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Traffic PAH and Other Air Pollutants in the Center of a Large City

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Abstract The presence of particulate PAH and mutagens and other air pollutants (soot, particles, CO, NMHC, NO, gas NO_y, SO_2, particulate metals, sulphate, chloride and bromide) was investigated in a busy street (60,000 vehicles each day) in Central Copenhagen and in a park-area adjacent to the street in the period January - March.

The concentrations of benzo(a)pyrene and benzo(e)pyrene (BeP) were 4.4 ± 1.2 and 4.4 ± 0.7 ng/m^3, respectively, in the busy street and 1.4 ± 0.6 and 1.3 ± 0.3 ng/m^3, respectively, in the park area. Applying BeP as PAH indicator the traffic contribution was estimated to be 80 % in the street. The weekdays distribution was as follows:

Working days: 90 %. Weekends: 60 %.

In the city park area the working days traffic contribution was estimated to be 40 %.

The simple chemical mass balance method performed to do these estimates applying the ratio between benzo(ghi)perylene and BeP and that between coronene and BeP was demonstrated as a control to give a satisfactorily description of the PAH contribution from traffic sources and from other sources in different cases:

A city traffic PAH profile was determined. The busy street PAH profile was very close to the city traffic one. The diurnal variation of PAH showed peaks in the morning and afternoon rush hours and the lowest concentrations in the night hours and was very close to the diurnal variation of the traffic gases, CO, NO and gas NO_y.

A method to differentiate between PAH contribution from petrol vehicles and those from diesel vehicles was developed and applied. It is concluded the PAH contributions from petrol vehicles and from diesel vehicles are comparable.

Contents

Preface

For many years it has been well known, that the group of Polycyclic Aromatic Hydrocarbons (PAH) contain several components with mutagenic and/or carcinogenic effect. 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 traffic is an important contributor. 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. Evaluation of the traffic contribution to PAH-emission, including a split between petrol and diesel driven vehicles
2. Determination of the PAH-level at different locations in Denmark..
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), Agency of Environmental Protection, City of Copenhagen (EPA) 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)
	Per Wrang
IT:	John Chr. Larsen
	Preben Aagaard Nielsen (part of time)
	Morten Poulsen (part of time)
EPA:	Jan Tønnesen
	Raymond Skaarup
dkT:	Allan Bang Jensen
DTU:	Jesper Schramm (part of time)

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 (DEPA, 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 (Risø-R-787, 1995).
2. Atmospheric PAH in Denmark (NERI No. 124, 1995).
3. Mutagenic activity in the center of Copenhagen (Technical Report No. 4, National Food Agency, 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.

1 Introduction

Polycyclic aromatic hydrocarbons (PAH) consists of carbon and hydrogen and can be conceived as consisting of fused rings of benzene. PAH belongs to the group of polycyclic organic matter (POM). Besides PAH, POM covers azaarenes, oxaarenes, thiaarenes and transformation products of these and PAH, e.g. nitro derivatives and quinones. Azaarenes, thiaarenes and oxaarenes can be conceived as a PAH, where a carbon atom in the ring system is replaced with a nitrogen, a sulphur and an oxygen atom, respectively. The environmental concern of PAH and other POM is caused by several of them are carcinogens and are present in polluted air. The compounds are formed by combustion, e.g. of petrol, oil and wood. In a historical view the interest started in the previous century by the discovery of the many cases of occupational skin cancer, e.g. workers in tar production. In 1933 the first carcinogenic PAH, benzo(a)pyrene (BaP), was identified in tar (Finlayson-Pitts and Pitts 1986).

The larger PAH (5 - 7 rings) covering most of the carcinogens are associated with particles in the atmosphere. Part of the 3 and 4 rings PAH is also present in ambient air in vapour phase (Nielsen and Pilegaard 1990). Oxa-, thia- and azaarenes have similar distribution between gas phase and particle association as PAH. Substituted PAH, e.g. quinones and nitro derivatives, have lower volatility than the parent PAH. A larger proportion of the 3 and 4 rings of these are associated with particles. The major part of the mutagens in ambient air have been shown to be particle-associated, bu the gas-particle distribution is dependent of the temperature and the pollution level (Fenger et al. 1990, Nielsen and Nielsen 1994).

Previous Danish investigations (Fenger et al. 1990, Nielsen and Nielsen 1994, Nielsen 1989, Nielsen and Pilegaard 1990, Ostenfeldt 1989) have shown ambient air measurements of PAH as well as measurements of the content of mutagenic activity are applicable indicator methods to investigate the content of carcinogens in ambient air. Several epidemiological investigations have tried to determine the influence of air pollution on the number of cancer incidents in the population. It appears 1 - 10 % of the incidence of lung cancer is caused by air pollution (Doll and Peto 1981, Speizer 1986). It is not the purpose of this report to evaluate these investigations, but it is an important, but unfortunately disregarded aspect, that the ambient air pollution with POM in the eighties and nineties has a relative lower content of unsubstituted PAH compared to the air pollution in the fifties and sixties and the air pollution in the working environment (Holmberg and Ahlborg 1983).

Several sources may contribute to the air pollution with PAH and other POM compounds, e.g. traffic, oil heating, wood stoves, municipal incinerators and industry. Also long-range transport of pollution from other countries may occur. In order to determine the importance of different sources the relative PAH composition of ambient air samples have been compared with that in exhaust and stack gases. Thus Sawicki (1962) and Brasser (1983) applied the ratio of pyrene to BaP, that of benzo(ghi)perylene to BaP and that of coronene to BaP to determine the contribution from traffic and that from domestic coal heating. In recent years, PAH emissions from traffic also has recognized attention as a tracer for pollution from traffic in connection with the phase-out of lead in petrol (Daisey et al. 1986). Many investigators have suggested that compositional differences in PAH resulting from the combustion of different fuels can be exploited for source identification (Daisey and Lioy 1981, Daisey et al. 1986, Gordon and Bryan 1973). In Denmark it is agreed that traffic, domestic heating and long-range transport is important sources of PAH and other mutagens (Fenger et al. 1990, Gudmundsson

1988, Kemp 1989, Nielsen and Nielsen 1994, Nielsen 1989, Nielsen and Pilegaard 1990, Nielsen et al. 1993, Ostenfeldt 1989). In a minor number of incidents PAH contribution from wood-stoves has been recognized in suburban areas (Nielsen 1989, Nielsen and Pilegaard 1990, Nielsen et al. 1993, Ostenfeldt 1989).

The purpose of this investigation was to determine the PAH traffic contribution in a busy street and to do at least a semiquantitative distinguishment beteeen the contribution from petrol vehicles and diesel engines. The PAH pollution was determined in a busy street (H. C. Andersens Boulevard) and a city park area close to the busy street (Tivoli). Besides PAH samples were collected in a bus street and a bus garage to provide informations on the PAH composition in the emissions from diesel engines. In the busy street and the city park area the following compounds were also determined: NO, gas NO_y, CO, NMHC, SO_2, particulate matter, soot, particulate mutagens, sulphur, chloride, bromide and metals. The PAH contribution from petrol and diesel engines have been determined by means of (a) factor analysis, (b) PAH composition (c) the busy street to city park ratio (d) weekdays variation (e) diurnal variation. A city traffic PAH profile has been determined. The results are detailed discussed in relation to the observations on inorganic components.

2 Measuring Program and Sites

The content of particulate PAH and mutagens was determined at four sites, a busy street in the Central Copenhagen, a site in a city park a few hundreds of meters from the busy street, a bus street in the Central Aarhus and a busgarage in the outskirts of Copenhagen.

Samples at the two latter sites were collected to determine the PAH profile in the exhaust from diesel vehicles. This programme only included PAH and mutagenicity determinations and only a minor number of samples was analyzed.

The major programme covered the **busy street** (H.C. Andersens Boulevard) and the **city park area** (Tivoli). The two sites were selected close to each other. The reason to this was based on the assumption that the two sites are expected to receive the same contribution of air pollutants from non-traffic sources, i.e. heating sources and long-range transport. By that any difference in air pollution level between the two sites can only originate from the different influence from traffic sources, where the traffic contribution at the busy street is larger than that in the city park area. The traffic intensity in the street was 60,000 cars each day, but also the streets in the neighbourhod had high traffic intensities. The street is situated north-south. The measuring station was at the eastern site of the street. The station has for many years been applied in Communality and regional air quality programmes (HLU 1993, Jensen et al. 1993, Municipality 1990). Measurements of PAH and mutagens have been performed earlier at this site (Nielsen 1989, Ostenfeldt 1989). The measuring programme was performed in the winter period (January - March), as this is often the period of the year with the highest air pollution levels.

The eastern part of the **city park** made up the west side of the street. The sampling station was placed at the location called Plænen, a bit north of the center of the city park. The city park is an amusement park in the summer period having an international reputation. No comparison of the air quality situation in a busy street and a city park area has been performed earlier in Denmark.

As shown in Table 1 a detailed characterization of the air quality was performed in the busy street and the city park area. The NMHC measurements were

the first ones of this kind in Denmark performed in a street.

The **bus street** was situated in the centre of a large town, Aarhus. A sunken road led to a covered street with stops for several bus lines and the monitor was placed close to the stops in the sunken road. Busses were the only cars within the first hundred meters of the sampler.

The **bus garage** was situated in an open area in the outskirts of Copnehagen. The monitor was placed near the workshop at the entrance to the parking area. For most wind directions and in windy conditions the influence from exhaust gases was moderate.

The winters in 1992 - 1994 were very mild, blowing and rainy almost without snow and with only a few days with temperatures below 0^0C. The measurements within this investigation were performed with a mean temperature of 2.7 ^0C. The dominant wind direction was that from west (51 %), followed by winds from south (22 %), north (16 %) and east (10 %). The wind direction distribution is typical for a mild winter. The wind speeds were typically 5 - 6 m/s. The westerly winds had the highest wind speeds (mean: 6.2 m/s) and the northerly winds the lowest wind speeds (mean: 4.3 m/s), although the difference is only minor. The wind speed and the ambient temperature was anticorrelated and a significant negative correlation was observed between these (r = -0.40, p < 0.001). In general, the weather was mild with winds from south (mean temperature: 3.7 ^0C) and west (mean temperature: 3.5 ^0C) and cold with winds from north (mean temperature: -0.5 ^0C) and east (mean temperature: 0.4 ^0C).

The local wind directions at the two sites were determined by the topography of the city and the dominant wind directions at both sites were those from south and north. The roughness of the surfaces caused the local wind speeds to be 3 - 4 times lower than that measured outside the city for all wind directions.

Table 1. Survey of the measuring program and the sites

Compounds	Busy street	City park	Bus street	Bus garage	Average time
Period	Jan.-March 92, Febr.-March 93	Jan.-March 92	Jan. 93	Nov. 92	
PAH	x	x	x	x	2-24 h
Mutagens	x	x	x	x	8-24 h
CO	x	x			30 min.
NO and gas NO$_y$*	x	x			30 min.
SO$_2$	x	x			30 min.
NMHC	x				60 min.
Soot	x	x			24 h
Particles	x	x			24 h
Metals	x	x			24 h
No. of PAH samples	88	50	5	6	

*Gas NO$_y$ is the sum of oxidized nitrogen compounds NO + NO$_2$ + HNO$_2$ + HNO$_3$ + PAN + PPN + NO$_3$ + 2 * N$_2$O$_5$ + gas phase organic nitrates. NO$_x$ = NO + NO$_2$ makes up typically 90 - 100 % of gas NO$_y$ in street air. In background areas the NO$_x$ proportion may be 50 - 75 % or even lower. For further details, see Nielsen *et al*. (1994).

3 Sampling and Analysis

Polycyclic aromatic hydrocarbons and mutagens: 24-h and in a minor number of cases 2 to 14-h samples of airborne particulate matter were collected using conventional Hi-Vol samplers with glass fibre filters. The sampling volumes were typic in the range 500 - 1500 m^3. Intercomparisons of the Hi-Vol samplers have earlier showed satisfactory results (Nielsen 1984b, Nielsen and Pilegaard 1990, Ostenfeldt 1989). The filters were stored in a freezer (-18 ^0C) untill the analysis.

The filters were extracted ultrasonically 3 times, 30 min. each time, with dichloromethane (*p.a.* Merck). The collected extracts were divided in two equal parts. One part was concentrated to 5 ml and applied to the mutagenicity tests. The concentration was performed in two steps: (a) Reducing of the solvent volume by rotary evaporation under reduced pressure at room temperature, (b) Concentration to 5 ml under pure nitrogen at 40 ^0C.

The other part was added known amounts of *m*-terphenyl, β,β'-binapthyl and benzo(c)-chrysene (internal standards) and concentrated to 0.25 ml. 1.5 ml *n*-hexane (Merck zur Rückstandsanalys) was added. The PAH fraction of the solution was isolated by means of (a) high-performance liquid chromatography (HPLC) (b) liquid-liquid extraction with a cyclohexane-dimethylformamide-water system.

(a) The 1.75 ml *n*-hexane-dichloromethane solution was fractionated by means of HPLC using *n*-hexane:dichloromethane (6:1) (2.0 ml/min) as eluent. The HPLC columns were packed with Nucleosil-Si-50-5. The PAH fraction was collected. The more polar POM compounds were washed out of the column system applying dichloromethane as eluent. The system was equilibrated with 60 ml *n*-hexane:dichloromethane (6:1) before the next fractionation was performed.

(b) The collected PAH fraction was concentrated to 1 ml. 2.0 ml cyclohexane (*p.a.* Merck) was added, and the solution was concentrated to 1.00 ml. The PAH in the concentrated cyclohexane solution was extracted with two 1.00 ml portions of water:dimethylformamide (*p.a.* Fluka) (1:9) by shaking for 10 min. each time. Then 1.80 ml water was added to the combined dimethylformamide extracts, and the PAH in the dimethylformamide:water solution was extracted with two 4.0 ml portions of cyclohexane by shaking for 10 min. each time. The combined cyclohexane phases were washed with 2.0 ml of water by shaking for 10 min., and concentrated to 0.20 ml. No direct determination of the recovery of the internal standards was performed. But comparisons of the GC gas chromatograms of the samples with those of a solution of the three internal standards suggested the recoveries of *m*-terphenyl and β,β′-binaphthyl were typical in the range 80 - 95 % and those of benzo-(c)chrysene in the range 90 - 100 %. Benzo(c)chrysene was applied as an internal standard for the higher PAH (5-7 rings).

The PAH samples were analyzed by capillary gas chromatography with on-column injection, a fused silica column coated with a methyl-silicone gum (SE-52, MEGA, crossbound, 25 m * 0.32 mm i.d., film thickness 0.1 - 0.15 μm) and flame ionization detection. The oven was programmed for 65 - 310 ^{0}C with 4 ^{0}C/min, 310 - 335 ^{0}C with 8 ^{0}C/min, and a constant temperature on 335 ^{0}C in 10 min.

CO: CO was determined by means of infrared light absorption in a two-channels instrument (Fuji Electric, ZRC) each 30 min. The absorption of the polluted air was determined in a measuring cell and in a reference cell. In the latter CO was transformed to CO_2 and the difference in the absorptivities was applied to calculate the CO concentration.

NO and gas NO_y: Measurements of NO and volatile NO_y were performed by a two chamber chemiluminecence monitor (Monitor Labs, 8840) each 30 min. The conversion of NO_y to NO was made by passing the filtered gas sample through 315 ^{0}C molybdenum chips. All oxidized N-species should be converted to NO (Nielsen *et al.* 1994). The converter efficiency was determined by gas phase titration of NO with O_3. The accuracy was within 1 - 2 %. The calibration was made with a reference gas diluted with zero air to the concentrations needed.

SO_2: SO_2 was determined by its fluorescence emission by irradiation of the polluted air sample with UV light (Monitor Labs, 8850). Light from a zinc lamp was sent through an interference filter (passing 214 nm light) into the measuring cell from where the fluorescence pass through a filter (passing 250 - 390 nm light) into a photomultiplier. The signal is proportional with the SO_2 concentration. The aromatic organic compounds (e.g. volatile PAH) which may give a false positive were removed by a scrubber. The calibration was made with a reference gas (Messer Griesheim, 12 ppm ± 2 %) diluted with zero air to the needed concentrations. The dilution was made by two mass flow controllers which were checked every 6 months with mercury sealed piston volumeters. The reference gas was regularly compared to a SO_2-permeation tube which permeation rate was

determined by weighing every two weeks. Corrections for atmospheric pressure variations were neglected calibrating the monitors.

NMHC: NMHC was determined by flame ionization detection (AAL-instrument, 526). The content of NMHC was removed by filter and the content of CH_4 was determined in a 4 min. period each hour. In the rest 56 min. the total content of volatile hydrocarbons was determined. The concentration of NMHC was achieved as the difference.

Particles: Particles were sampled on filters during 24h periods with an air flow volume of 60 m^3. The pore size of the filter was 1.2 μm. The filters were mounted in a filter holder having a 80 mm long mounter tube of 40 mm diameter pointing downwards. By that the filter is protected against rain, snow and sunshine. Each filter was conditioned and weighed before mounting in the filter holders. The filters in the filter holder was shifted once each week. After sampling the filters were conditioned in a week and then weighed. The particle concentration was determined as the weight difference divided by the flow volume.

Soot: Soot was collected on filters according to the well known OECD method applied as the standard method in many European countries. The sample flow was only 2.5 m^3 each day with a small inlet velocity in the sampling head. The darkness of the exposed filter was measured by reflectometric measurements.

Metals: The concentrations of elements on the filter samples were determined by ICP-MS (Inductively Coupled Plasma Mass Spectrometry) and PIXE (Proton Induced X-ray Emission Spectroscopy) (Jensen *et al.* 1992). A part of the filter sample corresponding to 15 m^3 was cut off and applied to the PIXE analysis. The rest of the filter sample corresponding to 45 m^3 was performed by ICP-MS. The ICP-MS determinations were performed by Per Solgaard, Risø National Laboratory, and the PIXE determinations by Kåre Kemp, National Environmental Research Institute. The results from the ICP-MS determinations and PIXE determinations were intercompared and agreed satisfactorily.

ICP-MS. The particle filter corresponding to 45 m^3 was brought into solution by digestion with HNO_3 and H_2O_2 in autoclave at 140 ^{0}C for 16 h. The clean solution were diluted and analysed on a Plasma Quad instrument from VG Elemental. The mass spectrum was scanned from 45 a.m.u. to 210 a.m.u. to cover elements from Sc to Pb including Rh and Re used as internal standards. The quantitative analysis was based on standard curves from external standard solutions.

In the PIXE analysis the particle filters were exposed to protons of high energy (2.5 MeV). The protons ejected electrons from the inner orbits and less bound electrons filled up the holes under emission of X-rays. The energy of the X-rays was characteristic for the elements from which they were emitted and the intensity was a measure for the amount of the element. By analysis of the X-ray spectrum it was possible simultaneously to determine all elements present above the detection limits and having an atomic number higher than 12 (aluminium and higher). The detection limits obtained were 2 ng/m^3 and higher by proton radiation in 2 min. for each filter. In most cases more than 15 elements could be determined.

4 Results and Discussion

4.1 General Air Pollution in the Measuring Period in a Central Busy Street and a City Park

Comparison of Inorganic Air Pollution Components in the Busy Street and in the City Park

Table 2 shows the 24-h levels of airborne inorganic components in the busy street and in the city park area in the period January - March 1992 and the ratio between the average levels of the inorganic components at the two sites. Besides, the average level of non-methane hydrocarbons (NMHC) in the busy street is also reported.

The highest ratios (3.2 - 5.2) between the **busy street** levels and the **city park** levels (**BS to CP** ratio) are observed for the group of compunds known to originate from traffic, *i.e.* CO (5.2), NO (4.8), Cu (4.7), Pb (3.7), Br (3.4) and gas NO_y (3.2), and from salting of the road (Cl, 4.7) to provide a non-freezing road-surface on days with frost.

NO and gas NO_y are gases primarily emitted from all kinds of vehicles. CO is primarily emitted from cars using petrol. Pb and Br are formed by the thermal decomposition of tetraalkyl lead compounds and the lead scavenger, ethylene dibromide, and by that emitted from vehicles using leaded petrol (Nielsen 1984a). A major source of particulate chloride had been resuspension of NaCl used for salting. The highest concentrations of Cl was observed on days with frost. An additionel source had been $PbCl_2$ from the combustion of leaded petrol containing the so-called lead scavenger, ethylene dichloride or 1,2-dichloroethane. Cu is not generel assumed to be a traffic associated component. But Maenhut *et al.* (1990) observed that particulate copper was intercorrelated with the content of particulate lead in filter samples of the street air in suburbs and the center of Brussels. About 72% of the total copper was estimated to originate from traffic source, the second source was soil dust (perhaps resuspension) (23 %). Also Danish observations support atmospheric Cu to originate from traffic sources (Keiding *et al.* 1986).

Two factors may decrease the street to park ratio for traffic air pollutants:

1) The contribution from outside city sources.
2) Biogenic emissions.

Three factors may increase the street to park ratio:

1) Chemical transformation.
2) Deposition.
3) Resuspension on the streets.

Although the deposition rates of gas NO_y (mainly NO_2 (Nielsen *et al.* 1992), particulate lead, bromide and copper are higher than those of NO and CO (Hewitt and Rashed 1991, Hummelshøj 1994) the two most important factors appear to be contribution from outside city sources and chemical transformation. The contribution from outside city sources is difficult to estimate as appropiate coincident measurements of CO in a background area is not available. Previous measurements (Fenger *et al.* 1990, Jensen and Stenfalk 1992, Nielsen and Pilegaard 1990) in a village 20 km outside of Copenhagen may perhaps suggest the contribution of CO from outside city sources is minor than that of gas NO_y species. Trans

Table 2. Comparison of NMHC and airborne inorganic components in the busy street and the city park area and the ratios between the air pollutant averages at the two sites for coincident measurements.

Compound	Busy street	City park area	BS to CP ratio	No. of BS samples	No. of CP samples
NO (ppb)	133 ± 13	28 ± 5	4.8	86	78
NO₂ (ppb)	164 ± 14	52 ± 6	3.2	86	78
SO₂ (ppb)	7.4 ± 0.7	4.4 ± 0.7	1.7	86	78
CO (ppm)	1.96 ± 0.14	0.38 ± 0.04	5.2	86	78
NMHC (ppm)	0.54 ± 0.05				78
Soot (µg/m³)	56 ± 5	23 ± 3	2.4	78	78
Particles (µg/m³)	94 ± 8	60 ± 6	1.6	78	78
Chloride (µg/m³)	5 ± 3	1.2 ± 0.6	4.3	23	23
Sulphate (µgS/m³)	2.7 ± 0.4	1.9 ± 0.3	1.4	27	27
Aluminium (µg/m³)	0.63 ± 0.16	0.28 ± 0.13	2.3	27	26
Calcium (µg/m³)	1.9 ± 0.4	0.75 ± 0.17	2.5	27	27
Iron (µg/m³)	1.7 ± 0.3	0.76 ± 0.16	2.2	27	27
Lead (µg/m³)	0.23 ± 0.04	0.062 ± 0.012	3.7	27	27
Potassium (µg/m³)	0.32 ± 0.05	0.22 ± 0.04	1.5	27	27
Zinc (µg/m³)	0.12 ± 0.02	0.051 ± 0.014	2.2	27	27
Silicon (µg/m³)	2.0 ± 0.5	0.7 ± 0.2	2.9	27	25
Bromide (ng/m³)	48 ± 9	14 ± 2	3.4	27	27
Antimony (ng/m³)	17 ± 4			11	
Barium (ng/m³)	49 ± 10	23 ± 7	2.2	24	10
Chromium (ng/m³)	14.6 ± 1.8	11.1 ± 1.2	1.3	27	27
Copper (ng/m³)	57 ± 9	12 ± 2	4.7	27	27
Manganese (ng/m³)	43 ± 8	14 ± 4	3.0	27	27
Molybdenum (ng/m³)	5.5 ± 1.5	2.3 ± 0.6	2.5	11	6
Nickel (ng/m³)	6.1 ± 1.1	5.7 ± 1.1	1.2	26	27
Strontium (ng/m³)	9.4 ± 1.8	5.5 ± 1.5	1.7	27	27
Tin (ng/m³)	9 ± 4	4.6		3	1
Titanium (ng/m³)	100 ± 19	38 ± 10	2.6	27	27
Vanadium (ng/m³)	12 ± 2	10 ± 2	1.2	23	24
Zirconium (ng/m³)	5.4 ± 1.1	3.0 ± 0.7	2.6	14	9
Platinum (pg/m³)	13 ± 10			1	
Season	January - March	January - March			

formation of a species will increase the street to park ratio, e.g. the transformation of NO to NO_2 by oxidation with ozone. This may be a reason to the street to park ratio of NO (4.8) is higher than that of gas NO_y (3.2). The reaction between ozone and NO is also the reason to that the difference between gas NO_y and NO (representing an upper limit for the NO_2 concentration (Nielsen *et al.* 1992)), is almost the same at the two sites, 31 ppb at the BS station and 24 ppb at the CP station. The difference on 7 ppb fits very well with an expected emission ratio between NO_2 and NO on 0.05.

The comparison of the inorganic traffic components levels at the two Copenhagen sites suggests the ratio of traffic component should be in the range of 4 (see also Section 4.3). The soot ratio (2.4) is lower than this suggesting other sources than traffic contributes to the soot content (see also the next section).

The distribution of gas NO_y from diesel vehicles and from petrol vehicles is calculated to be 55 to 45 assuming a gas NO_y (ppb) to CO (ppm) ratio in the atmosphere to be 90 and using following emissions ratios (R. Berkowicz, 1994, private communication):

gas NO_y (ppb)/CO (ppm) = 3.9 for diesel vehicles
gas NO_y (ppb)/CO (ppm) = 0.04 for petrol vehicles (without catalysts).

One group of compounds had BS to CP ratios relatively close to 1.0 showing their levels are about the same in the busy street and in the city park area, that is Ni (1.2), V (1.2), Cr (1.3), particulate sulphur (mostly sulphate) (Granby *et al.* 1994) (1.4), K (1.5) and SO_2 (1.7). The major sources of these compounds are non-traffic sources, *i.e.* Ni, V, particulate sulphur and SO_2 (heating, power plants and long-range transport from the Continent), Cr (industry) and K (power plants) (Jensen *et al.* 1993).

SO_2 had a different diurnal variation compared to that of CO, NO and gas NO_y. SO_2 had a maximum level in the early afternoon hours and a minimum level in the night hours, while CO, NO and gas NO_y had peaks in the morning and late afternoon traffic rush hours and minimum in the night hours. This suggests that the SO_2 emission primarily can be attributed to industry, power generation and heating with a typical daytime maximum and minor dependence on week days. However, SO_2 is not a good component for source identification. Other sources may be medium and long-range transport independent of local human activities, but probably depending of the growth of the day-time boundary layer, as well as a minor contribution from diesel engines.

The third group of compounds, called the resuspension group in the following sections, had BS to CP ratios between 2 and 3, despite none of the compounds are emitted from traffic sources. They were Al (2.3), Ca (2.5), Fe (2.2), Zn (2.2), Si (2.9), Ba (2.2), Mn (3.0), Mo (2.5), Ti (2.6) and Zr (2.6). Plotting the BS to CP ratios of particulate inorganic components towards Danish literature values of mass median diameter for the same compounds (Flyger *et al.* 1976) (see Fig. 1) revealed, the non-traffic related components in the third group had a higher mass median diameter than the non-traffic related compounds in the second group (V, Ni, S and K). Therefore, it is suggested the apparent traffic relation of the compounds in the third group is brought about by resuspension of road dust caused by the turbulence of the traffic in the street. Also, it is suggested road dust is enriched by the compounds in group 3 compared to the compounds in group 2. This enrichment appears reasonable, as the compounds in group 3 have higher deposition velocities than those in group 2 caused by the increase in particle diameter (Hummelshøj 1994). Applying the correlation between a certain compound, e.g. PAH, and the compounds in group 3 for source evaluation, it is important to have in mind that an uncritical use of the correlations will lead to an underestimate of the traffic contribution of e.g. PAH.

The data in Table 2 and Fig. 1 also suggest deposition and resuspension of the

components on small particles has only a minor effect on the air level of these compounds. First the BS to CP ratios of Cu (4.7), Pb (3.7) and Br (3.4) are not higher than that of the traffic related gas component CO (5.2) (CO is chosen as a reference value, as CO has an extreme low deposition velocity compared to that of NO_2 and most other gas NO_y compounds). Second the BS to CP ratios of the second group (Ni (1.2), V (1.2), S (1.4) and K (1.5)) are close to 1.0 and not higher than that of the gas component SO_2 (1.7) (part of the difference in the BS to CP ratios of Ni, V, S and SO_2 and 1.0 might be caused by emissions from diesel vehicles). Based on the results in Table 2 and Fig. 1, it is also suggested that deposition and resuspension of particle-associated PAH has only a minor effect on the air pollution levels of PAH. The deposition fluxes of PAH have been shown to be minor than those of particulate lead (Hewitt and Rashed 1991).
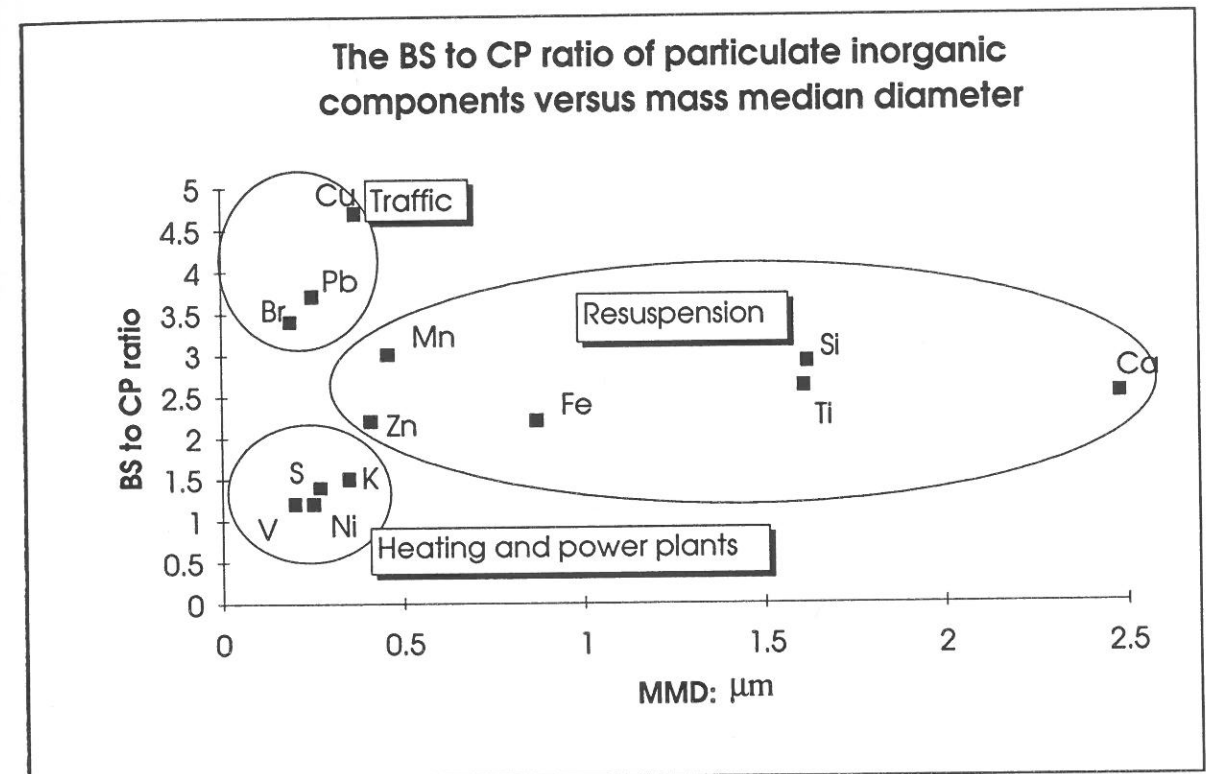

Figure 1. The ratio between the busy street (BS) concentrations and the city park (CP) concentrations of particulate inorganic components compared to their mass median diameter (µm) determined by Flyger et al. (1976).

Differences in Air Pollution Between Working Days and Weekends

Fig. 2 shows the following four ratios for the six different groups of air pollutants:
Working days busy street content (WOBS) to weekend busy street content (WEBS),
Working days city park content (WOCP) to weekend city park content (WECP),
Busy street weekends content (BSWE) to city park weekend content (CPWE),
and busy street working days content (BSWO) to city park working days content (CPWO).

Table 3 shows the working days content and the weekend content of NMHC and inorganic components in the busy street and in the city park area.
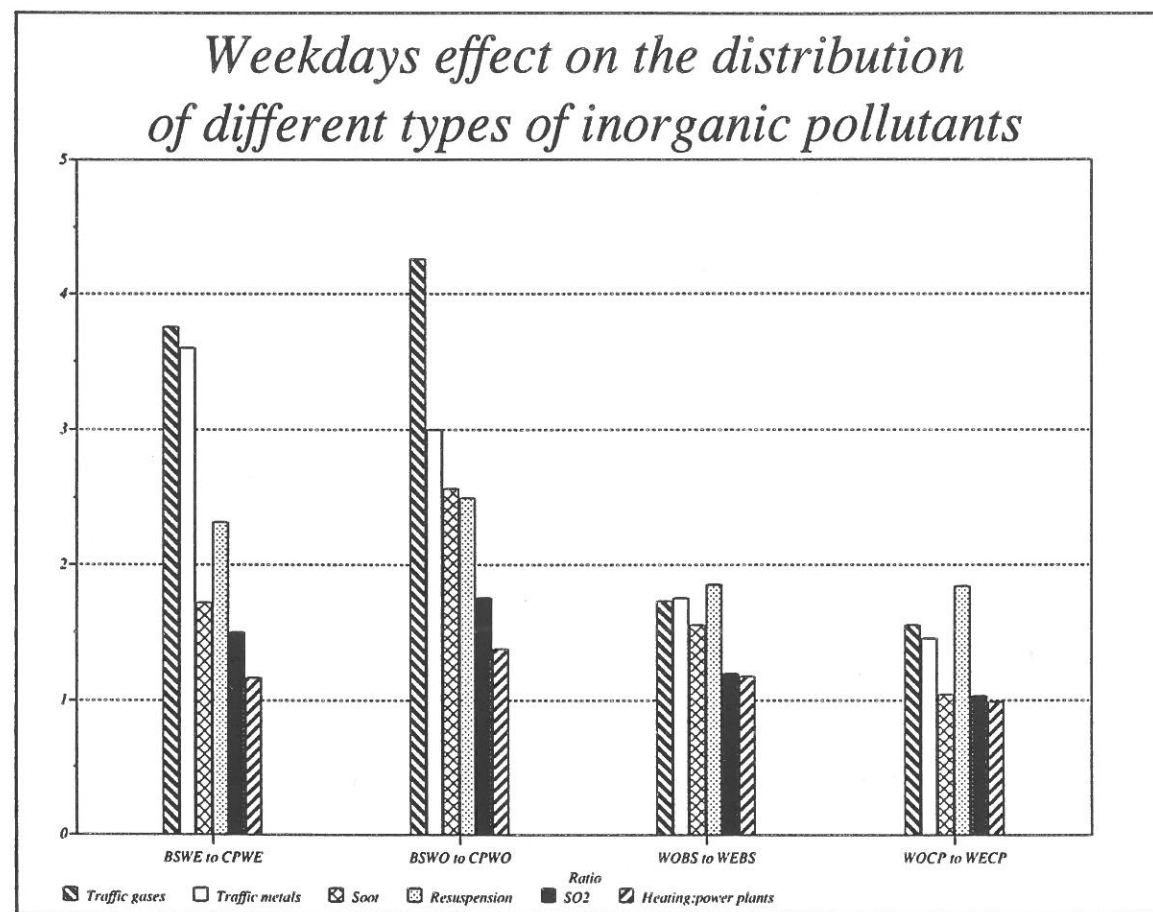

Figure 2. Comparison of the ratios of different group of inorganic pollutants on working days (WO) and weekends (WE) at the busy street (BS) and the city park (CP). The group are the following:
Traffic gases (NO_y, CO and NMHC),
Traffic metals (Pb, Cu and Br),
Soot,
Resuspended metals (Mn, Zn, Fe, Ti, Si and Ca),
SO_2 and
Heating and power plants particulate components (SO_4^{2-}, V, Ni, K)
(see also Fig. 1).

Table 3. Comparison of the working days content and the weekend content of NMHC and inorganic components in the busy street and in the city park area.

Compound	Busy street Working days*	Busy street Weekends**	City park area Working days*	City park area Weekends**
NO (ppb)	146 ± 17	74 ± 12	31 ± 6	13 ± 4
NO$_x$ (ppb)	178 ± 18	100 ± 14	56 ± 8	35 ± 9
SO$_2$ (ppb)	7.2 ± 0.6	6 ± 2	4.1 ± 0.7	4 ± 2
CO (ppm)	2.14 ± 0.18	1.26 ± 0.08	0.40 ± 0.06	0.27 ± 0.09
NMHC (ppm)	.. 0.61 ± 0.07	0.34 ± 0.05		
Soot (μg/m³)	59 ± 6	38 ± 10	23 ± 3	22 ± 12
Particles (μg/m³)	99 ± 10	72 ± 24	61 ± 7	58 ± 20
Chloride (μg/m³)	5.9 ± 3.3	2 ± 2	1.4 ± 0.8	1.0 ± 1.6
Sulphate (μgS/m³)	2.5 ± 0.4	2.9 ± 0.6	1.7 ± 0.2	2.3 ± 0.5
Aluminium (μg/m³)	0.64 ± 0.16	0.33 ± 0.12	0.24 ± 0.08	0.18 ± 0.11
Calcium (μg/m³)	2.1 ± 0.6	1.0 ± 0.4	0.9 ± 0.2	0.37 ± 0.09
Iron (μg/m³)	1.8 ± 0.4	1.0 ± 0.4	0.8 ± 0.2	0.49 ± 0.22
Lead (μg/m³)	0.25 ± 0.05	0.16 ± 0.04	0.060 ± 0.010	0.048 ± 0.020
Potassium (μg/m³)	0.33 ± 0.05	0.24 ± 0.07	0.21 ± 0.03	0.19 ± 0.05
Zinc (μg/m³)	0.12 ± 0.03	0.07 ± 0.02	0.045 ± 0.008	0.035 ± 0.015
Silicon (μg/m³)	2.1 ± 0.6	1.1 ± 0.6	0.7 ± 0.2	0.5 ± 0.3
Bromide (ng/m³)	54 ± 11	26 ± 6	15 ± 2	12 ± 3
Antimony (ng/m³)	17 ± 4	10		
Barium (ng/m³)	54 ± 15	36 ± 14	25 ± 9	15 ± 4
Chromium (ng/m³)	15 ± 2	11.3 ± 2.0	11.1 ± 1.4	11 ± 4
Copper (ng/m³)	61 ± 11	37 ± 10	13 ± 3	7 ± 3
Manganese (ng/m³)	45 ± 10	24 ± 11	14 ± 4	10 ± 5
Molybdenum (ng/m³)	6.2 ± 2.0	3.8 ± 1.3	2.5 ± 1.1	2.1 ± 0.5
Nickel (ng/m³)	6.0 ± 1.2	4.5 ± 1.4	5.4 ± 1.2	4.6 ± 1.6
Strontium (ng/m³)	10.3 ± 2.0	5.2 ± 1.7	5.8 ± 1.8	3.2 ± 0.9
Tin (ng/m³)	13	4.7	4.6	
Titanium (ng/m³)	106 ± 24	61 ± 23	37 ± 8	24 ± 9
Vanadium (ng/m³)	11 ± 2	10 ± 2	8.0 ± 1.9	9 ± 3
Zirconium (ng/m³)	5.8 ± 1.5	3.9 ± 1.5	3.2 ± 0.7	1.3
Season	January - March	January - March	January - March	January - March

*: Monday 10 am - Friday 10 am
**: Saturday 10 am - Sunday 10 am

The compounds have been divided in six groups in Fig. 2:

Traffic gases, *i.e.* CO and gas NO_y,
Traffic metals, *i.e.* Pb, Br and Cu,
Soot,
Resuspension group, *i.e.* Zn, Mn, Fe, Si, Ti and Ca,
SO_2,
and particulate components from heating sources and power plants, *i.e.* V, S, Ni and K.

Table 3 and Fig. 2 confirm the previous observations on the influence of the traffic on the levels of the components in the resuspension group. Thus their air pollution levels are almost a factor of two higher at both sites on working days with a high traffic intensity than in

weekends with a low traffic intensity. The BSWO to CPWO ratio (2.5) was almost the same as the BSWE to CPWE ratio (2.3). This reflects the working activities in the city park area on the working days also had caused resuspension of the components in the resuspension group. Otherwise, the BSWO to CPWO ratio should have been higher than the BSWE to CPWE ratio.

The content of the traffic components (CO, gas NO_y, Pb, Br and Cu) in the weekends was 57 % of that on the working days in the busy street. In the city park area the weekend content was 67 % of the working days content.

No weekend effect was observed on SO_2 and the other components originating from heating sources and power plants (V, Ni, S and K). Their ratios were close to 1.0 at both sites. In the busy street the ratios were about 1.2 and in the city park area the ratios were about 1.0.

Soot showed a mixed behaviour compared to that of the traffic components and that of the heating sources and power plants components. In the situations with heavy traffic (WOBS to WEBS ratio and BSWO to CPWO ratio) the soot ratios (1.6 and 2.6, respectively) were close to the traffic components ratios (1.75 and 3.0 - 4.3, respectively) showing the traffic as a source for soot. In the situations with minor traffic (WOCP to WECP ratio and BSWE to CPWE ratio) the soot ratios (1.05 and 1.7, respectively) were close to those of the heating sources and power plants components (1.0 and 1.2 - 1.5, respectively) showing other sources also are important soot sources.

Presence of NMHC and Correlation with Other Components

The investigation included the first measurements of NMHC in a busy street in Denmark. The average level of NMHC was 0.54 ± 0.05 ppm (see Table 2) and the weekend levels were 56 % of those on the working days (see Table 3). The latter value was almost the same as that observed for the traffic components (57 %) (CO, gas NO_y, Pb, Cu and Br) showing the traffic is the dominant NMHC source.

The investigation of the correlations between NMHC and the other components also confirmed this.

For the traffic gases the following correlations were observed:

NMHC (ppm) = (0.26 ± 0.03) * CO (ppm) + (0.03 ± 0.15), r = 0.77, p < 0.001,
NMHC (ppm) = (0.0033 ± 0.0002) * NO (ppb) + (0.10 ± 0.11), r = 0.88, p < 0.001
NMHC (ppm) = (0.0032 ± 0.0002) * NO_y (ppb) + (0.02 ± 0.11), r = 0.88, p < 0.001

Besides of these, NMHC showed significant positive correlations with all the other components being influenced of the traffic:

Traffic metals (Pb, Cu and Br): r = 0.73 - 0.81, P < 0.001
Soot and particles: r = 0.52 - 0.74, p < 0.001

Resuspension group (Fe, Ca, Si, Ti, Zn and Mn): r = 0.57 - 0.81, p < 0.01 to 0.001
Traffic PAH indicators (BghiP and Cor): r = 0.57, p < 0.001
DieselBeP, defined as BeP * ((MePh/Ph)-0.7)/4.8)): r = 0.51, p < 0.001
Other PAH indicators (BeP, BaP and BbjkF): r = 0.34 - 0.56, p < 0.01 to 0.001

The pollution with NMHC was highest on days with freeze and a significant negative correlation was observed with the temperature (r = -0.28, p ~ 0.01). This appears reasonable, as the combustion of petrol are more incomplete at cold weather conditions than at warm weather conditions. Furthermore, a stable atmospheric boundary layer occurs often at cold weather conditions having an accumulating effect on the air pollution.

A comparison of the NMHC levels in the busy street with previous measurements in a suburban area (0.23 ± 0.03 ppm) and a village (0.09 ± 0.04 ppm) (Fenger *et al*. 1990, Jensen and Stenfalk 1990, Nielsen and Pilegaard 1990) also confirmed the influence of the traffic on NMHC. Also the NMHC to CO ratio at the three sites (busy street, suburban area and village) support petrol vehicles being the major source of NMHC. The NMHC to CO ratio was 0.28, 0.30 and 0.24, respectively.

The correlations between NMHC and the components from the heating source and power plants gave a mixed picture. No significant correlation was attained between NMHC and particulate sulphur, V and Ni (r = 0.15 - 0.21, p > 0.05). A significant positive correlation was attained with K (r = 0.61, p ~ 0.001), and a weak significant positive correlation with SO_2 (r = 0.30, p < 0.01). But the fact that the correlations with the components from the heating source and power plants general are weaker or not significant compared to the fact that correlations between NMHC and all the components having relations to traffic support that NMHC originates mostly from traffic sources.

Occurrence of Platinum

The removal of lead from petrol and the introduction of vehicles equipped with catalyst containing platinum caused the possibility that the population may be exposed to platinum compounds. From time to time the possible health aspects for this exposure were discussed in the news papers. But part of the discussions was based on assumptions and relevant data for the exposure of humans for platinum compounds were missing. A single filter sample was most kind analyzed free by B. Rietz, Isotope Laboratory, Risø National Laboratory. The analytic method applied is described by Xilei *et al*. 1992. Determination of platinum in environmental samples does still belong to the expensive class of analysis.

The platinum content in the air in the busy street was 13 ± 10 pg/m³. This value represents an upper limit for the exposure of the population. The filter sample was selected from a day with high pollution. The atmospheric content of other components was as following: NO 351 ppb, gas NO_y 392 ppb, CO 4.7 ppm, NMHC 0.55 ppm, SO_2 11.6 ppb and soot 125 µg/m³. Therefore, a typic level of platinum in the atmosphere in busy streets is perhaps in the magnitude of 5 - 10 pg/m³, if one compares the levels of NO, gas NO_y, CO, NMHC and soot with the average levels reported in Table 2. But the ambient air level of platinum is expected to increase as the number of the cars equipped with catalysts increases.

Alt *et al*. (1993) analyzed the platinum content in 29 filter samples at their workplace in Dortmund and found an average level of platinum on 1.3 ± 0.5 pg/m³, but did not present any data on the traffic intensity nor the presence of other traffic air pollution components. Considering the data of Alt *et al*. (1993) did not appear to be busy streets measurements, it seems reasonable they generally found a lower ratio between platinum and airborne particulate matter (0.0006 - 0.13 mg/kg) than the single Danish busy street ratio on 0.1 mg/kg. The Danish value on 0.1 appears also reasonable compared to findings of platinum in roadside dust in California (0.037 - 0.68 mg/kg) (Alt *et al*. 1993) considering vehicles equipped with catalysts have been used several years in California. On the other hand, platinum contentrations ranging from 0.073 to 0.184 mg/kg air-

borne dust in samples of airborne particulate matter from Japan (Alt *et al.* 1993) appeared a bit low compared to the Danish value considering the requirement on vehicles equipped with catalyst in Japan was legislated several years ago.

It is beyond this report to do a health risk assessment of the exposure to ambient air platinum, but platinum-containing drugs are applied in the treatment of certain types of cancer. The doses the ambient air levels of platinum may cause are several orders of magnitude lower than those given to the cancer patients, although the latter doses cannot be considered as non-toxic (B. Rietz, personal communication, 1993).

4.2 Occurrence of PAH and Other Mutagens

Busy Street and City Park Area

Table 4 shows the levels of PAH and mutagens in the busy street, the city park area, a bus street and at a bus garage. There is no Danish air quality standard for these compounds, but in Germany the annual mean value of benzo(a)pyrene (BaP) is recommended to be below 10 ng/m^3 and in the Netherlands that of BaP is recommended to be below 1 ng/m^3. WHO recommends the annual mean value of BaP to be below 1 ng/m^3 (Sloof *et al.* 1989).

The mean value of BaP covering the winter months, January, February and March, was 4.4 ± 1.2 ng/m^3 in the busy street and 1.4 ± 0.6 ng/m^3 in the city park area. Thus the busy street level of BaP appears to be higher than the air quality limit value recommended in the Netherlands, but lower than that recommended in Germany, but the seasonal variation of BaP has not been determined. Considering the BaP levels probably are highest in the winter months, it cannot be concluded the three months measurements of BaP in the city park area suggest the BaP level in the city park area should exceed the air quality limit on 1 ng/m^3 recommmended in the Netherlands.

The dominant particle-associated PAH at the two sites were benzo(b)-+benzo(j)-+benzo(k)fluoranthene (BbjkF), benzo(ghi)perylene (BghiP), chrysene+triphenylene (Chr+TP), pyrene (Pyr), methylphenanthrenes (including 4,5-methylenephenanthrene and a minor contribution from methylanthracenes) (MePh), benzo(ghi)-fluoranthene+ benzo(c)phenanthrene (BhgiF+BcP), cyclopenteno(cd)pyrene (CcdP), coronene (Cor), fluoranthene (Fl), indeno(1,2,3-cd)pyrene (IP), BaP, benzo(e)pyrene (BeP) and benz(a)anthracene (BaA).

Previous measurements (Nielsen and Pilegaard 1990) have shown BbjkF, benz(a)fluoranthene (BaF), BeP, BaP, perylene (Per), IP, picene (Pic), BghiP, anthanthrene (Anthan) and Cor only is associated with particles. 70 - 80 % of CP, BaA and ChrTP are particle-associated, 50 - 60 % of benzo(b)napto(2,1-d)thiophene (BNT) and BghiF+BcP, ca. 40 % of Pyr and Fl and ca. 15 % of phenanthrene (Ph), anthracene and MePh.

The dominant part of the carcinogenic PAH is associated with particles, it is CP, BaA, Chr, BbF, BjF, BkF, BaP, IP and Anthan (IARC 1983). Therefore, it is reasonable to limit the investigation of the PAH occurrence to the particle-associated part.

Bus Street and Bus Garage

Table 4 also shows the concentrations of particle-associated PAH in a minor number of samples in a bus street in the center of large town and at a open bus garage. The purpose with these samples was to attain results to be ascribed to heavy duty vehicles and by that to attain information on the PAH composition in the emission from this type of traffic. The PAH emission composition is dependent of several factors, e.g. the engine conditions, the driving conditions, the PAH content in the fuel and the fuel composition. The advantage of using field sampling compared to laboratory measurements using the emission from an engine is, that the sample represents an average of emissions from several vehicles having

Table 4. Comparison of the concentrations (± 2σ) of particulate polycyclic aromatic hydrocarbons (PAH) (ng/m^3) and the particulate mutagenic activity (rev./m^3) at different sites.

Compound	Busy street	City park	Bus street	Bus garage
Dibenzothiophene	0.28 ± 0.08	0.07 ± 0.02	0.13 ± 0.12	0.09 ± 0.14
Phenanthrene	2.4 ± 0.9	0.9 ± 0.5	0.63 ± 0.20	0.6 ± 0.4
Anthracene	0.6 ± 0.2	0.18 ± 0.06	0.11 ± 0.05	0.06 ± 0.06
Methylphenanthrenes	7 ± 2	1.4 ± 0.4	3.0 ± 0.4	1.2 ± 1.0
Fluoranthene	5.6 ± 1.8	1.3 ± 0.8	0.6 ± 0.3	0.5 ± 0.4
Pyrene	7.3 ± 2.0	1.3 ± 0.6	0.47 ± 0.14	0.5 ± 0.3
Benzo(b)naptho-(2,1-d)thiophene	0.55 ± 0.16	0.18 ± 0.06	0.14 ± 0.05	0.052 ± 0.020
Benzo(ghi)-fluoranthene + benzo(c)phenanthrene	7.0 ± 1.4	1.5 ± 0.5	0.76 ± 0.15	0.8 ± 0.4
Cyclopenteno(cd)-pyrene	6.1 ± 1.7	1.5 ± 0.5	0.9 ± 0.3	0.4 ± 0.3
Benz(a)anthracene	4.1 ± 1.1	1.0 ± 0.4	0.5 ± 0.2	0.7 ± 0.5
Chrysene + triphenylene	7.9 ± 1.7	2.3 ± 0.8	1.0 ± 0.3	1.0 ± 0.4
Benzo(b+j+k)-fluoranthene	9.3 ± 1.9	2.9 ± 0.7	1.6 ± 0.5	1.8 ± 0.8
Benzo(a)fluoranthene	1.5 ± 0.3	0.40 ± 0.12	0.31 ± 0.18	0.19 ± 0.05
Benzo(e)pyrene	4.4 ± 0.7	1.3 ± 0.3	0.8 ± 0.3	0.6 ± 0.2
Benzo(a)pyrene	4.4 ± 1.2	1.4 ± 0.6	0.50 ± 0.13	0.45 ± 0.20
Perylene	1.2 ± 0.4[A]	0.14 ± 0.10[B]	0.04 ± 0.04	0.05 ± 0.06
Indeno(1,2,3-cd)-pyrene	4.5 ± 0.8	1.1 ± 0.3	0.43 ± 0.14	0.49 ± 0.20
Picene	0.73 ± 0.18	0.26 ± 0.08	0.09 ± 0.03	0.077 ± 0.019
Benzo(ghi)perylene	8.0 ± 1.3	1.5 ± 0.3	0.55 ± 0.19	0.7 ± 0.3
Anthanthrene	1.6 ± 0.3	0.27 ± 0.07	0.3 ± 0.3	0.13 ± 0.05
Coronene	5.8 ± 1.1	1.1 ± 0.2	0.5 ± 0.1	0.6 ± 0.2
TA98+S9	59 ± 29[C]	19 ± 4[D]	14 ± 7	12 ± 4[E]
TA98-S9	44 ± 20[C]	14 ± 3[D]	15 ± 13	12 ± 4[E]
TA98NR	32 ± 16[C]	8.7 ± 1.7[D]	6 ± 3	9 ± 3[E]
Season	Jan. - March	Jan. - March	January	November
No. of samples	76	51	5	6

[A]: 37 samples
[B]: 16 samples
[C]: 32 samples
[D]: 21 samples
[E]: 4 samples

different fuel composition *etc*. The disadvantage is, that the sample also may contain PAH from other sources. The concentrations of PAH were low in both types of samples, approx. 15 % of the BS levels and 50 % of the CP levels. The MePh to Ph ratio was 4.8, 2.0, 3.1 and 1.6, respectively, in the bus street, the bus garage, the BS and the CP area. The high content of alkylated PAH in diesel fuel causes diesel traffic to be a major source of this type of component. By that the MePh to Ph ratio can be used to evaluate whether the bus street and the bus garage samples have been "contaminated" with PAH from other sources. The low MePh to Ph ratio in the bus garage samples suggests this to be the case. This also implies the results from these samples cannot be used as a model for diesel traffic. On the other hand the MePh to Ph ratio in the bus street on 4.8 can be considered as a lower limit of a general value for the MePh to Ph ratio from diesel traffic, see also Section 4.4.

Comparison with Other PAH Measurements in the Nordic Countries

Table 5 and Figure 3 compare the results on PAH (BaP and/or BeP) in this investigations with the others observed in the Nordic countries during the last fifteen years. Only results with an adequate information on the sampling site and the traffic intensity have been included in this survey. The presentation includes the most active laboratories in the Nordic countries in the eighthies and nineties on PAH air pollution being international acknowledged for this work, e.g. the Central Institute and the National Institute of Air Pollution in Oslo (Möller *et al.* 1982), Stockholm University (Höglund and Wädding 1984, Löfroth 1990), the Swedish Water and Air Pollution Research Institute in Gothenburg (Lindskog and Brorström 1981) and Civilforsvarets analytiske-kemiske Laboratorium in Copenhagen (Madsen *et al.* 1982). The comparison is limited to the Nordic countries, as the infrastructure, the pattern of living traditions, the legislation *etc.* is similar in these countries. But the use of wood-stoves is much higher in the other Nordic countries at some locations. Higher concentrations may be observed in countries having much heavy industry or applying less advanced combustion technologies.

Although, the sampling and analytical methods, the meteorological conditions, the positions of the sampling sites, the composition of the art of vehicles *etc.* differ in the different investigations it is possible to draw some general conclusions from the comparisons in Table 5 and Figure 3:

1) The PAH air pollution level is highest in the large cities.
2) The PAH air pollution level is highest in streets with a high traffic intensity.
3) The PAH air pollution level decreases with increasing distance, both horizontal and vertical, from the traffic sources.
   At roof level or in city park areas the PAH pollution level appears to be 3 - 4 times minor than that at the busy street.
4) The PAH air pollution level is highest in the winter months.
5) The PAH air pollution level is highest in the day hours.

Table 6 also compares the PAH air pollution levels with those of the total content of mutagenic compounds. It appears from this comparison that the PAH and the mutagenic activity content of airborne particulate matter is close related, although it is possible to divide the results in two groups:

1) Having a ratio between (BaP and/or BeP) and the TA98+S9 mutagenic activity on 0.08 - 0.09.
2) Having the same ratio on 0.15 - 0.26.

Table 5. Comparison of PAH levels on different locations in Nordic countries

City	Location	Sampling site	Season	BaP (ng/m³)	BeP (ng/m³)	Reference
Copenhagen	Busy Street Central 60,000 cars/ 24 hours	1.2 m height at the road	January-March	4.4	4.4	Table 4
Copenhagen	City park Central	1.2 m height	January-March	1.4	1.3	Table 4
Copenhagen	Street 15,000 cars/ 24 hours	1.2 m height	April		1.7	Madsen *et al.* 1982
Copenhagen	Hospital area	1.2 m height	April		0.4	Madsen *et al.* 1982
Copenhagen	Street 15,000 cars/ 24 hours	Roof level ca. 22 m height	April		0.45	Madsen *et al.* 1982
Oslo	Center (day) Busy street 44,000 cars/ 24 hours	2 m height	Jan.-Febr.	11.9		Möller *et al.* 1982
Oslo	Center (night) Busy street 9,000 cars/ 24 hours	2 m height	Jan.-Febr.	3.8		Möller *et al.* 1982
Stockholm	Streets 22,000 cars/ 24 hours	1.5 m	October - March	1.8		Höglund and Wädding 1984
Gothenburg	Center	Roof level ca. 30 m height	February	2.1	1.7	Lindskog and Brorström 1981
Ähtäri	<100 cars/ 24 hours		February	1.5		Tuominen *et al.* 1988
Kastrup Airport	20,000 cars/ 24 hours	1.2 m height ca. 100 m from traffic	Dec. - Febr. and Oct. - March	2.5	2.4	Nielsen *et al.* 1993
Risø	6,000 cars/ 24 hours	1.2 m height ca. 400 m from road	Febr. - April	0.6	0.6	Nielsen *et al.* 1984
Gothenburg	Streets 23,600 cars/ 24 hours	1.5 m height			1.3	Löfroth 1990

PAH levels and traffic intensity
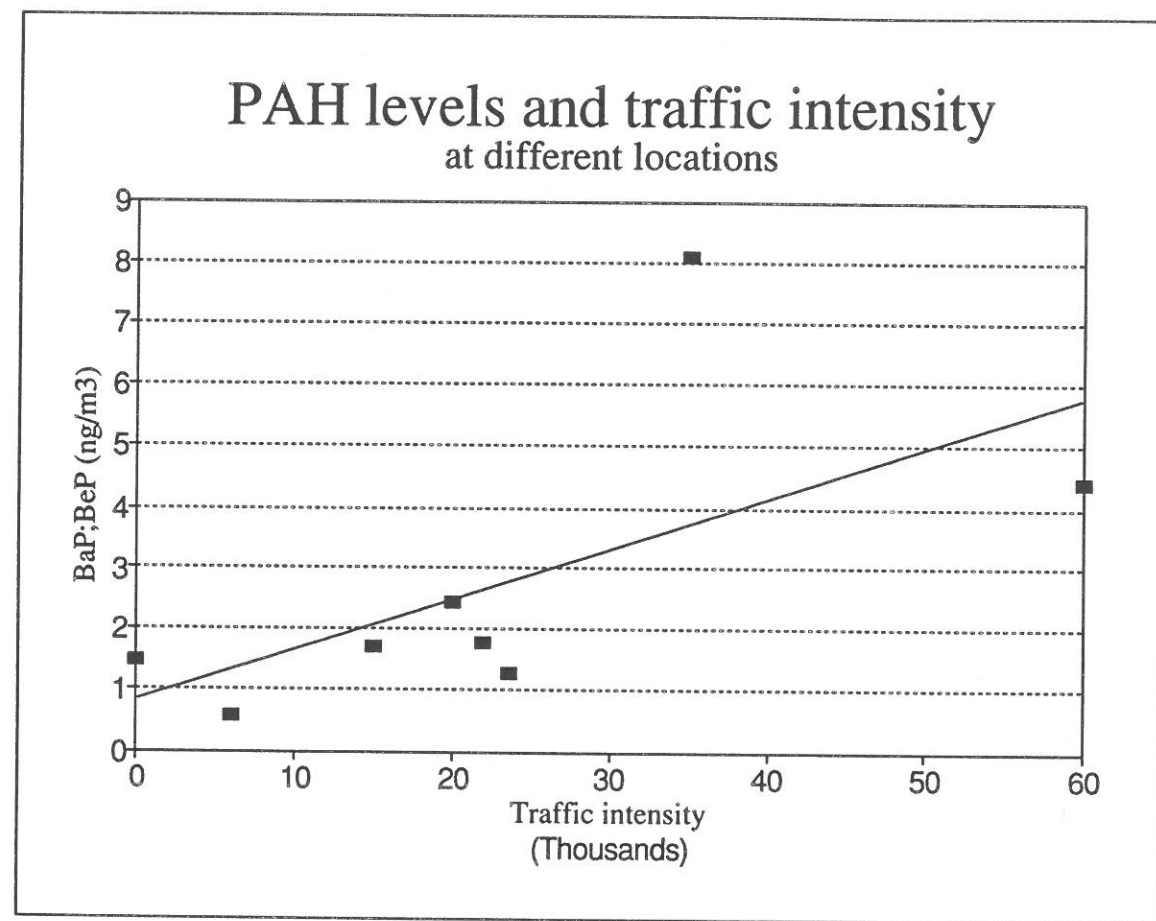### at different locations

Figure 3. Comparison of levels of benzo(a)pyrene (BaP) and/or benzo(e)pyrene (BeP) with the 24 hours traffic intensity at different sites in the Nordic countries. The correlation gives the following:

BaP (BeP) (ng/m³) = (8 ± 4) * 10^{-5} * 24 hours traffic intensity + (0.8 ± 2.1), r = 0.63, p ~ 0.1.

The results in the figure are from Table 5. The Oslo BaP and traffic intensity value used is the difference between day and night to correct for the heating contribution.

The former group includes the swedish results from Gothenburg performed by Stockholm University (Löfroth 1990) and the major part of the Danish results including busy street, city park and suburban measurements covering the period from 1986 - 1992.

The second group includes the Norwegian results performed by the Central Institute and the National Air Pollution Institute in Oslo (Möller *et al.* 1982) and the eight danish 1993 results from the busy street.

It was characteristic that all the measurements in the second group was performed at cold weather conditions with freeze, but further results are needed, before it is possible to conclude the PAH to mutagens ratio is higher at freezing conditions.

Table 6. Comparison of PAH levels and mutagenic acitivity at different locations in Scandinavia.

City	Location	BaP (ng/m³)	BeP (ng/m³)	TA98+S9 (rev./m³)	Ratio of BaP(BeP) to TA98+S9	No. of samples or reference
Copenhagen	Busy street 1992	6.0 ± 3.4	5.2 ± 1.7	72 ± 37	0.08	31
Copenhagen	Busy street 1993	2.8 ± 0.8	4.1 ± 1.0	13 ± 2	0.26	8
Copenhagen	City park	1.6 ± 0.7	1.1 ± 0.4	19 ± 5	0.07	18
Copenhagen	Busy street 1986 + 1987	9	8	91	0.09	Nielsen 1989
Oslo	Busy street (day)	11.9		79.5	0.15	Møller *et al.* 1982
Oslo	Busy street (night)	3.8		17.0	0.22	Møller *et al.* 1982
Kastrup	Street	2.4 ± 1.6	2.4 ± 1.4	32 ± 19	0.08	Fenger *et al.* 1990 Nielsen and Nielsen 1994
Gothenburg	Different sites		1.1 ± 0.3	12 ± 4	0.09	Löfroth 1990

4.3 Comparison of PAH with Other Air Pollutants and Meteorological Parameters

Comparison of PAH with Meteorological Parameters

Table 7 shows the wind distribution of PAH, mutagens and other air pollutants in the busy street and the city park area. The wind and temperature measurements were performed by Gunnar Jensen, Department of Meteorology and Wind Energy, at Risø National Laboratory. The local measurements of the wind direction showed wind at both sites either from the southern or the northern direction being controlled by the local topographic conditions.

The local wind-rates were a factor 3 to 4 minor than those measured at Risø caused by the higher roughness of the surface in the city. The local temperature measurements at both sites showed the same results as the Risø results. It was preferred to apply the Risø meteorological measurements, as the wind direction at Risø may give informations on possible distant air pollution sources, and the Risø wind-rates can be compared with the wind-rates measurements published in the national meteorological statistics (Larsen and Jensen 1983).

Generally, the weather conditions were colder at winds from the East and North sectors than at winds from the South and West sectors. The colder weather conditions might be the reason to the highest air pollution levels could be observed with winds from the East and North sectors. An additional reason might be long-range transport of polluted air from the Continent most often arrives with winds from the East sector. Thus, the most applied tracer of Continental long-range transport, sulphate or particulate sulphur, showed the highest concentrations with winds from the East sector, but the levels both in the busy street and the city park

area in the other wind sectors were only a factor of two lower.

The highest SO_2 levels were also observed with winds from the East sector. Most interesting the East sector also contains cases with strong elevated mutagenicity levels. This appears to confirm previous observations (Fenger *et al.* 1990, Nielsen and Nielsen 1994) on mutagens are formed by atmospheric reactions during transport. The formed mutagenic compounds appear to consist of nitroarenes as well as other types of POM.

The highest PAH concentrations were observed at low temperatures with significant negative correlations between (BaP, BeP, BghiP, Cor and BbjkF) and the temperature at both sites (see Table 8 and 9) (BS: $r = -0.33$ to -0.40, $p < 0.01$ to < 0.001 and CP: $r = -0.41$ to -0.57, $p < 0.01$ to < 0.001). Also, the BS-dieselBeP showed a significant negative correlation with the temperature ($r = -0.32$, $p < 0.01$).

The major source of CO and NMHC is traffic sources and both components are probably better indicators of organic pollutants from traffic sources than NO, gas NO_y, Pb, Br and Cu.

Significant negative correlations with temperature could be observed for BS-CO ($r = -0.32$, $p < 0.01$), CP-CO ($r = -0.57$, $p < 0.001$) and BS-NMHC ($r = -0.26$, $p < 0.05$).

The major reasons for the significant negative correlations between the temperature and the busy street PAH levels are, therefore, suggested to be:

1) The emission of PAH from the traffic is higher at cold weather conditions than at warm weather conditions.
2) Stable boundary layer occurs more often at cold weather conditions. By that the mixing of the emitted air pollutants is poorer, and the air pollutants are concentrated in the city atmosphere.

An additional reason, especially for the significant negative correlation between the temperature and the PAH levels in the city park area is the contribution from heating sources is higher at cold weather conditions than at warm weather conditions.

Correlations with Other Air Pollution Parameters

In contradiction to PAH the atmospheric soot content is continous measured each day at several stations in different surveillance programmes, e.g. the 1991 annual mean concentration of soot at the busy street was 45 µg/m³, the roof level concentration 22 µg/m³, the suburbs concentrations 17 - 26 µg/m³, and the concentrations in rural areas in Northern Zealands 6 - 7 µg/m³. In Copenhagen the urban background soot concentration had a maximum in 1985 on 35 µg/m³. Since 1989 the annual avarage levels has been constant on 22 µg/m³ (HLU 1993). The maximum in the middle of the eighthies is believed to be caused by an increase in the diesel traffic and by changes in the oil composition for heating (Municipality of Copenhagen 1990). As discussed in Section 4.1 traffic pollution has been the major source for soot in the street atmosphere on working days. In weekends the effect on the soot content of other sources, e.g. heating, can be observed, especially on locations distant from the streets. It was a request to this project to find correlations between the soot content and the PAH content. The purpose of this is to apply soot as an indicator for PAH in the daily surveillance of the air quality in Copenhagen. It is recognized soot measurements cannot replace PAH measurements nor mutagenicity measurements, but nevertheless the PAH-soot correlations can be applied to check, if further investigations of pollution of PAH and mutagens are needed, as well as to improve the health effects evaluation of

Table 7. Comparison of the wind distribution of PAH and other pollutants in the busy street and city park area and meteorological parameters.

Site	Compound or meteorological parameter	North	East	South	West	Total no. of samples
Busy street	BaP (ng/m³)	5 ± 3	9 ± 10	3.4 ± 0.8	3.7 ± 0.8	76
Busy street	BeP (ng/m³)	5 ± 2	7 ± 4	3.8 ± 0.9	3.9 ± 0.7	76
Busy street	BghiP (ng/m³)	10 ± 4	11 ± 6	6.3 ± 1.3	7.5 ± 1.5	76
Busy street	Cor (ng/m³)	7 ± 4	9 ± 6	4.4 ± 1.1	5.4 ± 1.3	76
Busy street	BbjkF (ng/m³)	11 ± 3	19 ± 14	7.9 ± 1.9	7.6 ± 1.3	76
Busy street	DieselBeP (ng/m³)	3.1 ± 1.6	2.1 ± 1.2	1.5 ± 0.5	2.3 ± 0.6	76
Busy street	TA98+S9 (rev/m³)	43 ±44	123 ±189	31 ±15	51 ±17	31
Busy street	TA98-S9 (rev/m³)	34 ±27	96 ±131	26 ± 9	38 ± 12	31
Busy street	TA98NR (rev/m³)	21 ±23	70 ±106	16 ± 5	28 ±10	31
Busy street	SO₂ (ppb)	7.7 ± 1.1	11 ± 5	7.5 ± 1.1	6.3 ± 0.6	76
Busy street	Sulphate (µgS/m³)	2.6 ± 0.3	5.7	3.0 ± 0.8	2.5 ± 0.4	25
Busy street	CO (ppm)	2.2 ± 0.4	1.9 ± 0.5	1.8 ± 0.2	1.85± 0.20	76
Busy street	NMHC (ppm)	0.46± 0.15	0.68 ± 0.19	0.49± 0.08	0.50± 0.06	68
Busy street	Soot (µg/m³)	71 ±14	64 ± 25	49 ± 6	54 ± 6	68
City park	BaP (ng/m³)	1.4 ± 0.7	4 ± 6	1.3 ± 0.6	1.1 ± 0.5	50
City park	BeP (ng/m³)	1.3 ± 0.5	2 ± 3	1.6 ± 0.7	1.0 ± 0.2	50
City park	BghiP (ng/m³)	1.7 ± 0.6	2 ± 2	1.5 ± 0.6	1.4 ± 0.3	50
City park	Cor (ng/m³)	1.2 ± 0.5	2.1 ± 1.7	1.0 ± 0.4	1.0 ± 0.2	50
City park	BbjkF (ng/m³)	3.6 ± 1.4	5 ± 5	3.4 ± 2.0	2.3 ± 0.5	50
City park	DieselBeP (ng/m³)	0.5 ± 0.4	0.13 ± 0.09	0.27± 0.13	0.5 ± 0.2	50
City park	TA98+S9 (rev/m³)	26 ± 6		21 ±10	17 ± 6	20
City park	TA98-S9 (rev/m³)	17 ± 4		19 ±10	13 ± 3	20
City park	TA98NR (rev/m³)	11 ± 5		9 ± 4	8 ± 2	20
City park	SO₂ (ppb)	3.7 ± 1.9	9 ± 8	5.0 ± 1.6	4.0 ± 0.8	50
City park	Sulphate (µgS/m³)	1.5 ± 0.2	4.7	2.1 ± 0.7	1.8 ± 0.3	26
City park	CO (ppm)	0.42± 0.14	0.6 ± 0.3	0.35± 0.11	0.37± 0.06	50
City park	Soot (µg/m³)	22 ± 6	30 ± 27	27 ± 6	22 ± 3	50
Outside city	Temperature (⁰C)	-0.3 ± 1.3	0.4 ± 1.3	3.7 ± 1.5	3.5 ± 0.7	85
Outside city	Wind-rate (m/s)	4.3 ± 0.6	5.1 ± 1.4	4.7 ± 0.7	6.2 ± 0.8	82

Table 8. Busy street coefficients (r) of correlations of PAH (benzo(a)pyrene BaP, benzo(e)pyrene BeP, benzo(ghi)perylene BghiP, coronene Cor, benzo(b)-+benzo(j)-+benzo(k)fluoranthene BhjkF and dieselBeP) with different air pollution components and outside city meteorological data.

Compound	BaP	BeP	BghiP	Cor	Bbjkf	DieselBeP
Benzo(a)pyrene		0.88***	0.79***	0.76***	0.92***	0.29**
Benzo(e)pyrene	0.88***		0.90***	0.89***	0.88***	0.57***
Benzo(ghi)perylene	0.79***	0.90***		0.81***	0.81***	0.51***
Coronene	0.76***	0.89***	0.81***		0.79***	0.47***
Benzo(bjk)fluoranthenes	0.92***	0.88***	0.81***	0.79***		0.27*
DieselBeP	0.29**	0.57***	0.51***	0.47***	0.27*	
TA98+S9	0.94***	0.87***	0.81***	0.85***	0.92***	0.13
TA98-S9	0.95***	0.88***	0.80***	0.84***	0.94***	0.13
TA98NR	0.95***	0.88***	0.79***	0.84***	0.93***	0.16
NO	0.40***	0.62***	0.70***	0.69***	0.42***	0.49***
Gas NO_x	0.40***	0.62***	0.69***	0.68***	0.42***	0.49***
CO	0.31**	0.54***	0.66***	0.61***	0.34**	0.43***
NMHC	0.34**	0.56***	0.57***	0.57***	0.35**	0.51***
SO_2	0.74***	0.71***	0.61***	0.61***	0.77***	0.03
Lead	0.54**	0.77***	0.84***	0.87***	0.53**	0.45*
Bromide	0.41*	0.68***	0.76***	0.78***	0.40*	0.49**
Copper	0.26	0.56**	0.62***	0.68***	0.24	0.52**
Manganese	0.27	0.37	0.40*	0.49*	0.25	0.17
Zinc	0.31	0.79***	0.75***	0.81***	0.69***	0.19
Iron	0.28	0.54**	0.55**	0.64***	0.26	0.44*
Titanium	0.28	0.59**	0.56**	0.66***	0.44*	0.25
Silicon	0.34	0.49*	0.46*	0.57**	0.32	0.29
Calcium	0.06	0.29	0.33	0.41*	0.04	0.36
Sulphate	0.62**	0.50*	0.40	0.40	0.61**	0.04
Vanadium	0.75***	0.70***	0.74***	0.71***	0.76***	0.13
Nickel	0.51**	0.46**	0.64***	0.53**	0.53**	0.17
Potassium	0.28	0.54**	0.71***	0.74***	0.26	0.17
Soot	0.63***	0.81***	0.73***	0.76***	0.66***	0.39**
Particles	0.21	0.28*	0.27*	0.29*	0.26*	0.05
Wind-rate	-0.13	-0.11	-0.15	-0.11	-0.13	0.05
Temperature	-0.33**	-0.40***	-0.38***	-0.36**	-0.38***	-0.32**

* : Significant, $p < 0.05$,
** : Significant, $p < 0.01$,
*** : Significant, $p < 0.001$.

Table 9. City park coefficients (r) of correlations of PAH (benzo(a)pyrene BaP, benzo(e)pyrene BeP, benzo(ghi)perylene BghiP, coronene Cor, benzo(b)-+benzo(j)-+benzo(k)fluoranthene BhjkF and dieselBeP) with different air pollution components and outside city meteorological data.

Compound	BaP	BeP	BghiP	Cor	BbjkF	DieselBeP
Benzo(a)pyrene		0.91***	0.88***	0.82***	0.80***	0.27*
Benzo(e)pyrene	0.91***		0.94***	0.88***	0.95***	0.16
Benzo(ghi)perylene	0.88***	0.94***		0.94***	0.90***	0.30*
Coronene	0.82***	0.88***	0.94***		0.86***	0.21
Benzo(bjk)fluoranthenes	0.80***	0.95***	0.90***	0.86***		0.05
DieselBeP	0.27*	0.16	0.30*	0.21	0.05	
TA98+S9	0.73***	0.77***	0.73***	0.67**	0.82***	0.42
TA98-S9	0.60**	0.61**	0.55*	0.47*	0.59**	0.36
TA98NR	0.66**	0.71***	0.75***	0.69**	0.71***	0.51*
NO	0.36**	0.38**	0.57***	0.53***	0.37**	0.44**
Gas NO_x	0.40**	0.44**	0.54***	0.56***	0.42**	0.46**
CO	0.36**	0.48***	0.56***	0.55***	0.53***	0.16
SO_2	0.72***	0.76***	0.68***	0.70***	0.75***	0.15
Lead	0.89***	0.90***	0.92***	0.90***	0.91***	0.20
Bromide	0.69***	0.66**	0.78***	0.71***	0.62**	0.43
Copper	0.56**	0.54*	0.64**	0.58**	0.51*	0.66**
Manganese	0.87***	0.88***	0.85***	0.85***	0.89***	0.16
Zinc	0.91***	0.92***	0.86***	0.88***	0.93***	0.01
Iron	0.55*	0.56**	0.59***	0.57**	0.56**	0.44
Titanium	0.79***	0.81***	0.72***	0.73***	0.83***	0.14
Silicon	0.74***	0.76***	0.73***	0.74***	0.80***	0.09
Calcium	0.23	0.25	0.42	0.37	0.29	0.33
Sulphate	0.73***	0.75***	0.68**	0.69***	0.79***	0.27
Vanadium	0.84***	0.83***	0.83***	0.82***	0.88***	0.35
Nickel	0.42	0.44	0.43	0.49*	0.50*	0.24
Potassium	0.82***	0.85***	0.81***	0.83***	0.87***	0.04
Soot	0.81***	0.87***	0.83***	0.79***	0.83***	0.15
Particles	0.40**	0.45**	0.35**	0.36**	0.47**	0.09
Wind-rate	-0.11	-0.23	-0.24	-0.24	-0.34**	0.24
Temperature	-0.41**	-0.53***	-0.57***	-0.52***	-0.58***	-0.07

* : Significant, $p < 0.05$,
** : Significant, $p < 0.01$,
*** : Significant, $p < 0.001$.

carcinogenic air pollutants in the air of Copenhagen. The following correlations between soot and PAH at the two sites, the busy street and the city park area, were observed:

Busy street:
BaP $(ng/m^3) = (0.172 \pm 0.026) * Soot (\mu g/m^3) - (4.6 \pm 4.4)$, r = 0.63, p < 0.001.
BeP $(ng/m^3) = (0.121 \pm 0.012) * Soot (\mu g/m^3) - (2.0 \pm 2.0)$, r = 0.81, p < 0.001.
BghiP $(ng/m^3) = (0.208 \pm 0.024) * Soot (\mu g/m^3) - (2.9 \pm 4.1)$, r = 0.73, p < 0.001.
Cor $(ng/m^3) = (0.192 \pm 0.020) * Soot (\mu g/m^3) - (4.3 \pm 3.4)$, r = 0.76, p < 0.001.
BbjkF $(ng/m^3) = (0.283 \pm 0.040) * Soot (\mu g/m^3) - (5.6 \pm 6.8)$, r = 0.66, p < 0.001.

City park:
BaP $(ng/m^3) = (0.155 \pm 0.016) * Soot (\mu g/m^3) - (2.3 \pm 1.3)$, r = 0.81, p < 0.001.
BeP $(ng/m^3) = (0.093 \pm 0.008) * Soot (\mu g/m^3) - (1.0 \pm 0.6)$, r = 0.87, p < 0.001.
BghiP $(ng/m^3) = (0.073 \pm 0.007) * Soot (\mu g/m^3) - (0.2 \pm 0.6)$, r = 0.83, p < 0.001.
Cor $(ng/m^3) = (0.059 \pm 0.007) * Soot (\mu g/m^3) - (0.3 \pm 0.5)$, r = 0.79, p < 0.001.
BbjkF $(ng/m^3) = (0.189 \pm 0.018) * Soot (\mu g/m^3) - (1.6 \pm 1.4)$, r = 0.83, p < 0.001.

It is suggested the busy street correlations are applied to street measurements of soot, and the city park measurements are applied to roof levels, backyards and city park areas measurements of soot. It shall be borne in mind all the PAH measurements were performed at winter time. As such the seasonal influence on the correlations are not known. Also the legislation to reduce pollution from diesel as well as petrol vehicles may effect not only the emission levels of PAH and soot but also their ratios. The suggested correlations do not take these circumstances into consideration.

Figure 4 shows the application of correlation coefficients to discriminate between major sources and minor ones shall be done with greatest possible care. The same precautions shall also be taken doing more elaborated correlation analysis, as e.g. factor analysis. Figure 4 shows the average correlation coefficients for the following 5 PAH (BbjkF, BaP, BeP, BghiP and Cor) with 5 different groups of inorganic source indicators. The average correlation coefficients have been investigated for the busy streets samples (71 PAH samples), the city park samples (56 samples) and the results for the two stations pulled together (125 PAH samples), respectively. In the combined sample set the results from the long-range transport episode (24. Jan. 1992, see Section 4.4) was omitted. The approach studying correlation coefficients for each station, as well as the approach pulling all the results together and omit the minor number of unusual cases are both scientific valid methods. Nevertheless, each approach leads to different results. If one study the correlation coefficients for the pulled group, this shows a decrase of the correlation coefficients in the following order: Traffic components, power plants, and heating and long-range transport. The busy street group shows a decrease of the correlation coefficients in the following order: Heating and long-range transport, traffic and power plant. While, the city park measurements show a decrease in the following order: Power plants, heating and long-range transport, and traffic.

Tables 8 and 9 present a detailed survey of the correlation coefficients of the 5 PAH mentioned above and of the estimated dieselBeP with other components at each of the two stations. In general, the 5 PAH had high correlation coefficients with the content of mutagens, but also significant correlation coefficients with most of the other components measured. One of the few exceptions was the soil component, Ca. The correlations with Mn at the BS station were poor, but high correlations were attained at the CP station. At the CP station the correlation coefficients with Ni were much poorer than those with particulate sulphur and V,
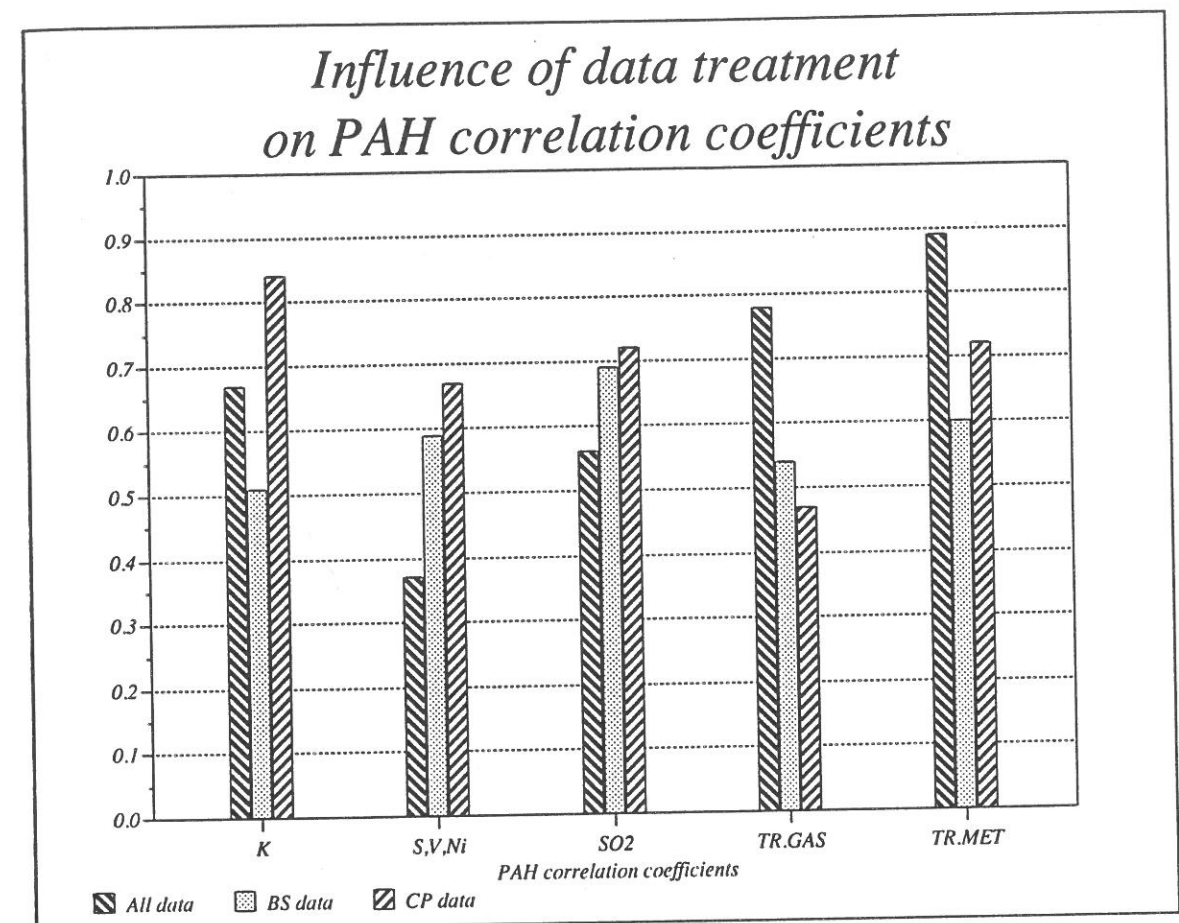
Figure 4. Influence of data treatment on PAH correlation coefficients. The graph shows the average correlation coefficients of the following 5 PAH (benzo(b)-+benzo(j)-+benzo(k)-fluoranthene, benzo(e)pyrene, benzo(a)pyrene, benzo(ghi)perylene and coronene) towards
K: Potassium (power plants),
S,V,Ni: Particulate sulphur, vanadium and nickel (heating sources and long-range transport)
SO_2:   (Heating sources and long-range transport)
TR.GAS: Traffic gases; NO, gas NO_y and CO
TR.MET: Traffic metals: Pb, Br and Cu.
The correlation coefficients have been determined for the following three groups:
BS data: Busy street measurements (71 PAH samples)
CP data: City park measurements (56 PAH samples)
All data: BS + CP measurements (125 PAH, samples, the two long-range transport samples on 24. Jan. 1992 (see Section 4.4) were excluded caused by the different nature of these two samples).

despite it is believed S, V and Ni originates from the same sources. Several of the correlation coefficients with the soil components, Fe, Si and Ti, were significant positive, despite soil is not a PAH source. As shown in Fig. 1 and discussed in the text in Section 4.1 turbulence from the driving traffic and resuspension processes may cause "false" correlations between traffic air pollutants and particulate metals on larger particles.

The analysis of the correlation coefficients showed that traffic, heating and long-range transport, power plants and perhaps incinerators (Zn) are possible PAH

sources, but as stated previous the correlation coefficient analysis cannot be applied to discriminate between major sources and minor ones.

The estimated dieselBeP correlation coefficients were generally poorer than those of the direct measured PAH. The reason to this is probably the precision of the dieselBeP determinations was poorer. First the uncertainty on the estimated dieselBeP concentrations includes the uncertainties on the determinations on three PAH, BeP, MePh and Ph. Second the estimation is based on assumptions on the MePh to Ph emission ratios from different sources. But very little is known e.g. on the effect of the fuel composition and driving conditions on these ratios. By that unknown daily variations are possible. Third the degradation rate of MePh in the atmosphere is much faster than that of Ph (Lindskog and Brorström 1981, Nielsen *et al.* 1983), e.g. the MePh to Ph ratio is very low in the long-range transport case on 24. Jan 1992 (see Section 4.4).

Nevertheless, the dieselBeP showed significant positive correlations with the other PAH, the traffic pollutants indicators, NO, gas NO_y, CO, NMHC, Pb, Br and Cu, and soot in the BS samples. But not with e.g. SO_2, S, V, Ni and K. In the CP samples the correlation coefficients were general poorer than those in the BS samples, but the transport time from the traffic sources to the sampling site is also longer. Still significant positive correlation coefficients in the CP samples were achieved with the major part of the traffic pollutants indicators. *i.e.* NO, gas NO_y, CO and Cu, but not with Pb and Br. The correlation coefficients with SO_2, S, V, Ni and K were neither significant in the CP samples.

Trend Analysis of PAH

Trend analysis of air pollutants requires continous daily measurements several years in order to be able to observe significant trends (Jensen *et al.* 1993). One of the reason is air pollutants concentrations are most dependent of the meteorological conditions. The different meteorological conditions may cause air pollutants variations being larger than those caused by changes in the emissions not only on a daily basis but also from one year to another .

The few PAH analysis performed so far is not a sufficient data material to draw any significant conclusions on whether the PAH content in busy street air in Copenhagen is increasing or decreasing. Nevertheless, if one compares the 1986+- 1987, 1992 and 1993 PAH measurements with coincident measurements of NO, gas NO_y, CO and SO_2 in Table 10, the results shown are not in contradiction with the following: The legislation requirements to pollutant emissions from petrol as well as diesel vehicles will cause the air pollution of organic pollutants to fall faster than the air pollution of inorganic gases.

The 1993 to 1992 ratio of the estimated dieselBeP is higher than the ratios of the inorganic gases, NO, gas NO_y, SO_2 and CO. Although this relative increase is not significant, it may reflect the atmospheric degradation of MePh will decrease by decreasing temperature. The average temperature was lower in the 1993 samples (-1.5 °C) than in the 1992 samples (+3.4 °C).

The 1992 results for the mutagenicity in Table 10 includes 24 samples, while the PAH 1992 results includes 68 samples. If one compares with Table 6 it should be obvious the mutagenicity ratios between the 1986 + 1987 samples and the 1992 ones are almost the same as the PAH ratios, at least for TA98+S9.

The low mutagenicity levels in the 1993 samples have been discussed in Section 4.2.

The first Danish PAH measurements (Campbell and Clemmesen 1956) were performed in the winter 1954 - 1995 and the summer 1955 at three different locations in Copenhagen and one in the suburbs. The average levels of BaP were 17 and 7 ng/m³, respectively, at the two types of sites in the winter season and 6

Table 10. Trend of PAH levels and other coincident parameters measured at a busy street in the center of Copenhagen

Compound	1986 + 1987 concentration	1992 concentration	1993 concentration	1986 + 1987 to 1992 ratio	1993 to 1992 ratio
Benzo(b+j+k)-fluoranthene (ng/m³)	22.1	9.5 ± 2.2	7.9 ± 1.8	2.33	0.83
Benzo(a)pyrene (ng/m³)	9.1	4.6 ± 1.4	2.8 ± 0.8	1.98	0.62
Benzo(e)pyrene (ng/m³)	8.3	4.4 ± 0.8	4.1 ± 1.0	1.89	0.92
Benzo(ghi)perylene (ng/m³)	14.3	8.1 ± 1.4	6.8 ± 2.1	1.77	0.83
Coronene (ng/m³)	11.9	5.9 ± 1.3	5.1 ± 1.6	2.02	0.87
DieselBeP (ng/m³)		2.2 ± 0.5	2.5 ± 0.8		1.14
NO (ppb)	187[a]	125 ± 13	125 ± 36	1.50	1.00
Gas NO_y (ppb)	225[a]	156 ± 14	155 ± 37	1.44	0.99
SO_2 (ppb)	13[b]	7.3 ± 0.8	7.0 ± 0.9	1.78	0.96
CO (ppm)		1.88 ± 0.15	2.1 ± 0.4		1.10
TA98+S9 (rev./m³)	91	72 ± 37	13 ± 2	1.26	0.19
TA98-S9 (rev./m³)	74	51 ± 27	21 ± 6	1.45	0.42
TA98NR (rev./m³)	48	38 ± 21	8.5 ± 1.8	1.26	0.22
Risø wind-rate (m/s)		5.8 ± 0.6	4.0 ± 1.3		
Risø temperature (°C)		3.4 ± 0.6	-1.5 ± 0.9		
No. of samples	8	68	8		

[a] 6 days

[b] 4 days

and 4 ng/m³, respectively, in the summer season, *i.e.* much higher levels than measured in the city park area in 1992. Measurements in London applying the same analytical method for several years (Commins and Hampton 1976) suggest the high PAH levels measured in the fifties have been real.

Evaluating the results in the fifties compared to nowadays PAH levels it shall be borne in mind the PAH proportion of the total amount of mutagens probably

have been much higher in the fifties than the 10 % observed nowadays. This was stated by an international working group (Holmberg and Ahlborg 1983) in Stockholm in 1981. The reason to the shift in the ratio between PAH and mutagens has probably been caused by two factors:

1) The more efficient combustion methods applied nowadays cause an increase in the emission ratio between transformation products of PAH and PAH.
2) The increase in emission of NO_x (Bos 1978, Brimblecombe and Stedman 1982) since the fifties has implied an increase in the formation of mutagenic transformation products of PAH in the atmosphere.

The increase in emission of NO_x has caused a shift in the atmospheric chemistry in Europe during the sixties and seventies and other parts of the Northern Hemisphere. At zero-level or low levels of NO_x the increase of the concentrations of organic pollutants causes a decrease of ozone and other photochemical oxidants. By that the primary organic pollutants and SO_2 are transformed slowly and are accumulated in the atmosphere. An example is the winter-time black smog episodes in London in the fourties and fifties. At increased NO_x levels the increase in emission of organic pollutants causes an increase in the concentrations of ozone and other photochemical oxidants. By that the transformation of primary organic pollutants and the process SO_2 to sulphuric acid proceeds faster and significant amounts of transformation products may be observed. An example is the so-called summertime white episodes in Southern Scandinavia in the seventies and eigthties (Nielsen *et al.* 1981).

More recent PAH measurements in the central Copenhagen were performed by Sørensen and Vester (1981), Nielsen (1989) and Nielsen *et al.* (1986). Sørensen and Vester found summer roof levels of BeP and BaP to be 0.3 and 0.2 ng/m³, respectively, in 1978, while Nielsen *et al.* (1986) and Nielsen (1989) found summer roof levels of BeP to be 0.7 ng/m³ and winter roof levels to be 1.8 ng/m³ in the period 1976 - 1982. A decrease on 11 % pr year on samples from February and June could be observed during those six years. The most recent PAH measurements in Copenhagen have been presented in Tables 5 and 10.

The PAH measurements have only been few and performed at different sampling sites and by using different sampling and analytical methods. In general, the PAH levels appear to follow the same trend with time as soot (Gudmundsson 1988, HLU 1993), although a decrease of soot in the period 1976 - 1982 was not observed. The soot measurements started at the end of the sixties with high levels. In the beginning of the seventies the soot levels were falling, but they increased again since 1976 - 1978 untill 1985. Since 1989 the soot concentrations appear to be constant at the same level as the beginning of the eightthies.

4.4 Evaluation of PAH Traffic Contribution Including Speciation between Diesel and Petrol Vehicles

Factor Analysis of PAH and Other Chemical Components

Theory of the factor analysis. In this paragraph the data have been examined for any structure that can explain the correlation between not one, but several components. For this purpose the factor analysis has been used. In general the model assumes that the observed data can be represented by the following model:

$$x_t = A \; f_t + \xi(o, \sigma^2)$$

x_t is a vector representing all the observations $(x_1...x_n)$ on the t' the day, here x_1 to x_n is the n chemical compounds measured a day t. The source profile A is a $(m \; x \; n)$ matrix where the m columns represents the sources (or factors) and the n rows is the n chemical compounds loading on the m'the source. The elements in the source profile are denounced as the factor loadings and in this analysis the unit of the elements is ng (n'the chemical compound) per µg dust from the m'the source for the inorganic compunds and PAH, whereas the units for for mutagenic activity the units are rev. The facscores f_t is in this model a vector that represents the source distribution of dust from the $f_1..f_m$ sources.

The model assumes that the chemical compounds can be described by a linear combination of the source profile and source distributions, without any chemical transformation during the transport from the source to the measuring location.

The data analysis is performed on the correlation matrix for x_t that corresponds to a rewritten model for the the normalized variables *i.e.*:

$$y_t = \frac{(x_t - E(x_t))}{S(x_t)}$$

The analysis of the normalized variables y_t can be reformulated in a similar linear model as for x_t and is here written as:

$$y_t = B \; g_t$$

where

$$B = S_x A S_f^{-1}$$

The interpretation of the matrix B in the linear model then becomes different from the definition of A. By comparing the model for x_t and y_t it is seen that the B matrix represents a normalized source profile. In the comparison between the two source profiles the presences of noise on the chemical compounds have been neglected. S_x represents a diagonal matrix consisting of the std. dev. of the chemicals, and S_f represents a diagonal matrix consisting of the std.dev. of the factor contributions. The values in S_f have to be determined by an additional equation:

$$y_{txp}(t) = \sum \alpha_i g_i(t)$$

This equation represents a mass balance of particulate matter, *i.e.*, the sum of all the normalized source contributions is equal to the particulate matter at day t. The variance on the different sources is then determined by

$$\sigma_{f,i}^2 = \alpha_i^2 \sigma_{g,i}^2$$

where α_i is found by mutilple regression.

The rank of correlation matrices R_x determines the number of sources present in the model, *i.e.*, the number of non-independent linear equations in the system. The rank of the correlation matrices is determinated by the number of eigenvalues which have a none zero values. However, in practice all the eigenvalues are

different from zero. This is caused by the presence of noise in the model, and the rank determination is therefore often based on a specified threshold, or an a prior knowledge of the data in the model (e.g., the actual number of sources involved).

The solution for **B** is found by the eigenvalues and eigenvectors, and the solution is denounced as the principal component solution. This solution is rather unrealistic, as factor 1 describes the highest amount of variance and factor 2 less etc. The factors are in this solution ranked by the amount of variance, whereas in a physical system this does not always imply for which reason the matrix **B** is rotated based on a set of specified criteria. The widely used criterion is the "simply structure" approach (Richman 1986). In the analysis of PAH component the Varimax rotation has been used. This rotation does not allow for any internal correlation between the factors assuming that the different source contributions are uncorrelated. Based on this model two sources that have a high correlation creates only one factor/source or introduce an overlap in the loadings.

Finally the facscores (the source contributions) are estimated from a least square fit of

$$Min(\varepsilon^2) = \sum_t (x_t - Af_t)^2$$

where ε^2 is determined by the estimated communalities found by the factor analysis. The resulting facscores f_t can then be estimated as

$$f_t = (A'\Sigma^{-1}A)^{-1}A'\Sigma^{-1}x_t$$

where Σ contains a diagonal with the communalities (Konradsen 1984).

Data analysis. In the analysis of the PAH the data have been restricted to include only PAH of which the dominant amount is related to the particulate matter (*i.e.* 4 rings and more) and the mutagens. Furthermore only the metals of the inorganic components have been included. The data have further been reduced to include only the days where all the selected chemical compounds have been present. This includes in all 28 days in total including both the busy street station (HCA) and the city park station (Tivoli), corresponding to 14 days at HCA and 14 days at Tivoli.

The two stations have been treated as one station and merged into one data base. The data can by that be viewed as an artificial time series consisting of 28 days with the first 14 days contribution from HCA and the next 14 days from Tivoli.

Results. By analyzing all the data presents, *i.e.*, the inorganic compounds and the organic compounds (including the PAH and mutagens) it is expected to see following sources:

  - LRT Long range transport
  - Traffic (petrol and diesel)
  - Soil (resuspension)
  - Fuel
  - Chlorine Source

The traffic source is expected to be highly correlated to the Soil factor, due to the resuspension from the streets caused by the turbulence created by passing cars.

As for the LRT source the correlation with other sources tends to be zero because of the source configuration which has longer timescale (transportation

time from, e.g. the eastern countries). Nevertheless correlation to other sources can be introduced by special meteorological situations, e.g. periods with low inversion heights. Here the concentrations of all constituents increase due to the lack of turbulence mixing with "clean air". This spike in time gives correlation between all sources as all concentrations rise within the same short period. To take this into account the days with a strong inversion have been removed from the data. The high level of concentrations is here related to a lack of mixing due to the stratified atmosphere.

Figure 5. The figure shows the normalized Cl facsores specifying the days that belong to the two different locations.

Table 11. The source profile for the four factor solution with both station included.

Compound	Auto-factor (+ resuspension)	Soil-factor	Cl-factor	LRT/Fuel-factor
Al	17.1	13.7	3.13	7.53
Si	85.8	52.8	11.2	17.9
S	28.2	5.26	16.2	45.9
Cl	35.9	139	182	0.0
K	9.14	4.55	0.477	3.93
Ca	93.9	49.6	5.78	0.0223
Ti	4.48	2.32	0.483	0.892
V	0.315	0.0649	0.00787	0.363
Cr	0.135	0.225	0.0121	0.0616
Mn	1.86	1.20	0.168	0.304
Fe	95.5	36.7	6.85	15.2
Ni	0.0317	0.0464	0.0	0.216
Cu	4.21	1.08	0.365	0.541
Zn	6.61	1.98	0.347	1.80
Br	4.01	0.884	0.206	0.334
Pb	19.2	3.50	0.960	3.00
Soot	4.190	0.651	0.363	0.286
BNT	0.0558	0.00824	0.00	0.00162
BcPBghiF	0.980	0.143	0.0529	0.0139
CP	1.18	0.195	0.0157	0.00
BaA	0.701	0.0811	0.0376	0.0741
ChrTP	0.841	0.0813	0.0499	0.156
BbjkF	0.835	0.0799	0.0419	0.0979
BaF	0.204	0.0268	0.00935	0.00773
BeP	0.592	0.0675	0.0360	0.0316
DieselBeP	0.284	0.0230	0.0317	0.00
BaP	0.571	0.0598	0.0188	0.0480
IP	0.638	0.0386	0.0201	0.103
Pic	0.111	0.00798	0.00638	0.0121
BghiP	1.23	0.107	0.0465	0.184
Anthan	0.273	0.0345	0.00483	0.0335
Cor	1.03	0.119	0.0400	0.0967
TA98+S9	5.00	0.613	1.09	0.4810
TA98-S9	3.43	0.196	0.793	0.355
TA98NR	2.94	0.218	0.609	0.0710

In the statistical analysis of the data it is found that a factor solution with four factors can be explained resonably. The chosen solution can explain approximately 80 % of the variance of the system, commumalities (the explained variance distributed on the chemical compounds) ranging from 70 % to 90 %.
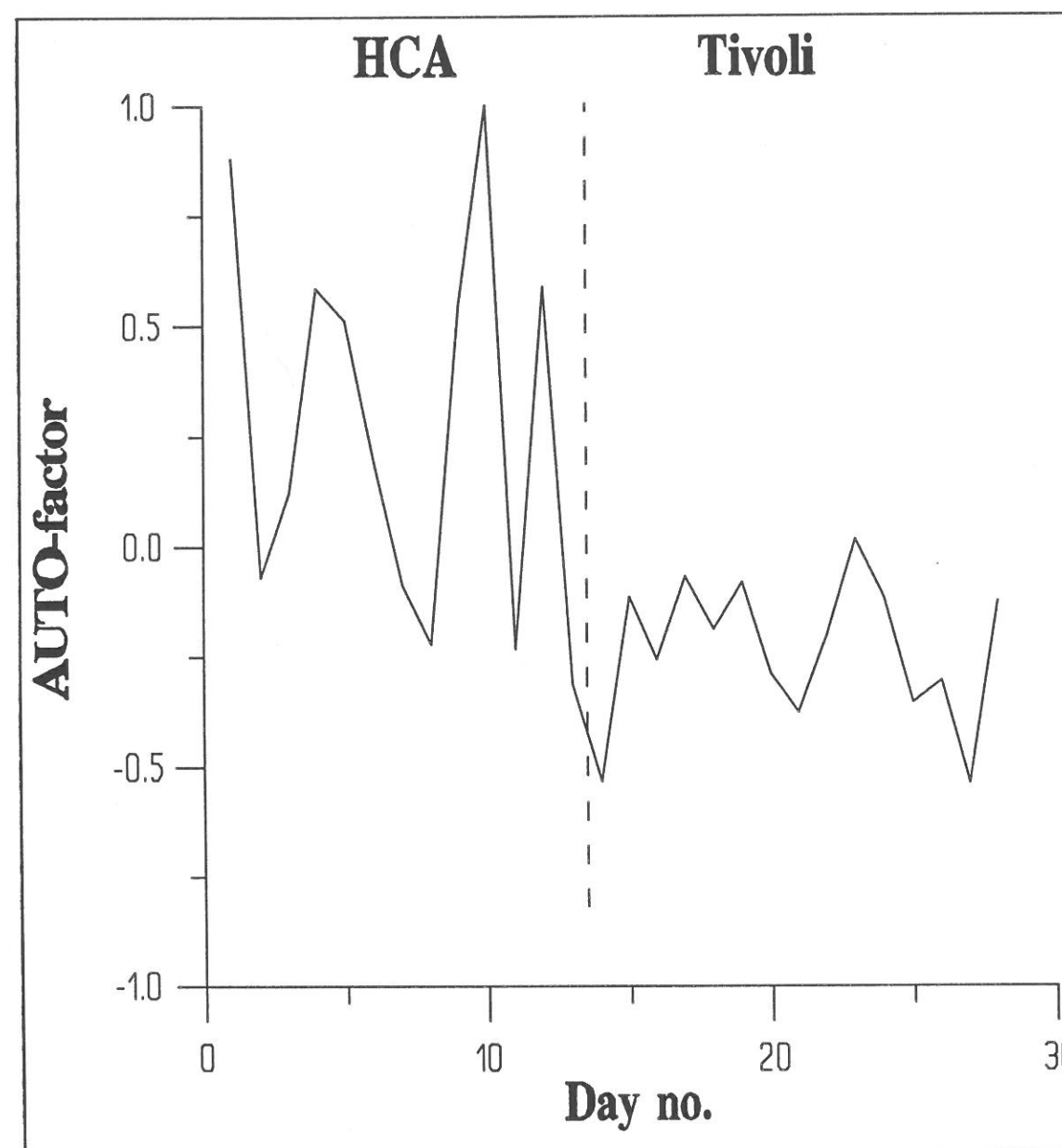
Figure 6. The figure shows the normalized Auto facsores specifying the days that belong to the two different locations.

The conclusion regarding the source profile is as follows (see Table 11). The Soil and Auto factor is highly correlated. By using the orthogonal rotations there was a major overlap for the distribution of the soil the metals, Al, Si, Ca, Fe, Ti, Mn and Zn on the Auto factor and the Soil one. The part of the seven elements associated with the Auto factor is believed to represent that part resuspended by the turbulence from the traffic (See also Fig. 1). On the other hand also Cu appeared both on the Auto and Soil factor. Nevertheless, it is believed that Cu is related to the Auto factor and that Cu is a distinct traffic tracer (See Section 4.1).

The PAH's are solely coming from the Auto sources and only small not significantly contributions comes from other sources. The mutagens also originates from the traffic sources with minor contributions from the other sources. The relations to the Cl factor probably reflects an influence of the temperature.
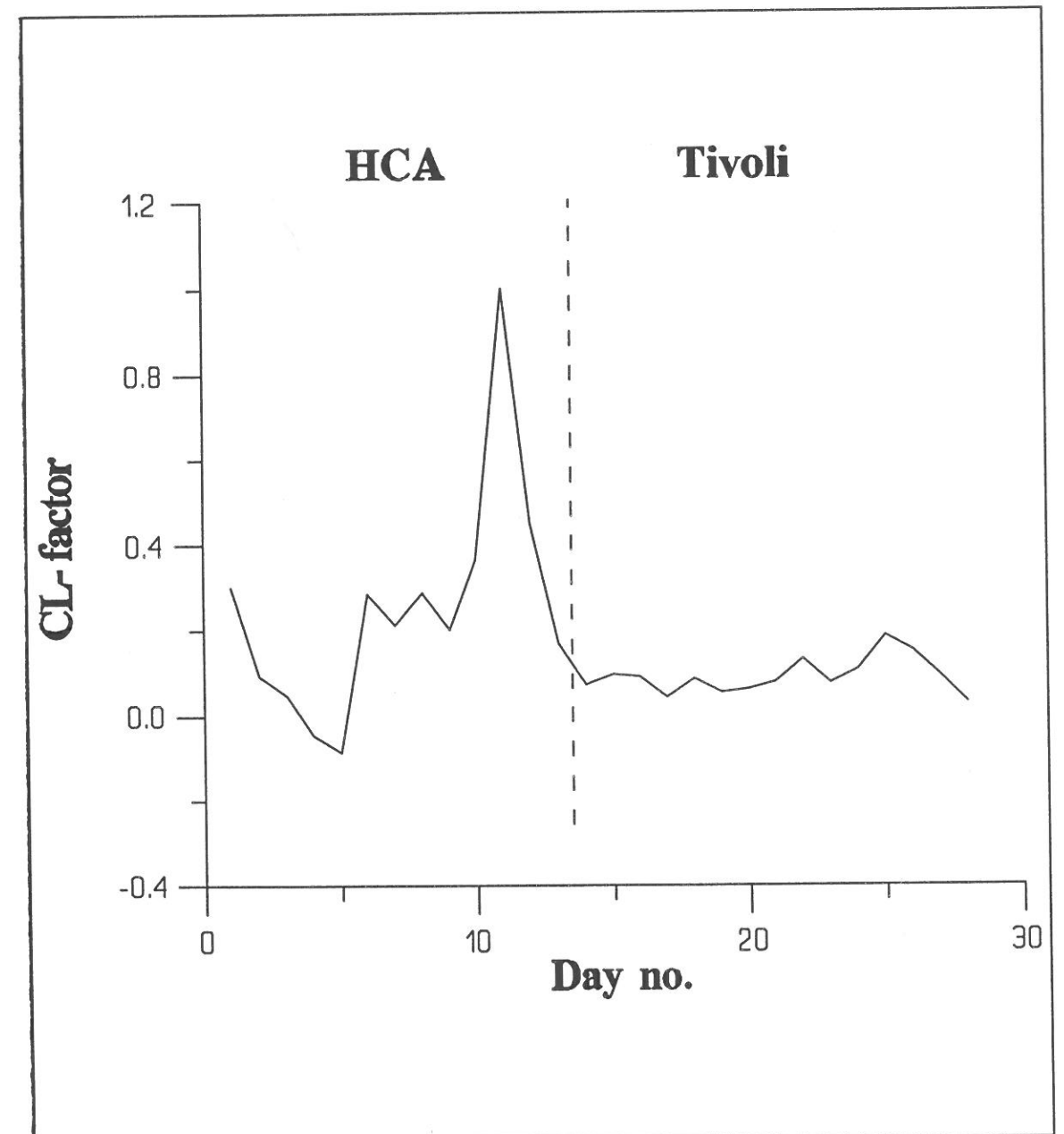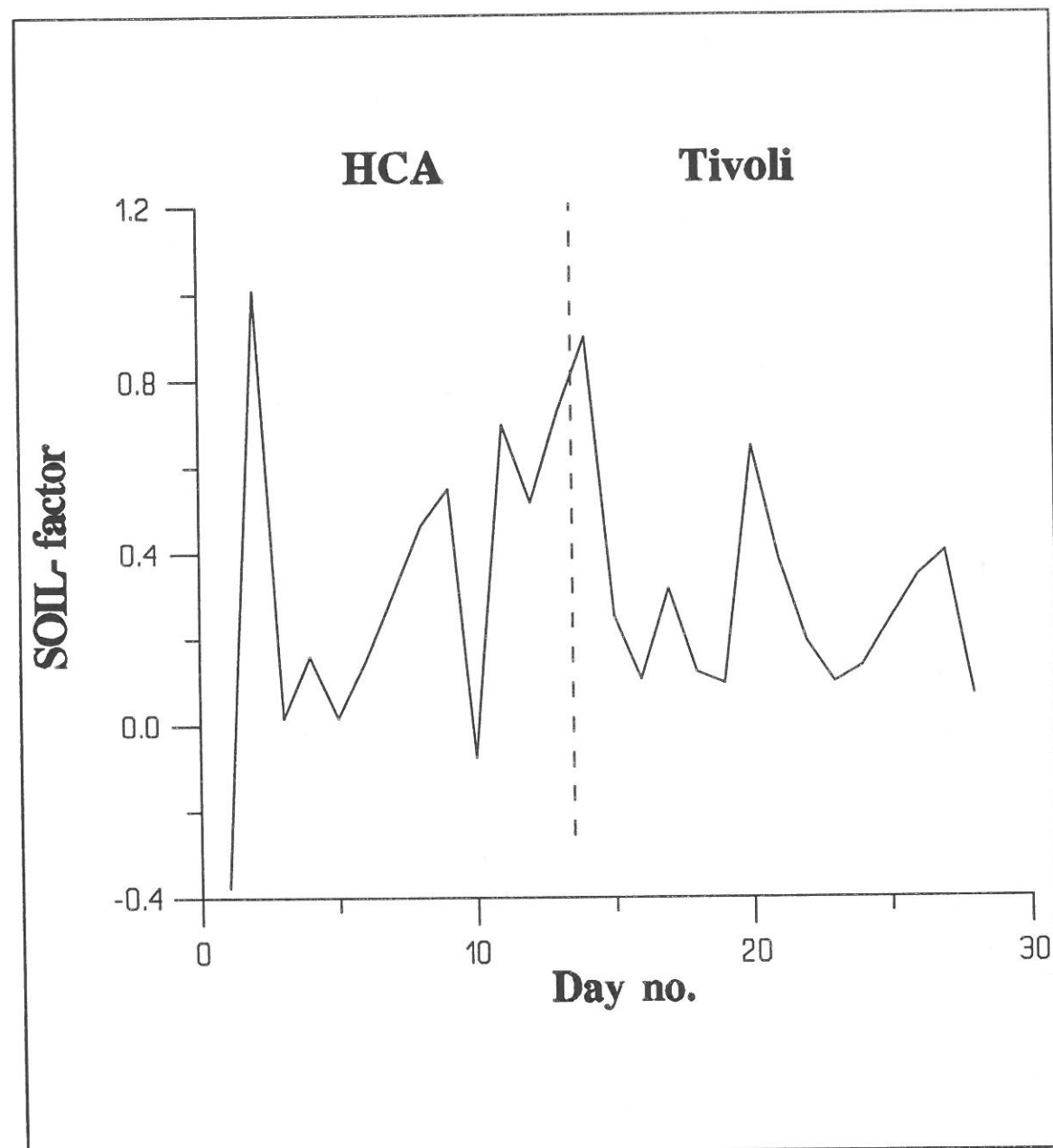

Figure 7. The figure shows the normalized Soil facsores specifying the days that belong to the two different locations.

The Cl factor is interpreted as an artifact factor caused by the contribution of the salt spreading due to ice on the roads. The factor is therefore highly related to the temperature. Another source to the Cl factor is seaspray, i.e., spray from the sea is transported to the air during high wind speeds and transported over land. However, the pike on the Cl factor is most likely explained as salting the roads as a winter precaution (see Figure 5).

All the facscores are shown in the Figures 5 - 8. It is seen that unrealistic nega-

tive values appeared in one factor, namely the Auto factor. This may be caused by using the orthogonal factor rotation, which does not allow for factor correlations, and the Auto source is highly correlated to the Soil source (see also Figure 1). Figure 6 shows that the contribution from traffic on HCA is approximately three times higher than the Tivoli contribution when adding a threshold to the Auto-facscores that removes all negative factorscores.
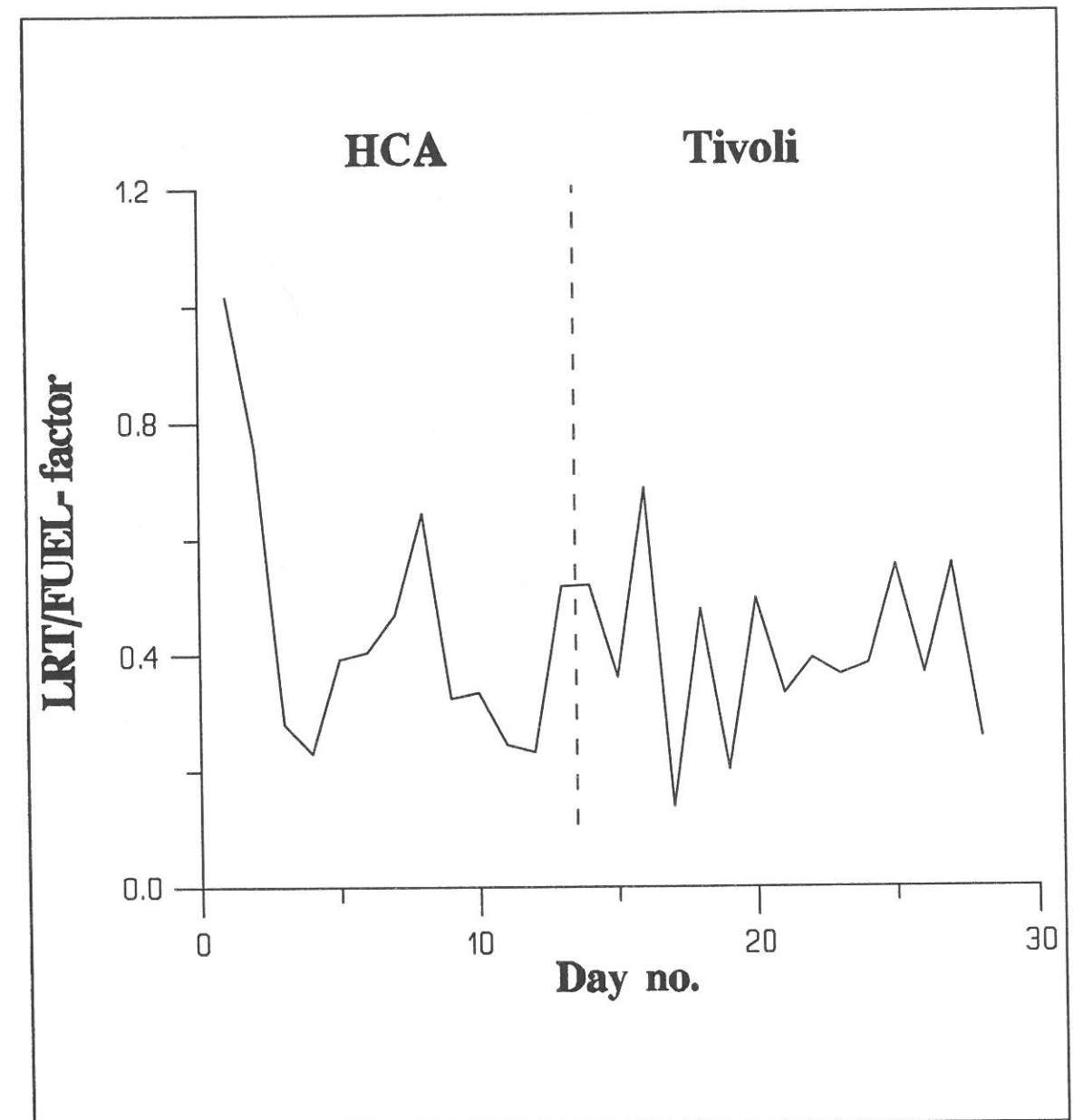
Figure 8. The figure shows the normalized LRT/FUEL facsores specifying the days which belong to the two different locations.

The Cl factor (see Figure 5) shows systematic behavior as the pikes of facscores appeared at both the HCA and the Tivoli station, although the pike as expected is much minor at the Tivoli station.

The LRT/Fuel and Soil factors, see Figure 7 and 8, both show a similar level on both stations with only a slightly higher level of the Soil factor at the HCA

station. Thus, this confirmed that the major part of the contribution from resuspension of the vehicles at HCA is covered by the Auto-factor.

The general conclusions of the factor-analysis are:

Nearly all the contributions of PAH are related to the traffic factor. The contribution from the traffic is approximately 3 times higher at HCA than at Tivoli.

The factor-analysis with an ortogonal variation failed in a perfect discrimation between Soil and Auto components due to source correlation from resuspension.

Applicability of MePh/Ph Ratio to Estimate the Diesel Contribution

The PAH rich diesel fuel contains a relatively high content of alkylated PAH compared to the content of the parent PAH. The reason to this is low temperature PAH formation (petrogenesis) produces mixtures enriched in alkyl-susbstituted PAH and other kinetically favored compounds in contradiction to high temperature processes (combustion and pyrolysis) encouraging the generation of unsubstituted (thermodynamically favored) compounds (Youngblood and Blumer 1975). The emission amount of PAH and mutagens, and the emission ratio of the alkylated PAH compared to the unsubstituted from diesel engines depends on the fuel composition, the PAH content and the PAH composition in the fuel and lubricant, and the engine operating conditions (Barbella et al. 1989, Jensen and Hites 1983, Rasmussen 1990, Schramm 1993, Schramm et al. 1993). Thus at low combustion temperature and low exhaust temperature the MePh/Ph ratio is high, while it decreases with increasing combustion and exhaust temperature. Nevertheless, compared to other sources, e.g. petrol engines, the MePh/Ph emission ratio is higher from diesel engines as Benner et al. (1989) most elegantly showed in a recent roadway tunnel study. Benner et al. (1989) calculated the MePh/Ph ratio from diesel engines to be 4.5 and the ratio from petrol engines to be 0.6. Considering the difference in the driving conditions between city traffic and roadway tunnel traffic the ratios of Benner et al. (1989) is suggested to represent a lower limit value for city traffic.

Fig. 9 shows the MePh to Ph ratio at different sites. The ratio values from this investigation is the ratio between the mean concentration of particulate MePh and that of particulate Ph. These values should be the same as the ratio between the mean concentration of total MePh and that of total Ph, as the gas to particle distributions of MePh and Ph previous (Nielsen and Pilegaard 1990) had been found to be the same (see Section 4.2). The MePh/Ph ratio falls in the following order: Diesel exhaust gas (5.5) (from Westerholm et al. 1991), bus street (4.8), BS;WO (3.6), bus garage (2.0), BS;WE (1.8), CP;WO (1.6), petrol exhaust gas (0.7). The value of diesel exhaust gas on 5.5 from Westerholm et al. (1991) was achieved from a Swedish bus in a test simulating the driving in an European city. This value agreed reasonable with the value on 4.8 observed in a bus street. The advantages/dis-advantages applying field sampling and applying single engines in laboratory tests have been discussed in Section 4.2. The diesel exhaust gas value on 5.5 agreed even better if one comparred it with the bus street value of the mean of the MePh/Ph ratio (5.4 ± 1.7). The fall of the MePh to Ph ratio in the range, BS;WO (3.6), BS;WE (1.8) and CP;WO (1.6), agreed with the expectations on the PAH traffic contribution in these three type of samples. The low MePh to Ph ratio observed in the bus garage samples have been discussed in Section 4.2.
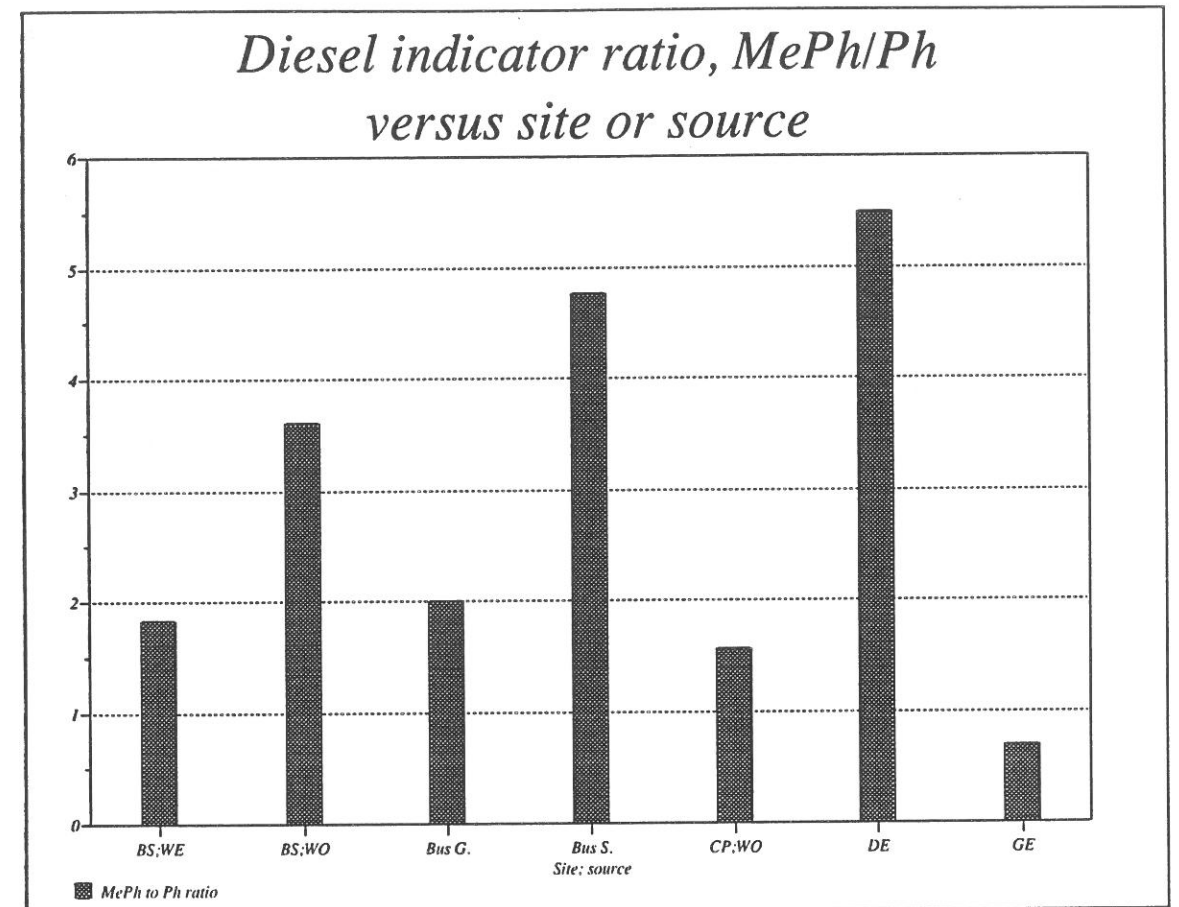
Figure 9. The diesel traffic indicator ratio, methylphenanthrenes to phenanthrenes ratio (MePh/Ph), at different sites or from different sources. BS;WE: Busy street, weekends, BS;WO: Busy street, working days, Bus G.: Bus garage, Bus S.: Bus street, CP;WO: City park, working days, DE: Heavy-duty diesel truck exhaust gas, GE: Petrol-powered vehicle exhaust gas.

Comparison of results from the busy street and the city park

Table 12 compares the PAH levels in the busy street and city park on 41 coincident measuring days covering the following period of the week: Monday 10 am - Saturday 10 am. The PAH results are compared with those of other air pollution components. The traffic related PAH, Cor, BghiP and dieselBeP, had the highest BS to CP ratio, 6.6, 6.4 and 5.8, respectively. The other PAH, BaP, BeP and BbjkF, had BS to CP ratios in the range of 3.7 to 4.2. The set of 14 mutagenicity results had lower BS to CP ratios, in the range of 2.5 to 3.2.

Table 12. Comparison of the busy street and the city park levels of PAH (benzo-(a)pyrene, benzo(e)pyrene, benzo(ghi)perylene, coronene, benzo(h)- + benzo(j)- + benzo(k)fluoranthene and dieselBeP), those of other air pollution components and outside city meteorological data on 41 coincident measuring days in the period January - March 1992.

Compound	Busy street	City park	BS to CP ratio	No. of days
Benzo(a)pyrene (ng/m³)	5.5 ± 1.7	1.5 ± 0.7	3.7	41
Benzo(e)pyrene (ng/m³)	4.8 ± 1.2	1.1 ± 0.4	4.2	41
Benzo(ghi)perylene (ng/m³)	9.3 ± 2.0	1.5 ± 0.3	6.4	41
Coronene (ng/m³)	6.7 ± 1.8	1.0 ± 0.3	6.6	41
Benzo(bjk)fluoranthene (ng/m³)	10 ± 3	2.6 ± 0.7	4.0	41
DieselBeP (ng/m³)	2.6 ± 0.7	0.45 ± 0.19	5.8	41
TA98+S9 (rev./m³)	57 ± 19	20 ± 6	2.8	14
TA98-S9 (rev./m³)	38 ± 13	15 ± 3	2.5	14
TA98NR (rev./m³)	30 ± 11	9.4 ± 2.0	3.2	14
NO (ppb)	138 ± 17	30 ± 7	4.6	41
Gas NO$_y$ (ppb)	169 ± 17	55 ± 8	3.1	41
CO (ppm)	2.04 ± 0.19	0.37 ± 0.06	5.5	41
SO$_2$ (ppb)	7.6 ± 1.1	4.5 ± 1.1	1.7	41
Lead (µg/m³)	0.25 ± 0.05	0.067 ± 0.017	3.8	17
Bromide (ng/m³)	52 ± 11	15 ± 3	3.4	17
Copper (ng/m³)	59 ± 11	13 ± 3	4.6	17
Sulphate (µgS/m³)	2.7 ± 0.5	2.0 ± 0.4	1.4	17
Vanadium (ng/m³)	12 ± 3	10 ± 3	1.2	15
Nickel (ng/m³)	6.7 ± 1.5	6.3 ± 1.4	1.1	16
Potassium (µg/m³)	0.34 ± 0.06	0.23 ± 0.05	1.4	17
Soot (µg/m³)	56 ± 7	23 ± 4	2.4	41
Particles (µg/m³)	95 ± 11	63 ± 7	1.5	41
Wind-rate (m/s)	5.9 ± 0.7	5.9 ± 0.7		39
Temperature (°C)	3.4 ± 0.8	3.4 ± 0.8		41

The BS to CP ratio is affected by different sources and process. As discussed in Section 4.1 traffic sources (e.g. CO), resuspension (e.g. the resuspension group), atmospheric depletion (e.g. NO) and deposition processes (e.g. the resuspension group) will increase the BS to CP ratio.

The BS to CP ratio will be diminished by the interference of following:
Other sources (e.g. SO$_2$, particulate sulphur, V, Ni and K), background contribution (e.g. gas NO$_y$) and atmospheric formation.

Furthermore, it shall be borne in mind comparing the BS to CP ratios of PAH and mutagens with those of inorganic pollutants that the PAH and mutagens were sampled in the height of 1.2 m close to the kerbroad in the busy street, while the concentrations of the inorganic pollutants were determined in 3 m height. A PAH intercomparison presented in the joint final report (see Foreword) suggests the PAH concentrations are diminished with 30 % in the heigth of 3 m compared to those in the height of 1.2 m.

The results of Jensen and Stenfalk (1990) and Jensen *et al.* (1993) suggest the background contributions of CO and Cu are in the magnitude of 5 - 10 % of the BS levels. Recent data of Br and Pb in background areas in Western Europe exists (Hopper *et al.* 1991, Jensen *et al.* 1993, Kemp and Manscher 1993) but it is difficult to apply these to do an estimate of the contribution of outside-city sources, as the amount of tetraalkyl lead compounds and ethylene dibromide in petrol has been decreasing the latest years.

The lower BS to CP ratios for the mutagenicities compared to those of PAH are real and not an artifact caused by the different number of samples. E.g. the BS to CP ratio of BbjkF was 3.7 in the set of 14 samples and 4.0 in the set of 41 samples. The reason to the decrease of the BS to CP mutagenicity ratio could be atmospheric processes forming new mutagenic compounds. The relative increase of mutagens at the CP site is minor, *ca.* 30 %.

The BS to CP ratios of the traffic related PAH, BghiP (6.4), Cor (6.6) and dieselBeP (5.8), are in the same magnitude as those of the other traffic pollutants, CO (5.5) and Cu (4.6). While the group of source indifferent PAH, BaP (3.7), BeP (4.2) and Bbjkf (4.0), had ratios in the same magnitude as Pb (3.8) and Br (3.4) and much higher ratios than SO$_2$ (1.7), S (1.4), V (1.2), Ni (1.1) and K (1.4). The different sizes of the sample sets had no significant influnce on the results, e.g. the BS to CP ratio of BbjkF was 3.9 in the set of 17 samples compared to 4.0 in the set of 41 samples.

The BS to CP ratios showed that traffic sources have been the major ones for PAH air pollutants in the busy street.

City Traffic PAH Profile

It appears reasonable to assume the contributions from long-range transport, power plants and heating sources are the same or almost the same in the city park area and in the busy street considering the distance between the two sites only are a few hundred of meters. If one can neglect the influence of atmospheric chemical processes, deposition and resuspension processes, the only difference at the two sites is the distance to the traffic sources. Therefore, the PAH difference level between the two sites can be ascribed to originate only from traffic sources. In the following the PAH difference levels have been utilized for the calculation of of a city traffic PAH profile. *The city traffic PAH profile is the PAH profile one would determine for city air, if vehicles were the only PAH source.* So far, the PAH composition in car exhaust has been evaluated from measurements of the exhaust from individual cars or from measurements in traffic tunnels (Daisey *et al.* 1986, Grimmer *et al.* 1980). None of these methods are perfect. The PAH composition differs from car to car and is dependent on driving conditions, fuel, lubricant and engine conditions (Pedersen *et al.* 1980). The advantage of the method used in the following is the PAH has originated from the exhaust from a great numbers of cars driving in a pattern typic for city traffic.

The presumptions for the method are:

1) significant positive correlations of the individual PAH difference values, e.g. ΔBghiP and ΔBeP in Fig. 10.
2) traffic emissions are the major PAH source at the busy street sampling site.
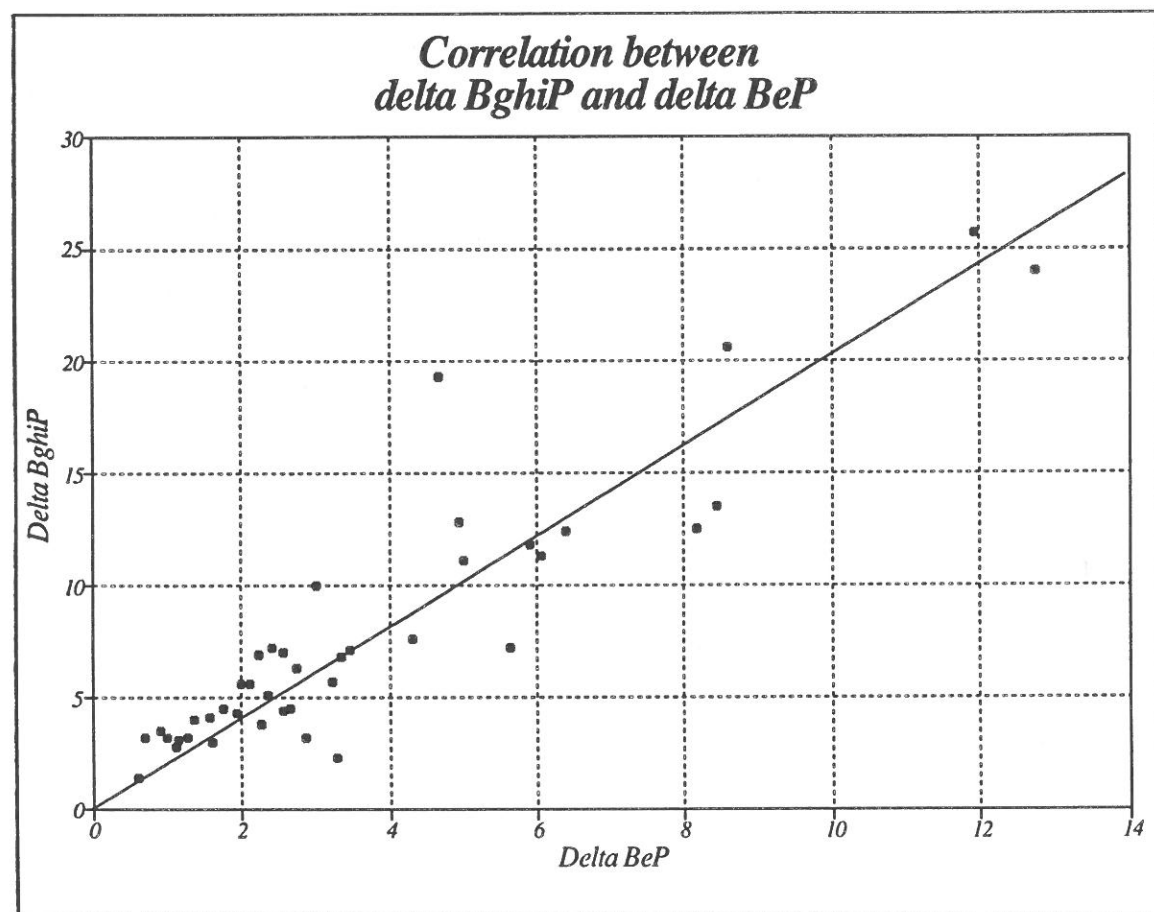
Figure 10. Correlation between ΔBghiP and ΔBeP with the y-intercept value forced to zero. ΔBghiP = the difference between the level of benzo(ghi)perylene in the busy street and that of BghiP in the city park. ΔBeP = the difference between the level of benzo(e)pyrene in the busy street and that of BeP in the city park. ΔBghiP = (2.02 ± 0.17) * Δ BeP, r = 0.91, p < 0.001.

Four statistical methods to determine the PAH city traffic PAH profile have been tested:
1) Linear regression analysis of the ΔPAH values to the ΔBeP value with the y-intercept value forced to zero, see Fig. 10.
2) Linear regression analysis without forcing the y-intercept to zero.
3) The mean of the ratio between ΔPAH and ΔBeP.
4) The ratio between the mean of ΔPAH and the mean of ΔBeP.

Method 1 was choosed as the final method, as it was the only method not giving neither the highest ΔPAH to ΔBeP ratio nor the lowest one for any of the 13 PAH components in Fig. 11, although the difference in the applied results between the four methods was only minor.
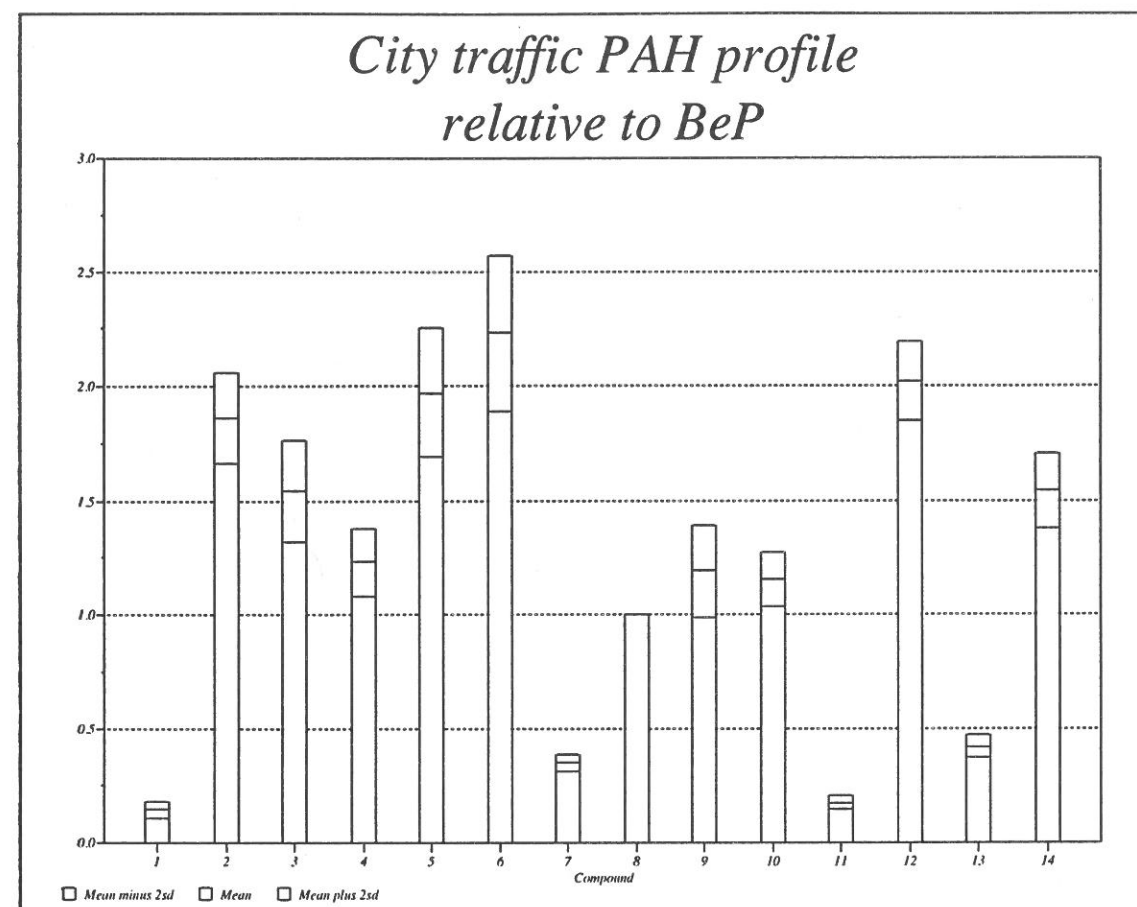
Figure 11. The PAH composition (relative to benzo(e)pyrene) from traffic sources in the city. Identity of the PAH: 1. Benzo(b)naphtho(2,1-d)thiophene, 2. Benzo(ghi)fluoranthene +benzo(c)-phenanthrene 3. Cyclopenteno(cd)pyrene, 4. Benz(a)anthracene, 5. Chrysene + triphenylene 6. Benzo(b)- + benzo(j)- + benzo(k)fluoranthene, 7. Benzo(a)fluoranthene, 8. Benzo(e)pyrene, 9. Benzo(a)pyrene, 10. Indeno(1,2,3-cd)pyrene, 11. Picene, 12. Benzo(ghi)perylene, 13. Anthanthrene, 14. Coronene. The middle levels in the columns in the figure show the mean values. The upper levels the mean values + 2σ. The lower levels the mean value - 2σ. The values are achieved from the linear regression analysis of ΔPAH towards ΔBeP with the y-intercept value forced to zero, see Fig. 10. The correlation coefficient, r, ranged from 0.70 to 0.91, p < 0.001.

Fig. 11 shows the results for the ratios of the 13 different ΔPAH to ΔBeP. The ratio of compound no. 8, ΔBeP, has been included, although its ratio is defined to be 1.0 ± 0.0. BeP is choosed as a reference compound, because it is relative stable in the atmosphere and source indifferent. Fig. 11 shows also the accuracies on the determined ΔPAH/ΔBeP ratios. The dominant PAH in the city traffic exhaust are BbjkF, Chr+TP, BghiP, BghiF+BcP, CP, Cor, BaA, BaP and IP. Thus, the dominant PAH in ambient air are the same in city traffic exhaust gases. The accuracies on the determined ΔPAH/ΔBeP ratio varied from 9 to 24 % with an average on 14 ± 2 %. In general, the accuracies were lowest for the dominant PAH, e.g. BghiP (9 %), and highest for the less abundant PAH, e.g. BNT (24 %).

Fig. 12 shows the PAH composition from city traffic sources, the PAH composition in the fortyone 24-h samples from the busy street and the same number of samples from the city park. As one can see from the figure, BghiF+BcP, CP, BghiP and Cor are emitted in relatively high amounts from traffic sources. This

was also observed in a recent study of PAH pollution at an international airport (Fenger et al. 1990, Nielsen and Pilegaard 1990, Nielsen et al. 1993). Most interesting the results in Fig. 11 and Fig. 12 on the BghiP/BeP (2.02 ± 0.17) and Cor/BeP (1.54 ± 0.16) ratios from this investigation applying the developed difference measurements approach fit very well with previous estimates (Nielsen and Pilegaard 1990, Nielsen et al. 1993). These estimates were based on literature values and measurements from traffic tunnels (Nielsen 1984b, Nielsen 1989, Nielsen and Pilegaard 1990). The previous values were 2.0 and 1.5, respectively (Nielsen and Pilegaard 1990).

Figure 12. Comparison of the PAH composition (relative to benzo(e)pyrene) from traffic sources in the city, in a busy street and in a city park area. Identity of the PAH: See Fig. 11.

Fig. 12 shows the PAH composition in the busy street is close to the PAH city traffic profile suggesting the traffic is the PAH major source in the busy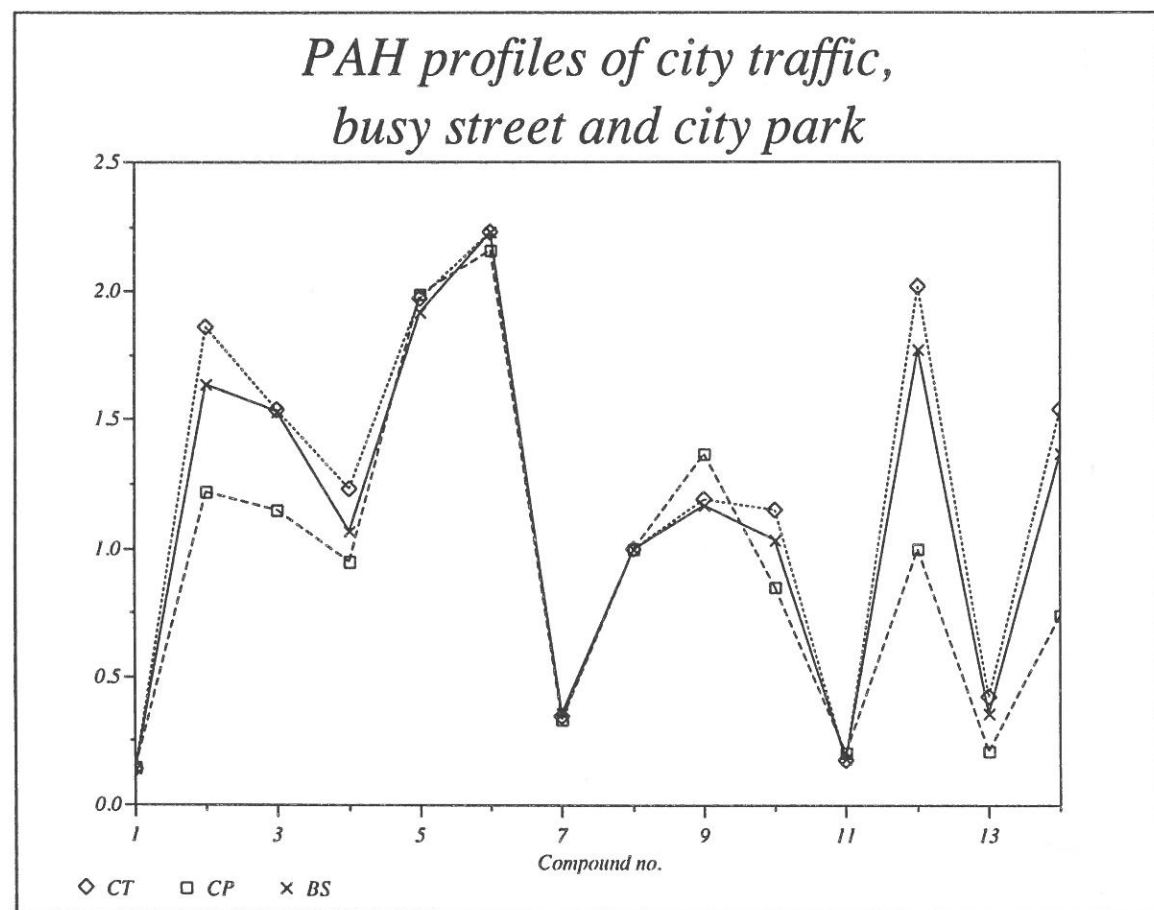 street. In the city park area, it is obvious from Fig. 12, that other PAH sources also are important PAH air pollution sources.

Fig. 13 shows the determination of the diesel BeP proportion of the total city traffic BeP contribution. The approach applied is the same as used in Fig. 10. One presumption using this approach is ΔdieselBeP gives a significant positive correlation with ΔBeP. In all the three tested modifications the correlation was significant (r = 0.69 - 0.86, p < 0.001). The second presumption is atmospheric reactions has not changed the ratio between the level of MePh and that of Ph. As one can see in Fig. 13 the MePh/Ph ratio during the long-range transport episode (see also later) was extreme low suggesting degradation of MePh. The BeP diesel propor-

tion is equal to the slope in the linear regression analysis. If one exclude the long-range transport episode in the analysis the BeP diesel proportion changes to 0.64 ± 0.07 from 0.54 ± 0.10. The third presumption for the application of the method is an adequate estimate of the MePh/Ph ratio in diesel exhaust gases. If one applies an value on 7.0 instead of 5.5 the slope changes to 0.50 ± 0.07 instead of 0.64 ± 0.07. From the factor analysis the BeP diesel proportion can be calculated to be 0.47 (From the Auto-factor in Table 11). Thus, the different results suggest, that the BeP diesel exhaust contribution and the BeP petrol exhaust contribution is comparable.

Compared to this Gudmundsson (1988) have estimated the PAH emission from petrol vehicles to make up 80 - 85 % and that from diesel vehicles to make up 15 - 20 %. The PAH emission factors Gudmundsson (1988) applied were almost the same for both types of vehicles. If one assumes the emission pr. km ratios for the heavier PAH, including BeP, are 1.3 to 1.0 for diesel vehicles compared to the same type of petrol vehicles (Lies et al. 1981, NAS 1981) and corrects the calculations of Gudmundsson (1988) for the increase in the number of diesel vehicles the latest years (Iversen 1993, Municipality of Copenhagen 1990), the petrol cars contribution appears to be about 60 % and the diesel vehicles contributions appears to be about 40%.

Handa et al. (1984) collected 1-h samples in two different traffic tunnels and compared their measurements of 6 PAH with coincident counts of the traffic intensity and traffic composition. The PAH diesel proportion varied from 29 to 71 % with an average on 59 ± 7 %. For BaP the diesel proportion was 61 and 70 % in the two tunnels. The vehicles were driving with a speed on 80 km/h.

Benner et al. (1989) determined the content of 20 PAH in gas phase as well as particulate phase in a traffic tunnel study and analyzed the results by means of factor analysis. The PAH diesel proportion varied from 0 (BbjkF) to 94 % (C_2-phenanthrenes). The diesel proportion of the 10 alkylated phenanthrenes was 90.8 ± 1.4 %. For phenanthrene the diesel proportion was 56 %. For the 4 to 6 ring parent PAH the diesel proportion was 22 ± 15 %, and for BeP and BaP it was 10 and 16 %, respectively. Benner et al. (1989) did not estimate the accuracy of their calculations, but the calculated concentrations of the 4 - 6 ring PAH were typic 1.5 times higher than the measured concentrations. For BeP the calculated concentration was 1.7 times higher than the measured one.

Li and Kamens (1993) and Pistikopoulos et al. (1990) applied both a chemical mass balance model factor analysis combined with different atmospheric chemical reactivities on a data set with PAH measurements on samples from the top of a tall tower in Paris. The PAH distribution between residential heating, petrol vehicles and diesel vehicles was 20 ± 6, 53 ± 4 and 27 ± 2 %, respectively, in the investigation of Li and Kamens (1993) and 11 ± 5, 57 ± 4 and 32 ± 2 %, respectively, in the investigation of Pistikopoulos et al. (1990).

Different investigations applying different approaches have shown diesel vehicles as well as petrol vehicles are important PAH sources. The diesel proportion of the total traffic contribution varies from 15 to 70 %. Although part of this variance maybe can be explained by differences in the composition of vehicles and differences in the driving conditions, the major reason to the discrepancies is probably the state of the art. Therefore, it appears most reasonable to conclude diesel and petrol PAH emissions are comparable and much further research are needed to establish their relative importance. The approach developed within this project shows the particulate MePh and Ph measurements can be applied to determine a semiquantitative diesel PAH chemical mass balance expression.
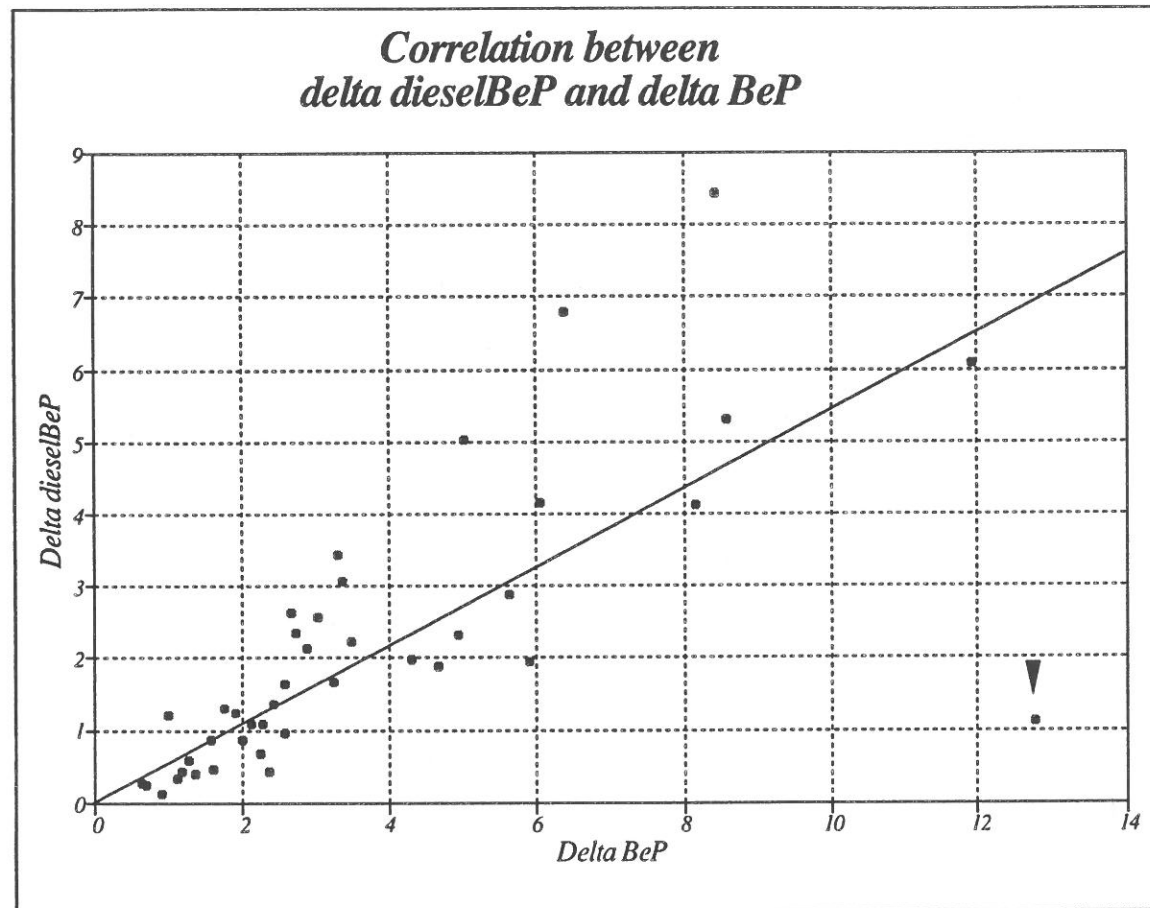
Figure 13. Determination of the PAH (as benzo(e)pyrene (BeP)) diesel proportion of the total city traffic PAH (as BeP) contribution. The y-intercept value is forced to zero. The PAH diesel proportion = the slope = 0.54 ± 0.10 (r = 0.69, p < 0.001). ΔBeP = the difference between the BeP level in the busy street and that in the city park. ΔdieselBeP = the difference between the estimated diesel traffic contribution to the BeP level in the busy street and that to the BeP level in the city park. If one exclude the long-range transport episode data, see later in this chapter, i.e. the point in the lower right corner from the correlation analysis, the PAH diesel proportion = 0.64 ± 0.07 (r = 0.86, p < 0.001). If one also assumes an appropiate value for the diesel exhaust gas ratio between methylphenanthrenes and phenanthrene should be 7.0 instead of 5.5, the PAH diesel proportion = 0.50 ± 0.07 (r = 0.81, p < 0.001).

Comparison of Working Days and Weekend PAH Levels in a Busy Street

In Fig. 2 in Section 4.1 the WOBS to WEBS ratios of traffic gases (1.7), traffic metals (1.8), soot (1.55), resuspension group (1.9), SO_2 (1.2) and particulate components from heating and power plants (1.2) were shown. Fig. 14 shows the busy street levels of PAH (BaP, BeP, BghiP, Cor, BbjkF and dieselBeP) on working days (Monday 10 am - Friday 10 am) and in weekends (Saturday 10 am - Sunday 10 am). The WOBS to WEBS ratios of the six components were 1.4, 1.45, 1.8, 2.0, 1.3 and 1.6, respectively. Thus, the group of traffic related PAH (BghiP, Cor and dieselBeP) has WOBS to WEBS ratios (1.6 - 2.0) close to the traffic related inorganic components (1.7 - 1.8). The source indifferent PAH group (BaP, BeP and BbjkF) had WOBS to WEBS ratios being slightly lower (1.3 - 1.45). Fig. 15

shows the mutagenicity levels in the busy street on working days and in weekends. The WOBS to WEBS ratios for TA98+S9, TA98-S9 and TA98NR were 1.3, 1.1 and 1.2, respectively.
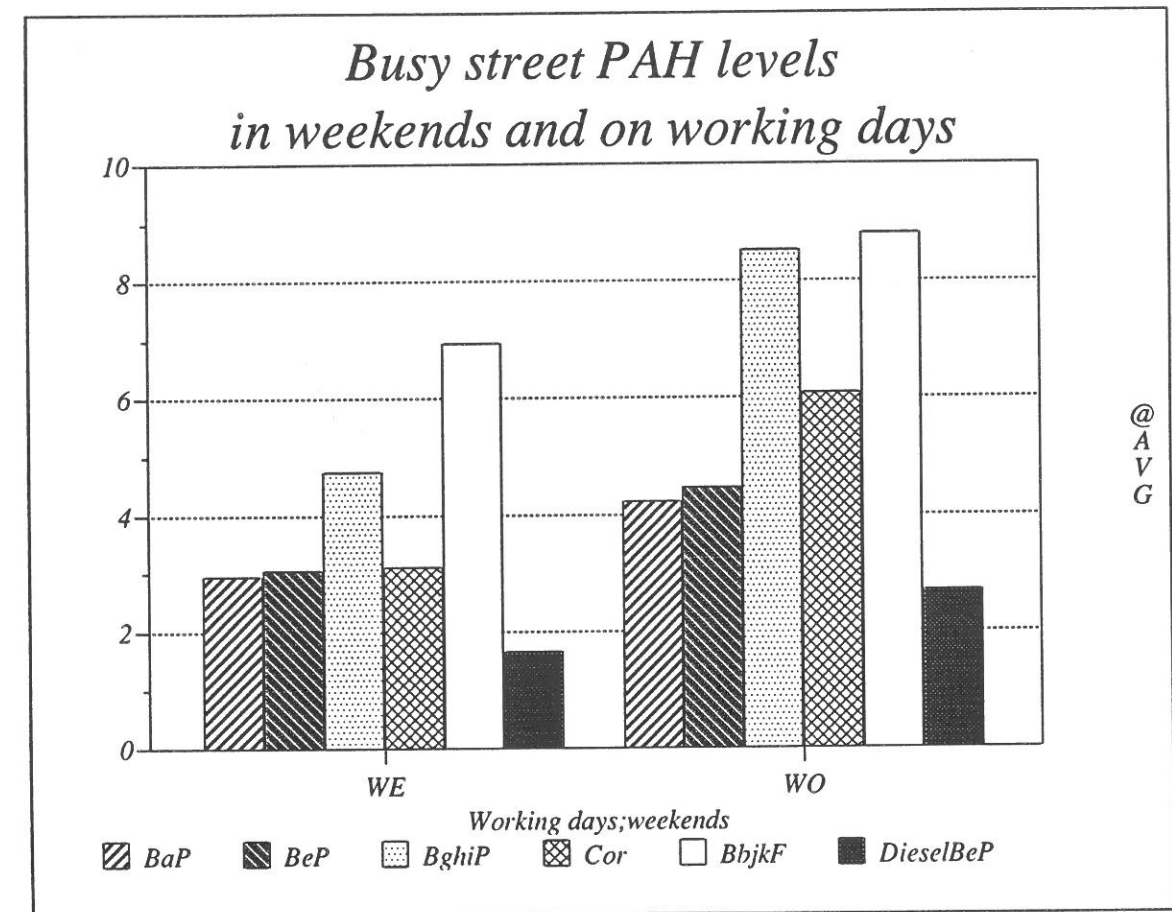
Figure 14. Comparison of working days (WO) and weekends (WE) PAH levels (ng/m³) in a busy street. Identity of the PAH: BaP. benzo(a)pyrene, BeP. benzo(e)pyrene, BghiP. benzo(ghi)perylene, Cor. coronene, BbjkF, benzo(b)- + benzo(j)- + benzo(k)fluoranthene, DieselBeP. diesel traffic contribution of benzo(e)pyrene.

Thus, the range of of the PAH and mutagenicity ratios falls in the order: Traffic related PAH, source indifferent PAH and mutagenicity. The same range of order was observed, when one previous in Section 4.4 compared their BSWO to CPWO ratios. The concentrations of ozone and other photochemical oxidants are typic higher in weekends than on working days in city areas (Fenger 1984). Therefore, the simular behaviour of mutagens comparing their WOBS to WEBS ratios as well as their BSWO to CPWO ratios with those of PAH support atmospheric formation of mutagens also takes place in city air and not only in long-range transported air masses (Fenger et al. 1990, Nielsen and Nielsen 1994, Nielsen and Pilegaard 1990). The enhancement of the mutagenic activity by means of atmospheric processes has also been discussed by Löfroth (1990).

Considering the PAH their WOBS to WEBS ratios as well as their BSWO to CPWO ratios confirm traffic being a major source for these air pollutants in the busy street area.

Figure 15. Comparison of working days (WO) and weekends (WE) mutagenicity levels (rev./m³) in a busy street. Identity of the mutagenicty tests: TA98S9. TA98 + S9, TA98_S9. TA98 - S9. TA98NR. TA98NR - S9.
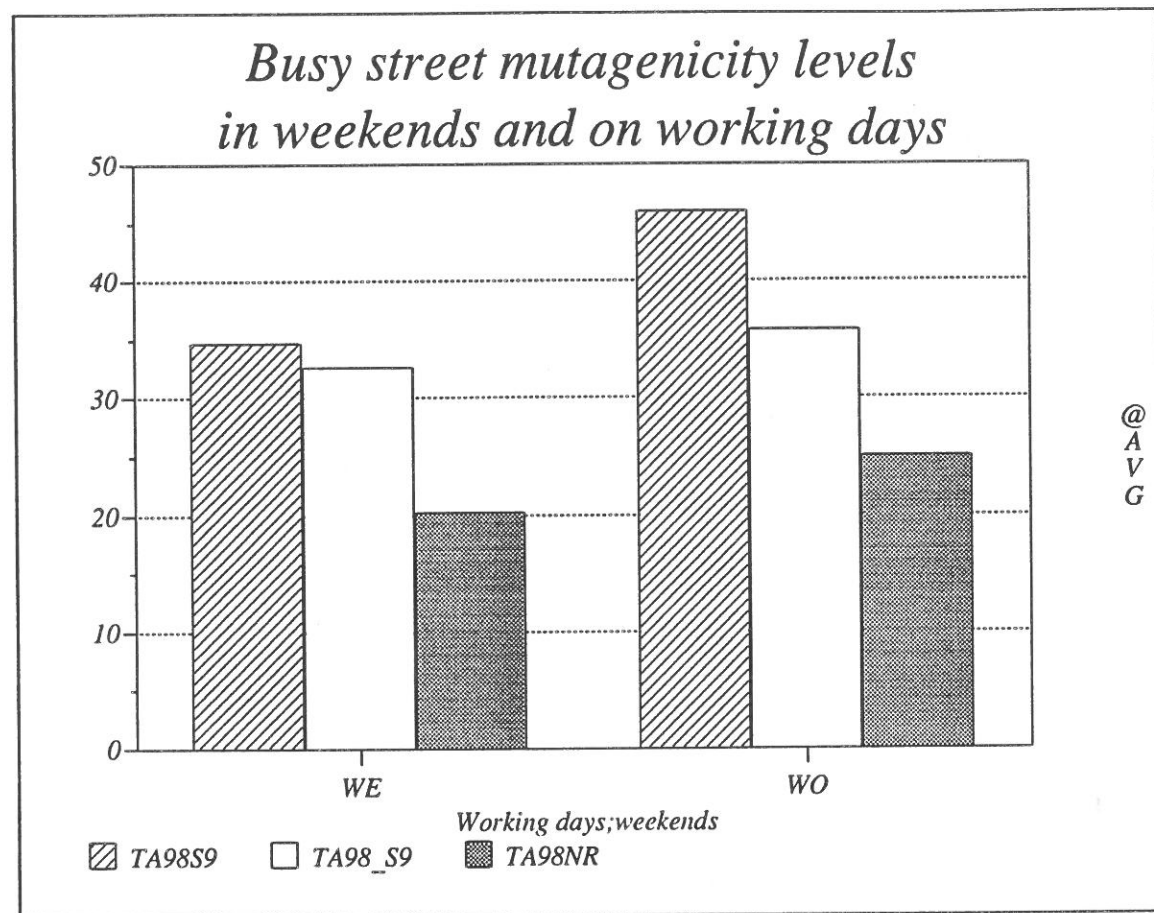
This is also confirmed by Fig. 16. The BghiP to BeP and Cor to BeP ratios are applicable indicators for the PAH traffic contribution proportion (cf. Fig. 12). Fig. 16 shows the BghiP to BeP and Cor/BeP ratios at different sites. The ratios fall in the same range as one would expect the traffic contribution proportion to fall:

City traffic (CT, 2.02 and 1.54), busy street working days 1992+1993 (BS;WO, 1.89 and 1.40), busy street working days 1986+1987 (BS86, 1.80 and 1.36), busy street weekends 1992 (BS;WE, 1.40 and 1.0), suburban (SU, 1.10 and 0.90), city park (CP, 1.00 and 0.74), village (VL, 0.90 and 0.75) and a agricultural area (AA, 0.96 and 0.47).

In general, the BghiP/BeP ratio and the Cor/BeP ratio follows the same pattern and range. The only exception is the agricultural area has a higher BghiP/BeP ratio than the village, while the Cor/BeP ratio is highest in the village area.

Representative values of BghiP/BeP and Cor/BeP emission ratios from non-traffic sources, e.g. heating sources, have been discussed earlier (Nielsen 1984b, Nielsen 1989, Nielsen and Pilegaard 1990). All field samples are influenced by traffic pollution. But nevertheless, a minor number of the PAH samples collected in Danish investigations can be applied to assess maximum values for the BghiP/BeP and Cor/BeP ratios from non-traffic sources. The Greater Copenhagen samples from 1954 and 1955 of Campbell and Clemmesen (1956) gives an indication on the pretraffic ratio of BghiP/BeP(BaP). The mean ratio between BghiP and BaP was 0.87 ± 0.24 in this investigation. Sørensen and Vester (1981) determined the PAH content in long-range transported polluted air from the Continent in
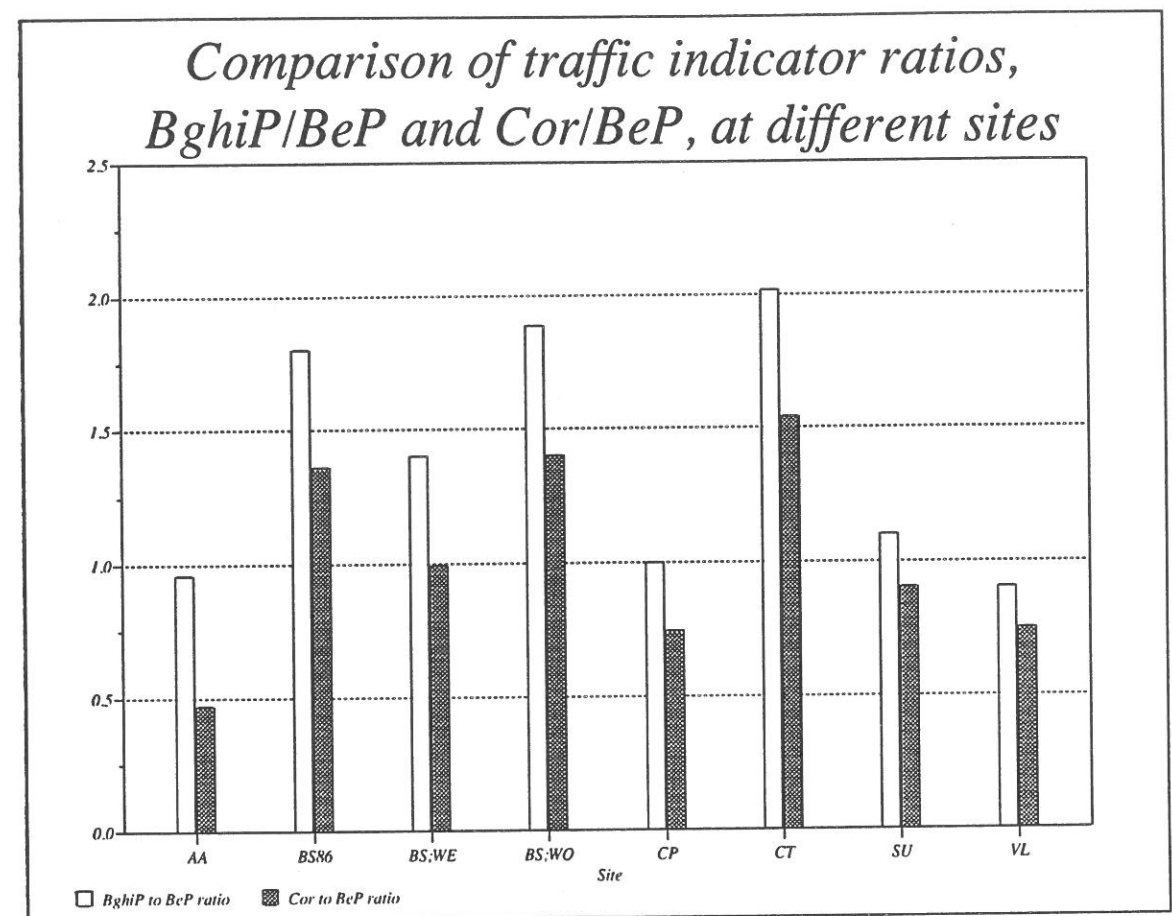
Figure 16. Comparison of the traffic indicator ratios, benzo(ghi)perylene (BghiP) to benzo(e)pyrene (BeP) and coronene (Cor) to BeP, at different locations. Identity of the locations: AA. Agricultural area (Risø), BS86. Busy street 1986 + 1987, BS;WE: Busy street, weekends (1992), BS;WO. Busy street, working days (1992 + 1993), CP. City park, CT. City traffic, SU. Suburban area (Kastrup), VL. Village (Dragør).

samples from South Langeland with winds from south. They observed a mean ratio between BghiP and BeP on 0.89 ± 0.20 in these samples. Nielsen and Pilegaard (1990) observed a mean ratio between BghiP and BeP on 0.97 ± 0.08 and between Cor and BeP on 0.69 ± 0.16 in southern wind samples from the northern part of a village (Dragør) in the southern part of Amager. These samples consisted mainly of long-range transported PAH from the Continent and a contribution from heating and traffic sources in the village.

Comparing the previous assesment of a BghiP/BeP ratio on 0.8 from non-traffic sources (Nielsen and Pilegaard 1990) with the results in Fig. 16, and the results of Campbell and Clemmesen (1956), Nielsen and Pilegaard (1990) and Sørensen and Vester (1981), it is recommended still to apply this value on 0.8. The documentation for a non-traffic Cor/BeP emission ratio value is poorer than that for the BghiP/BeP ratio and the results are less consistent (Nielsen 1984, Nielsen 1989, Nielsen and Pilegaard 1990). Therefore, it is suggested to apply a value on 0.3 for the Cor/BeP ratio from non-traffic sources.
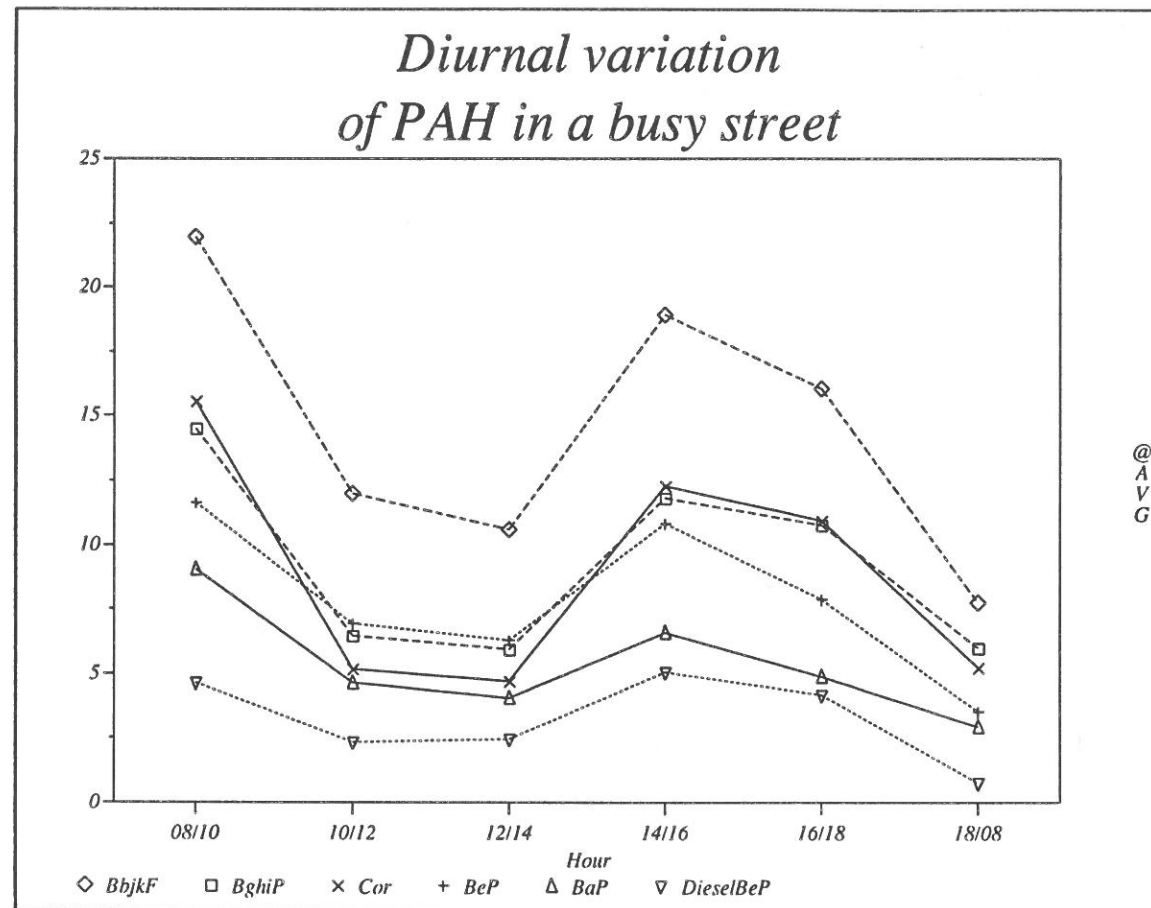
Figure 17. Diurnal variation of PAH in a busy street in the period 10. March 8^{00} - 12. March 8^{00} 1993 showing peak values of PAH in the morning and the afternoon hours following the traffic pattern. The values are the average of two periods covering following hour periods: 8^{00} - 10^{00}, 10^{00} - 12^{00}, 12^{00} - 14^{00}, 14^{00} - 16^{00}, 16^{00} - 18^{00} and 18^{00} - 8^{00}. The identity of the PAH: BbjkF. benzo(b)- + benzo(j)- + benzo(k)fluoranthene, BghiP. benzo(ghi)perylene, Cor. Coronene, BeP. benzo(e)pyrene, BaP. benzo(a)pyrene, dieselBeP. the estimated contribution of BeP from diesel traffic.

Figs. 17 and 18 show the average diurnal variation of PAH (BeP, BaP, BbjkF, BghiP, Cor and the estimated dieselBeP), CO, SO$_2$, NO and gas NO$_y$ in the busy street covering a 48-h period in March 1993. In general, the air pollution level was elevated. Thus, the mean levels of the 5 PAH (BeP, BaP, BbjkF, BghiP and Cor) were 1.45 ± 0.24 times higher than those in Table 4. The levels of CO, NO and gas NO$_y$ were 1.5 - 1.6 times higher than those in Table 3, while the SO$_2$ level was 2.0 times higher than that in Table 3.

The traffic gases, CO, NO and gas NO$_y$, had peaks in the rush hours, 8 - 10 am and 4 - 6 pm, and minimum in the lunch hours 0 - 2 pm and in the night hours 6 pm - 8 am. SO$_2$ showed a total different diurnal variation with a peak in the lunch hour 0 - 2 pm and very small variation in the day hours.

The diurnal variations of the PAH had greatest similarities with those of the traffic gases. The PAH had also a morning peak and a minimum at lunch time, but the afternoon peak fell at 2 - 4 pm and not at 4 - 6 pm suggesting the SO$_2$ sources also were important PAH sources. This appeared also reasonable consider
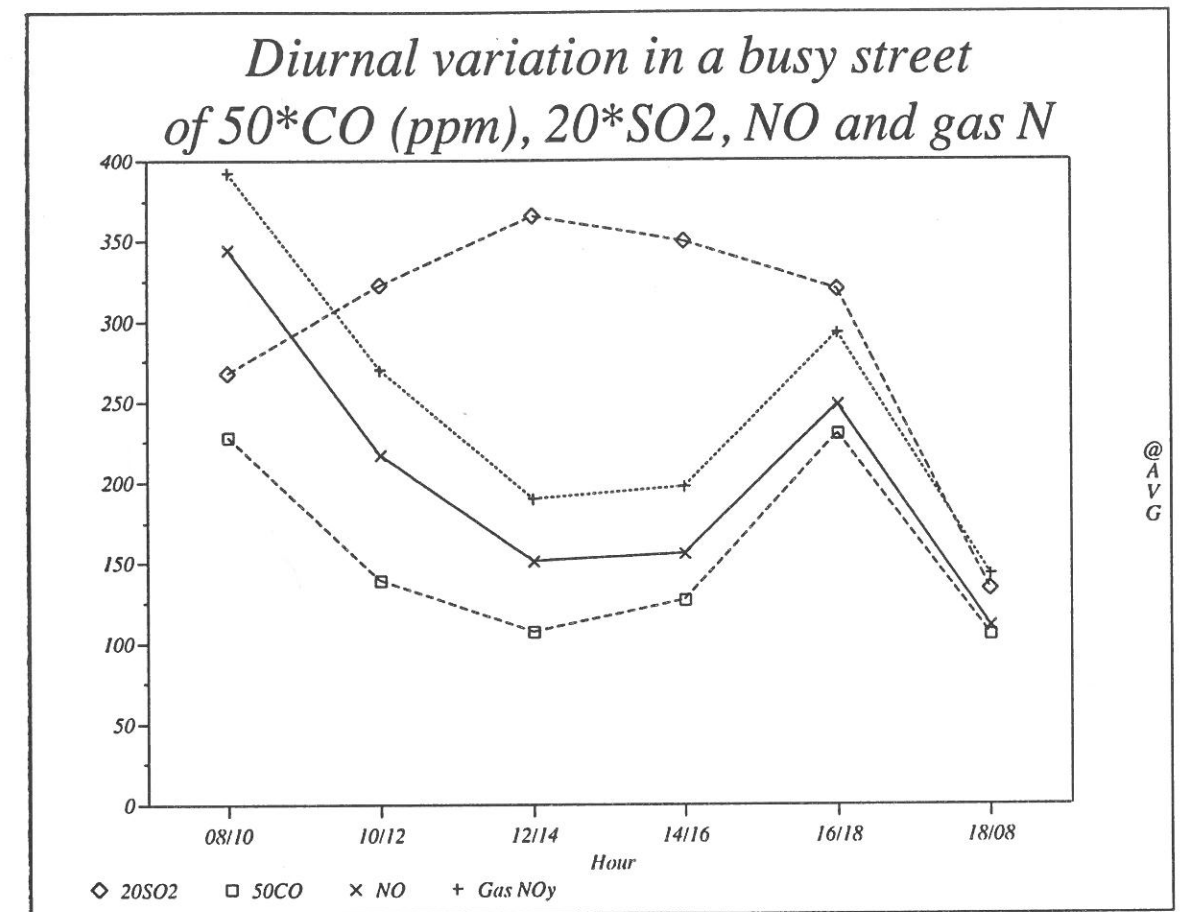
Figure 18. Diurnal variation of CO (50 times the ppm concentration), NO (ppb) and gas NO$_y$ (ppb), traffic pollution components, and SO$_2$ (100 times the ppb concentration) originating mainly from heating, power plants and long-range transport. CO, NO and gas NO$_y$ have a similar diurnal variation as PAH in Fig. 17, while SO$_2$ shows a different pattern with a maximum in the lunch hours.

ing the relative high SO$_2$ concentrations. A simple simulation of the BeP diurnal variation by means of a linear combination of the CO and SO$_2$ values suggested 60 % of BeP should originate from traffic sources and 40 % from the SO$_2$ sources (r = 0.67, p < 0.05).

The BghiP/BeP (1.18) and Cor/BeP (1.15) ratios were lower than the typic BS working days ratios (1.89 and 1.40, respectively, see Fig. 16) and similar to the BS weekend ratios (1.40 and 0.99, respectively) also suggesting an increased contribution of PAH from non-traffic sources. It should be mentioned the reason to the small difference between the BghiP and Cor concentrations is not known. Applying the BghiP/BeP and Cor/BeP ratios the BeP traffic contribution is suggested to be 50 ± 37 % being in accordance with the other estimate on 60 %. The PAH diurnal variation showed in Fig. 17, therefore, appeared to show a day with increased PAH contribution from non-traffic sources.

Influence of Long-Range Transport on 24. January 1992 on the Composition of Air Pollutants in the Busy Street and the City Park

In general, the SO$_2$ levels were low in the period Jan. - Febr. 1992 (Table 2) compared to those the previous years, even though the air pollution with SO$_2$ has been decreasing since 1986 (Jensen et al.. 1993). In opposition to this the con-

centrations of particulate matter, NO and gas NO_y (Table 2) were relative high compared to the situation the previous years. A SO_2 episode (see Fig. 19) was observed on 24. - 25. January. Compared to the mean levels in Table 2 SO_2 had increased with a factor of 3.7 at the BS station and a factor of 5.2 at the city park station. The contribution from long-range transport from the Continent was confirmed by the wind direction and the elevations of the concentrations of other long-range transport air pollutants tracers, particulate sulphur, V, Ni, soot and particles. The elevation of these components at the busy street station was 2.1, 2.5, 2.1, 2.0 and 1.4, respectively, compared to the mean levels in Table 2. At the city park station the elevation was 2.5, 3.1, 2.1, 3.3 and 2.0, respectively. As shown in Fig. 19 no increase in the concentrations of CO was observed on January 24. - 25. But some of the other traffic indicators showed an increase. Thus the concentrations of Pb and Br were increased with a factor of 1.6 and 1.3, respectively, at the busy street station and a factor of 2.7 and 2.0, respectively, at the city park station.

The elevations of mutagens and PAH on 24.-25. January compared to the mean levels (Table 4) were even higher than those of SO_2. Thus the content of mutagens was increased with a factor of 7.4 - 7.9 at busy street station. BeP was increased with a factor of 4.6 at the busy street station and a factor of 5.8 at the city park station.

Fig. 20 compares the relative content of PAH traffic tracers (CcdP, BghiP, Anthan and Cor) in the long-range transport episodes with the mean situations in the busy street and at the city park and with their relative content from city traffic sources. As one can see from Fig. 20 the relative content of all four PAH traffic tracers fell in the range:

City traffic, mean busy street, busy street LRT epsiode, mean city park, city park LRT episode.

Thus Fig. 20 shows the decrease of the traffic PAH contribution proportion during the long-range transport episode and by that the long-range transport has affected the PAH composition. Most interesting, the simple chemical mass balance method applying the developed ratios, BghiP/BeP and Cor/BeP, for traffic as well as non-traffic sources was able to give a satisfactorily description of the traffic and non-traffic contributions of BeP during the long-range transport episode. The BghiP/BeP and Cor/BeP ratios were 1.48 and 1.28, respectively, in the LRT-BS case and 0.80 and 0.66 in the LRT-CP case. Thus the traffic BeP contribution proportion was 68 ± 23 % at the busy street station and 15 ± 29 % at the city park station. The total contribution from heating and long-range transport shall be the same at the two stations. This was also the case, the BeP contribution from heating and long-range transport at the busy street station was 6.5 ng/m³ (0.32 * 20.25) and that at the city park station was 6.4 ng/m³ (0.85 * 7.49).

The simple chemical mass balance method also gave a satisfactorily description of the heavy increase of the heating+LRT BeP contribution under the LRT episode comparing this data set with the set of 41 coincident measured samples in Table 11. The BghiP/BeP and Cor/BeP ratios were 1.94 and 1.40, respectively, in the 41 samples from the busy street station and 1.36 and 0.91, respectively, in those from the city park station. The traffic BeP contribution proportion can be calculated to be 90.5 ± 5 % at the BS station and 47.5 ± 3 % at the CP station. The mean heating+LRT BeP contribution was 0.46 and 0.58 ng/m³, respectively, at the two stations. Thus, the heating+LRT BeP contribution has increased with a factor on 12 during the long-range transport episode.

The relative content of the traffic PAH tracers decreases in the order CT, BS, BS;LRT, CP, CP;LRT. Also the long-range transport contribution of PAH had caused the relative content of the traffic PAH tracers to decrease, although the decrease only had been minor.
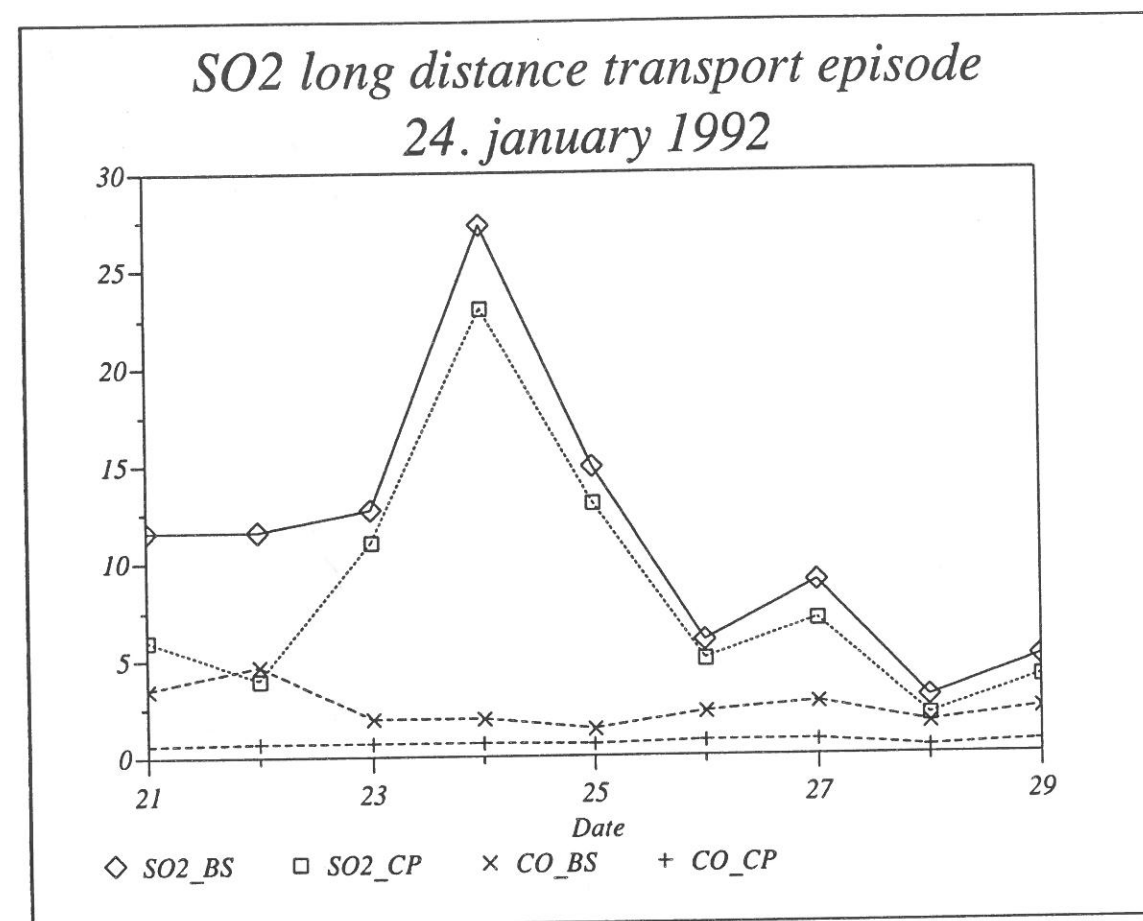
Figure 19. Elevation of the SO_2 levels in the busy street (BS) and the city park (CP) in the period 24. Jan. 10^{00} - 25. Jan. 10^{00} caused by long-range transport contribution from the Continent. The traffic component, CO, was not elevated. The 24 h levels of SO_2 and CO are shown for the period 21. Jan 10^{00} - 30. Jan. 10^{00}.
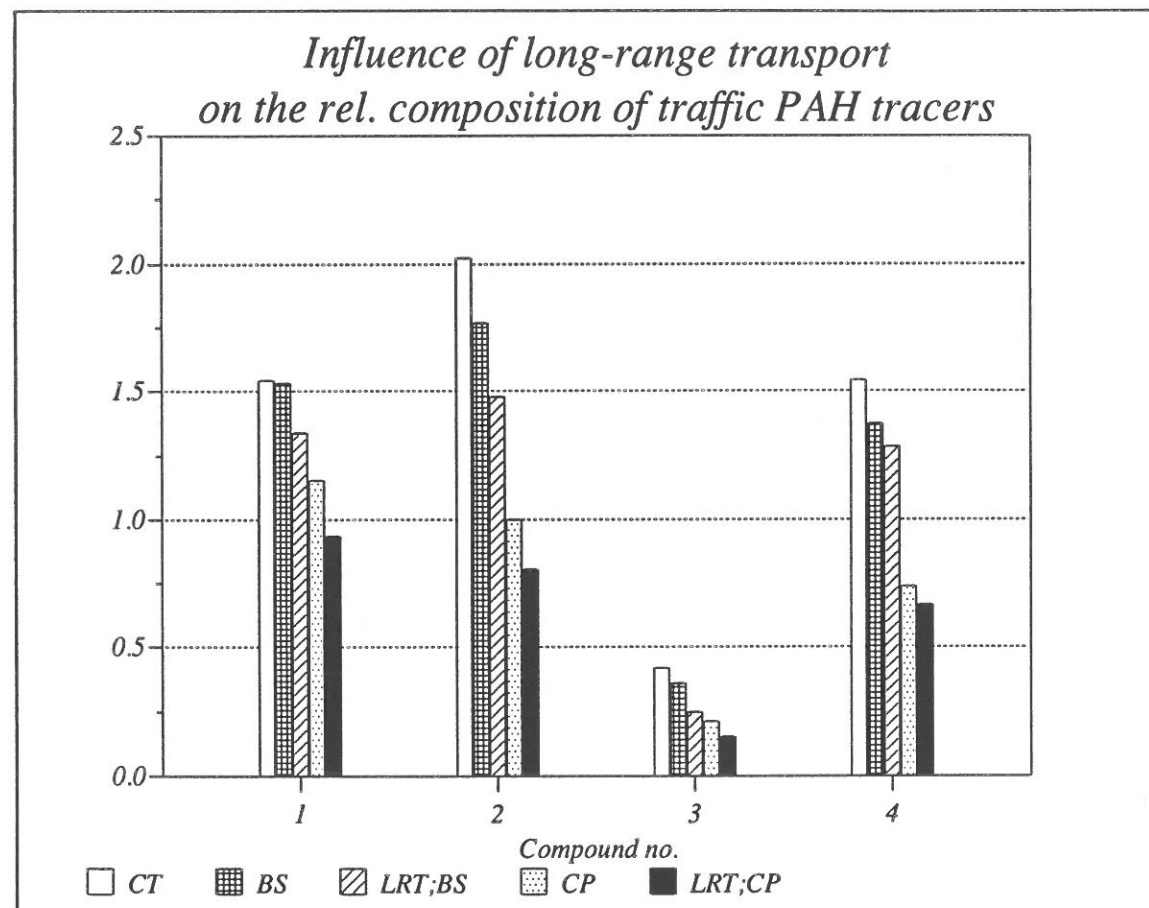
Figure 20. Comparison of the relative composition of traffic PAH tracers (relative to benzo(e)pyrene) during the long-range transport episode with the average conditions. Identity of the PAH compounds: No. 1. cyclopenteno(cd)pyrene, 2. benzo(ghi)perylene, 3. anthanthrene, 4. coronene. Identity of the situations: CT. city traffic composition, BS. average busy street composition, LRT;BS. busy street composition on 24. Jan., CP. average city park composition, LRT;CP. city park composition on 24. Jan. 1992.

Influence of Ambient Temperature on Traffic Emissions of PAH and Mutagens

It is known the traffic fuel consumption is higher at winter-time than at summer-time despite the speed is not higher and the length of the distance is the same (Erik Iversen, private communication, 1994). This implies the combustion of the fuel is more inefficient at lower temperatures than at higher ones, and the emissions of organic pollutants may be higher at winter-time. Recent Swedish results have shown cases where the PAH emission increased with a factor 5 - 6 at winter-time conditions compared to summer-time conditions (Westerholm 1994). The seasonal variation of CO in busy streets is typic minor than a factor of two with the highest concentrations in the winter months. The major source of CO should be petrol engines. The seasonal variation of BghiP, an indicator of PAH from traffic, was found to be a factor 2 - 5 in urban street air as shown in the joint final report (see the Foreword).

The following negative correlations confirmed the traffic emission of PAH is relative much higher at low ambient temperatures:

BghiP (BS) (ng/m^3) / CO (BS) (ppm) = -(0.44 ± 0.09) * temperature (^{0}C) + (5.61 ± 1.89), r = -0.51, p < 0.001.

Cor (BS) (ng/m^3) / CO (BS) (ppm) = -(0.37 ± 0.09) * temperature (^{0}C) + (4.20 ± 1.82), r = -0.46, p < 0.001.

Correspondingly a significant correlation was observed between the ambient temperature and the ratio between the traffic contribution of BeP and CO (r = -0.49, p < 0.001). The measurements applied in the correlations were performed in the period January - March 1992 and covered the ambient temperature range -3 to +8 ^{0}C. It should be obvious the observed correlations shall not be extrapolated to do quantitative conclusions on the PAH traffic contributions at summertime. Nevertheless, the results explain that the seasonal variation oF BghiP and other PAH in urban street air is higher than that of CO. Relative to CO the levels of PAH fall with ca. 30 %, if the ambient temperature increases from 2 to 5 ^{0}C.

Table 13 shows the monthly variation of PAH, mutagens and inorganic components in the busy street and in the city park area. The dominant wind directions had been westerly winds (SW, W or NW). Only one sample from the March period occurred with winds from south. In the January + February set the 24-h mean temperature ranged from -2.5 to 6 ^{0}C with a mean on 2.1 ^{0}C, and the 24-h mean wind speed ranged from 3 to 10 m/s with a mean on 4.9 m/s. In the March set the 24-h mean temperature ranged from 3 to 7 ^{0}C with a mean on 5.3 ^{0}C, and the 24-h mean wind speed ranged from 3 to 10 m/s with a mean on 6.7 m/s. The single sample in the March set having winds from the south showed the lowest traffic contribution of PAH in the city park area of all the 17 samples, but besides of this none of the air pollution parameters at the two sites in the south wind sample showed any characteristic features different from the those observed in the others 16 samples.

At both stations the traffic air pollution parameters (traffic PAH, traffic gases and traffic metals) showed a decrease in the March set compared to the January + February set.

In the busy street the major source of PAH and mutagens should be the traffic. All the PAH and mutagens showed a larger decrease than the traffic gases and metals in the March set. The decrease of the traffic gases and metals was approximately 30 % minor than the decrease of PAH and mutagens. Thus, the busy street comparison supports the relative emissions of PAH and mutagens from traffic decreases with increasing ambient temperature.

At the city park area the traffic contribution of PAH and mutagens was estimated to be minor than 50 % (see the following). Both the two PAH groups (traffic PAH indicators, BghiP and Cor, and the so-called source indifferent PAH, BeP, BaP, BbjkF and IP) and the mutagens showed a decrease in the March set compared to the January + February set. The decrease varied from 20 to 50 % and was larger for the traffic PAH group than for the mutagens. The traffic gases showed also a decrease on about 60 %, while the traffic metals showed a decrease on about 40 %. The decrease of the mutagens and most of the PAH in the March set is perhaps larger than one should expect, if one neglects the temperature effect on traffic emissions of PAH and mutagens and considers

a) the PAH and mutagens traffic contribution is minor than 50 % of the total contributions

b) the decrease on about 50 % of the traffic inorganic pollutants

c) the unchanged levels of the other particulate inorganic pollutants, S, V, Ni and K.

Table 13. Comparison of the March to January + February air pollution levels of PAH, mutagens and inorganic components in the busy street site and at the city park site covering measuring days, where all parameters were determined at both sites.

Components	Busy Street: Mean (March) / Mean (Jan. + Febr.)	City Park: Mean (March) / Mean (Jan. + Febr.)
Traffic PAH (BghiP, Cor)	0.38 - 0.40	0.50 - 0.57
Other PAH (BeP, BaP, BbjkF, IP)	0.37 - 0.50	0.49 - 0.80
Mutagens (TA98+S9, TA98-S9, TA98NR)	0.38 - 0.43	0.61 - 0.73
Traffic gases (CO, NO, gas NO_y)	0.52 - 0.59	0.35 - 0.48
Traffic metals (Cu, Pb, Br)	0.56 - 0.75	0.53 - 0.72
Soot	0.66	0.67
Particles	0.93	0.94
SO_2	0.66	0.75
Other metals (S, K, V, Ni)	0.94 - 1.06	0.84 - 1.06
Temperature	5.3 ^{0}C and 2.1 ^{0}C	5.3 ^{0}C and 2.1 ^{0}C
Wind speed - outside city	6.7 m/s and 4.9 m/s	6.7 m/s and 4.9 m/s
No. of measurements	5 and 12	5 and 12

It appears from Table 13 that despite of the increase in the ambient temperature and maybe the increased turbulence caused by the higher mean wind speed the levels of S, K, V and Ni were the same in the two sets. Also the amount of particles was almost the same in the two sets. This suggests the air pollution contribution from heating sources, power plants and other non-traffic sources had been the same in the two set.

The observations of Institute of Toxicology in their report (see the Foreword) on the ratio between the content of mutagens on the busy street and that in the city park area was larger in January + February than in March can be explained by the following:
a) The contributions of mutagens from non-traffic sources in the city park area appear to be the same in the January + February set and in the March set.
b) The traffic contribution had decreased in the March set at both stations.
c) The traffic is the dominant source of mutagens in the busy street, while the traffic contribution of mutagens in the city park area is important, but not dominant.

Evaluation of the PAH Traffic Contribution

The results of seventy-six 24-h samples and 12 short term samples of PAH from a busy street and fifty-one 24-h samples from a city park area have been detailed analyzed. The analysis showed 80 % of the busy street PAH content applying BeP as PAH indicator originated from traffic having the following distribution:
Working days (89 ± 5 %) and weekends (59.5 ± 3.5 %).
The 51 samples from the city park area covering the weekdays period Monday 10 am - Saturday 10 am showed a traffic contribution on 39 ± 11 %. If one limited the analysis to the weekdays period Monday 10 am - Friday 10 am the traffic contribution was 41 ± 9 %. The estimates was achieved by means of a simple chemical mass balance method. This was demonstrated to give a satisfactorily description of the PAH contributions from traffic sources and those from other sources in the following cases:

1) Short-term samples in the busy street
2) Long-range transport episode
3) Coincident measuring days in the busy street and the city park area.

Besides the results from the chemical mass balance method the following results also showed the dominance of traffic sources in the busy street on working days:

1) The factor analysis.
2) The similarity between the diurnal variation of PAH and of the traffic gases, CO, NO and gas NO_y.
3) The elevation of the PAH concentrations on working days compared to weekends.
4) The similarity between the busy street PAH profile and the estimated one from city traffic.
5) The elevation of the PAH concentrations in the busy street compared to those in the city park area.

The investigation performed covering the months January - March. Investigating other seasons traffic should also turn up to be the major source in busy streets and an important source to city background air. As shown long-range transport of PAH occasionally may affect the PAH levels even in busy streets in Copenhagen. During the measuring period (Jan. - March 1992) the SO_2 levels were lower than normal for this period of the year, even though one takes the decreasing trend of SO_2 into consideration. The winter meteorological conditions can show great variations from one year to another. These variations may also cause higher PAH contributions from heating sources and long-range transport than found in this investigation. The contribution of mutagens from long-range transport will be higher than that of PAH. A minor number of observations (Fenger *et al.* 1990, Nielsen and Nielsen 1994) suggest the increase to be about a factor of 1.5. However, this does not mean the traffic contribution proportion of mutagens will be lower than that of PAH considering the relative high emission of mutagens from diesel-powered vehicles (Löfroth 1990, Salmeen *et al.* 1985).

The PAH contribution from diesel vehicles and that from petrol vehicles appeared to be comparable. A method to determine the diesel part of the total traffic contribution was developed. Considering the scattering results different investigators have achieved evaluating the diesel part by means of different methods one shall at present only apply such methods to do semiquantitative conclusions.

5 Conclusions

The concentrations of benzo(a)pyrene and benzo(e)pyrene (BeP) were 4.4 ± 1.2 and 4.4 ± 0.7 ng/m³, respectively, in a busy street in Central Copenhagen and 1.4 ± 0.6 and 1.3 ± 0.3 ng/m³, respectively, in an adjacent city park area. The samples in the busy street was taken in 1.2 m height close to the traffic. The traffic intensity was 60,000 vehicles each day. The investigation covered the winter months January - March. The winter was mild with a mean temperature on 2.7 °C. The major PAH source in the street was the traffic. In the city park area traffic was also an important source, but not the major one.

Applying BeP as PAH indicator the traffic contribution was estimated to be 80 % in the street. The weekdays distibution was as follows:

Working days: 90 %. Weekends: 60 %.

In the city park area the working days traffic contribution was estimated to be 40 %.

The simple chemical mass balance method performed to do these estimates applying the ratio between benzo(ghi)perylene and BeP and that between coronene and BeP was demonstrated as a control to give a satisfactorily description of the PAH contribution from traffic sources and from other sources in the following cases:

1) Short term samples in the busy street.
2) A comparison at the two sites at an episode with long-range transport and inversion.
3) Coincident measuring days in the busy street and the city park area.

A city traffic PAH profile was determined. The busy street PAH profile was very close to the city traffic one. The diurnal variation of PAH showed peaks in the morning and afternoon rush hours and the lowest concentrations in the night hours and was very close to the diurnal variation of the traffic gases, CO, NO and gas NO$_y$.

A method to differentiate between PAH contribution from petrol vehicles and those from diesel vehicles was developed and applied. The method was compared with similar attempts in investigations in other countries. In this investigation it is concluded the PAH contributions from petrol vehicles and from diesel vehicles are comparable.

Inversion and long-range transport episode from the Continent was random in this investigation covering a mild winter. But it was demonstrated such episodes may affect the PAH levels and composition even in the busy street.

It is suggested there is a minor formation of mutagenic compounds relative to the PAH during the transport to the city park area. These accords with previous Danish observations on formation on mutagens relative to PAH during long-range transport.

Summary

The presence of PAH, mutagens and other air pollutants (soot, particles, CO, NMHC, NO, gas NO$_y$, SO$_2$, particulate metals, sulphate, chloride and bromide) was investigated in a busy street in Central Copenhagen and in a park-area adjacent to the street. The diurnal variation of PAH was determined and compared with the diurnal variation of the air pollutant gases, CO, NO, gas NO$_y$ and SO$_2$. Besides the content and composition of PAH and the content of mutagens was determined in a bus street in the Central Aarhus and in a bus garage area in the outskirts of Copenhagen.

The concentrations of benzo(a)pyrene and benzo(e)pyrene (BeP) were 4.4 ± 1.2 and 4.4 ± 0.7 ng/m³, respectively, in the busy street and 1.4 ± 0.6 and 1.3 ± 0.3 ng/m³, respectively, in the city park area. It was evaluated applying BeP as PAH indicator, that 80 % of the PAH content in the busy street originated from traffic sources. The weekdays distribution was as follows:

Working days: 89 ± 5 %, weekends: 59.5 ± 3.5 % being in accordance with the variation in the traffic intensity.

In the park area the traffic contribution was 39 ± 11 % of the total PAH contribution for the weekdays period Monday 10 am - Saturday 10 am. If the analysis was limited to the weekdays period Monday 10 am - Friday 10 am the traffic contribution was 41 ± 9 %. The estimates was achieved by means of a simple chemical mass balance method. This was demonstrated as a control to give a satisfactorily description of the PAH contribution from traffic sources and that from other sources in the following cases:

1) Short-term samples in the busy street.
2) Long-range transport episode with comparison of the two sites.
3) Coincident measuring days in the busy street and the city park area.

The following results and observations support the dominance of traffic sources in the busy street:

1) Results from the factor analysis.
2) The similarity in the diurnal variation of PAH and that of the traffic gases, CO, NO and gas NO$_y$.
3) The increase of PAH on working days compared to weekends.
4) The similarity between the busy street PAH profile and the estimated one from city traffic.
5) The elevation of the PAH concentrations in the busy street compared to those in the city park area.

The PAH contribution from diesel vehicles and that from petrol vehicles appeared to be comparable. A method to determine the diesel part of the total traffic contribution was developed. The reliability of the method appeared not to be poorer than similar methods developed by investigators in other countries.

The investigation performed covering the months January - March. Investigating other seasons traffic should also turn up to be the major source in busy streets and an important source to city background air. As shown long-range transport of PAH occasionally may affect the PAH levels even in busy streets in Copenhagen. During the measuring period (Jan. - March 1992) the SO$_2$ levels were lower than normal for this period of the year, even though one takes the decreasing trend of SO$_2$ into consideration. The winter meteorological conditions can show great variations from one year to another. These variations may also cause higher PAH

contributions from heating sources and long-range transport than found in this investigation. The mutagenic contribution from long-range transport will be higher than that of PAH. A minor number of observations (Fenger *et al.* 1990, Nielsen and Nielsen 1994) suggest the increase to be about a factor of 1.5. However, this does not mean the traffic contribution proportion of mutagens will be lower than that of PAH considering the relative high emission of mutagens from diesel-powered vehicles (Löfroth 1990, Salmeen *et al.* 1985).

Resume

Forekomsten af PAH, mutagener og andre forurenende komponenter (sod, partikler, CO, NMHC, NO, gas NO_y, SO_2, partikulære metaller, sulfat, chlorid og bromid) er undersøgt i en trafikeret gade i det Centrale København, H. C. Andersens Boulevard, og i et nabo-beliggende parkområde, Tivoli. Døgnvariationen af PAH i den trafikeret gade er blevet bestemt og sammenlignet med døgnvariationen af forureningsgasserne, CO, NO, gas NO_y og SO_2. Desuden er PAH-sammensætningen og indholdet af mutagener blevet bestemt i en bustrafik-gade i det centrale Aarhus og i et busgarage-område i udkanten af København.

Koncentrationerne af benz(a)pyren (BaP) og benz(e)pyren (BeP) var henholdsvis 4.4 ± 1.2 ng/m^3 og 4.4 ± 0.7 ng/m^3 i den trafikerede gade og henholdsvis 1.4 ± 0.6 og 1.3 ± 0.3 ng/m^3 i parkområdet. Med BeP som PAH-indikator er det vurderet, at 80 % af PAH-indholdet i den trafikeret gade hidrører fra trafikken. Ugefordelingen er som følgende:

Hverdage 89 ± 5 % og weekender 59.5 ± 3.5 %.

Trafik-bidraget i park-området er vurderet til 39 ± 11 % dækkende følgende del af ugen mandag kl. 10 - lørdag kl. 10. For ugeperioden mandag kl. 10 - fredag kl. 10 blev trafik-bidraget beregnet til 41 ± 9 %.

Beregningerne af trafik-bidraget er opnået ved hjælp af en enkel kemisk masse balance metode. Metoden er påvist at give en tilfredsstillende beskrivelse af PAH-bidraget fra trafikale kilder så vel som bidraget fra andre kilder (boligopvarmning og fjerntransport) i følgende tre typer af situationer:

1) Døgnvariation i den trafikeret gade.
2) Fjern-transport-episode med inversion.
3) Sammenligning af målinger på sammenfalde måledage i den trafikeret gade og parkområdet.

Følgende forhold støtter, at trafikken er den dominerende PAH-kilde i den trafikeret gade:

1) Resultaterne fra faktor-analyse.
2) Ligheden i døgnvariationen af PAH og døgnvariationen af trafik-gasserne, CO, NO og gas NO_y.
3) Forhøjelsen af PAH-koncentrationerne på hverdage sammenlignet med weekender.
4) Ligheden mellem PAH-profilen i den trafikeret gade med en PAH-profil, som er blevet bestemt for bytrafik.
5) Forhøjelsen af PAH-niveauerne i den trafikeret gade sammenlignet med niveauerne i parkområdet.

PAH-bidraget fra dieseltrafik og fra benzin-trafik synes at være sammenlignelig. En metode til at bestemme dieseltrafik-andelen af det totale trafik-PAH-bidrag er blevet udviklet. Metodens pålidelighed synes at være fuld højde med tilsvarende metoder udviklet i udlandet.

Undersøgelsen har dækket perioden januar - marts. Såfremt at man undersøgte andre årstider skulle det forventes, at trafikken ligeledes er PAH-hovedkilden i den trafikeret gade samt en væsentlig kilde til PAH-forureningen i bybaggrundsluften. Undersøgelsen har vist, at fjerntransport og inversion lejlighedsvis kan forårssage, at bidraget fra non-trafikale kilder bliver sammenlignelig med bidraget fra trafikale kilder i trafikeret gader. I den undersøgte periode (januar - marts 1992) synes SO_2 niveauerne lavere end normalt, også når man tager hensyn til den

faldende tendens af SO_2 niveauerne i Danmark. Den undersøgte vinter-periode var præget af mild vejr og få frostdage med lav vindhastighed og inversion. De meteorologiske forhold kan vise stor variation fra en vinter til en anden. Disse forhold kan medføre, at der vil være vintre med et højere PAH-bidrag fra boligopvarmning og fjerntransport end det, der blev observeret i denne undersøgelse. De mutagene bidrag fra fjerntransport vil være højere end PAH-bidraget. Tidligere observationer i Danmark (Fenger *et al.* 1994, Nielsen and Nielsen 1994) indikerer, at den relative mutagenicitets-forøgelse er omkring en faktor 1,5. Dette indebærer ikke, at trafik-mutagenicitets-bidraget vil være lavere end bidraget af PAH, eftersom diesel-trafikken har et relativt højt bidrag af mutagener (Löfroth 1990, Salmeen *et al.* 1985).

Acknowledgements

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Traffic PAH and Other Air Pollutants in the Center of a Large City

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Abstract (Max. 2000 characters)

The presence of particulate PAH and mutagens and other air pollutants (soot, particles, CO, NMHC, NO, gas NO_y, SO_2, particulate metals, sulphate, chloride and bromide) was investigated in a busy street (60,000 vehicles each day) in Central Copenhagen and in a park-area adjacent to the street in the period January - March.

The concentrations of benzo(a)pyrene and benzo(e)pyrene (BeP) were 4.4 ± 1.2 and 4.4 ± 0.7 ng/m^3, respectively, in the busy street and 1.4 ± 0.6 and 1.3 ± 0.3 ng/m^3, respectively, in the park area. Applying BeP as PAH indicator the traffic contribution was estimated to be 80 % in the street. The weekdays distribution was as follows:

Working days: 90 %. Weekends: 60 %.

In the city park area the working days traffic contribution was estimated to be 40 %.

The simple chemical mass balance method performed to do these estimates applying the ratio between benzo(ghi)perylene and BeP and that between coronene and BeP was demonstrated as a control to give a satisfactorily description of the PAH contribution from traffic sources and from other sources in different cases:

A city traffic PAH profile was determined. The busy street PAH profile was very close to the city traffic one. The diurnal variation of PAH showed peaks in the morning and afternoon rush hours and the lowest concentrations in the night hours and was very close to the diurnal variation of the traffic gases, CO, NO and gas NO_y.

A method to differentiate between PAH contribution from petrol vehicles and those from diesel vehicles was developed and applied. It is concluded the PAH contributions from petrol vehicles and from diesel vehicles are comparable.

Descriptors INIS/EDB

AIR POLLUTION MONITORING; AUTOMOBILES; CARCINOGENS; COMPARATIVE EVALUATIONS; DENMARK; DIESEL FUELS; EMISSION; GASOLINE; MUTAGENS; POLLUTANTS; POLYCYCLE AROMATIC HYDROCARBONS; ROAD TRANSPORT