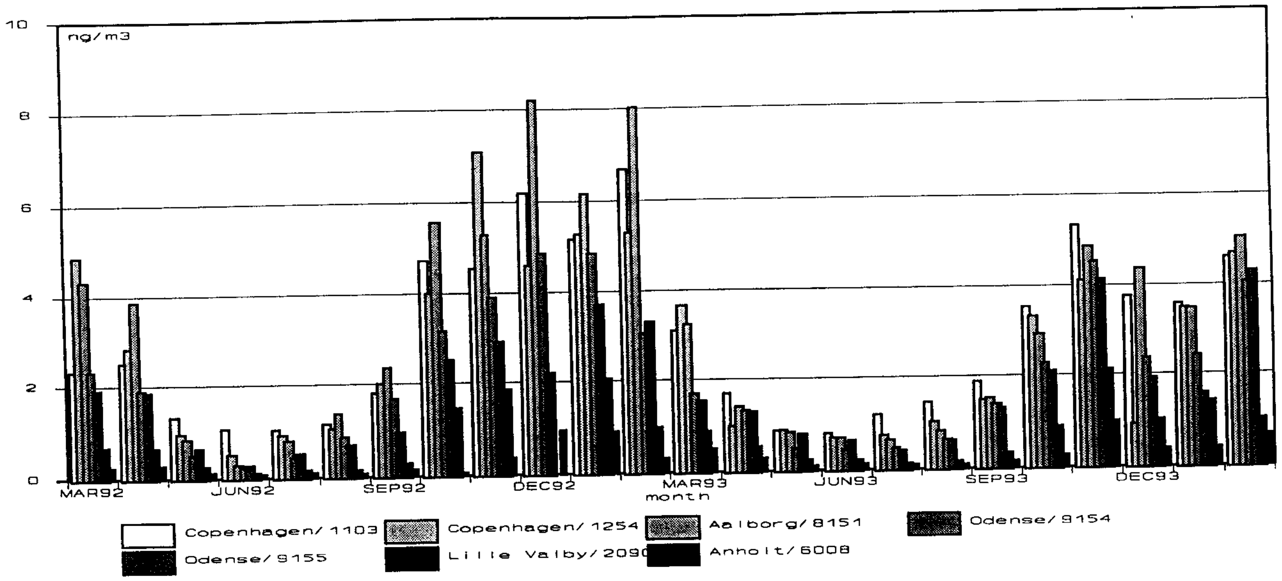

*Figure 4.2.* Monthly average concentration of pyrene for each station from March 1992 to February 1994.

*Table 4.2.* The range of the pyrene concentrations in ng/m$^3$ measured in summer and winter periods at different stations.

| Station | Summer (ng/m$^3$) | Winter (ng/m$^3$) |
|---|---|---|
| All stations | 0.1 - 1.4 | 0.09 - 8.2 |
| Copenhagen/1103 | 0.8 - 1.4 | 3.5 - 6.7 |
| Copenhagen/1257 | 0.5 - 1.0 | 3.3 - 7.1 |
| Aalborg/8151 | 0.3 - 1.4 | 2.9 - 8.2 |
| Odense/9154 | 0.2 - 0.9 | 2.3 - 4.9 |
| Odense/9155 | 0.3 - 0.8 | 1.6 - 4.1 |
| Lille Valby/2090 | 0.1 - 0.3 | 0.9 - 2.1 |
| Anholt/6008 | 0.10 - 0.15 | 0.09 - 1.0 |

*Benzo(b+j+k)fluoranthene*

It should be noted that the results for benzo(b+j+k)fluoranthene are a sum of 3 individual isomers. The highest concentration level of benzo(b+j+k)fluoranthene were measured in the winter period 1992-93. This level was 25-50% higher than in the winter period 1993-94. The winter levels were 3-18 times higher than the summer levels. The summer concentrations were at the same level for both periods. The levels for urban areas were 2-8 times higher than for the rural areas, with Odense/9155 as the least polluted urban station. Maximum values were measured at Copenhagen/1257 in November 1992 and February 1993. See *Figure 4.3* and *Table 4.3.*

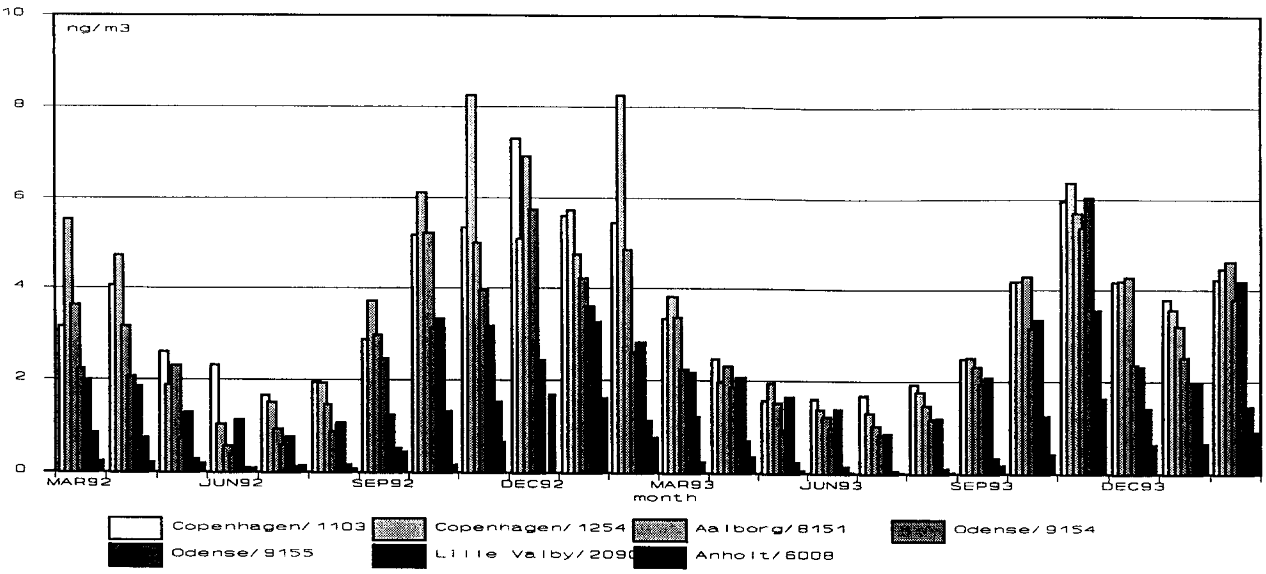

*Figure 4.3.* Monthly average concentration of benzo(b+j+k)fluoranthene for each stations from March 1992 to February 1994.

*Table 4.3.* The range of the benzo(b+j+k)fluoranthene concentrations in ng/m$^3$ measured in summer and winter periods at different stations.

| Station | Summer (ng/m$^3$) | Winter (ng/m$^3$) |
|---|---|---|
| All stations | 0.07 - 2.6 | 0.2 - 7.3 |
| Copenhagen/1103 | 1.6 - 2.6 | 4.2 - 7.3 |
| Copenhagen/1257 | 1.0 - 1.9 | 3.6 - 8.3 |
| Aalborg/8151 | 0.6 - 2.3 | 3.2 - 6.9 |
| Odense/9154 | 0.4 - 1.2 | 2.4 - 5.7 |
| Odense/9155 | 0.8 - 1.7 | 2.0 - 6.0 |
| Lille Valby/2090 | 0.07 - 0.3 | 1.2 - 3.6 |
| Anholt/6008 | 0.10 - 0.21 | 0.2 - 1.7 |

### *Benzo(e)pyrene*

The highest concentration levels of benzo(e)pyrene were measured in the winter period 1992-93. This level was 25-50% higher than in the winter period 1993-94. The winter levels were 3-5 times higher than the summer levels. The summer concentrations were at the same level for both periods. The levels for urban areas were 2-10 times higher than for the rural areas, with Odense/9155 as the least polluted urban station. Maximum values were measured at Copenhagen/1257 in November 1992 and February 1993. See *Figure 4.4* and *Table 4.4*

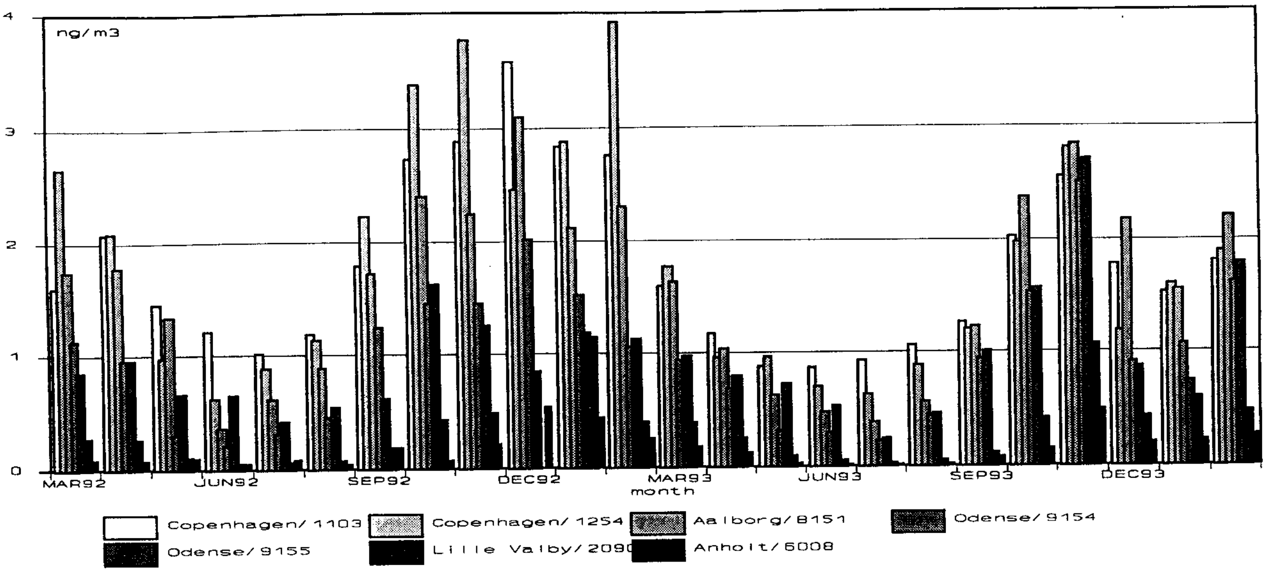

*Figure 4.4.* Monthly average concentration of benzo(e)pyrene for each station from March 1992 to February 1994.

*Table 4.4.* The range of the benzo(e)pyrene concentrations in ng/m$^3$ measured in summer and winter periods at different stations.

| Station | Summer (ng/m$^3$) | Winter (ng/m$^3$) |
|---|---|---|
| All stations | 0.02 - 1.9 | 0.1 - 3.9 |
| Copenhagen/1103 | 0.9 - 1.4 | 1.5 - 3.6 |
| Copenhagen/1257 | 0.6 - 1.9 | 1.2 - 3.9 |
| Aalborg/8151 | 0.4 - 1.3 | 1.5 - 3.1 |
| Odense/9154 | 0.2 - 0.5 | 0.9 - 2.5 |
| Odense/9155 | 0.2 - 0.7 | 0.7 - 2.7 |
| Lille Valby/2090 | 0.02 - 0.2 | 0.1 - 0.5 |
| Anholt/6008 | 0.02. - 0.10 | 0.08 - 0.5 |

### *Benzo(a)pyrene*

As described in 3.2 only 85% of the result from the second year are presented. The winter concentration levels were 5-10 times higher than the summer levels. The levels for urban areas were 4-30 higher than for the rural areas. Maximum values were measured at Copenhagen/1103 and Odense/9155 in november 1993. See *Figure 4.5* and *Table 4.5.*

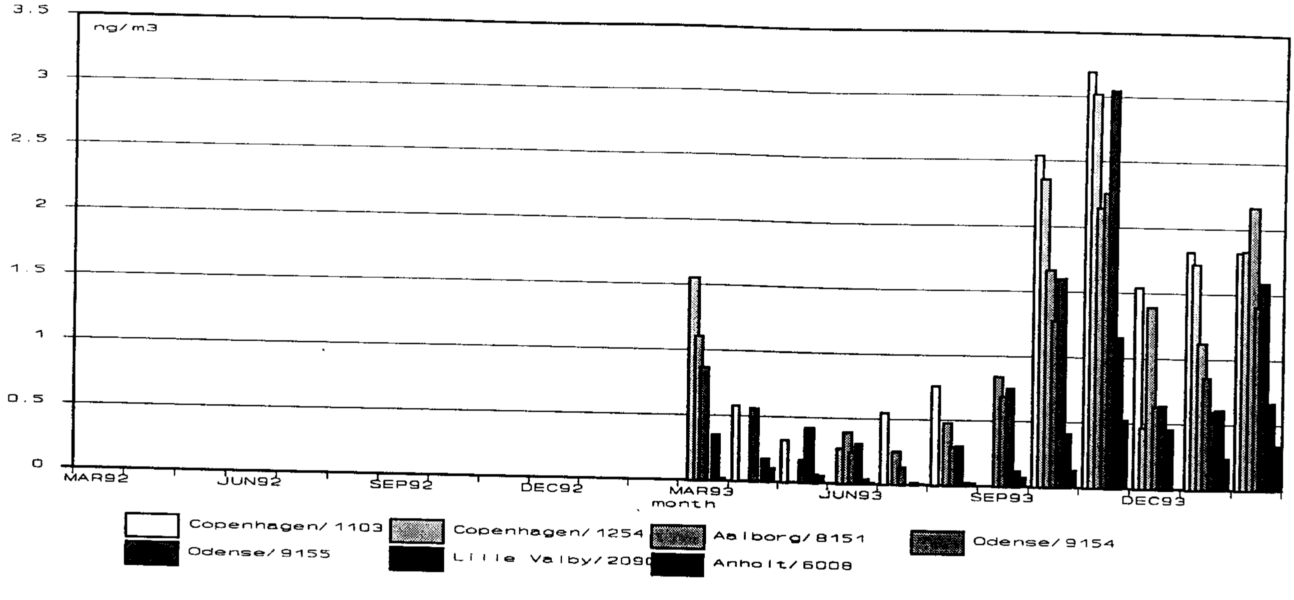

*Figure 4.5* Monthly average concentrations of benzo(a)pyrene for each stations from March 1993 to February 1994.

*Table 4.5* The range of the benzo(a)pyrene concentrations in ng/m$^3$ measured in summer and winter periods at different stations.

| Station | Summer (ng/m$^3$) | Winter (ng/m$^3$) |
|---|---|---|
| All stations | 0.01 - 0.6 | 0.14 - 3.2 |
| Copenhagen/1103 | 0.3 - 0.6 | 1.5 - 3.2 |
| Copenhagen/1257 | 0.3 | 0.5 - 3.0 |
| Aalborg/8151 | 0.3 - 0.5 | 1.1 - 2.2 |
| Odense/9154 | 0.1 - 0.3 | 0.6 - 2.7 |
| Odense/9155 | 0.3 - 0.4 | 0.6 - 3.1 |
| Lille Valby/2090 | 0.01 - 0.06 | 0.4 - 1.2 |
| Anholt/6008 | 0.01 - 0.06 | 0.14 - 0.5 |

*Indeno(1,2,3-cd)pyrene*

The highest concentration levels of indeno(1,2,3-cd)pyrene were measured in the winter period 1992-93. This level was 25-50% higher than in the winter period 1993-94. The winter levels were 3-5 times higher than the summer levels. The summer concentrations were at the same level for both periods. The levels for urban areas were 2-18 times higher than for the rural areas, with Odense/9155 as the least polluted urban station. Maximum values were measured at Aalborg /8151 in December 1992. See *Figure 4.5* and *Table 4.5.*

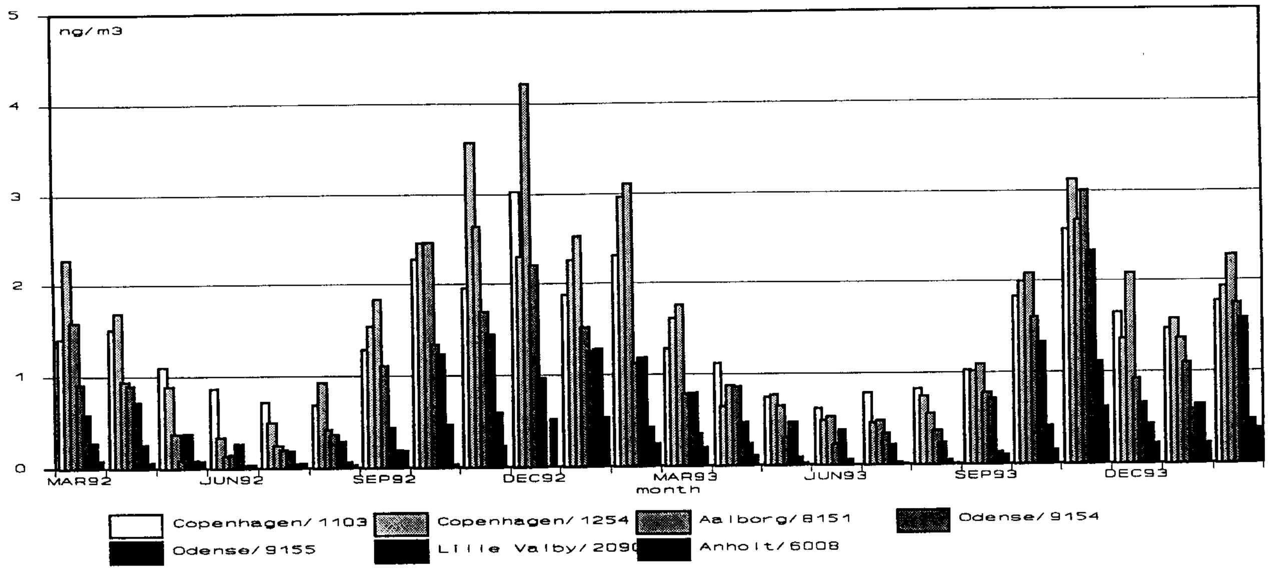

*Figure 4.6.* Monthly average concentration of indeno(1,2,3)pyrene for each station from March 1992 to February 1994.

*Table 4.6.* The range of the indeno(1,2,3-cd)pyrene concentrations in ng/m$^3$ measured in summer and winter periods at different stations.

| Station | Summer (ng/m$^3$) | Winter (ng/m$^3$) |
|---|---|---|
| All stations | 0.01 - 1.1 | 0.04 - 4.4 |
| Copenhagen/1103 | 0.6 - 1.1 | 1.5 - 3.0 |
| Copenhagen/1257 | 0.3 - 0.9 | 1.4 - 3.6 |
| Aalborg/8151 | 0.1 - 07 | 2.1 - 4.2 |
| Odense/9154 | 0.1 - 0.7 | 0.9 - 4.4 |
| Odense/9155 | 0.2 - 0.5 | 0.7 - 2.3 |
| Lille Valby/2090 | 0.03 - 0.1 | 0.4 - 1.2 |
| Anholt/6008 | 0.01 - 0.09 | 0.04 - 0.5 |

### *Benzo(ghi)perylene*

The highest concentration levels of fluoranthene were measured in the winter period 1992-93. This level was 25-50% higher than in the winter period 1993-94. The winter levels were 4-6 times higher than the summer levels. The summer concentrations were at the same level for both periods. The levels for urban areas were 20-44 times higher than for the rural areas, with Odense/9155 as the least polluted urban station. Maximum value was measured at Copenhagen/1257 in November 1992. See *Figure 4.7* and *Table 4.7.*

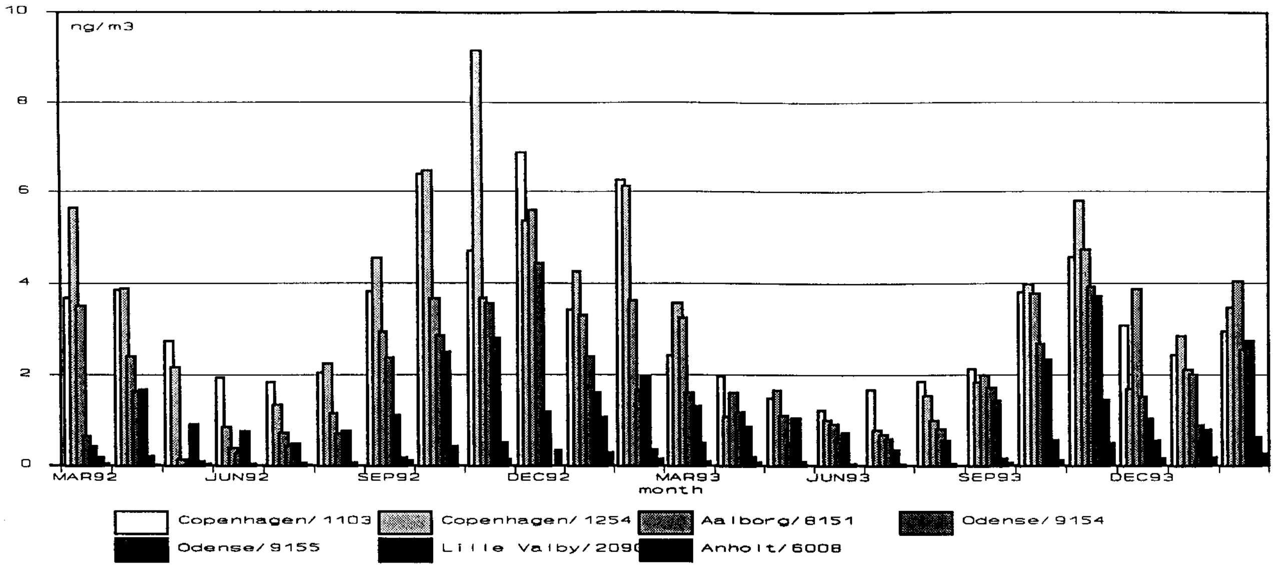

*Figure 4.7.* Monthly average concentration of benzo(ghi)perylene for each station from March 1992 to February 1994.

*Table 4.7.* The range of the benzo(ghi)perylene concentrations in ng/m$^3$ measured in summer and winter periods at different stations.

| Station | Summer (ng/m$^3$) | Winter (ng/m$^3$) |
|---|---|---|
| All stations | 0.01 - 2.8 | 0.03 - 9.2 |
| Copenhagen/1103 | 1.2 - 2.8 | 2.4 - 6.9 |
| Copenhagen/1257 | 0.8 - 2.3 | 1.7 - 9.2 |
| Aalborg/8151 | 0.1 - 1.1 | 2.1 - 5.6 |
| Odense/9154 | 0.01 - 0.8 | 1.5 - 4.4 |
| Odense/9155 | 0.3 - 1.0 | 1.0 - 3.7 |
| Lille Valby/2090 | 0.02 - 0.1 | 0.4 - 1.4 |
| Anholt/6008 | 0.01 - 0.07 | 0.03 - 0.5 |

## 4.2 PAH profiles

*Copenhagen/1103*

The PAH profiles for winter and summer periods were different. The winter profile showed the highest concentrations of fluoranthene, pyrene, benzo(b+j+k)fluoranthene and benzo(ghi)perylene. Benzo(e)pyrene, benzo(a)pyrene and indeno(1,2,3-cd)pyrene were measured to be the half of the concentration of the other PAH. The summer profile showed the highest concentrations for benzo(b+j+k)-fluoranthene and benzo(ghi)perylene, whereas fluoranthene and pyrene were found in the same concentrations as benzo(e)pyrene and indeno(1,2,3-cd)pyrene. Benzo(a)pyrene was measured in the lowest concentration, i.e. only half of the concentration of fluoranthene, pyrene, benzo(e)pyrene and indeno(1,2,3-cd). See *Figure 4.8* and *Table 4.8.*

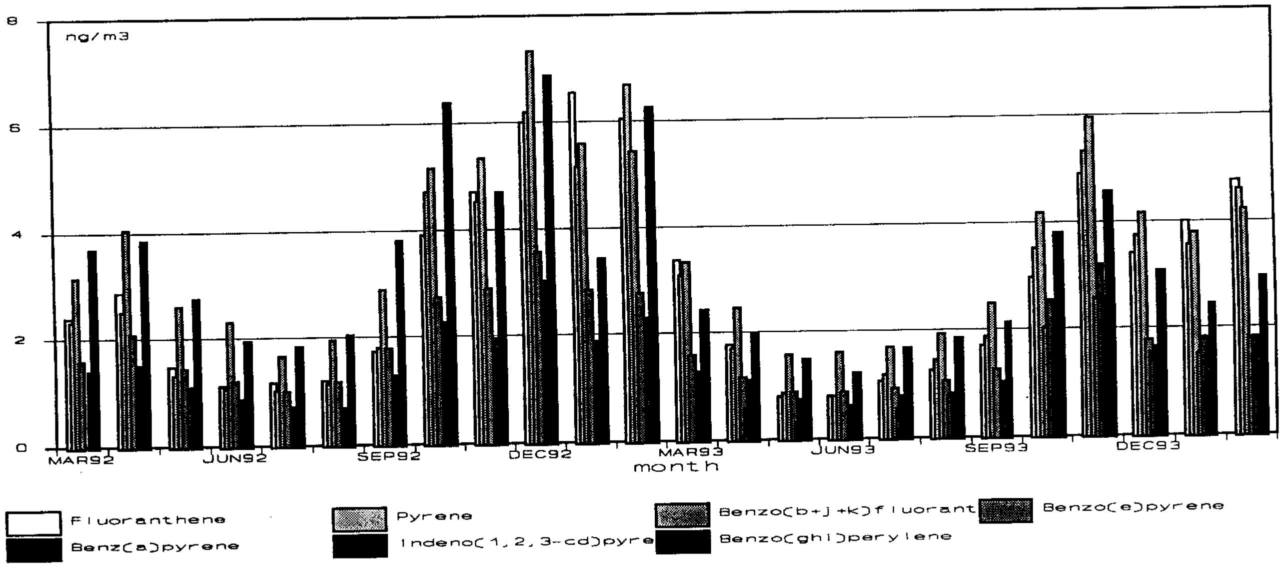

*Figure 4.8.* Monthly average concentrations of PAH at Copenhagen/1103 from March 1992 to February 1994.

*Table 4.8.* The range of the PAH concentrations in ng/m$^3$ measured in summer and winter periods at Copenhagen/1103.

| PAH | Summer (ng/m$^3$) | Winter (ng/m$^3$) |
|---|---|---|
| All PAH measured | 0.6 - 2.8 | 1.5 - 6.9 |
| Fluoranthene | 0.8 - 1.5 | 3.0 - 6.5 |
| Pyrene | 0.8 - 1.4 | 3.5 - 6.7 |
| Benzo(b+j+k)fluoranthene | 1.6 - 2.6 | 4.2 - 7.3 |
| Benzo(e)pyrene | 0.9 - 1.4 | 1.5 - 3.6 |
| Benzo(a)pyrene | 0.3 - 0.6 | 1.5 - 3.2 |
| Indeno(1,2,3-cd)pyrene | 0.6 - 1.1 | 1.5 - 3.0 |
| Benzo(ghi)perylene | 1.2 - 2.8 | 2.4 - 6.9 |

*Copenhagen/1257*

The PAH profiles for winter and summer periods were different. The winter profile showed the highest concentrations of fluoranthene, pyrene, benzo(b+j+k)fluoranthene and benzo(ghi)perylene. Benzo(e)pyrene, benzo(a)pyrene and indeno(1,2,3-cd)pyrene were measured to be the half of the concentration of the other PAH. The summer profile showed the highest concentration for benzo(b+j+k)-fluoranthene and benzo(ghi)perylene, whereas fluoranthene and pyrene were found in the same concentrations as benzo(e)pyrene and indeno(1,2,3-cd)pyrene. The only result for benzo(a)pyrene in summer period was lower than the rest of the concentrations. See *Figure 4.9* and *Table 4.9.*

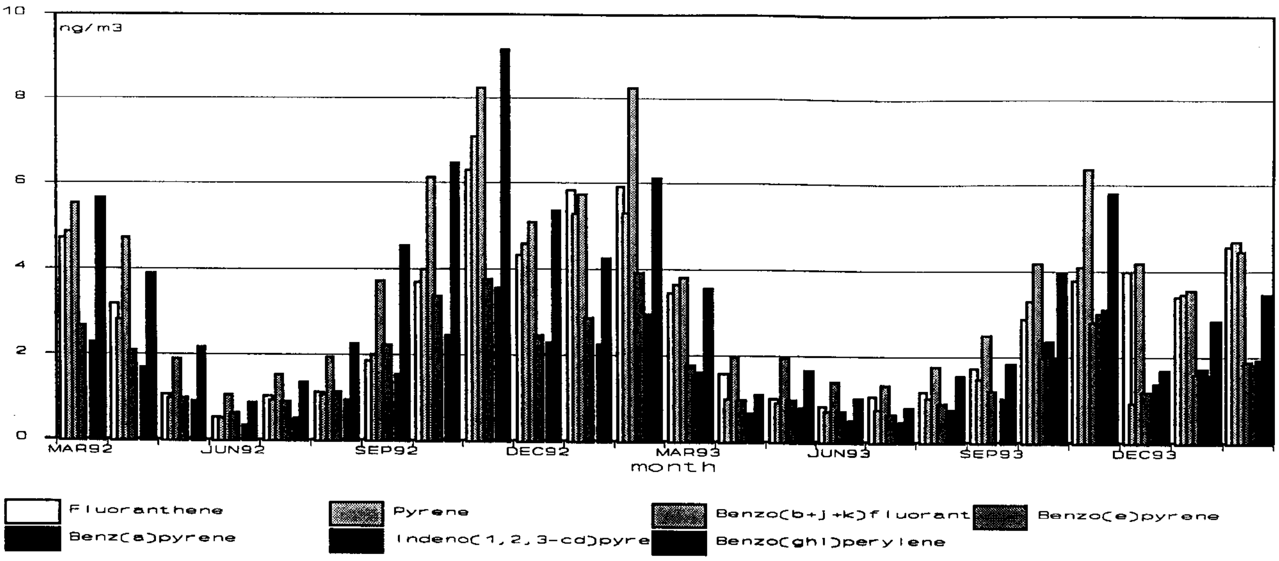

*Figure 4.9.* Monthly average concentrations of PAH at Copenhagen/1257 from March 1992 to February 1994.

*Table 4.9.* The range of the PAH concentrations in ng/m$^3$ measured in summer and winter periods at Copenhagen/1257.

| PAH | Summer (ng/m$^3$) | Winter (ng/m$^3$) |
|---|---|---|
| All PAH measured | 0.3 - 2.3 | 1.2 - 9.2 |
| Fluoranthene | 0.5 - 1.2 | 2.9 - 6.3 |
| Pyrene | 0.5 - 1.0 | 3.3 - 7.1 |
| Benzo(b+j+k)fluoranthene | 1.0 - 1.9 | 3.6 - 8.3 |
| Benzo(e)pyrene | 0.6 - 1.9 | 1.2 - 3.9 |
| Indeno(1,2,3-cd)pyrene | 0.3 - 0.9 | 1.4 - 3.6 |
| Benzo(ghi)perylene | 0.8 - 2.3 | 1.7 - 9.2 |
| Benzo(a)pyrene | 0.3 | 0.5 - 3.0 |

*Aalborg/8151*

The PAH profiles for winter and summer periods were different. The winter profile showed the highest concentrations of fluoranthene, pyrene and benzo(b+j+k)fluoranthene. Benzo(ghi)perylene were measured to be 75% and benzo(e)pyrene, benzo(a)pyrene and indeno(1,2,3-cd)pyrene to be 50% of the concentration of fluoranthene, pyrene and benzo(b+j+k) fluoranthene. The summer profile showed the highest concentration for fluoranthene, pyrene and benzo(b+j+k)fluoranthene and benzo(ghi)perylene, whereas benzo(e)pyrene, benzo(a)pyrene and indeno(1,2,3-cd)pyrene were found in half the concentrations of the other.
See *Figure 4.10* and *Table 4.10.*

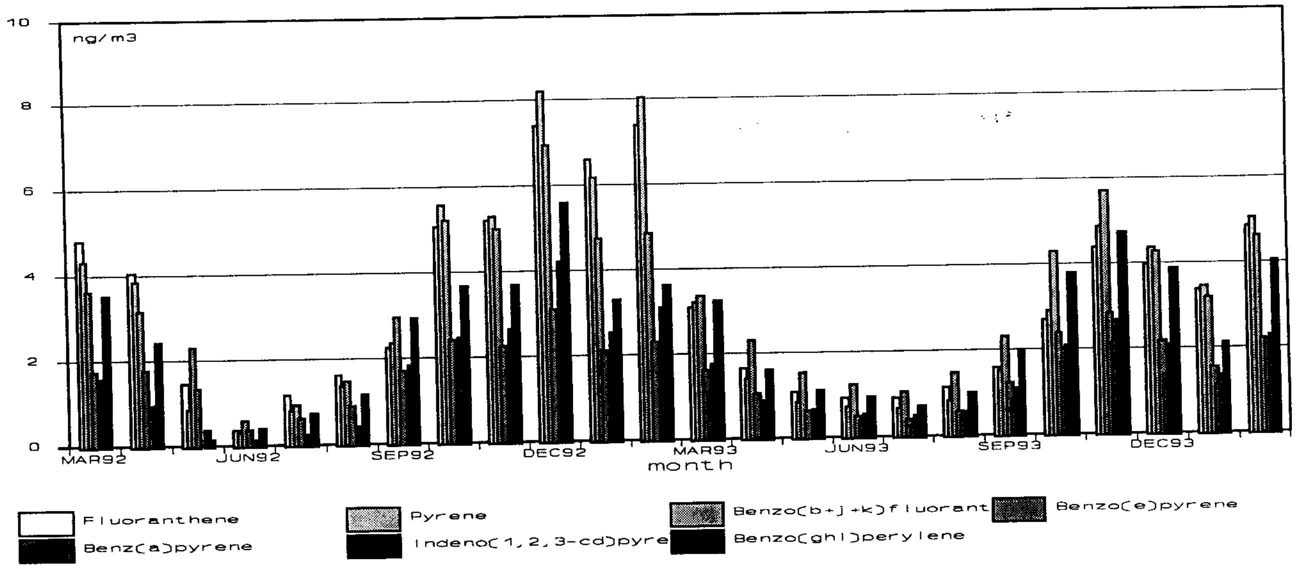

*Figure 4.10.* Monthly average concentrations of PAH at Aalborg/8151 from March 1992 to February 1994.

*Table 4.10.* The range of the PAH concentrations in ng/m$^3$ measured in summer and winter periods at Aalborg/8151.

| PAH | Summer (ng/m$^3$) | Winter (ng/m$^3$) |
|---|---|---|
| /All PAH measured | 0.1 - 1.6 | 1.5 - 7.4 |
| Fluoranthene | 0.4 - 1.6 | 2.7 - 7.4 |
| Pyrene | 0.3 - 1.4 | 2.9 - 8.2 |
| Benzo(b+j+k)fluoranthene | 0.6 - 2.3 | 3.2 - 6.9 |
| Benzo(e)pyrene | 0.4 - 1.3 | 1.5 - 3.1 |
| Benzo(a)pyrene | 0.3 - 0.5 | 0.5 - 3.0 |
| Indeno(1,2,3-cd)pyrene | 0.1 - 0.7 | 2.1 - 4.2 |
| Benzo(ghi)perylene | 0.1 - 1.1 | 2.1 - 5.6 |

*Odense/9154*

The PAH profiles for winter and summer periods were the same. The profiles showed the highest concentrations of fluoranthene, pyrene and benzo(b+j+k)fluoranthene. Benzo(ghi)perylene were measured to be 75% and benzo(e)pyrene and indeno(1,2,3-cd)pyrene were measured to be 50% and benzo(a)pyrene 40% of the concentration of fluoranthene, pyrene and benzo(b+j+k)fluoranthene. See *Figure 4.11* and *Table 4.11.*

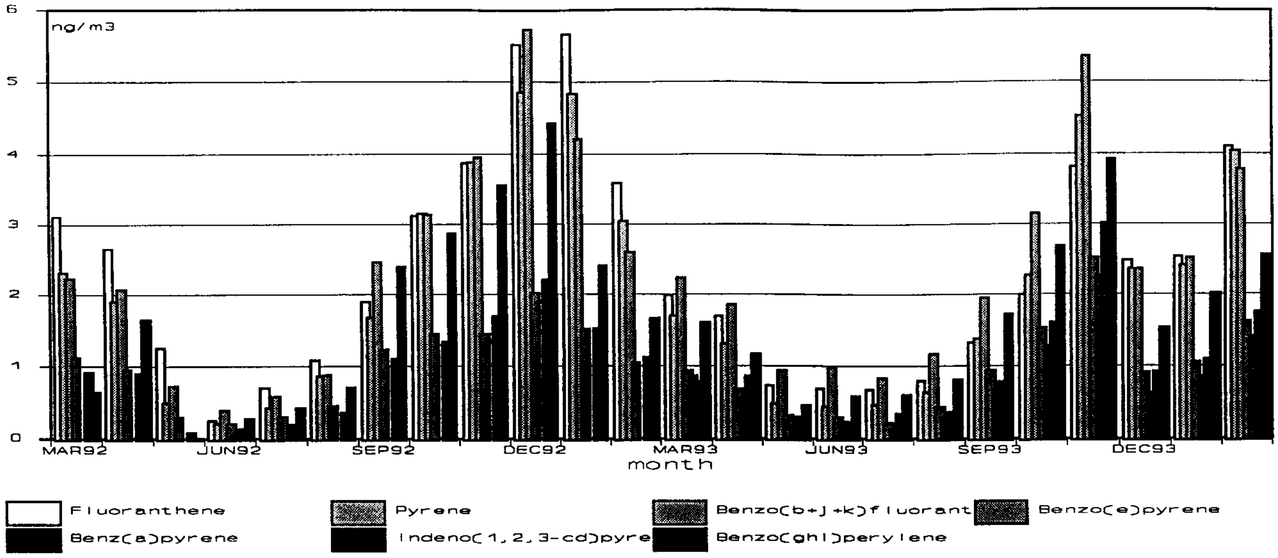

*Figure 4.11.* Monthly average concentrations of PAH at Odense/9154 from March 1992 to February 1994.

*Table 4.11.* The range of the PAH concentrations in ng/m$^3$ measured in summer and winter periods at Odense/9154.

| PAH | Summer (ng/m$^3$) | Winter (ng/m$^3$) |
|---|---|---|
| All PAH measured | 0.01 - 1.3 | 0.9 - 5.7 |
| Fluoranthene | 0.3 - 1.1 | 2.0 - 5.7 |
| Pyrene | 0.2 - 0.9 | 2.3 - 4.9 |
| Benzo(b+j+k)fluoranthene | 0.4 - 1.2 | 2.4 - 5.7 |
| Benzo(e)pyrene | 0.2 - 0.5 | 0.9 - 2.5 |
| Benzo(a)pyrene | 0.1 - 0.3 | 0.6 - 2.7 |
| Indeno(1,2,3-cd)pyrene | 0.08 - 0.7 | 0.9 - 4.4 |
| Benzo(ghi)perylene | 0.01 - 0.8 | 1.5 - 4.4 |

*Odense/9155*

The PAH profiles for winter and summer periods were the same. The profiles showed the highest concentrations of fluoranthene, pyrene and benzo(b+j+k)fluoranthene. Benzo(ghi)perylene were measured to be 75% and benzo(e)pyrene, benzo(a)pyrene and indeno(1,2,3-cd)pyrene were measured to be 50% of the concentration of fluoranthene, pyrene and benzo(b+j+k)fluoranthene. See *Figure 4.12* and *Table 4.12.*

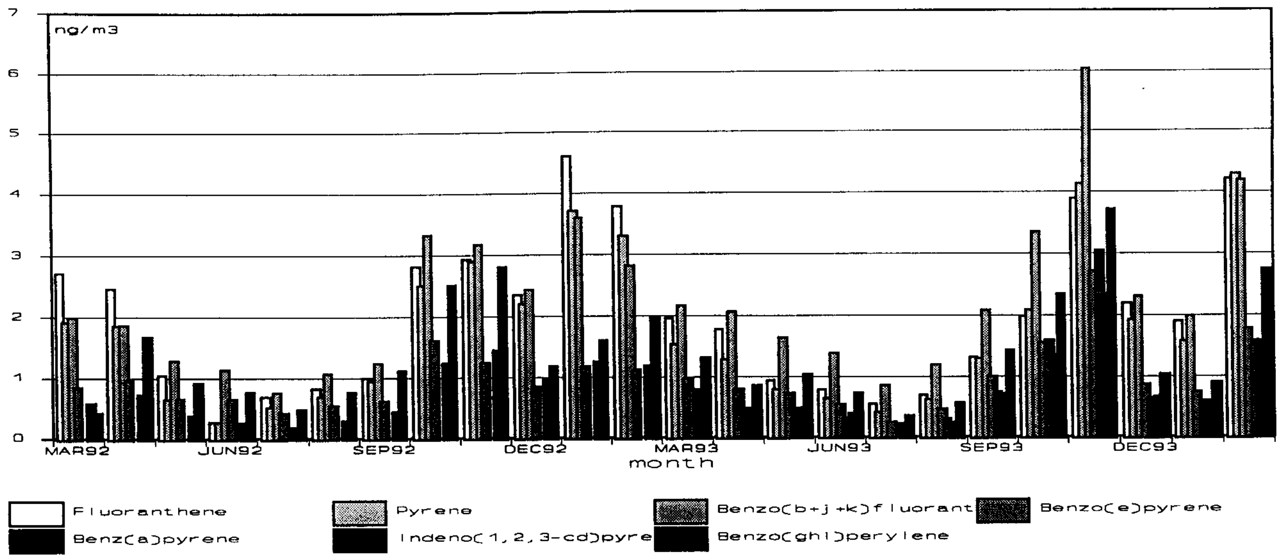

*Figure 4.12.* Monthly average concentrations of PAH at Odense/9155 from March 1992 to February 1994.

*Table 4.12.* The range of the PAH concentrations in ng/m$^3$ measured in summer and winter periods at Odense/9155.

| PAH | Summer (ng/m$^3$) | Winter (ng/m$^3$) |
|---|---|---|
| All PAH measured | 0.2 - 1.0 | 0.6 - 4.6 |
| Fluoranthene | 0.3 - 1.0 | 1.9 - 4.6 |
| Pyrene | 0.3 - 0.8 | 1.6 - 4.1 |
| Benzo(b+j+k)fluoranthene | 0.8 - 1.7 | 2.0 - 6.0 |
| Benzo(e)pyrene | 0.2 - 0.7 | 0.7 - 2.7 |
| Benzo(a)pyrene | 0.3 - 0.4 | 0.6 - 3.1 |
| Indeno(1,2,3-cd)pyrene | 0.2 - 0.5 | 0.7 - 2.3 |
| Benzo(ghi)perylene | 0.3 - 1.0 | 1.0 - 3.7 |

*Lille Valby/2090*

The PAH profiles for winter and summer periods were the same. The profile showed the highest concentrations of fluoranthene, pyrene and benzo-(b+j+k)fluoranthene. Benzo(ghi)perylene, benzo(e)pyrene, benzo(a)pyrene and indeno(1,2,3-cd)pyrene were measured to be the half of the concentration of the other PAH. See *Figure 4.13* and *Table 4.13.*

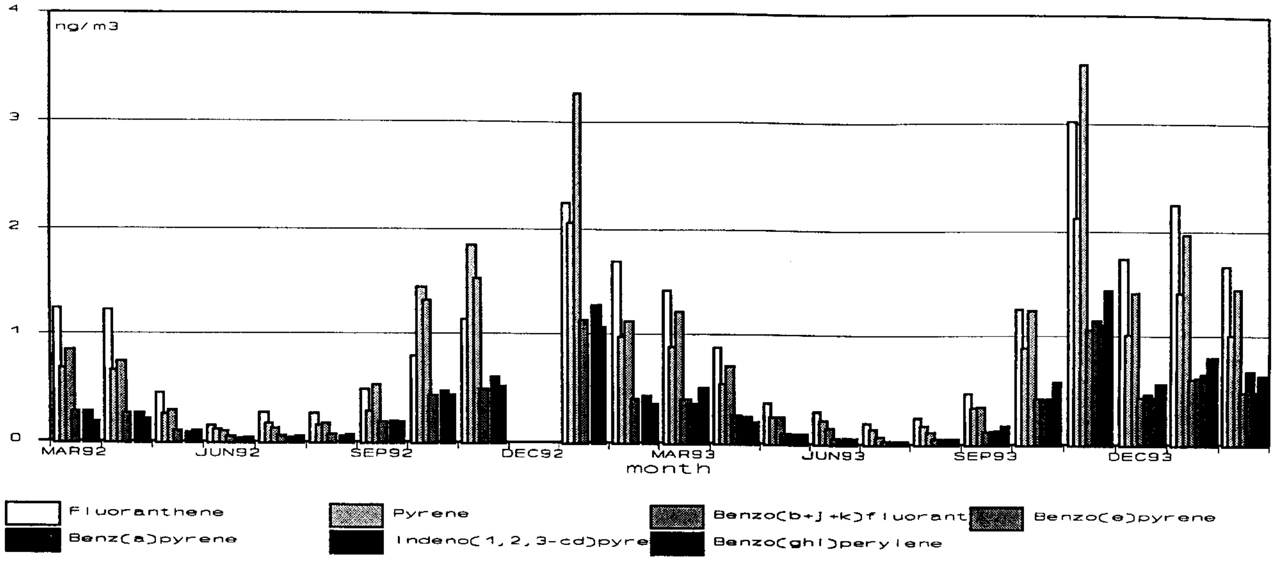

*Figure 4.13.* Monthly average concentrations of PAH at Lille Valby/2090 from March 1992 to February 1994.

*Table 4.13.* The range of the PAH concentrations in ng/m$^3$ measured in summer and winter periods at Lille Valby/2090.

| PAH | Summer (ng/m$^3$) | Winter (ng/m$^3$) |
|---|---|---|
| All PAH measured | 0.01 - 0.4 | 0.3 - 3.6 |
| Fluoranthene | 0.1 - 0.4 | 0.8 - 3.0 |
| Pyrene | 0.1 - 0.3 | 0.9 - 2.1 |
| Benzo(b+j+k)fluoranthene | 0.03 - 0.3 | 1.1 - 3.6 |
| Benzo(e)pyrene | 0.03 - 0.1 | 0.1 - 0.5 |
| Benzo(a)pyrene | 0.02 - 0.06 | 0.4 - 1.2 |
| Indeno(1,2,3-cd)pyrene | 0.03 - 0.09 | 0.4 - 1.3 |
| Benzo(ghi)perylene | 0.02 - 0.1 | 0.4 - 1.5 |

*Anholt/6008*

The PAH profiles for winter and summer periods were different. The winter profile showed the highest concentrations of fluoranthene and benzo(b+j+k)fluoranthene. Pyrene was measured to be 75% and benzo(e)pyrene, benzo(a)pyrene and indeno(1,2,3-cd)pyrene to be 40% of the concentrations of fluoranthene and benzo(b+j+k)fluoranthene. The summer profiles showed the highest concentrations for fluoranthene, whereas pyrene and benzo(b+j+k)fluoranthene were measured to be 75% and benzo(e)pyrene, benzo(a)pyrene, indeno(1,2,3-cd)pyrene and benzo(ghi)perylene to be 40% of the concentrations of fluoranthene. See *Figure 4.14* and *Table 4.14*.

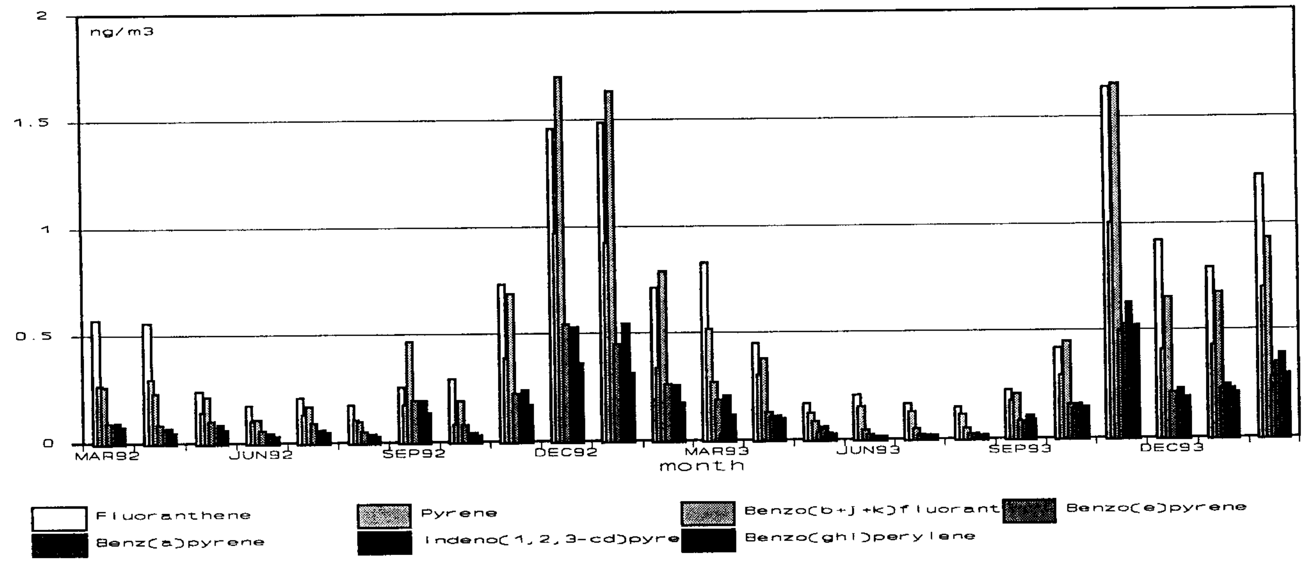

*Figure 4.14.* Monthly average concentrations of PAH at Anholt/6008 from March 1992 to February 1994.

*Table 4.14.* The range of the PAH concentrations in ng/m$^3$ measured in summer and winter periods at Anholt/6008.

| PAH | Summer (ng/m$^3$) | Winter (ng/m$^3$) |
|---|---|---|
| All PAH measured | 0.01 - 0.24 | 0.03 - 1.5 |
| Fluoranthene | 0.15 - 0.24 | 0.3 - 1.5 |
| Pyrene | 0.10 - 0.15 | 0.09 - 1.0 |
| Benzo(b+j+k)fluoranthene | 0.04 - 0.21 | 0.2 - 1.7 |
| Benzo(e)pyrene | 0.02 - 0.10 | 0.08 - 0.5 |
| Benzo(a)pyrene | 0.01 - 0.06 | 0.1 - 0.5 |
| Indeno(1,2,3-cd)pyrene | 0.01 - 0.09 | 0.04 - 0.5 |
| Benzo(ghi)perylene | 0.01 - 0.07 | 0.03 - 0.5 |

# 5 Discussion

## 5.1 Method evaluation

*Parallel sampling*

As mentioned in chapter 3 it was not possible to optimize the procedure for sampling and handling the samples for the PAH determination. It was necessary to use daily samples, which were sampled for other purposes, i.e. especially designed for the TSP and PIXE analysis (see 3.1). A parallel sampling was carried out at Lille Valby for examination of any losses of PAH due to treatment of the filters. The results from the comparisons showed some differences in the concentration of PAH between the two stations, but the differences were not significant at 95%-level (*Table 5.1*). Taking the uncertainty of the analytical procedure into account (see 3.2) it was not possible to see any differences in the data from the parallel stations, which means that the special treatment in relation to the TSP and PIXE analysis did not influence the results significantly.

*Accuracy*

The total uncertainty on the measured concentrations of the PAH was a result of a number of parameters, e.g. sampling efficiencies, stability (degassing and chemical reaction) of PAH on the filter, losses during storage and handling, losses in the extraction procedure, variation in sampling volume and accuracy in the analytical procedure. The variation of the sample volume was less then ± 5% and therefore negligible. It was beyond the scope of this study to investigate problems like sampling efficiency and degassing during sampling time. As described in 3.2 a substantial work has been made to determine the accuracy of the PAH analysis.

*Table 5.1.* Correlation coefficients, slopes and intercepts from the correlation analysis between PAH concentrations from the simultaneous sampling at Lille Valby/2090 and Lille Valby/2098.

| | Correlation coefficient | Slope | Intercept |
|---|---|---|---|
| Fluoranthene | 0,8378 | 1,065 | -0,027 |
| Pyrene | 0,7291 | 0,799 | -0,013 |
| Benzo(b+j+k)fluoranthene | 0,7291 | 0,799 | -0,013 |
| Benzo(a)pyrene | 0,7982 | 0,822 | 0,022 |
| Indeno(1,2,3-cd)pyrene | 0,5644 | 0,897 | -0,018 |
| Benzo(ghi)perylene | 0,7924 | 0,801 | -0,019 |

## 5.2 PAH-levels compared with other studies

PAH levels measured in different studies can not always be directly compared, however in table 5.2 several different studies are summarised. *Table 5.2* shows the results of investigations where the sampling technique (filters, particulate matter) and the degree of urbanisation were comparable to this study.

*Table 5.2.* PAH-results (average values) from different studies in ng/m$^3$.

| PAH | Germany, Duisburg 1) | Germany 2) | Germany, Berlin 3) | Germany, Berlin 4) | Austria, Vienna 5) | Yugoslavia, Zagreb 6) | Sweden, Stockholm 7) | U.K., 4 cities 8) | Denmark, Copenhagen 9) | Denmark, 3 cities 10) |
|---|---|---|---|---|---|---|---|---|---|---|
| Fluoranthene | 40 | | 30 | 7.4-14 | 52-94* | 34 | 1.3-5.9* | | 2.9-30* | 0.3-7.4* |
| Pyrene | 28 | | 33 | 9.4-15* | 55-95* | | 1.3-7.7* | 5.0-15* | 2.7-33* | 0.2-8.2* |
| Benzo(b+k)-fluoranthene | 34 | 25-55* | 17 | 1.3-2.9* | 10-30* | 22 | 3.3-5.0* | 0.5-2.2* | 8.9-34* | 0.4-8.3* |
| Benzo(e)-pyrene | 13 | 10-25* | | 1.1-4.5* | 4.6-13* | | 2.6-4.2* | | 3.4-9* | 0.2-3.9* |
| Indeno(1,2,3-cd)pyrene | 7.3 | 5-15* | 7.5 | 0.8-0.6* | 4.5-13* | 11 | 1.8-3.4* | | 4.3-14* | 0.1-4.4* |
| Benzo(ghi)-perylene | 8.3 | 10-15* | 9.3 | 1.8-1.9* | 8.5-20* | | 4.7-7.7* | 0.6-2.3* | 9.3-21* | 0.01-9.2* |
| Number of samples | | ca. 30+30 | >500 | 28+26* | ca. 50 | 89 | 27+27 | 99 | 7 | 96 |
| Site | town centre | 2 residential areas heated by oil and by coal* | 21 sites | Prevailing emissions from vehicles and from domestic heating by coal* | Near centre, at the intersection of 2 busy roads *different season | Various sites. Industrial town | 5 summer and 3 winter sites in ordinary streets. Prevailing domestic heating by oil | Centre of urban areas *Winter data | Centre of urban areas *Winter data | Centre of urban area *winter data |
| Period | Dec.1977-Mar.1978 | Oct.1978-Apr.1979 | Jan. 1982-Jan. 1983 | Oct.1983-Jan.1984 | Aug.1983-Aug.1984 | Winters 1977-1983 | 1980-1983 | Jan.-Dec.-1991 | 1986-1987 | Mar.1992-Feb.1993 |

| | |
|---|---|
| 1-7) | *Menichini, 1992* |
| 8) | *Halsall et al., 1993* |
| 9) | *Nielsen, 1989* |
| 10) | This investigation |

*Differences between investigations*

Although the sample technique and the degree of urbanisation should be comparable, the results display significant variations. Comparison of the measurements should be carried out with great prudence, due to the fact that they were performed according to different procedures and conditions for sample collection, and different analytical methods were used. *Menichini* (1992) has reviewed the factors affecting the results: Meteorological conditions (wind velocity, thermal inversions, scavenging effect by snow and rain, ambient temperature), the time of day (total PAH daytime concentrations were found to be reduced to the half of the night values in Oslo), number of sampling sites, the characteristics of the sampling site (height of surrounding buildings, height of sampling site, ventilation), the sampling parameters (length of each sampling period).

*Comparison of PAH at urban areas*

The PAH concentration levels measured at urban areas in this study were compared to the results in other studies. The concentrations were at the same levels as the Swedish and partly the English studies (see *Table 5.2)*, but they were considerable lower than in the other studies. Most of the studies were made between 1977 and 1987. Only the English study and this study were made during the nineties. The development in different combustion techniques (e.g. in power plant, industry, cars, house heating etc.) have been improved concerning the emission of pollutants and at the same time the authorities issued lower limit values for emission of many pollutants. This might be one of the reasons to the decrease of the PAH concentrations the eighties to the nineties.

*Comparison of PAH at rural areas*

Only a few data from rural areas were available, however the rural data from this study could be compared with two other studies. The results from Anholt/6008 were compared with the Swedish study from the rural area Rörvik, situated only 100 km from Anholt/6008 (*Lundén, 1990*) (See *Table 5.3*). The Swedish study were made during February and May 1990. These result were compared only with the results from February and May in this study. Although the samples from the two studies were collected with 3 years interval, the concentrations were very similar with a somewhat higher values at Rörvik for most of the PAH. This could be expected because Anholt/6008 are situated more distant to the source than Rörvik. The results from Lille Valby were compared to an other Danish study, where samples were collected at Risø *(Nielsen et al., 1984)*, 1.5 km from Lille Valby/2090. The Risø samples were collected from mid February to mid May in 1982. These result were compared to the February, March and April PAH concentrations from this study. In spite of the samples being collected with an interval of 12 years, there are no obvious differences between the concentration levels found at the two studies.

*Table 5.3.* Results in ng/m$^3$ a from 1 Swedish (the west coast of Sweden) and 1 Danish rural station (the island Anholt), situated 100 km from each other, separated by the sea (Kattegat).

| PAH | Rörvik, Sweden (*Lundén*, 1990) | | Anholt/6008, Denmark (this studie) | |
|---|---|---|---|---|
| Fluoranthene | 0.81 - 1.6 | 0.21 - 0.42 | 0.71 - 1.22 | 0.17 - 0.24 |
| Pyrene | 0.64 - 1.9 | 0.25 - 0.37 | 0.34 - 0.69 | 0.13 - 0.14 |
| Benzo(b+k)fluoranthene | 0.28 - 0.79 | 0.06 - 0.11 | 0.79 - 0.93 | 0.09 - 0.22 |
| Benzo(e)pyrene | | | 0.26 - 0.28 | 0.01 - 0.10 |
| Benzo(a)pyrene | 0.05 - 0.21 | 0 .02 - 0.03 | 0.35 | 0.06 |
| Indeno(1,2,3-cd)pyrene | 0.13 - 0.43 | 0.03 - 0.10 | 0.26 - 0.39 | 0.03 - 0.09 |
| Benzo(ghi)perylene | 0.25 - 0.61 | 0.04 - 0.06 | 0.18 - 0.29 | 0.03 - 0.03 |
| Number of samples | 2 | 2 | 2 | 2 |
| Period | Feb. 1990 | May 1990 | Feb. 1993 and 1994 | May 1992 and 1993 |

*Table 5.4.* Results in ng/m$^3$ from Risø and Lille Valby. Risø and Lille Valby are situated 1.5 kilometre from each other.

| PAH | Risø, Denmark *(Nielsen et al., 1984)* | Lille Valby, Denmark (this study) |
|---|---|---|
| Fluoranthene | 1.2 ± 0.6 | 0.9 - 1.7 |
| Pyrene | 1.3 ± 0.8 | 0.5 - 1.0 |
| Benzo(b+j+k)fluoranthene | 1.3 ± 0.5 | 0.7 - 1.5 |
| Benzo(e)pyrene | 0.6 ± 0.2 | 0.3 - 0.5 |
| Benzo(a)pyrene | 0.6 ± 0.2 | 0.2 - 0.7 |
| Indeno(1,2,3-cd)pyrene | 0.7 ± 0.2 | 0.2 - 0.5 |
| Benzo(ghi)perylene | 0.6 ± 0.2 | 0.2 - 0.6 |
| number of samples | 30 | 6 |
| period | Mid February to mid April 1982 | March and April in 1992, February, March and April 1993 and February 1994 |

## 5.3 PAH levels at urban and rural locations and seasonal variations

*Urban and rural locations*

The PAH levels measured in urban areas were significantly higher than in rural areas, because the latter are not directly exposed to anthropogenic sources of PAH. The physical removal and transport of airborne particles is a function of the particle size and the meteorological conditions (*Baek et al., 1991a*). Atmospheric particulate matter tends to have a bimodal mass distribution. Most of the PAH exhibited uni-modal distributions, with the particle size exclusively localised between 0,4 to 1,1 µm (*Baek et al., 1991b*). Particles of this size will not be removed efficiently by rain or dry deposition and may be transported over long distances. The concentrations in the rural areas are mainly due to long range transport within Denmark or from our neighbouring countries.

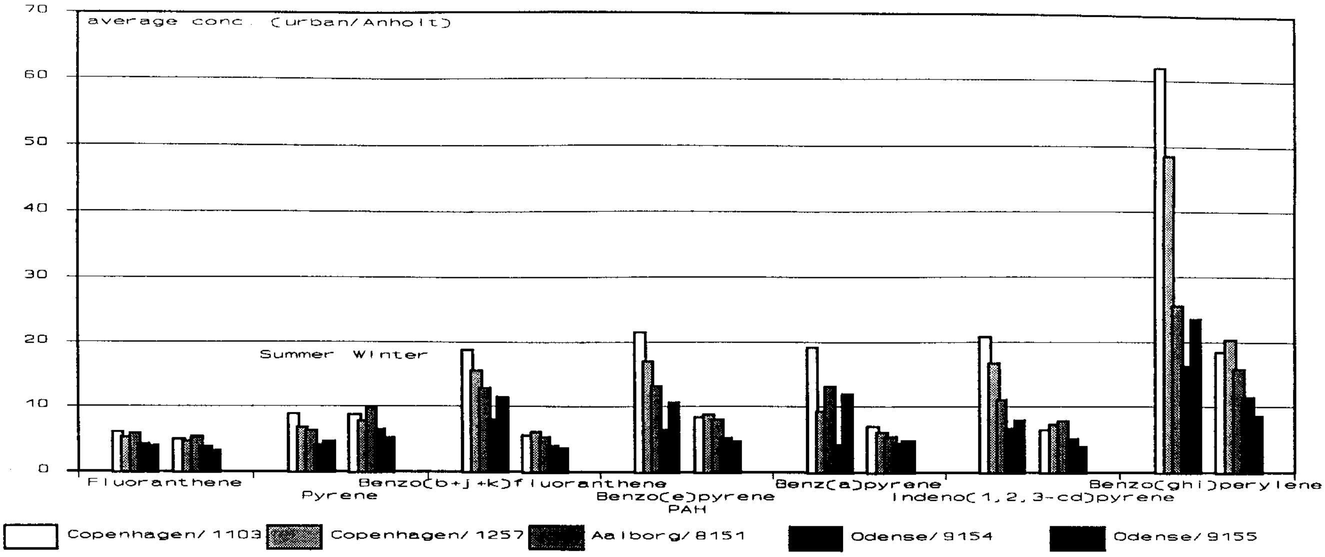

*Figure 5.1.* Ratio between the concentration of PAH in the urban areas and in the rural area Anholt/6008 - both summer and winter data.

*Ratios, urban/rural*

As seen in the *Figure 5.1* and the *Table 5.5* fluoranthene showed the lowest and most constant ratio between the 5 urban sample sites and the rural area sample site, whereas pyrene, benzo(b+j+k)fluoranthene, benzo(e)pyrene, benzo(a)pyrene and indeno(1,2,3-cd)pyrene showed more or less the same ratio and pattern between the cities, with Copenhagen/1103, Copenhagen/1257 and Aalborg/8151 as the highest. Benzo(ghi)perylene showed a much higher ratio i.e. 9-20 calculated on basis of the winter samples and 16-63 in summer periods. These high ratios are a result of the very low concentration at Anholt/6008 both summer and winter, while the benzo(ghi)perylene concentration especially at Copenhagen/1103 and Copenhagen/1257 were high. These high benzo(ghi)perylene concentrations will be discussed further in chapter 5.4 and 5.6.

*Table 5.5.* The range of the ratios between average concentrations in the urban areas and in the rural area Anholt/6008.

| PAH | All data | Summer data | Winter data |
|---|---|---|---|
| Fluoranthene | 3-5 | 4-6 | 3-5 |
| Pyrene | 5-9 | 4-8 | 5-10 |
| Benzo(b+j+k)fluoranthene | 4-8 | 8-18 | 3-6 |
| Benzo(e)pyrene | 6-10 | 7-22 | 5-8 |
| Indeno(1,2,3-cd)pyrene | 4-8 | 7-21 | 4-8 |
| Benzo(ghi)perylene | 9-25 | 16-63 | 9-20 |

*Ratios, other countries*

Few results are reported from the analysis of samples collected simultaneously in rural areas and at urban sites. Data reviewed by *Menichini* (1992) show that the ratios in The Netherlands are 2-3, in USA 3-10 and in Australia 5, but because the individual PAH were not specified, it is not possible to conclude, whether any significant differences can be observed between these studies.

*Seasonal variations*

The results from all the stations showed a seasonal variation having the highest concentrations during the winter time. Various factors, possibly concomitant, are indicated to explain this: domestic heating, which is commonly considered to be the most important; winter meteorological conditions, particularly temperature inversion, which slow down the dispersion of air pollutants; temporary closure of factories in summer; possibly, chemical PAH reactivity (photochemistry and, presumably, thermal chemistry), (*Menichini, 1992*).

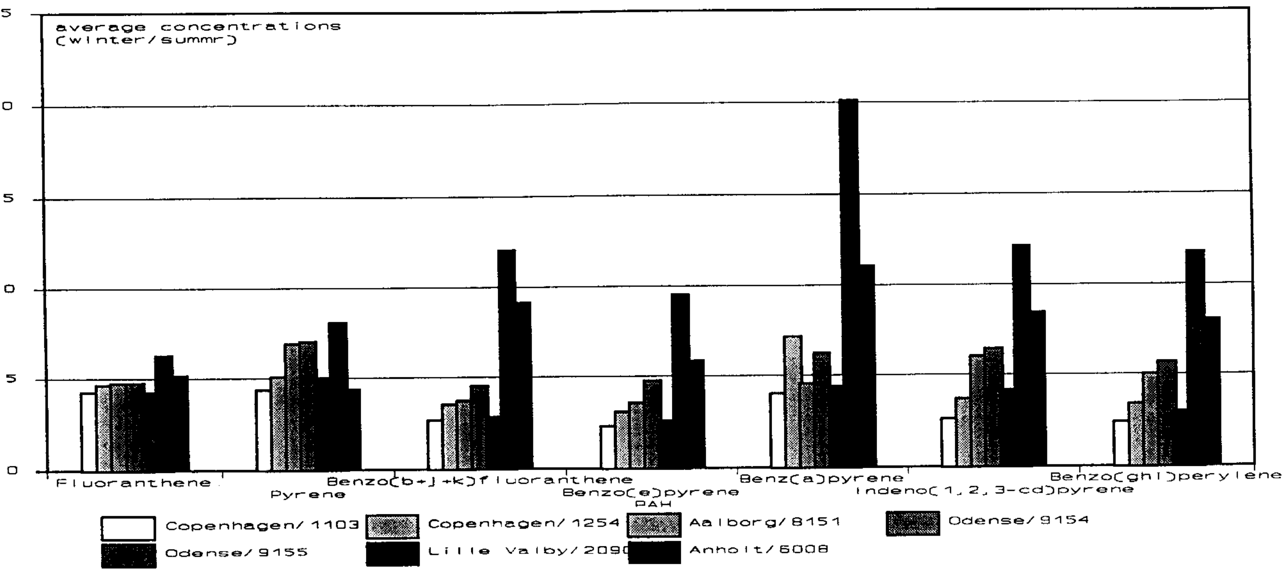

*Figure 5.2.* The ratios between the concentrations of PAH during winter and summer at different stations.

*Ratios, winter/summer*

As seen in *Figure 5.2* and *Table 5.6* the ratios between the concentrations during the winter and summer periods in the urban areas do not differ a lot from the ratios found at the rural area Anholt/6008, whereas the rural area Lille Valby/2090 shows a bigger difference between summer and winter levels. The explanation could be that domestic heating in winter periods is a major source to PAH in this area, but not to the same extent in the cities. The differences seems not to be correlated with the molecular masses of the PAH. The biggest differences in the ratios between winter and summer levels in urban areas were observed at Odense/9154, due to relatively lower concentrations during the summer period.

*Table 5.6.* Ratios between concentration during winter and summer in urban and rural areas in Denmark and other countries.

| PAH | Urban 5 cities, Denmark 1) | Urban Vienna, Austria, 2) | Urban Stockholm, Sweden 2) | Urban 4 cities, U.K., 3) | Rural, Lille Valby/2090 Denmark 1) | Rural, Anholt Denmark 1) | Rural, Rörvik, Sweden, 4) |
|---|---|---|---|---|---|---|---|
| Fluoranthene | 4-5 | 2 | 5 | | 6 | 5 | 4 |
| Pyrene | 4-7 | 2 | 6 | 1-3 | 8 | 4 | 4 |
| Benzo(b+k)-fluoranthene | 3-5 | 3 | 2 | 2-4 | 12 | 9 | 6 |
| Benzo(e)pyrene | 2-5 | 3 | 2 | | 9 | 6 | |
| Benzo(a)pyrene | 4-7 | 4 | 2 | 1-5 | 20 | 12 | 5 |
| Indeno(1,2,3-cd)-pyrene | 3-6 | 3 | 2 | | 12 | 8 | 4 |
| Benzo(ghi)perylene | 2-6 | 2 | 2 | 2-4 | 12 | 8 | 9 |
| Period | 1992-1994 | 1983-1984 | 1980-1983 | 1991 | 1992-1994 | 1992-1994 | 1990 |

1) This investigation
2) *Menichini, 1992*
3) *Hasall et al., 1993*
4) *Lundén, 1990*

*Ratios, other countries*

*Table 5.6* also shows the ratios found in other investigations. The ratios between winter and summer levels seem to be higher in Danish cities than in cities in other countries. The explanation could be that the contribution of PAH from domestic heating is more important in Danish cities because of the relatively low intensity of traffic and higher space heating demand. The Swedish and the Danish situations are more alike. The Danish and Swedish rural station did not differ in term of ratios between the winter and summer levels.

## 5.4 PAH profiles at urban and rural locations and seasonal variations

*Normalisation to benzo(e)pyrene*

In order to evaluate the compositional differences in the PAH profiles, the concentrations of PAH were normalized with respect to benzo(e)pyrene, which is photochemically stable and predominately found in the particulate phase as described by *Grimmer et al., (1980).*

*Winter profiles*

As seen in *Figure 5.3* and *Table 5.7*, which is based on the average concentrations for the winter samples, the urban areas had the same normalized PAH-profile during winter periods, but different from the rural areas. The urban areas had a lower ratio than the rural areas for fluoranthene and benzo(b+j+k)fluoranthene, the same ratio for pyrene and indeno(1,2,3-cd)pyrene and a higher ratio for benzo(ghi)perylene.

### *Summer profiles*

The summer profiles for the urban areas (see *Figure 5.3* and *Table 5.7*) were similar compared to each other and different from that of the rural areas. The urban areas had a lower ratios for fluoranthene and pyrene, the same ratio for benzo(b+j+k)pyrene and indeno(1,2,3-cd)pyrene and a higher ratio for benzo(ghi)perylene.

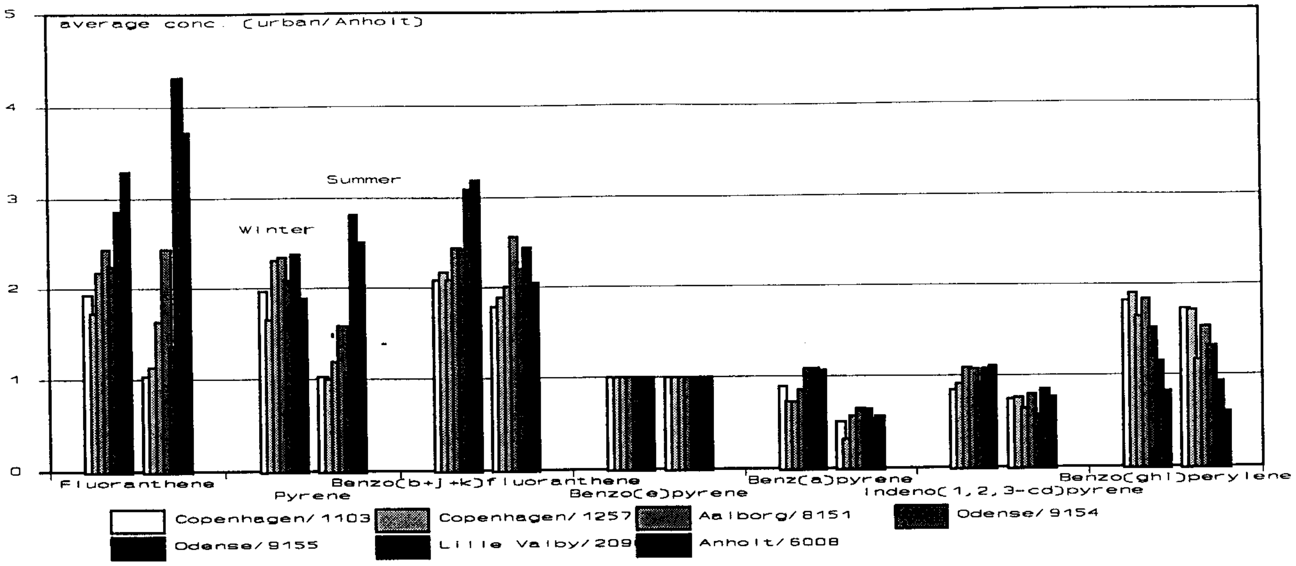

*Figure 5.3.* Concentration of PAH from urban and rural areas normalized to benzo(e)pyrene, averaged for winter (left columns) and summer data (right columns).

*Table 5.7.* Concentrations of PAH from urban and rural areas normalized to benzo(e)pyrene, averaged for summer and winter data.

| | Urban areas | | Rural areas | |
|---|---|---|---|---|
| PAH | winter | summer | winter | summer |
| Fluoranthene | 1.7-2.4 | 1.0-2.4 | 2.8-3.3 | 3.7-4.4 |
| Pyrene | 1.6-2.4 | 1.0-1.6 | 1.9-2.4 | 2.6-2.8 |
| Benzo(b+j+k)fluoranthene | 2.1-2.4 | 1.8-2.6 | 3.1-3.2 | 2.0-2.4 |
| Benzo(e)pyrene | 1 | 1 | 1 | 1 |
| Benzo(a)pyrene | 0.7-1.1 | 0.4-0.7 | 1.1 | 0.5 |
| Indeno(1,2,3-cd)pyrene | 0.8-1.1 | 0.6-0.8 | 1.1 | 0.8-0.9 |
| Benzo(ghi)perylene | 1.5-1.9 | 1.1-1.7 | 0.8-1.2 | 0.6-0.9 |

*Summer-winter profiles*

The differences between the summer and winter profiles as seen in *Figure 5.3* were not only a result of change in emission sources but also due to phase distribution and photochemical reactions. According to *Baek et al. (1991b)* the gas-particle distribution of PAH variate with respect to the molecular weights and the temperature, so about 30% of fluoranthene and pyrene are found in the particle phase in winter periods and only 10% in summer periods. This means that three times as much fluoranthene and pyrene are found in the particle phase in the winter periods compared with the summer periods. For the higher molecular weight benzo(e)pyrene, benzo(a)pyrene and benzo(b+k)fluoranthene *Baek et al. (1991b)* have found a significant lower difference in the phase distribution during summer and winter with about 90% bound to the particle phase in winter periods and about 80% in summer periods. It is only a difference of about 10%. For the high molecular weight indeno(1,2,3-cd)pyrene and benzo(ghi)perylene *Baek et al. (1991b)* have shown that almost 100% found in the particle phase during both summer and winter.

*Fluoranthene and pyrene*

In the urban areas the ratios for fluoranthene and pyrene were lower during the summer periods than during the winter periods. This is in accordance with the phase distribution described above. However, the ratios for fluoranthene and pyrene in the rural areas were higher during the summer periods and one explanation could be that there are more particles (soil dust) in the rural areas during the summer periods (soil drift), on which the gas phase fluoranthene and pyrene can condensate.

*Benzo(b+j+k)fluoranthene*

The ratios for benzo(b+j+k)fluoranthene in the urban areas were the same during the summer and winter periods, but in the rural areas the ratio was higher during the winter period. This cannot be explained by differences in the phase distribution, but could instead be due to a higher degradation rate during the summer than during the winter combined with the distance from the sources.

*Benzo(a)pyrene*

The ratios for benzo(a)pyrene were lower in the summer periods for both urban and rural areas. This is properly due to a higher degradation rate during the summer period.

*Indeno(1,2,3-cd)pyrene*

The ratios for indeno(1,2,3-cd)pyrene were the same for the urban and the rural areas, but the summer ratios were lower than the winter ratios. This might be due to differences in sources e.g. residential heating in winter time (see Cap. 5.6). The degradation rate combined with the distance to the sources do not seem to have any influence because there is no differences between the ratios for the urban and rural areas.

*Benzo(ghi)perylene*

The ratios for benzo(ghi)perylene were higher for urban areas than for rural areas and there were no differences between the summer and winter periods. The high ratios for urban areas were due to emission from traffic.

*Other investigations*

The ratios observed in Denmark and Sweden are quite similar for all the PAH. The ratios observed in the Austrian study with respect to fluoranthene and pyrene shows the reverse picture, with higher ratios in summer than in winter (*Table 5.8*). However the ratios for fluoranthene and pyrene were very high both summer and winter so different sources are properly the explanation.

*Table 5.7.* Concentrations of PAH normalized to benzo(e)pyrene for summer and winter periods at urban and rural areas found in other investigations

| | Vienna[1] Austria | | Stockholm[1] Sweden | |
|---|---|---|---|---|
| PAH | winter | summer | winter | summer |
| Fluoranthene | 7.2 | 11 | 1.4 | 0.5 |
| Pyrene | 7.3 | 12 | 1.8 | 0.5 |
| Benzo(b+k)fluoranthene | 2.3 | 2.2 | 1.2 | 1.3 |
| Benzo(e)pyrene | 1.0 | 1.0 | 1.0 | 1.0 |
| Benzo(a)pyrene | 1.2 | 0.8 | 0.5 | 0.4 |
| Indeno(1,2,3-cd)pyrene | 1.0 | 1.0 | 0.8 | 0.7 |
| Benzo(ghi)perylene | 1.5 | 1.8 | 1.8 | 1.8 |

[1] *(Menichini, 1992)*

## 5.5 Correlations between PAH and inorganic components

*Application of correlation analysis*

The PAH concentrations, which have been measured at rural and at urban monitoring stations, showed many different types of fluctuations and trends due to variation of the emissions, physical/chemical transformation, deposition and meteorological conditions. The correlation or covariation between the PAH and other components can give some indications about the origin of the PAH. However, because correlations can be caused by a common third factor, e.g. the meteorology, the correlation can never be the proof of the origin, but only an indication. Conclusions about the origin must also be based on other observations, e.g. the PAH profile and differences between locations.

*Monthly averages*

The present investigations were based on monthly averages of the PAH concentrations only. Therefore the fluctuations at a shorter time scale have been removed. The analysis was based on seasonal fluctuations and trends over the two years monitoring period.

*Fluctuations and trends of inorganic pollutants*

Many inorganic components show a clear seasonal variation. Only graphs from selected stations is shown in the following. The components, which originate from house heating show high concentrations during the winter and low concentrations during the summer (*Figure 5.4*). This is more or less the same for the pollutants from traffic, but in this case the variation is mainly caused by bad dispersion during the winter (*Figure 5.5*). The lead pollution has been decreasing during the measuring period due to the increasing number of petrol driven cars with three-way catalysts, which require lead free petrol. The pollutants from soil dust varies with the wind speed and the humidity, which means, that the concentration of TSP and the soil components are high during springtime and early summer period (*Figure 5.6*). The variation of the long range transported pollutants, e.g. S, depends on the transport situation, but it is often high during April and May (*Figure 5.7*).

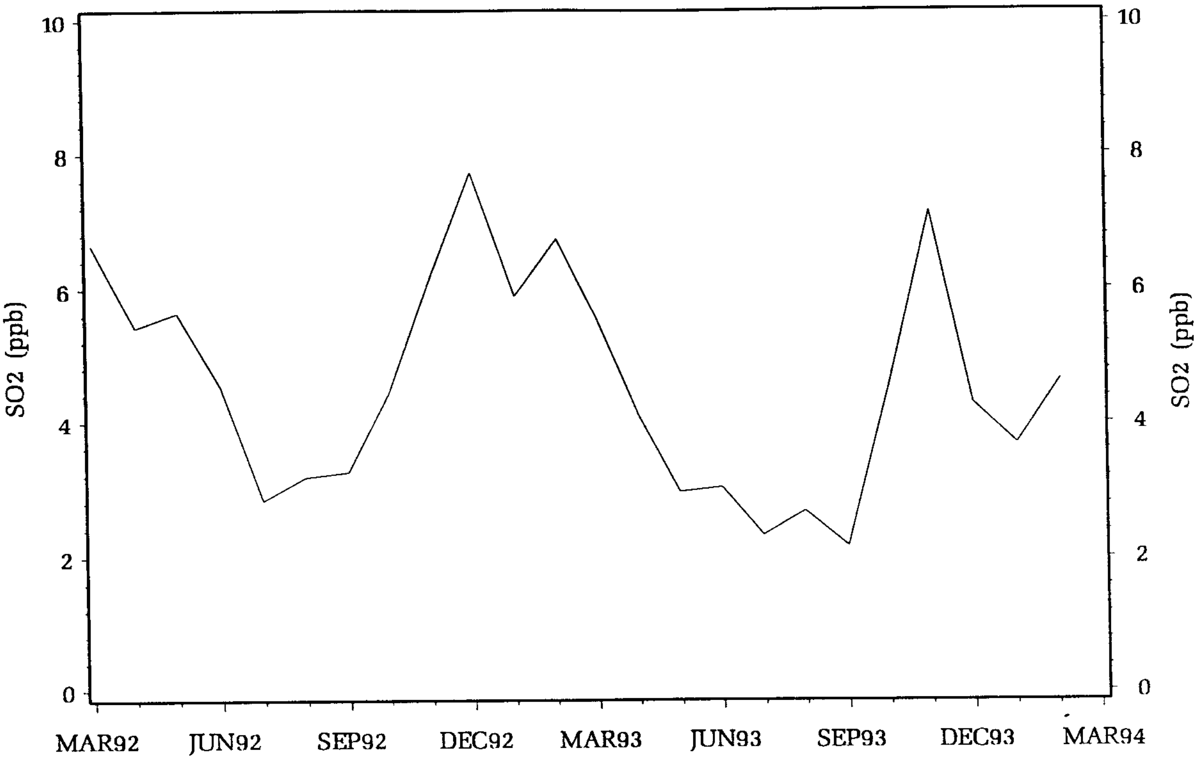

*Figure 5.4.* The monthly average concentration of $SO_2$, which is an indicator of air pollution from house heating, measured at Copenhagen/1257.

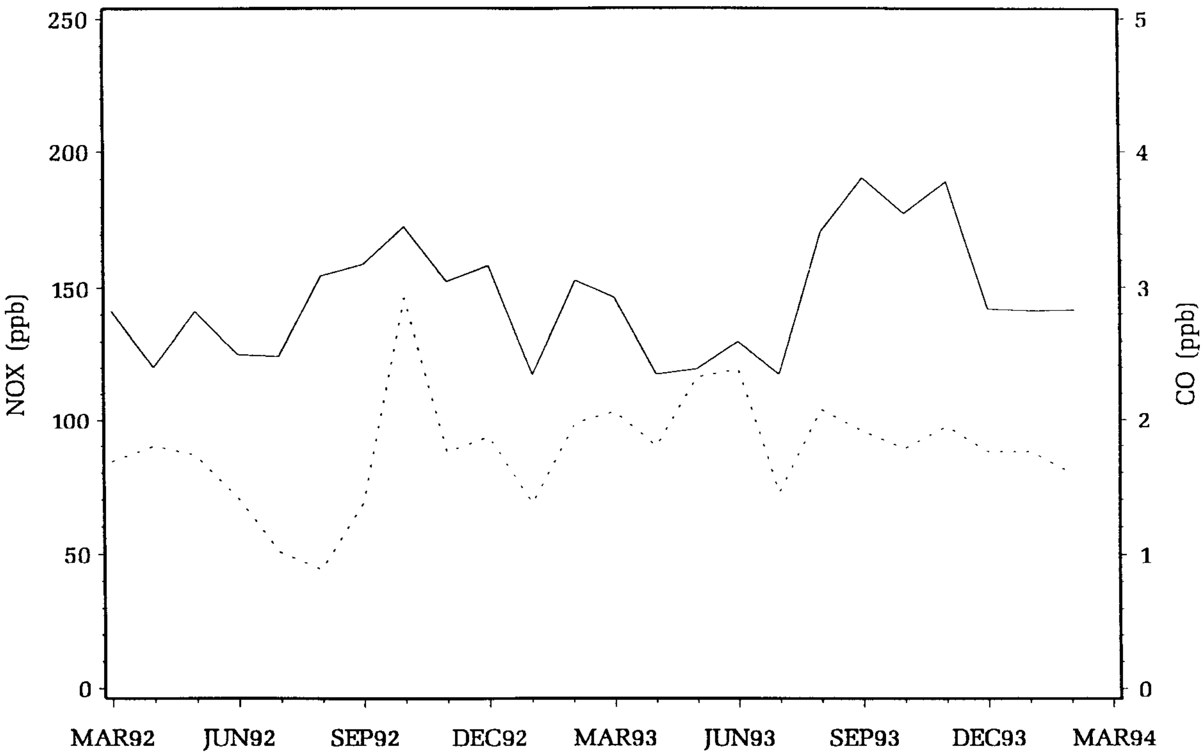

*Figure 5.5.* The monthly average concentrations of $NO_x$ (solid line) and CO (dotted line), which are indicators of air pollution from road traffic, measured at Copenhagen/1103.

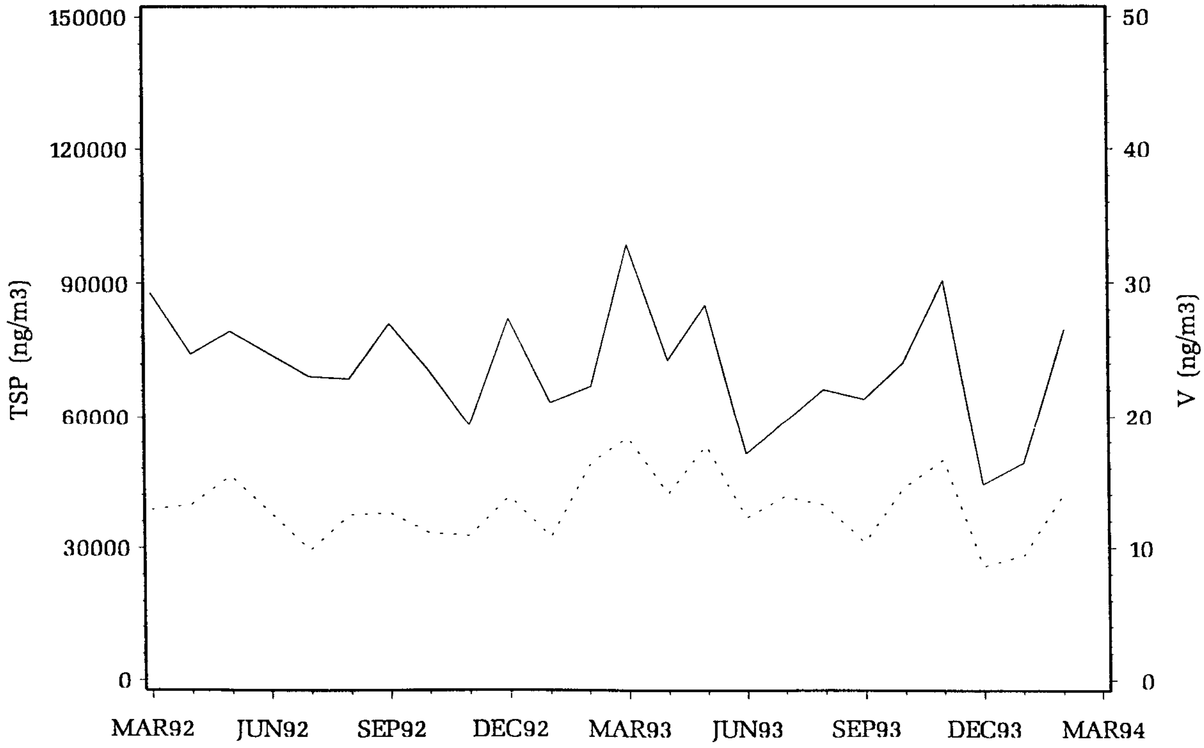

*Figure 5.6.* The monthly average concentrations of TSP (Total Suspended Particulates)(solid line) and V (dotted line), which are indicators of resuspended soil dust and combustion of heavy fuel oil respectively, measured at Copenhagen/1257.

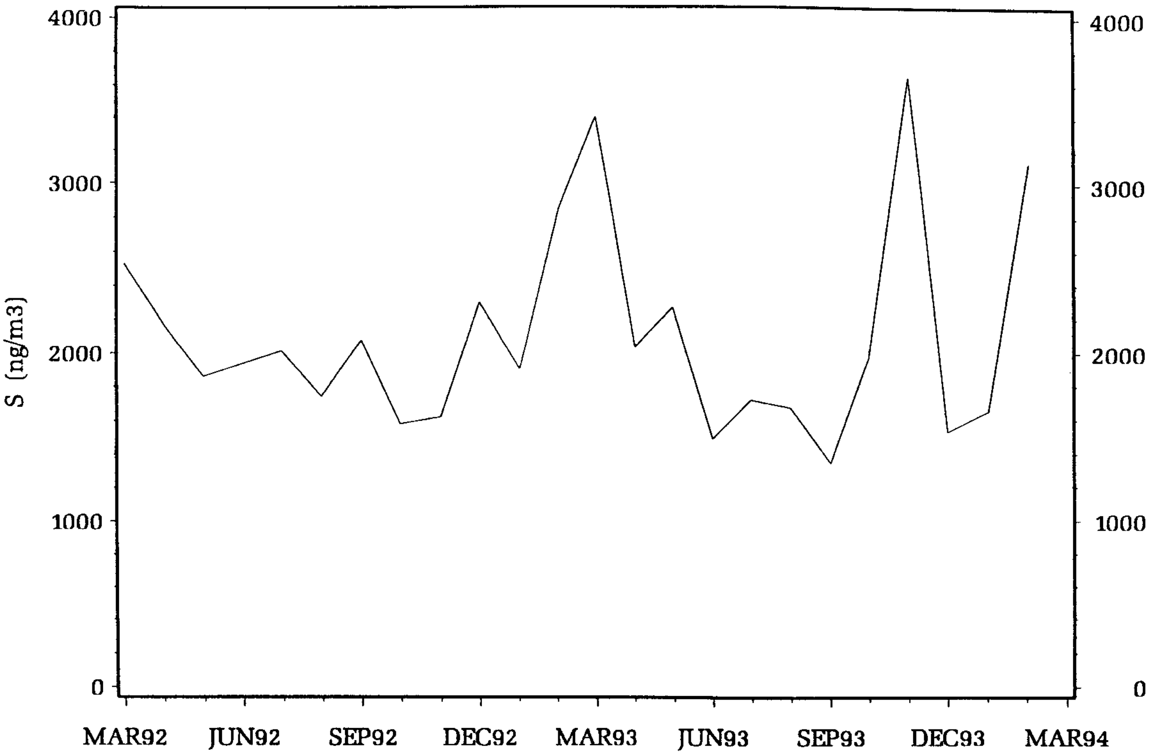

*Figure 5.7.* The monthly average concentration of S, which is an indicator of long range transported air pollution, measured at Copenhagen/1257.

*Correlations between inorganic pollutants*

Good correlations were generally observed between inorganic pollutants from the same sources. The correlation was good between Si, K and TSP (r=0.7-0.9), all from soil dust. The correlation between NO, $NO_x$ and CO (CO was only measured at Copenhagen/1103 in this period) from the road traffic was also good (r=0.6-0.9), but lowest for CO to NO and $NO_x$. The correlation between lead and NO, $NO_x$ and CO was generally lower than expected. This might be caused by the significant negative trend for lead during the period. The data analyses have also been carried out by use of lead-data adjusted for this trend, see below.

*Long range transport*

The concentration of sulphate is a good indicator for long range transport, because it is present in significant concentrations most of the time and because it does not show regular seasonal fluctuations and is independent of house heating demand, and local dispersion of pollutants. The correlation between sulphate and the measured PAH was weak at all locations, indicating an unimportant contribution from foreign sources. The correlation coefficients for the PAH and sulphate are shown in *Table 5.9*.

*Table 5.9.* Correlationcoefficients (r) for sulphate S to the measured PAH at different stations.

| Station | 1103 | 1257 | 9154 | 9155 | 8151 | 2090 | 6001 |
|---|---|---|---|---|---|---|---|
| Fluoranthene | 0.23 | 0.31 | 0.13 | 0.25 | 0.12 | 0.25 | -0.27 |
| Pyrene | 0.17 | 0.38 | 0.17 | 0.30 | 0.13 | -0.08 | -0.19 |
| Benzo(b+k)fluoranthene | 0.11 | 0.37 | 0.27 | 0.46 | 0.17 | 0.09 | -0.42 |
| Benzo(e)pyrene | 0.04 | 0.35 | 0.35 | 0.55 | 0.18 | 0.07 | -0.30 |
| Benzo(a)pyrene | 0.15 | 0.51 | 0.44 | 0.41 | 0.18 | 0.24 | -0.34 |
| Indeno(1,2,3-cd)pyrene | 0.12 | 0.42 | 0.39 | 0.29 | 0.11 | 0.002 | -0.28 |
| Benzo(ghi)perylene | 0.01 | 0.32 | 0.20 | 0.39 | 0.19 | 0.13 | -0.31 |

*Soil dust*

No significant correlations have been observed between the measured PAH and the soil dust and the elements (Si and K) in the dust, indicating that the PAH were not present at the coarse particles, *Table 5.10 and 5.11*. This is in accordance with *Baek et al., 1991*.

*Table 5.10.* Correlationcoefficients (r) for silicium (Si) to the measured PAH at different stations.

| Station | 1103 | 1257 | 9154 | 9155 | 8151 | 2090 | 6001 |
|---|---|---|---|---|---|---|---|
| Fluoranthene | -0.59 | -0.48 | -0.50 | -0.46 | -0.30 | -0.32 | -0.43 |
| Pyrene | -0.60 | -0.31 | -0.51 | -0.43 | -0.30 | -0.34 | -0.36 |
| Benzo(b+k)fluoranthene | -0.61 | -0.38 | -0.42 | -0.19 | -0.29 | -0.20 | -0.34 |
| Benzo(e)pyrene | -0.64 | -0.29 | -0.33 | -0.04 | -0.26 | -0.18 | -0.36 |
| Benzo(a)pyrene | -0.44 | -0.11 | -0.20 | -0.12 | -0.31 | -0.17 | -0.37 |
| Indeno(1,2,3-cd)pyrene | -0.60 | -0.32 | -0.332 | -0.21 | -0.32 | -0.19 | -0.34 |
| Benzo(ghi)perylene | -0.63 | -0.22 | -0.39 | -0.10 | -0.32 | -0.17 | -0.36 |

*Table 5.11.* Correlationcoefficients (r) for potassium (K) to the measured PAH at different stations.

| Station | 1103 | 1257 | 9154 | 9155 | 8151 | 2090 | 6001 |
|---|---|---|---|---|---|---|---|
| Fluoranthene | -0.81 | -0.17 | 0.02 | -0.14 | 0.16 | 0.27 | -0.08 |
| Pyrene | -0.81 | -0.01 | 0.03 | -0.11 | 0.13 | 0.23 | 0.04 |
| Benzo(b+k)fluoranthene | -0.82 | -0.15 | 0.11 | 0.14 | 0.17 | 0.39 | 0.01 |
| Benzo(e)pyrene | -0.81 | -0.06 | 0.20 | 0.27 | 0.17 | 0.40 | 0.03 |
| Benzo(a)pyrene | -0.53 | 0.10 | 0.22 | 0.13 | 0.04 | 0.38 | -0.02 |
| Indeno(1,2,3-cd)pyrene | -0.81 | -0.07 | 0.20 | 0.11 | 0.11 | 0.37 | 0.08 |
| Benzo(ghi)perylene | -0.78 | -0.02 | 0.07 | 0.17 | 0.08 | 0.39 | 0.05 |

*Space heating and power generation*

$SO_2$ has been used as an indicator for combustion of coal and oil (gas and fuel oil). $SO_2$ showed clear seasonal fluctuations like the PAH and the correlations were good ($r = 0.6 - 0.94$) indicating some contribution from space heating except at the station in Aalborg. The contribution from space heating could be lower due to extensive use of district heating, *Table 5.12*. However, as mentioned earlier the dispersion is normally strong during summertime causing lower pollution. Therefore it is not possible by the monthly time resolution to estimate the contribution from these sources. No correlations were observed between the measured PAH and V from heavy fuel oil. Because the use of wood for space heating correlates strongly with the use of coal and oil, the correlation could indicate contribution of PAH from wood burning. A better estimate could be made by combining the results from the detailed studies of PAH in Copenhagen *(Nielsen et al., 1995)*.

*Table 5.12.* Correlationcoefficients (r) for sulphur dioxide ($SO_2$) to the measured PAH at different stations.

| Station | 1103 | 1257 | 9154 | 9155 | 8151 | 6001 |
|---|---|---|---|---|---|---|
| Fluoranthene | 0.62 | 0.78 | 0.72 | 0.75 | 0.13 | 0.86 |
| Pyrene | 0.56 | 0.79 | 0.75 | 0.78 | 0.14 | 0.86 |
| Benzo(b+k)fluoranthene | 0.67 | 0.77 | 0.75 | 0.82 | 0.29 | 0.95 |
| Benzo(e)pyrene | 0.65 | 0.72 | 0.78 | 0.81 | 0.35 | 0.92 |
| Benzo(a)pyrene | 0.53 | 0.70 | 0.71 | 0.73 | 0.25 | 0.84 |
| Indeno(1,2,3-cd)pyrene | 0.64 | 0.80 | 0.79 | 0.78 | 0.14 | 0.93 |
| Benzo(ghi)perylene | 0.58 | 0.73 | 0.57 | 0.61 | 0.24 | 0.94 |

*Traffic and lead*

The best indicator of the pollution from petrol driven cars is lead in the air. During the two years of measurements of PAH, the lead concentration decreased significantly (*Figure 5.8*) and the correlations between lead and the PAH were not strong, (*Table 5.13*) The negative trend of the lead concentration has been removed by dividing the measured lead concentration with the linear regression line for the lead concentration versus time. The correlations between the adjusted lead concentration and the PAH were much stronger indicating a contribution from petrol driven cars at all urban stations. Also in this case the correlation is not a clear proof for the origin of the PAH, because the correlation or a part of it could be due the common third factor, the dispersion fluctuation.

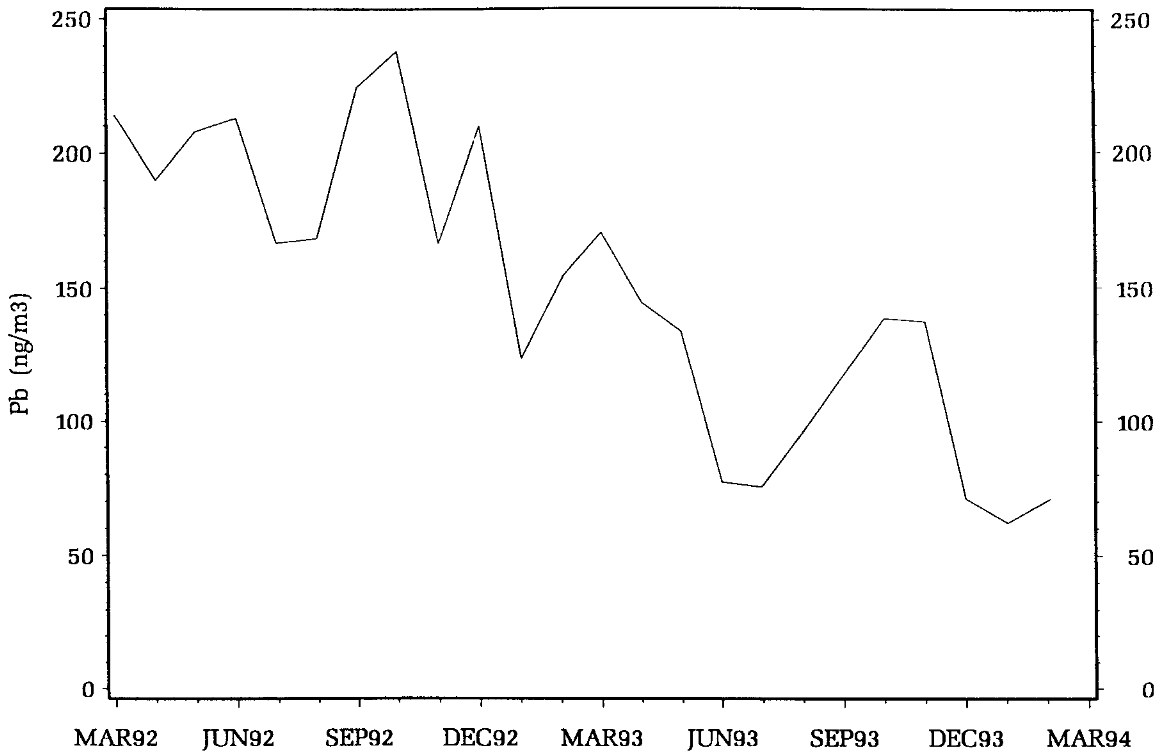

*Figure 5.8.* The monthly average concentration of Pb, which is an indicator of air pollution from petrol driven cars, measured at Copenhagen/1257. The negative trend is due to increasing use of lead-free petrol.

*Table 5.13.* Correlationcoefficients (r) for lead (Pb) to the measured PAH at different stations.

| Station | 1103 | 1257 | 9154 | 9155 | 8151 | 2090 | 6001 |
|---|---|---|---|---|---|---|---|
| Fluoranthene | 0.54 | 0.22 | 0.45 | -0.09 | 0.41 | 0.76 | 0.64 |
| Pyrene | 0.50 | 0.39 | 0.41 | -0.05 | 0.39 | 0.68 | 0.65 |
| Benzo(b+k)fluoranthene | 0.64 | 0.34 | 0.40 | 0.05 | 0.35 | 0.75 | 0.48 |
| Benzo(e)pyrene | 0.67 | 0.48 | 0.46 | 0.18 | 0.38 | 0.72 | 0.57 |
| Benzo(a)pyrene | 0.55 | 0.30 | 0.09 | 0.06 | -0.04 | 0.76 | 0.68 |
| Indeno(1,2,3-cd)pyrene | 0.61 | 0.38 | 0.37 | 0.11 | 0.27 | 0.69 | 0.60 |
| Benzo(ghi)perylene | 0.67 | 0.55 | 0.45 | 0.18 | 0.25 | 0.76 | 0.62 |

*Traffic and the trend of lead*

The significant negative trend of lead has not been observed for the PAH concentrations. The increased use of lead free petrol did not lead to significant changes in the PAH emission from petrol driven cars, caused by other composition of petrol (more aromatics and increasing PAH concentration) or collection at the catalysts (decreasing PAH concentration). This could be because the emissions of the measured PAH are low compared to other sources and the above correlations between lead and the PAH were due to dispersion fluctuations or because of the main contribution from petrol driven cars are from a low percentage of badly maintained older cars.

*Traffic and CO*

The concentration of CO has only been measured at the station in Copenhagen/1103. CO is a good indicator for petrol driven cars. The correlations between CO and the PAH were fair (r = 0.6-0.7) for all PAH, except for benzo(a)pyrene, which is unstable.

*Traffic and $NO_x$*

$NO_x$ ($NO+NO_2$) is in urban areas mainly emitted from petrol and diesel driven vehicles. $NO_x$ has been measured at 4 of the urban stations and at 1 rural station (Lille Valby/2090). The correlations between $NO_x$ and the measured PAH were highest at the rural station and in Odense and Aalborg and lowest in Copenhagen, *Table 5.14.*

*Table 5.14.* Correlationcoefficients (r) for nitrogen oxides ($NO+NO_2$) to the measured PAH at different stations.

| Station | 1103 | 1257 | 9155 | 8151 | 2090 |
|---|---|---|---|---|---|
| Fluoranthene | 0.37 | 0.17 | 0.14 | 0.46 | 0.81 |
| Pyrene | 0.44 | 0.42 | 0.32 | 0,53 | 0.71 |
| Benzo(b+k)fluoranthene | 0.40 | 0.34 | 0.61 | 0.72 | 0.80 |
| Benzo(e)pyrene | 0.41 | 0.48 | 0.72 | 0.76 | 0.75 |
| Benzo(a)pyrene | 0.27 | 0.37 | 0.72 | 0.67 | 0.91 |
| Indeno(1,2,3-cd)pyrene | 0.42 | 0.44 | 0.60 | 0.68 | 0.72 |
| Benzo(ghi)perylene | 0.43 | 0.56 | 0.63 | 0.68 | 0.87 |

*Factor analysis*

The factor analyses were performed on all raw data. In the annex is listed the correlation coefficients between the pollutants and the factors found in the analysis. In addition the explained variance are shown.

*Factor analysis, TSP, Si, K, NO, $NO_x$, CO and lead*

Factor analyses have been carried out on all data. Results from these analyses are summarized in the annex. At all stations all the PAH were associated with the same factor. The measured PAH may mainly be from the same types of sources. The PAH were never the same factor as the soil dust factor (TSP, Si and K) in accordance with the above conclusions. At many stations most of the pollutants (NO, $NO_x$ and CO) from the road traffic were associated with the same factor as the PAH. The Pb corrected for the negative trend was clearly associated with this factor.

*Factor analyses, $SO_2$, V and S*

At some stations the PAH factor did also include $SO_2$, i.e. the rural stations and Jagtvej in Copenhagen, which indicates significant contribution from space heating with PAH. At the other stations the factor analyses indicated smaller contributions from space heating. S was never associated with the PAH factor, which indicates, that the PAH do not originate from foreign sources. V (from fuel oil) was at most of the stations associated with the soil factor and never with the PAH factor, which indicates that fuel oil combustion is not a significant source of PAH.

*Further investigations*

It is not possible by the correlation analysis for the measured PAH as monthly averages and the measured inorganic pollutants alone to conclude on the origin of the PAH, but the analysis indicated significant contributions from space heating and road traffic, but a final conclusion requires supplement from other observations, especially the more detailed (in time and more PAH) investigation in Copenhagen.

## 5.6 Estimates of PAH contribution from different sources

*Sources*

PAH are widespread environmental contaminants. They are emitted to the atmosphere from both natural (forest fires and volcanic eruptions) and anthropogenic sources. The anthropogenic sources can be divided into stationary and mobile categories. The stationary sources include industrial plants, power and heat generation, space heating, incineration and open fires. The mobile sources include petrol-engine vehicles, diesel-engine vehicles, trucks, airplanes, and ships (*Bjørnseth, Ramdahl, 1985*). The amount of PAH released from any process is mainly dependent on raw materials and the combustion technology. Estimations of PAH emissions in Sweden and Norway have been made by *Bjørseth and Ramdahl (1985)*. The relative importance of different sources varies depending on the industrial profile of each country.

*Table 5.15.* Estimates of PAH emission from Denmark, Norway and Sweden *(Alfheim, Ramdahl, 1986).*

| | Denmark | | Norway | | Sweden | |
|---|---|---|---|---|---|---|
| | t/year | % | t/year | % | t/year | % |
| Space heating | 28.5 | 48 | 49.5 | 51 | 105 | 50 |
| Industrial production | 1.2 | 2 | 23.1 | 24 | 48.3 | 23 |
| Power generation | 0.5 | 1 | 0.2 | <1 | 6.7 | 3 |
| Incineration | 7.5 | 12 | 4.0 | 4 | 4.0 | 2 |
| Mobile sources | 21.9 | 37 | 20.1 | 21 | 47.1 | 22 |

The emission data from Denmark, Norway and Sweden showed in *Table 5.15* is based on statistical data and the relative emission factors for the different types of sources. About half of the PAH emissions from both Denmark, Norway and Sweden was calculated to come from the space heating. The contribution from industrial production in Sweden and Norway was about one forth, while the contribution in Denmark was negligible. On the other hand Denmark has more solid waste incineration, and a lager contribution from mobile sources.

### *Traffic exhaust and space heating*

In Denmark the urban air traffic exhaust and space heating are therefor the main sources to the PAH pollution. In order to quantify the contribution from these sources to the urban air, ratios between individual PAH have been used e.g. the ratio between indeno(1,2,3-cd)pyrene and benzo(ghi)perylene. Benzo(ghi)perylene is omitted in higher quantities from traffic than from space heating. According to *Jaklin, Krenmayr (1985)* ratio between indeno(1,2,3-cd)pyrene and benzo(ghi)perylene should be 0.37 for the PAH profile for traffic exhaust and 0,90 for space heating. As seen in *Figure 5.9* the 2 years average ratios were very different between the urban areas and the rural area with the highest ratios for the latter. The ratio for Copenhagen/1103 and Copenhagen/1257 were the lowest (0.46-0.48) indicating that the main source was the traffic. For the other 3 urban areas the ratios were higher (0.57-0.58) indicating that lager contribution to the PAH concentrations came from space heating. The rural area Lille Valby/2090 showed a ratio of 0.98 and the rural area Anholt/6008 showed a very high ratio of 1.37.

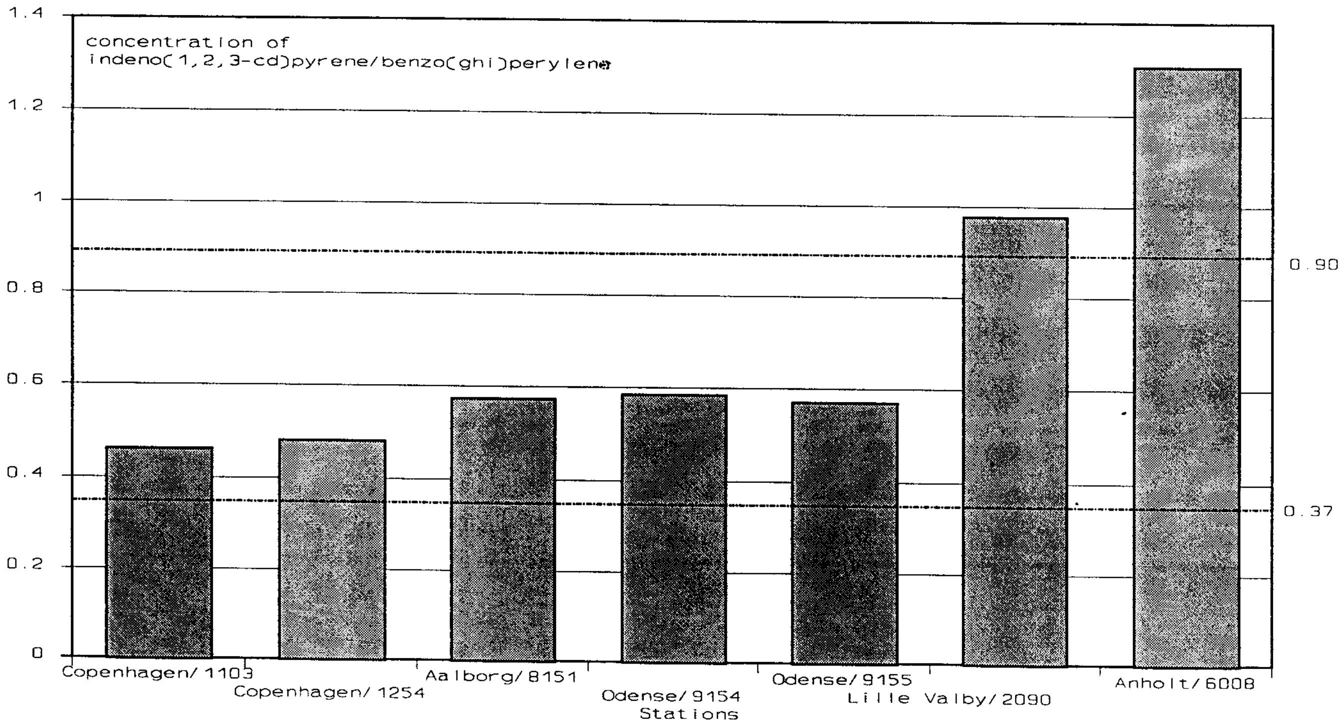

*Figure 5.9.* Average for 2 years values of the ratios of indeno(1,2,3-cd)pyrene and benzo(ghi)-perylene at all stations.

*Urban sites*

The ratios between indeno(1,2,3-cd)pyrene and benzo(ghi)perylene for the urban areas in the summer periods (*Figure 5.10)* were lower than the winter ratios indicating a higher contribution from the traffic during summer. In the winter periods the ratios for the Copenhagen stations, Copenhagen/1103 and Copenhagen/1257 were increased with 12-14%, whereas the ratios for the other urban sites were increased with 23-43%. This indicates that the traffic was the main source to the PAH pollution at the two Copenhagen sites even during winter periods. For the other urban sites the space heating contributed to the PAH pollution during the winter periods.

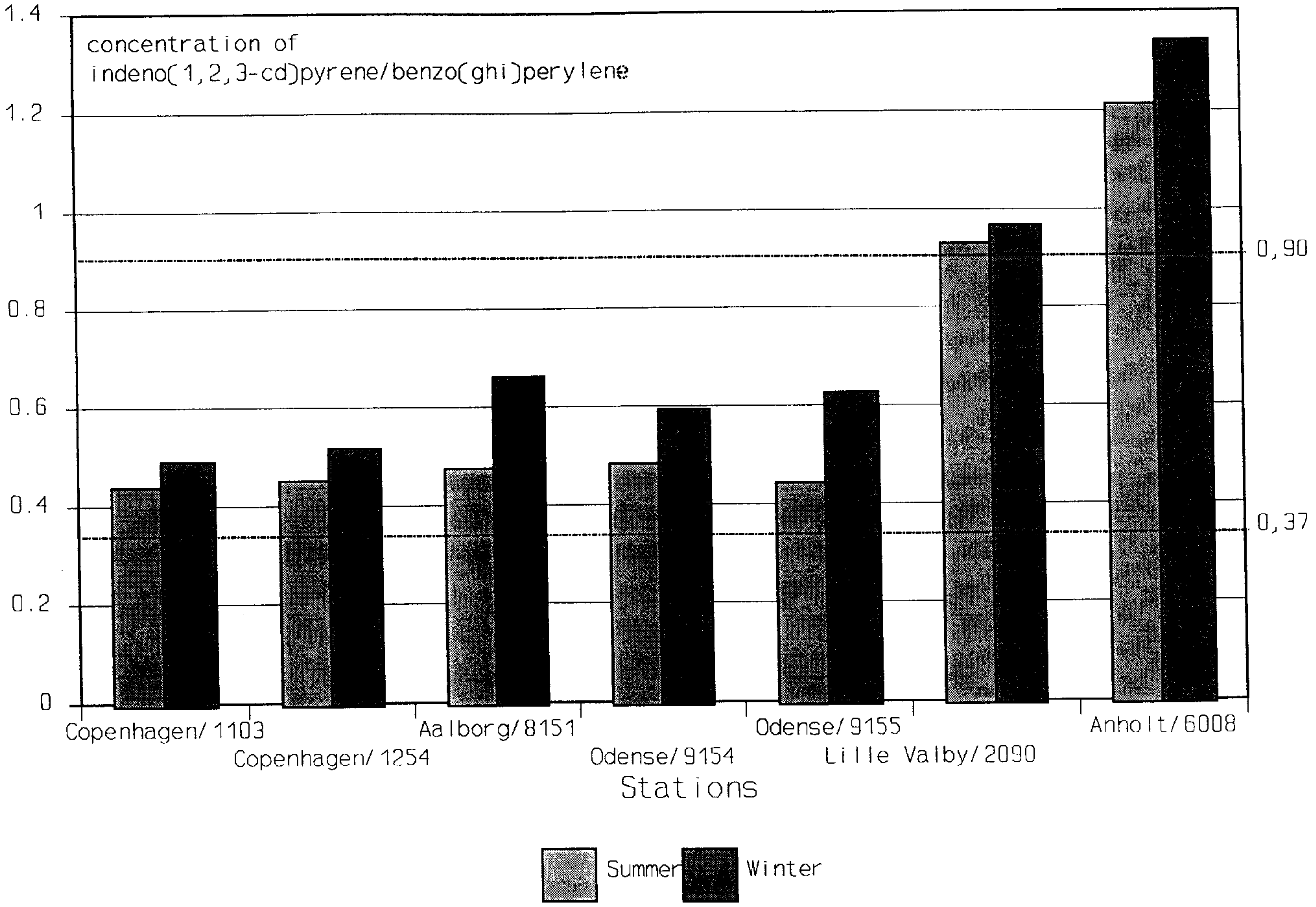

*Figure 5.10.* Average for summer and winter values of the ratios of indeno(1,2,3-cd)pyrene and benzo(ghi)perylene at the urban stations, and rural areas.

*Rural sites*

The ratios for the rural areas were high both summer (0.93 and 1.21) and winter (0.97 and 1.34) (see *Figure 5.10*). Although the ratios were increased during winter periods, which could be explained by a bigger contributions from space heating, the ratios in the summer periods were far too high to be explained by a significant contribution from traffic. The ratios must depend on other phenomenons. Photochemical degradation is likely to be a parameter. According to *Howard et al. (1991)* the photochemical half-life for indeno(1,2,3-cd)pyrene is almost twice as long as for benzo(ghi)perylene. As benzo(ghi)perylene degraded twice as fast as indeno(1,2,3-

cd)pyrene the ratios will always increase as a function of the distance from the sources. This can explain that the ratio measured at Anholt/6008 was higher than at Lille Valby/2090, which is much closer to the sources than Anholt/6008. Furthermore it should be taken into account that the ratio-source relation as pointed out by *Jaklin and Krenmayr (1985)* can only be used close to the sources.

## 5.7 PAH levels compared to WHO's guideline

*WHO's guideline*

Denmark has no limit values for PAH. WHO's guidelines for air states as follows (*WHO, 1987*):

> "Owing to its carcinogenicity, no safe level of PAH can be recommended. There is no known cancer threshold for benzo(a)pyrene, the most thoroughly studied PAH, nor is there an ambient mixture of PAH that does not contain benzo(a)pyrene and other substances for which there is sufficient evidence of carcinogenicity.
>
> A number of different risk estimates for PAH have been made, based primarily on using benzo(a)pyrene as the index compound. The US EPA has offered an upper-bound lifetime cancer risk estimate of 62 per 100.000 exposed people per µg benzene-soluble coke-oven emission per $m^3$ ambient air. Assuming a 0.71% content of benzo(a)pyrene in these emissions, it can be estimated that 9 out of 100.000 people exposed to 1 ng benzo(a)pyrene per $m^3$ over a lifetime would be at risk of developing cancer."

*Toxic equivalency factors*

Other PAH than benzo(a)pyrene are known to be carcinogenic. *Nisbet, LaGoy* (1992) has assigned toxic equivalency factors for different PAH relative to benzo(a)pyrene. In *Table 5.16* is shown the toxic equivalency factors relevant for this.

*Table 5.16.* Toxic equivalency factors (TEF) for PAH relative to benzo(a)pyrene assigned by *Nisbet and LaGoy* (1992).

| PAH | TEF |
|---|---|
| Fluoranthene | 0.001 |
| Pyrene | 0.001 |
| Benzo(b)fluoranthene | 0.1 |
| Benzo(k)fluoranthene | 0.1 |
| Benzo(a)pyrene | 1 |
| Indeno(1,2,3-cd)pyrene | 0.1 |
| Benzo(ghi)perylene | 0.01 |

As seen in *Table 5.17* the concentration of benzo(a)pyrene at the urban stations measured in this study, were close to 1 ng/m$^3$ (see WHO's guidelines above), whereas the concentrations at the rural station are below one third of this value.

*Benzo(a)pyrene$_{equiv.}$*

By using the TEF from *Table 5.16* on the average concentrations measured in this study to calculate the benzo(a)pyrene equivalence (benzo(a)pyrene$_{\text{equiv.}}$) from all the PAH, it can be estimated (*Table 5.17)* that the extra contribution of benzo(a)pyrene$_{\text{equiv.}}$ from the other PAH was between 25% and 50% of the benzo(a)pyrene$_{\text{equiv.}}$ from benzo(a)pyrene. This elevates the concentration of the carcinogenic content in the air from urban sites in Denmark up above the WHO concentration of 1 ng/m$^3$.

*Table 5.17.* Average concentration (over 2 years) of benzo(a)pyrene in ng/m$^3$ and benzo(a)-pyrene$_{\text{equiv.}}$ in ng/m$^3$ calculated by toxic equivalency factors assigned by *Nisbet and LaGoy* (1992).

| Station | Concentration of benzo(a)pyrene | benzo(a)pyrene$_{\text{equiv.}}$ exclusive benzo(a)pyrene | benzo(a)pyrene$_{\text{equiv.}}$ inclusive benzo(a)pyrene |
|---|---|---|---|
| Copenhagen/1103 | 1.5 | 0.5 | 2.3 |
| Copenhagen/1257 | 1.6 | 0.6 | 2.4 |
| Aalborg/8151 | 1.2 | 0.5 | 2.1 |
| Odense/9154 | 0.8 | 0.4 | 1.4 |
| Odense/9155 | 1.0 | 0.3 | 1.3 |
| Lille Valby/2090 | 0.3 | 0.1 | 0.4 |
| Anholt/6008 | 0.2 | 0.1 | 0.3 |

*Nisbet and LaGoy* (1992) has assigned toxic equivalency factors for other PAH than showed in *Table 5.16*, but for almost all of them the toxic equivalency factor are very low or the concentration i air are so low that they will not contribute significantly to additional benzo(a)pyrene$_{\text{equiv.}}$. The only exception could be benzo(a)anthracene, which according to *Nisbet and LaGoy (1992)*, has a toxic equi-valency factors of 0.1 and occurs in more or less the same concentrations as indeno(1,2,3-cd)pyrene (*Nielsen, 1989*) (*National Institute of Standards and Technology*, 1992). Benzo(a)anthracene could contribute with 5-10% more benzo(a)pyrene$_{\text{equiv.}}$. Future investigations on PAH in particulate matter should therefore include measurement of benzo(a)anthracene.

# 6 Conclusion

*Levels of PAH*

The concentration of the measured PAH in the air were 0.01-9.2 ng/m$^3$. The highest concentrations (average of all compounds) were found in Copenhagen and the lowest at the rural area Anholt. The concentrations in the urban areas were 3-63 times higher than on Anholt. The concentrations in winter periods in relation to summer periods were 2-6 times higher in the urban areas and 6-12 times higher in the rural areas. The levels were comparable with investigations made in other countries in the nineties, but lower than earlier investigations properly due to the improvements in combustion techniques with respect to the emission of PAH. In order to describe the trends this investigation can be used as the basis for a following study in the future.

*Limit values*

Denmark has no limit values for PAH, but the concentrations of benzo(a)pyrene$_{equiv.}$ in the cities were higher or at the same level as the value of 1 ng/m$^3$ recommended by WHO. If exposed to this concentration over a lifetime, according to the US EPA, 9 out of 100 000 will be at risk of developing cancer. The average concentration of benzo(a)pyrene$_{equiv.}$ were 2 ng/m$^3$ in Copenhagen and 0.3 at Anholt.

*The origin of PAH*

The ratio between indeno(1,2,3-cd)pyrene and benzo(ghi)perylene indicated that the main contribution of PAH to the urban air came from the traffic. It has not been possible generally to confirm this by the correlation between the measured PAH as monthly averages and the measured inorganic pollutants alone. Important chemical transformations of the PAH might occur in the summer months. A final conclusion require supplement from other observations, e.g. to the more detailed (in time and numbers of measured PAH) investigation in Copenhagen *(Nielsen et al., 1995)*. However some indication of contributions from road traffic as well as from space heating has been observed. No indication was observed of transport of PAH from our neighbour countries.

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# ANNEX. Factor analysis for PAH and measured inorganic pollutants.

## Initial Factor Method: Principal Components

Copenhagen / 1103
Factor Pattern

| | Factor 1 | Factor 2 | Factor 3 |
|---|---|---|---|
| Si | -0.68314 | 0.64506 | 0.01541 |
| S | 0.19545 | 0.83307 | 0.04181 |
| V | -0.34423 | 0.83791 | 0.19146 |
| K | -0.85147 | 0.26411 | 0.03714 |
| Pb* | 0.70666 | 0.49190 | 0.41052 |
| TSP | -0.18930 | 0.86212 | 0.30868 |
| $SO_2$ | 0.56639 | 0.60092 | -0.38619 |
| NO | 0.67945 | -0.16402 | 0.67676 |
| $NO_2$ | -0.71015 | 0.44234 | -0.25894 |
| $NO_x$ | 0.64643 | -0.12145 | 0.70113 |
| CO | 0.77821 | 0.00775 | 0.29142 |
| Fluoranthene | 0.93775 | 0.17304 | -0.18666 |
| Pyrene | 0.95421 | 0.13481 | -0.12965 |
| Benzo(b+j+k)fluoranthene | 0.96270 | 0.15050 | -0.17954 |
| Benzo(e)pyrene | 0.94581 | 0.08364 | -0.20768 |
| Benzo(a)pyrene | 0.78190 | 0.04690 | -0.31866 |
| Indeno(1,2,3-cd)pyrene | 0.96376 | 0.17732 | -0.13636 |
| Benzo(ghi)perylene | 0.92400 | 0.04545 | -0.20365 |

Variance explained by each factor

| Factor 1 | Factor 2 | Factor 3 |
|---|---|---|
| 10.199047 | 3.579101 | 1.843164 |

Final Communality Estimates: Total = 15.621313

* Lead corrected for trend

Copenhagen / 1257
Factor Pattern

| | Factor 1 | Factor 2 | Factor 3 |
|---|---|---|---|
| Si | -0.11000 | 0.93449 | 0.04747 |
| S | 0.54403 | 0.44444 | 0.59583 |
| V | 0.21723 | 0.67760 | 0.51013 |
| K | 0.13759 | 0.83949 | 0.18738 |
| Pb* | 0.69251 | 0.50728 | -0.36919 |
| TSP | 0.44143 | 0.83651 | 0.18171 |
| $SO_2$ | 0.84382 | -0.01541 | 0.32730 |
| NO | 0.67716 | 0.34484 | -0.61325 |
| $NO_2$ | -0.11457 | 0.79247 | -0.23083 |
| $NO_x$ | 0.61016 | 0.47631 | -0.61769 |
| Fluoranthene | 0.82905 | -0.45273 | 0.16954 |
| Pyrene | 0.92836 | -0.23319 | 0.04916 |
| Benzo(b+j+k)fluoranthene | 0.91081 | -0.34453 | 0.05477 |
| Benzo(e)pyrene | 0.92464 | -0.23151 | -0.06934 |
| Benzo(a)pyrene | 0.79354 | -0.03825 | 0.17208 |
| Indeno(1,2,3-cd)pyrene | 0.95712 | -0.25167 | 0.02534 |
| Benzo(ghi)perylene | 0.94819 | -0.15996 | -0.13006 |

Variance explained by each factor

| Factor 1 | Factor 2 | Factor 3 |
|---|---|---|
| 8.283157 | 4.687818 | 1.826101 |

Final Communality Estimates: Total = 14.797076

* Lead corrected for trend

Aalborg / 8151
Factor Pattern

| | Factor 1 | Factor 2 | Factor 3 |
|---|---|---|---|
| Si | -0.01650 | 0.91684 | 0.11597 |
| S | 0.40385 | 0.70917 | 0.32899 |
| V | 0.09442 | 0.90752 | 0.08773 |
| K | 0.40837 | 0.80076 | 0.26537 |
| Pb* | 0.83981 | 0.40568 | -0.06662 |
| TSP | 0.35913 | 0.87412 | 0.22848 |
| $SO_2$ | 0.49324 | 0.59969 | -0.05382 |
| NO | 0.88062 | 0.05487 | -0.45835 |
| $NO_2$ | 0.30302 | 0.79589 | -0.45389 |
| $NO_x$ | 0.85528 | 0.15773 | -0.48497 |
| Fluoranthene | 0.81501 | -0.37326 | 0.37199 |
| Pyrene | 0.84927 | -0.37543 | 0.29900 |
| Benzo(b+j+k)fluoranthene | 0.94206 | -0.30324 | 0.06053 |
| Benzo(e)pyrene | 0.94505 | -0.26438 | -0.01149 |
| Benzo(a)pyrene | 0.82297 | -0.31063 | -0.05409 |
| Indeno(1,2,3-cd)pyrene | 0.90353 | -0.37248 | 0.09041 |
| Benzo(ghi)perylene | 0.90017 | -0.34216 | 0.07593 |

Variance explained by each factor

| Factor 1 | Factor 2 | Factor 3 |
|---|---|---|
| 8.485464 | 5.552396 | 1.159078 |

Final Communality Estimates: Total = 15.196937

* Lead corrected for trend

| Odense/9154<br>Factor Pattern | | |
|---|---|---|
| | Factor 1 | Factor 2 |
| Si | -0.23071 | 0.86084 |
| S | 0.50129 | 0.75939 |
| V | 0.33676 | 0.86023 |
| K | 0.32835 | 0.85357 |
| Pb* | 0.81773 | 0.13245 |
| TSP | 0.42047 | 0.83177 |
| $SO_2$ | 0.85098 | 0.18524 |
| Fluoranthene | 0.82913 | -0.36974 |
| Pyrene | 0.90643 | -0.35564 |
| Benzo(b+j+k)fluoranthene | 0.95460 | -0.25526 |
| Benzo(e)pyrene | 0.97614 | -0.14576 |
| Benzo(a)pyrene | 0.83170 | 0.02183 |
| Indeno(1,2,3-cd)pyrene | 0.97828 | -0.12298 |
| Benzo(ghi)perylene | 0.89700 | -0.27945 |

Variance explained by each factor

| Factor 1 | Factor 2 |
|---|---|
| 7.921912 | 3.973272 |

Final Communality Estimates: Total = 11.895184

* Lead corrected for trend

Odense/9155
Factor Pattern

| | Factor 1 | Factor 2 | Factor 3 |
|---|---|---|---|
| Si | 0.28333 | 0.89118 | 0.09915 |
| S | 0.78468 | 0.36181 | 0.37757 |
| V | 0.70748 | 0.61712 | 0.15451 |
| K | 0.56621 | 0.71770 | 0.24455 |
| Pb* | 0.76618 | 0.52353 | -0.14533 |
| TSP | 0.64988 | 0.70367 | 0.16915 |
| $SO_2$ | 0.76182 | -0.37521 | 0.34777 |
| NO | 0.87074 | 0.14103 | -0.43156 |
| $NO_2$ | 0.59322 | 0.74260 | -0.04429 |
| $NO_x$ | 0.87215 | 0.21971 | -0.40196 |
| Fluoranthene | 0.51215 | -0.72054 | 0.39359 |
| Pyrene | 0.63745 | -0.71736 | 0.20816 |
| Benzo(b+j+k)fluoranthene | 0.84674 | -0.50496 | 0.01937 |
| Benzo(e)pyrene | 0.91189 | -0.36218 | -0.04827 |
| Benzo(a)pyrene | 0.83407 | -0.41027 | -0.26064 |
| Indeno(1,2,3-cd)pyrene | 0.82862 | -0.53521 | -0.02891 |
| Benzo(ghi)perylene | 0.80791 | -0.41721 | -0.18360 |

Variance explained by each factor

| Factor 1 | Factor 2 | Factor 3 |
|---|---|---|
| 9.229802 | 5.399423 | 1.059945 |

Final Communality Estimates: Total = 15.689171

* Lead corrected for trend

Lille Valby / 2090
Factor Pattern

| | Factor 1 | Factor 2 | Factor 3 |
|---|---|---|---|
| Si | -0.20506 | 0.74471 | 0.46603 |
| S | 0.26236 | 0.80477 | -0.39058 |
| V | 0.65607 | 0.59662 | -0.30317 |
| K | 0.40784 | 0.79292 | 0.38080 |
| Pb* | 0.93637 | 0.16792 | -0.24050 |
| NO | 0.91972 | 0.08058 | -0.07929 |
| $NO_2$ | 0.80602 | -0.20367 | -0.45145 |
| $NO_x$ | 0.92058 | -0.05618 | -0.26991 |
| Fluoranthene | 0.93784 | -0.08636 | -0.04707 |
| Pyrene | 0.86397 | -0.31194 | 0.28330 |
| Benzo(b+j+k)fluoranthene | 0.95814 | -0.11543 | 0.24035 |
| Benzo(e)pyrene | 0.93364 | -0.11654 | 0.29845 |
| Benzo(a)pyrene | 0.96832 | 0.00051 | -0.01695 |
| Indeno(1,2,3-cd)pyrene | 0.90905 | -0.16268 | 0.34836 |
| Benzo(ghi)perylene | 0.97860 | -0.07297 | 0.14540 |

Variance explained by each factor

| Factor 1 | Factor 2 | Factor 3 |
|---|---|---|
| 10.064831 | 2.429697 | 1.319529 |

Final Communality Estimates: Total = 13.814058

* Lead corrected for trend

Anholt/6008
Factor Pattern

| | Factor 1 | Factor 2 | Factor 3 |
|---|---|---|---|
| Si | -0.42564 | 0.71121 | 0.52587 |
| S | -0.32108 | 0.76156 | -0.40985 |
| V | 0.11091 | 0.87199 | -0.28607 |
| K | -0.01289 | 0.87323 | 0.43667 |
| Pb* | 0.70777 | 0.37534 | -0.50100 |
| $SO_2$ | 0.95349 | 0.09700 | 0.17655 |
| Fluoranthene | 0.93761 | 0.01474 | -0.12982 |
| Pyrene | 0.93335 | 0.11811 | -0.10097 |
| Benzo(b+j+k)fluoranthene | 0.96254 | -0.06954 | 0.22797 |
| Benzo(e)pyrene | 0.97078 | 0.01766 | 0.09574 |
| Benzo(a)pyrene | 0.84134 | -0.06273 | 0.04299 |
| Indeno(1,2,3-cd)pyrene | 0.98060 | 0.05650 | 0.09520 |
| Benzo(ghi)perylene | 0.98212 | 0.02724 | 0.09155 |

Variance explained by each factor

| Factor 1 | Factor 2 | Factor 3 |
|---|---|---|
| 7.959948 | 2.786164 | 1.106685 |

* Lead corrected for trend

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