Applications of Source Receptor Models Using Air Pollution Data in Stockholm

Undergraduate Thesis

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Abstract

Relating ambient concentrations of air pollution data to their sources is essential to improve the air quality in urban areas. In this thesis varimax rotated principal component analysis (PCA), chemical mass balance model (CMB) and absolute principal component analysis (APCA) are used to identify and quantify different source contributions in air pollution data from Stockholm (Hornsgatan, Enskede, Kista, Gubbängen and Söderledstunneln).

Obvious diesel and gasoline components are received in all PCA-models using PAH-, alkane- and naphtalene-data. PAH with high molecular weight e.g. coronene are characteristic for gasoline vehicle emissions. For diesel vehicles PAH with low moleculer weight (e.g. pyrene, phenanthrene and fluoranthene) and alkanes with high molecular weight (decane – pentadecane) dominate the emissions.

CMB indicates that gasoline exhaust accounts for 73% and diesel for 27% of the PAH concentrations due to traffic related at Hornsgatan 1991 and 1994-97. Corresponding values for Enskede are 87% from gasoline vehicles and 13% from diesel vehicles. In Kista 71% of the traffic related PAH concentrations are from gasoline vehicle emissions and 29% from diesel vehicle emissions. For the individual PAH only pyrene from diesel emissions exceed the gasoline emissions of pyrene at Hornsgatan and in Kista.

The result of APCA of PAH data at Hornsgatan indicate quite a different result compared to the CMB result. One reason for the lack of consistence can be that too few samples were available.

A method for analysing PAH in tyres was developed. Substantial amounts of PAH are found in the 8 analysed tyres, but the concentrations vary from 64 to 445 ppm. From the analysis of tyres done no obvious systematic differences in PAH concentration between different makes and years can be observed.

Contents

1. Introduction

1.1 Purpose and background

Emissions of hydrocarbons have negative effects on the environment and human health. A national environmental objective in Sweden is to reduce emissions of carcinogenic compounds by 90% in urban areas in the future using 1995 as a base year [1]. More information on the contribution by different sources to the total emissions is needed to reach this objective. The main source of hydrocarbons in larger Swedish cities is vehicle-emissions.

This undergraduate thesis is a part of a project that will identify the dependence of different sources for dispersion and occurrences of carcinogenic compounds in Stockholm. The thesis will identify gasoline and diesel traffic profiles from measurements in a traffic tunnel (Söderledstuneln) in the winter 1998-99.

Beside data from Söderledstunneln measurements of ambient air in1999 and 2000 will complete the information about carcinogenic compounds in Stockholm.
Earlier ambient measurements of PAH from Hornsgatan, Enskede and Kista together with elemental data from Gubbängen are analysed in this thesis.

Relating the ambient concentrations of these compounds to their sources is essential to be able to improve the air quality in the urban areas. Chemical mass balance model (CMB), varimax rotated principal component analysis and absolute principal component analysis (APCA) will be used to characterise and quantify different source contributions of carcinogenic compounds in Stockholm.

Highly aromatic oil is used in the production of tyres. Therefore tyres could be a significant PAH source in urban areas. Very little is known about total PAH concentration and PAH-profiles in tyres. A method for analysing the PAH content in tyres is proposed in this thesis.

1.2 Hydrocarbons

Hydrocarbons is a wide group of compounds, occurring both in the gas phase and on particles, with different effects on the environment and human health. Therefore it is important to know emissions and occurrences of individual compounds. Aldehydes, for example, are irritants and potential carcinogenic compounds and alkenes can form carcinogenic epoxide-metabolites. Mono-aromatic compounds, for example benzene, can cause leukaemia and several Polycyclic Aromatic Compounds (PAC) that include Polycyclic Aromatic Hydrocarbons (PAH) are mutants and carcinogens [2]. Hydrocarbons can also have secondary effects participating in ozone forming processes [3].

PAH are defined in Sweden as compounds with three or more benzene rings. U.S EPA[#] -standard define PAH as compound with two or more benzene rings and this definition is in international use. Because of double bonds the structures are plane and the molecules can penetrate membranes and cause mutations and cancer [4].

PAH are formed by incomplete combustion of organic matter and the main sources in Sweden are domestic wood burning and road traffic [1]. Other possible anthropogenic

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[#] EPA= Environmental Protection Agency

sources are tyres, road asphalt, roofing tar pots [5], oil heating, municipal incinerators and industry (e. g. aluminium and iron production). Natural sources can be forest fires, volcanoes and geologic transformations [4]. In larger Swedish cities road traffic dominate the emissions.

Depending on molecular weight PAH are partitioned between a gas phase and particulate phase. PAH can also be solved in water droplets in the atmosphere. Phenanthrene is mainly present in gas phase and coronene in particulate phase. Ambient temperature and moisture also influence the partitioning of PAH between phases [1].

PAH and other hydrocarbons can be removed from the atmosphere by photochemical reactions, but the removal occurs mainly through dry or wet deposition [6]. Other pollutants such as ozone, nitrogen oxides, and sulphur dioxide or oxidising organic compounds may enhance the photochemical oxidation of PAH activated by ultraviolet radiation [1].

PAH are lipophilic, persistent and they can bioaccumulate. These compounds can therefore have significant biological activity despite lower traffic-emissions compared to other compounds. Benzo(*a*)pyrene is often used as a tracer for PAH, it is the most studied of the PAH and is carcinogenic to animals. Benzo(*a*)pyrene was identified in coal tar 1933, in domestic soot 1949 and 1952 in ambient particles [7].

1.3 Airborne elements on fine particles
Most elements are metals. Heavy metals are the elements that have most influence on the environment. Some metals are essential for life but for example mercury, cadmium and lead have no known positive function for plants, animals and human beings. Atmospheric transport occurs mainly through the particulate phase and removal from atmosphere is both due to wet and dry deposition. One of the goals set up by the city council of Stockholm is to stop the enrichment of heavy metals to the environment [8]. There are both global and local emissions and the lack of dominating point sources in Stockholm make the diffuse sources significant. Metals are emitted in the ore mining, production and the usage of metal products. Iron, zinc, copper, nickel, vanadium, arsenic and lead are emitted through the combustion of coal and vanadium and nickel in oil combustion. Due to the successive elimination of lead in gasoline the lead emissions from gasoline vehicles have declined substantially during the last decade [9].

1.4 Emissions from road traffic
There are regulated and unregulated exhaust emissions from vehicles. Regulated emissions by law in Sweden (g/km) are carbon monoxide, nitrogen oxides, unburned fuel hydrocarbons and particles. Law does not regulate for example PAH and individual hydrocarbons, but there are recommended health risk levels for several other compounds [2].

Several factors influence the traffic emissions of PAH and other pollutants such as fuel composition, exhaust after-treatment devices, ambient temperature, driving conditions, type of motor and it's condition [1, 10].

Environmentally classified diesel fuels (MK1) were introduced in Sweden 1991 and this fuel reduces the emissions of PAH at least a factor of 5 but the relative emission of individual PAH is similar to conventional diesel fuel [1]. A decline of PAH emissions

with 15% for light duty vehicles due to more cars equipped with catalysts and 70% for heavy duty trucks because of the introduction of environmentally classified diesel fuel (MK1) were expected in Stockholm 1990-98 [11]. A corresponding decline in ambient PAH levels at Hornsgatan is not observed, perhaps due to fluctuations in vehicle composition and meteorological variations or contributions from other sources that are not subject to the same decline.

Accurate source apportionment of PAH and other pollutants from different vehicles is therefore important for identification of optimal measures for decreasing emissions. The use of PAH profiles as source signatures in receptor modelling such as CMB are of renewed interest because of the elimination of lead from gasoline [12]. It has been suggested that selected PAH could be used as tracers for emissions from motor vehicles. Low molecular weight PAH as phenanthrene, fluoranthene and pyrene are characteristic for diesel vehicles and high molecular weight as coronene and benzo(*ghi*)perylene for gasoline vehicles [13]. For heavier alkanes the emission rates are much higher for diesel vehicles than for gasoline vehicles [3]. This is also true for particles and soot, but emissions of carbon monoxide and lighter hydrocarbons are smaller compared to gasoline vehicles [10].

Emission factors from different vehicles have been estimated based on chassis dynamometer measurements. Before these measurements vehicles are always serviced. There are big differences between vehicles depending on how they operate. A tunnel study can give real world emission data from mobile sources [3]. The data of hydrocarbons, particles and traffic from the Söderledstunnel from winter 1998-99 will give these real world emission factors for traffic in Stockholm.

Nielsen 1996 examined the diurnal variation of particulate associated PAH in Copenhagen and proposed another method than receptor modelling for differentiating between PAH contribution from gasoline vehicles and those from diesel vehicles. By measuring PAH both at a street carrying only diesel buses, a busy street and a park area different contributions can be estimated. By taking the ratio of different PAH to for example CO, which originate from traffic, the traffic contributions can be estimated. At low combustion temperature and low exhaust temperature as in diesel vehicles the ratio of methylphenanthrenes to phenanthrenes is high. In the buss-street this ratio was 4.8 which is in good agreement with dynamometer measurements of diesel vehicles. This was used to determine source apportionment from diesel and gasoline vehicles [14].

Vehicle exhaust consists of combustion products and unburned gasoline or diesel. The degree of unburned fuel can be as much as 60% [15]. Emissions from vehicles beside exhaust also include vaporisation of gasoline during driving and parking conditions and evaporation of motor-oil. The degree of vaporisation can be calculated successfully from the fuel content. Therefore representative samples of fuel from Stockholm will later be analysed as a part of the project.

1.5 Emission from Tyres
Ahlbom and Duus 1994 proposed that tyres could be a significant PAH source because 1.5 litre highly aromatic oil (HA-oil) is required for the production of every passenger tyre. The PAH content in the HA-oil is 700ppm - 30 % depending on definition and analytical method. According to Ahlbom's and Duus' calculations 14 tons of PAH are released yearly due to tyre wear on Swedish roads. This is based on an estimation of

7000 ppm of PAH in the HA-oil, 20% HA-oil in the tyres and 10 000 tons of particles due to wear of tyres.

Emission factors in μg/km for tyres have been calculated for comparison with exhaust emission factors. For car tyres the factor is 28 μg/km and for truck-tyres 140 μg/km. A PAH content of 700 ppm is used in these emission factors. If these factors are real the emissions from tyres would predominate the emissions from exhaust pipe for cars equipped with a catalyst or trucks which use environmentally classified fuel [16]. A study made in Germany show on much lower PAH content and emission from tyres [17]. Measurements of wear and tear of tyres, wet hold ability on road and noise from tyres with and without HA-oil show no significant differences [18]. Therefore the usage of HA-oil in tyres seems to be unnecessary.

PAH from tyres probably to a great extent occur as coarse particles, not inhalable and only local spreading to for example urban run off water. On Hornsgatan roof levels of particulate associated PAH are about 1/50 of the level in the street, one explanation could be PAH in coarse particles from tyres.

However very few analyses have been made on PAH in tyres, and in most studies the total PAH content have been analysed and not individual PAH. This work proposes a method for analysis of individual PAH in tyres, to get source profiles and an estimation of the PAH-levels in tyres.

1.6 Varimax Rotated Principal Component Analysis

Principal component analysis (PCA) is a multivariate method finding patterns of correlation within large data matrices. In PCA the original data matrix X is broken down into two smaller matrices P representing the variable (loadings) and T representing the sample (scores) information. The product of these two matrices is an approximation of the original matrix, X= T P'+E, E is a matrix of residuals. In a graphical sense, samples are represented by points in a k-dimensional space, where k are the number of variables. The first principal component (PC) is a line through k-space that explains most of the variance in the data, the second PC explains most of the variance that is left and so on. Loadings describe relations between the original variables and the PC by cosinus of the angle between the original variable axis and the PC. Scores describe the distance from origin to the orthogonal projection of the sample on the PC. All extracted PCs are mutually orthogonal and the result can be visualised in two-dimensional loading and scores plots. A maximum of k principal components can be extracted but due to correlation between variables less than k PC's may approximate the original data matrix. [19].

Varimax rotation attempts to minimise the number of variables with high loadings on a factor. The result becomes easier to interpret after rotation and the PC's becomes like fingerprints for the sources [20].

The data matrices are often auto-scaled before principal component analysis. This procedure includes mean-centre and variance set to unity. Auto-scaling give all variables the same influence on the model and variables with small numerical values can influence the model as much as variables with high values.

Principal component analysis is sensitive for outliers. Outliers are samples that differ from the other samples having much lower or higher concentration. The occurrences of outliers can have several reasons for example contamination or instrumental problems in sampling or analysis. These samples should be omitted from further modelling. If the outlier is due to an extreme value depending on meteorological or temporary emissions one must consider if this due to normal variation or not. Outliers are omitted because they can affect the model sometimes making an additional PC only explaining the outlier.

Swietlicki *et al.* 1996 used varimax rotated principal component analysis on 313 fine fraction samples from Bily Kriz in the Czech Republic. Eighteen elements were used as variables and 8 samples were identified as outliers. A small number of missing values (below the detection limit) were replaced by random values. Six significant sources were identified on the basis of prior knowledge. The first source was a combination of ferrous and non-ferrous smelters, coal combustion, wood processing, industry and traffic. The other five sources were soil dust, oil combustion, coal combustion, secondary sulphate and sea spray [21].

Biegalski *et al.* 1998 found that oil-and coal-combustion, road salt, mining, incineration and smelting were anthropogenic sources to aerosols of the rural of the Great Lakes by using varimax rotated principal component analysis. 1000 samples with an aerodynamic diameter of 10μm or less were collected by a high volume sampler at three Canadian monitoring stations. The samples were analysed by neutron activation analysis for about 30 trace elements. Earth crust's was the natural source found in the analysis [22].

Miguel *et al.* 1997 used principal component analysis, factor analysis and cluster analysis on trace element data from Madrid and Oslo. The results of the statistical analysis suggests that chemical elements in the street dust can be classified into three groups: "urban" elements (Ba, Cd, Co, Cu, Mg, pb, Sb, Ti and Zn), "natural" elements (Al, Ga, La, Mn, Na, Sr, Th and Y) and elements of mixed origin (Ca, Cs, Fe, Mo, Ni, Rb, Sr and U). "Urban" elements are mostly anthropogenic and are primarily from traffic and from weathering and corrosion of building materials. Resuspended soil dust is the most significant "natural" source [23].

Sjögren *et al.* 1995 performed PCA on physical and chemical characteristics of ten different diesel fuels from four suppliers. PCA of a subset of the data representing the chemical composition yielded three significant principal components explaining 80% of the variance. Three principal components indicating at least three latent variables, corresponding to the suppliers, in the data set. This study showed that using PCA it was possible to describe complex mixtures such as diesel fuels by a few principal components. Chemical characteristics of fuels may be reduced to a few general characteristics represented by for example the polycyclic aromatic hydrocarbons 1-methylphenanthrene and picene. Although some of the compounds that contributed to the principal components was considered as trace constituents, they were representative for the variation between different fuels [19].

Westerholm *et al.* 1994 used principal component analysis to study the relationship between PAH contents in diesel fuels and PAH contents in the exhaust emissions from diesel vehicles. The PAH in the exhaust consist of uncombusted fuel and PAH formed

during incomplete combustion. A correlation between PAH of diesel fuels and PAH in the exhaust emissions was observed indicating that a selection of diesel fuels with low PAH content can reduce the PAH emission from diesel vehicles [24].

1.7 Chemical Mass Balance model

CMB models use the chemical and physical characteristics of both gases and particles measured at sources and receptors to both identify the presence of and quantify source contribution estimates [25]. Significant sources and their profiles must be identified. The relative compositions of different species in the source emissions form the source matrix A. The corresponding composition in the ambient air samples form a receptor profile, the C matrix. They are related through the matrix-equation $C = A*S$, where S is the source contribution estimates of the identified sources. The equation is solved by multiple linear regression.

To take considerations of errors in sampling and chemical analysis the regression can be weighted by the variances in both receptor (σ_{aij}^2) and source profiles (σ_{Ci}^2). The input data uncertainties are used both for weighting the relative importance of the input data to the model solution and for estimating uncertainties in the source contribution estimates [26]. The solution $S = (A^T V A)^{-1} C V A^{T\ \#}$ include a diagonal matrix V with the element $v_{ii} = (\sigma_{Ci}^2 + \Sigma \sigma_{aij}^2 * s_j^2)^{-1}$ in the diagonal. An iteration process is then required because s_j (source contribution) is not known. The weighting regression gives standard errors (STDERR) in the source contribution estimates (SCE) by diagonal elements in the matrix $(A^T V A)^{-1})^{1/2}$ [27]. The standard error is an indicator of the precision or certainty of each SCE. The value of the standard errors depends on the uncertainties in the input data and the amount of co-linearaity among source profiles [28].

In the literature several methods how to calculate a variance-estimate in source and receptor profiles are proposed, but in most applications the estimate of the variance is set to some percentage of the profile value for example 10 or 20%.

Beside the assumption that all significant sources must be identified and characterised as already mentioned there are at least additional five. The species in the model should be almost inert and the source contribution should be constant during the measuring period. As in ordinary multiple linear regression errors should be random and normally distributed, there must be more species than sources and the sources should not be co-linear. Almost never all of these assumptions are fulfilled, but the CMB-model can handle some deviations as outlined by Hopke [28].

It is better to do a CMB- model for every individual sample and then taking the mean of the CMB out put. If first taking the mean of all samples and then use this as input to the CMB-model important information is lost [29]. In the literature CMB models have been applied using both elemental data and volatile organic compounds.

Chow *et al.* 1992 determined the sources which contributed to ambient concentrations of PM 10 (particulate matter with aerodynamic diameter equal to or less than 10 μm) in San Joaquin Valley, California by applying CMB using source profiles specifically determined for the study area. Species analysed and used as input in the model were organic and elemental carbon, nitrate sulphate, ammonium and elements. Standard

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[#] A^T is the transpose and A^{-1} is the inverse of the matrix A.

deviations determined from replicated sampling and chemical analysis were used in the weighted regression. Primary geological material was the largest contributor at all monitoring sites [26].

Mukund *et al.* 1995 present the result of modelling the temporal and spatial variabilities in the source contributions of measured volatile organic compounds (VOC) in Columbo, Ohio. The region does not contain any large industrial point source. VOC emissions are therefore dominated by mobile sources. Three-hour samples from 3 separate 2-day campaigns at six different monitoring sites were used to study both temporal and spatial trends. Nineteen VOC were selected for the model. The five profiles used were derived from different databases in which different analytical and sampling methods have been used. Therefore 20% uncertainty were used in source profiles. In receptor profiles the uncertainty was estimated to be10%. Vehicle exhaust, gasoline vapour and natural gas were main sources for most VOC at all six sites. Spatial differences were small because the main sources are mobile and homogeneously distributed over the area. Burning of natural gas is an important contributor to urban light hydrocarbons. The other source profiles used were industrial solvent and chlorinated solvent usage. Diurnal changes in the contribution of vehicle exhaust, gasoline vapour and natural gas were observed. Vehicle exhaust varied with the traffic frequency and gasoline vapour source varied not only temporally but also spatially during the day. The gasoline vapour source was important in urban and industrial areas during the day and at residential sites during the evening and night. The natural gas source was repressed by the other sources and became more dominating as the other sources decreased [30].

Schauer *et al.* 1996 included PAH in the chemical mass balance models and examined the atmospheric stability of the particulate associated organic compounds used. The initial step was to identify and exclude compounds that appeared to be significantly modified during transport from source to receptor. The ratios of ambient concentrations to emission rates were calculated and plotted. If the ratio differed more than two standard deviations of the ratio of concentration to emission rate observed for conserved reference materials: elemental carbon, fine particle aluminium and fine silicon particle the specie was excluded. For example, all PAH with molecular weight less than 252 (benzo(*k*)fluoranthene) were not used in the model [31].

Venkataraman *et al.* 1994 used CMB with modified source profiles to reflect reactive decay of PAH in the atmosphere. Vehicular exhaust and meat-cooking emissions were used as source profiles. The vehicular source profile was taken from measurements in a tunnel. Particulate PAH and elemental carbon data from two Los Angeles sites were used as receptor profiles. The conclusion was that 90% of the PAH came from automobile emissions, but at the residential site (Upland) meat cooking contributed between 20 and 75% of the four–ring PAH. An uncertainty of 10% was assumed for sample losses including volatilisation, extraction recovery and degradation before analysis [12].

1.8 Absolute Principal Component Analysis
Absolute principal component analysis (APCA) is a multivariate method based on varimax rotated principal component analysis, giving source profiles in absolute units without receptor profiles. Absolute principal component scores (APCS) are calculated for every sample by using the loading matrix from varimax rotated PCA. A regression of the total mass of the species included in the analysis on these APCS gives source

contribution estimates for the sources identified in the PCA. Finally a regression of the measured concentration versus every individual species on the derived source contributions estimates will give quantitative source profiles [32].

Swietlicki *et al.* 1996 receive source profiles in absolute units using another technique, the varimax rotated principal component analysis is followed by a scaling procedure [33].

Thurston *et al.* 1985 performed APCA on particulate elemental data from a monitoring site in Metropolitan, Boston. Five fine mass particle source classes (soil, motor vehicle, coal related, oil and salt aerosols) and six coarse particle source classes (soil, motor vehicle, refuse incineration, residual oil, salt and sulphate aerosols) were identified and the their source profiles were calculated [32].

Swietlicki *et al.* 1996 used data on 14 trace element, SO_2, NO_2 and O_3 from Lund, Sweden in APCA calculations. The major sources were identified and the pollutants were apportioned to the identified sources. The dominant sources for the measured species were resuspended road dust, automobile and diesel emissions, combustion of oil and coal, ferrous and non-ferrous smelters and sea spray [33].

2. Experimental

2.1 Monitoring sites, sampling and analytical methods

The samples taken at Hornsgatan were collected during two periods April-May and May-June 1991 and 1994-98, the period mean values were used in the PCA-models. In 1991 only one sample was available. Totally 11 samples from Hornsgatan were used in the calculations. Together with PAH sampling, traffic measurements in Hornsgatan were also made see figure 2.1.
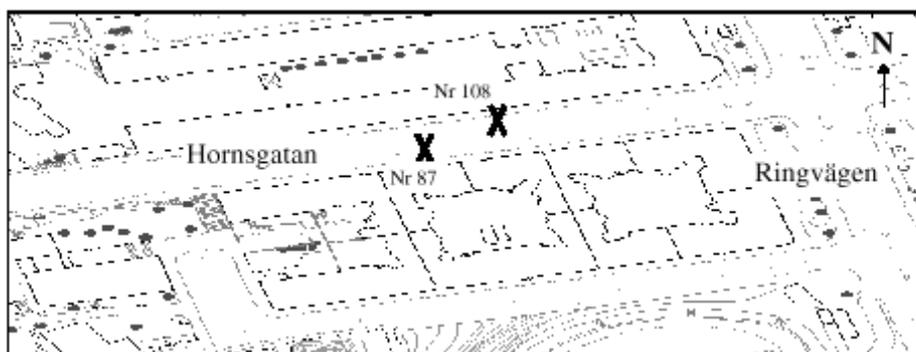
Figure 2.1 The monitoring site at Hornsgatan.

Sixteen two-day PAH samples were collected in January, February and March 1997 at Enskede and Kista. Figure 2.2 is a map showing the monitoring site at Enskede, which is located, in a residential neighbourhood where wood burning may be an important PAH source. The road with highest traffic in the neighbourhood is Nynäsvägen with 83 000 vehicles every 24 hours. Nynäsvägen is located 1 km from the monitoring site.
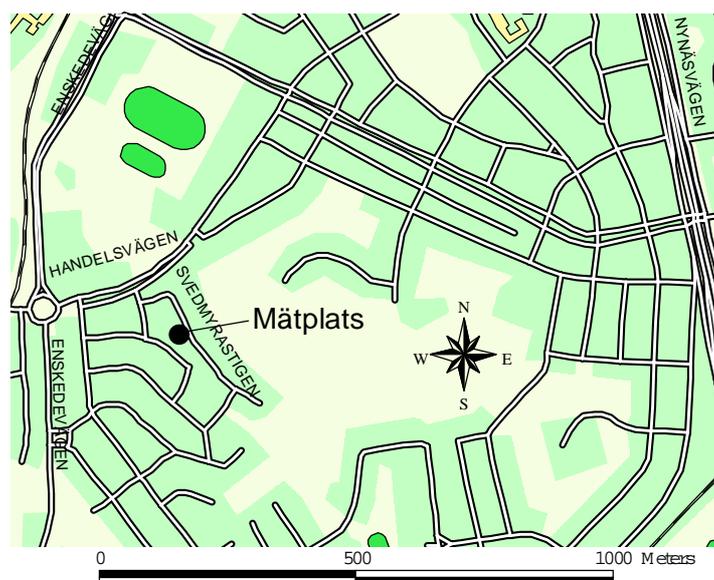
Figure 2.2 Monitoring site in Enskede.

The monitoring site at Kista (figure 2.3) is located in an area with terrace-houses and domestic wood burning is not as frequent as in Enskede. There are no heavily trafficked roads nearby the monitoring site.
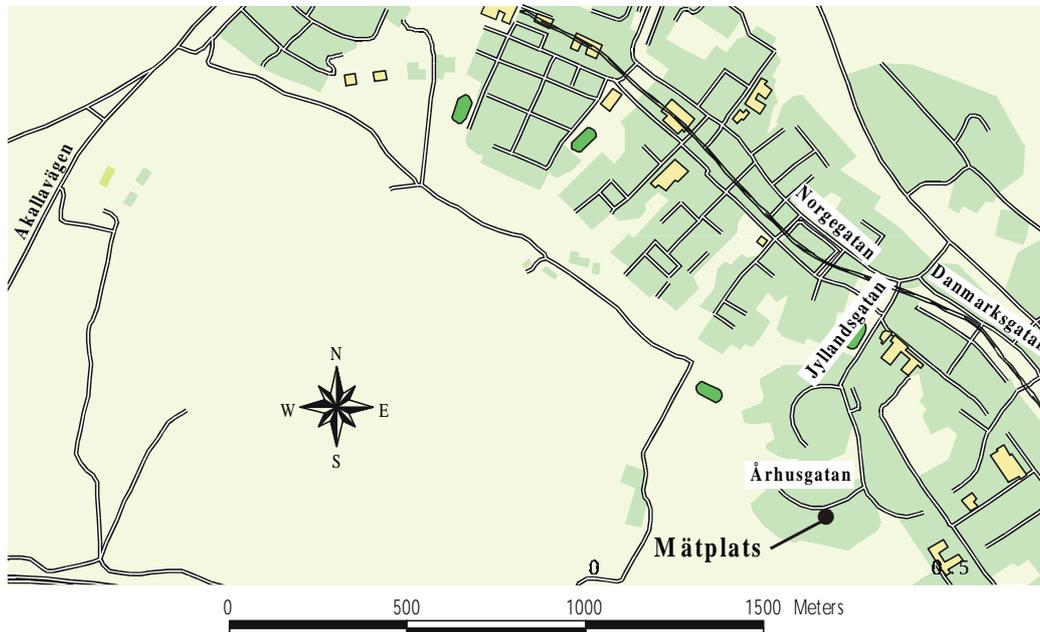
Figure 2.3 Monitoring site in Kista.

The Söderledstunnel is underground the centre of Stockholm in the North -South direction. The tunnel is 1500 metres and have two bores, one for south travelling vehicles and one for north travelling vehicles see figure 2.4. Monitoring sites were 100 metres (Åsö) and 1 km (Noa) from the entrance in the northwards bore. Equipment for monitoring different VOC, PAH, particulate matter (mass, number and chemical composition) and also NO_x and CO were stationed at the monitoring sites during the campaign in December 1998, January and February 1999. The tunnel-bore is sloping slightly upward and it is ventilated by fans in the ceiling and air is moving with the traffic see figure 2.4. The intention is to subtract the Åsö values from Noa to get an estimate of vehicle emissions in the tunnel and to obtain emission factors.
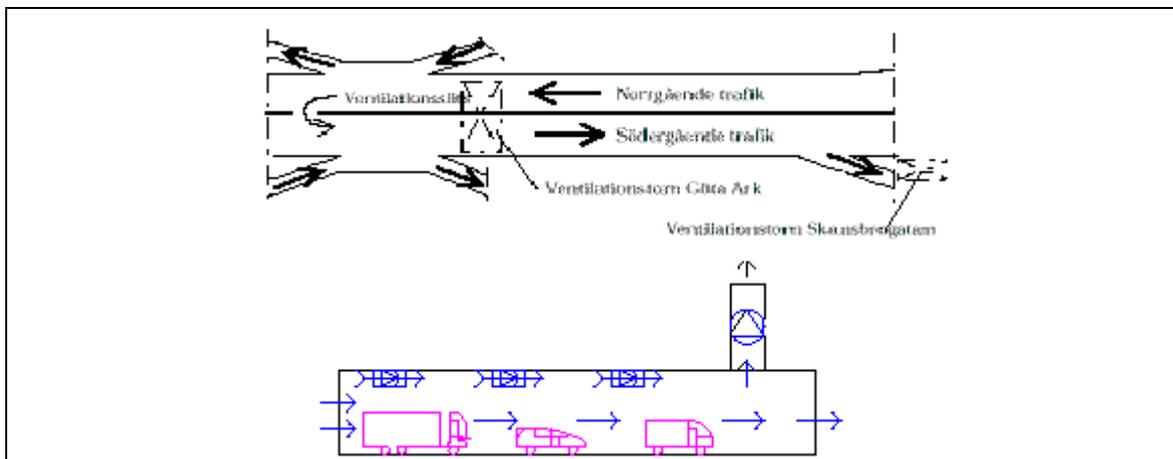
Figure 2.4 The Söderledstunnel

PAH data from Rörvik 1994-96 were used as background profiles in the CMB models. Rörvik is a rural and coastal monitoring-station 40 km south of Gothenburg. Sampling periods were one week and sampling frequencies one week every month. Sampling and analytical methods are described in table 2.1 and in detail in Brorström-Lundèn *et al.*1994.

Gubbängen is a suburb south of Stockholm and the monitoring site is situated 1.5 km from Högdalens waste incineration station and 200m from Nynäsvägen (described above). In total 182 samples were taken during March 1989 to April 1996. No samples were taken during 1994. The sampling period was about six days.

Sampling and analytical methods for data used in different models are summarised in table 2.1. References where detailed information can be found are also given.

Table 2.1 Sampling and analytical methods.

Specie	Monitoring site	Year	Monitoring time	Sampling method	Extraction	Clean up procedure	Analysis	Reference
PAH	Rörvik	1994-96	1 week	High volume sampler with glass fibre filter and PUF	Soxhlet extraction with acetone for 24 h	!0% deactivated silica gel column, eluated with pentane	HPLC with fluores-cence detector	34
PAH	Hornsgatan Enskede Kista	1991, 1994-98	2 days 2 days	High volume sampler with glass fibre filter and PUF	Soxhlet extraction with dichloro-methane for 24 h	!0% deactivated silica gel column, eluated with cyclo-hexane	LC-GC on line with FID detection	35
PAH	Söderleds-tunneln	1998-99	1h to 1 day	High volume sampler with filter and PUF	Soxhlet extraction with dichloro-methane for 24 h	!0% deactivated silica gel column, eluated with hexane	GC/MS	36, 37
alkanes>6C	Söderleds-tunneln	1998-99	1 h	Tenax adsorbent			GC/MS	10
Elements	Gubbängen	1989-96	6 days	Low volume sampling with filters (mainly fine particles)			PIXE	38

PUF = Poly Urethane Foam, PIXE = Particle Induced X-ray Emission analysis

2.2 Varimax Rotated Principal Component Analysis
Varimax Rotated Principal Component Analysis was made on the sum of particulate and semi-volatile PAH in Hornsgatan, Kista and Enskede using SPSS-Statistical data program. The data matrices were auto-scaled (mean-centred and variance set to unity) columnwise. Separate models for each of the three sites were made and also a model including all three sites. The two models including Enskede and Kista used 20 different PAH as variables and the models including Hornsgatan used 14 different PAH. Data of seven different dimethylphenanthrenes were excluded from Enskede and Kista models

since there were no standard including dimethylphenanthrenes available, therefore their chemical identification is uncertain.

Varimax Rotated Principal Component Analysis was also made on elemental data from Gubbängen. The models used 16 different elements as variables, 182 samples from 1989-1996 as objects and the data matrix was auto-scaled columnwise. Because only 8 samples have data for every element missing values were replaced by the overall mean.

Seven alkanes (nonane to pentadecane) and three naphtalenes from the measurements in the Söderledstunnel 1998-99 were used for Varimax Rotated Principal Component Analysis in SPSS. In total 104 samples were analysed from both Åsö and Noa, but because of problems with the sampling-pumps mainly at Noa, only 49 samples have positive values when subtracting Åsö from Noa. One PCA model with these 49 samples and one model with 104 samples from Åsö were made. Undecane was eliminated from the analysis because of several missing values.

Nine samples from the Söderledstunnel (4 samples from Åsö and 5 from Noa) were analysed for 49 different PAH both in particulate and semi-volatile phase. An attempt to do varimax rotated PCA on these nine samples was also made. All the data from the tunnel were auto-scaled columnwise before the principal component analysis in SPSS.

The criterion for determining the number of components to be extracted was that the eigenvalue should exceed one times the mean eigenvalue. However this is not always the best approximation of the data. Scores plots in higher PC and loading plots together with scree plots (a plot of component number vs. eigenvalue) are always studied before determining the number of significant PC.

To confirm the PCA-result hierarchical cluster analysis on some sets of data used in principal component analysis have also been made, using SPSS data program. The data matrices were auto-scaled and outliers identified in the PCA were eliminated before the cluster analysis.

2.3 Chemical Mass Balance Model

A Chemical mass balance model with three sources and 10 different PAH as variables was made. PAH-data from Hornsgatan were used as receptor profiles. The three sources were gasoline vehicles, diesel vehicles and background. Calculations were made in Microsoft Excel.

Source profiles of the diesel and gasoline source were calculated by using emission factors from laboratory dynamometer testing. Percentage of vehicles with or without catalyst and the per cent use of diesel MK I vs. diesel MK III are given for in table 2.2. The emission factors of the PAH used in the models are shown in table 2.3 and the complete source profiles are given in Appendix 2.

Table 2.2 Percentage of vehicles with or without catalyst and the per cent use of diesel MK I vs. MK III in Stockholm [39].

year	Light duty vehicles without catalyst	Light duty vehicles with catalyst	Heavy duty truck Diesel MK III	Heavy duty truck Diesel MK I
1991	60%	40%	100%	0%
1994	50%	50%	50%	50%
1995	45%	55%	10%	90%
1996	40%	60%	7%	93%
1997	35%	65%	3%	97%
1998	30%	70%	0%	100%

Table 2.3 Emission factors for light and heavy-duty vehicles in μg/km including both particles and gas phase associated PAH [11].

	Light duty vehicles		Heavy duty truck	
	gasoline, no catalyst	gasoline with catalyst	diesel III	diesel I
Phenanthrene	91	28	267	40
Anthracene	28	5	28	3
1-Methylphenanthrene	16	1	99	10
Pyrene	22	3	212	70
Benz(a)antracene	4	0.4	4	<0.1
Chrysene/Triphenylene	4	1	1	0.2
Benzo(b&k)fluoranthene	5	1	0.5	<0.1
Benzo(e)pyrene	3	0.2	<0.1	<0.1
Benzo(a)pyrene	6.6	0.3	0.2	<0.1
Indeno(1,2,3,-cd)pyrene	2	0.4	<0.1	<0.1
Benzo(gih)perylene	6	0.5	<0.1	<0.1
Coronene	2	0.5	<0.1	<0.1
Fluoranthene	21	5	83	24

Background source profile was taken from measurements in Rörvik 1994-96 and from Kista and Enskede 1997 see profile plot in figure 2.5. PAH data from Rörvik in March 1995 have more than ten times higher concentrations of PAH than the other months. This is probably due to an air pollution episode. Since this sample influence the profile and also the CMB-model, giving a very high background contribution in 1995, the sample was excluded.

In 1997 when Kista and Enskede data were used as background profile two models were made, one with 10 different PAH for comparison with the other years in which only ten PAH are available, and one model with 13 different PAH.
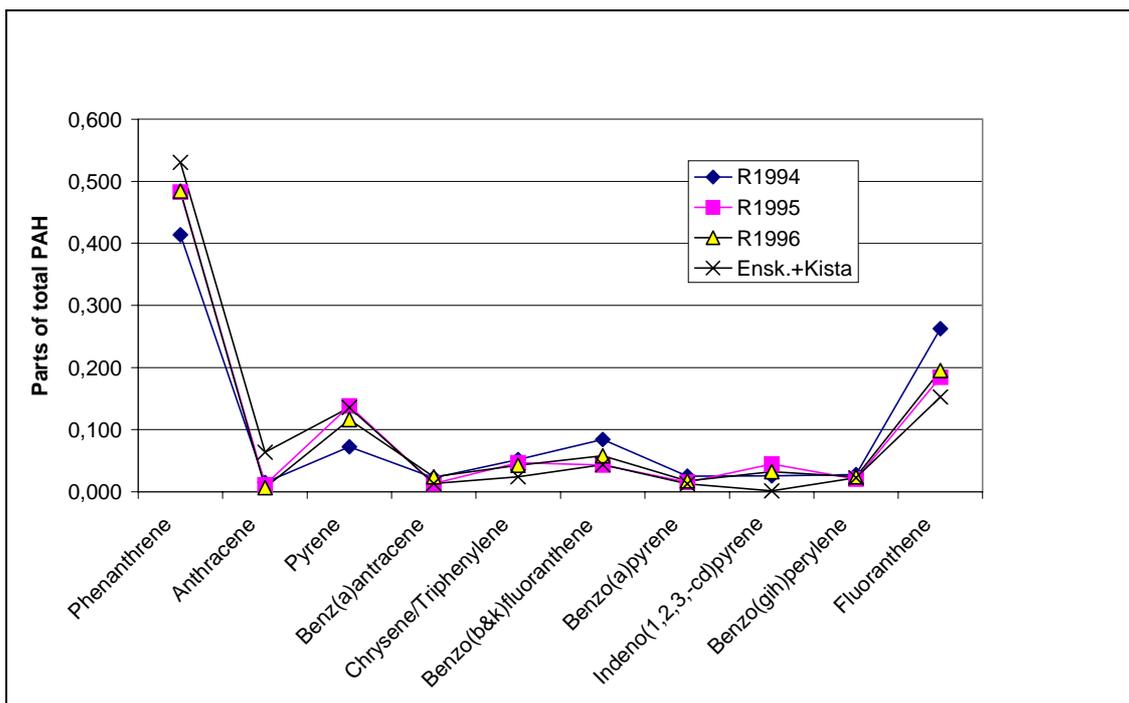
Figure 2.5 Background profiles 1994-96 from Rörvik (March sample 1995 excluded) and 1997 from Enskede and Kista.

In the receptor profiles and the background profile from Kista and Enskede benzofluoranthenes include both benzo(*b & k*)fluoranthene and benzo(*a & j*)fluoranthene. In the source profiles benzofluoranthenes corresponds only to benzo(*b & k*)fluoranthenes. In the gasoline and diesel source profiles chrysene also include triphenylene but in all other profiles chrysene is separated from triphenylene.

Atmospheric reactions have not been considered in the models because in Hornsgatan the distance from emission to sampling site is very short. The lifetimes for phenanthrene, anthracene, fluoranthene and pyrene are 11 to 3 hours [40]. The time from emission to sampling is only some minutes. The partitioning between gas and particulate associated phase does not matter if modelling the sum of the two phases.

Different values of the standard deviation in the weighted least squares regression was tested. A 20% standard deviation in receptor profile and 10% in source profile gave the best mass recovery and relevant standard errors (STDERR). This is outlined for one sample in table 2.4. The different combinations of standard deviation are shown in table 2.4 and it is obvious that 10% deviation in source profiles and 20% deviation in receptor profile gave the best ratio of calculated to measured and highest TSTAT- values (SCE/STDERR). A TSTAT-value greater than 2,0 shows that the relative precision of the source contribution estimates is high and that the source is significant [28]. A deviation of 20% in source profiles and 40% in receptor profile gave the same ratio of calculated to measured but lower TSTAT- values. The different combinations were tested for every sample. For the majority of samples10% deviation in source profile and 20% deviations in receptor profile gave the best ratio of calculated to measured and highest TSTAT- values. Only in a few cases 20% deviation in source profiles and 50% deviation in receptor profile gave a marginally better calculated to measured ratio.

Table 2.4 Different per cent values of the standard deviation in receptor (σ_{Ci}) and source profiles (σ_{Ai}) for the sample from period 1 (April-May) 1994. The measured mass of the 10 PAH was 190.5 ng/m^3.

σ_{Ci}	σ_{Ai}	source	SCE ng/m3	STDERR	TSTAT (SCE/ STDERR)	calculated/ measured for total PAH
20%	20%	gasoline	139	32	4,3	
		diesel	49	19	2,6	
		background	12	16	0,8	
		total	200			1,05
20%	40%	gasoline	157	52	3,0	
		diesel	44	27	1,6	
		background	7	25	0,3	
		total	209			1,10
40%	20%	gasoline	120	51	2,4	
		diesel	54	32	1,7	
		background	17	26	0,7	
		total	191			1,00
20%	10%	gasoline	120	25	4,8	
		diesel	54	16	3,3	
		background	17	13	1,3	
		total	191			1,00
50%	20%	gasoline	117	61	1,9	
		diesel	55	40	1,4	
		background	18	31	0,6	
		total	189			0,99

An attempt to do CMB on PAH data from Kista and Enskede were also made. The same diesel and gasoline source profiles as in Hornsgatan 1997 were used. Background sources were either the profile from Rörvik 1996 or measurements 1997 from Rosenlundsgatan at roof level. In one CMB model for Enskede a profile for domestic wood burning [1] were used instead of the background profile. Finally models with only the two sources; gasoline and diesel vehicle exhaust were made on PAH data from Enskede and Kista. Thirteen different PAH were used in these models and concentrations below the detection limit in receptor profiles was replaced by 0,01to make the modelling possible. A standard deviation of 10% in receptor profiles and 20% in source profile gave the best ratio of calculated to measured total concentration and highest TSTAT- values.

For CMB modelling of the elemental data from Gubbängen 1989-96 source profiles were taken from literature [26]. Four sources were identified from varimax rotated PCA and therefore four sources were selected from literature for CMB: paved road dust, fireplace burning, crude oil combustion and motor vehicle. Because invalid results a CMB model with output from varimax rotated PCA as source profiles were made. Both three and four sources were used.

2.4 Absolute Principal Component Analysis

APCA due to Thurston's method [32] was made both using PAH data from Hornsgatan and using the alkane-and naphtalene-data from Söderledstunneln (Noa-Åsö). Calculations were made in Microsoft Excel. Outliers identified in varimax rotated PCA were excluded. The PAH data from Hornsgatan was also used for APCA-calculations in Matlab using Swietlicki's method [33].

2.5 Analysis of PAH- content in tyres

In a pilot experiment about 0.5 g of crumbs from a Bridgestone tyre were extracted with dicloromethane in a Soxhlet apparatus for 24 hours. The extract was removed and the same crumb was extracted again. This procedure was repeated giving totally three extracts: 24, 48 and 72 hours-extract. The extracts were evaporated to dryness in a rotary evaporator and washed out with acetone. Fifteen µl DIST-B internal standard (0.15 ng/µl D_{10}-Phenantrene and 2,2'-binaphthyl) was then added about 2 % of the 24-hour extract before evaporation with an aliquot of 10% deactivated silica gel in hexane under nitrogen pressure. The powder was added to a 12 cm (6 mm i.d.) silica gel column. The first alifatic- fraction was eluated with 4ml hexane and the second PAH-fraction with 14ml hexane. Fraction II was evaporated and washed with acetone and evaporated to a volume of 300µl before injection on gas chromatography-mass spectrometry (GC-MS). The gas chromatograph (Hewlett Packard 5890 series II) was equipped with a split/splitless injector (injector temperature 285 °C) and a fused-silica capillary column (30 m × 0.25 mm i.d., HP5-MS, Hewlett-Packard, USA). The temperature program was as follows: Initial temperature 110 °C for 1 min, rate 7 °C/min, final temperature 300 °C for 10 min. The interface temperature of the mass selective detector (Hewlett Packard 5971A) was set at 300 °C, and the ion source temperature at 200 °C. The MS was operated in the electron ionisation, EI, mode at 70 eV. The quantitative analysis was made in the selected ion monitoring (SIM) mode. A PAH standard mixture with internal standards was used for determination of retention times and response factor calculations using molecular ions (M+).

After this pilot experiment seven more tyre crumbs were analysed. To see if there is a time variation in the PAH content, Michelin tyres from 1993, 1995, 1997 and from three different periods in 1998 were analysed in the same way as described above. All these tyres were for wintertime use and the Bridgestone tyre had nails. To compare different manufacturers a Gislaved tyre from week 15 1999 was also analysed.

The 48 and 72-hours extracts were treated in the same way except that 7 and 4µl DIST-B internal standard were added to about 4 and 6% of the extracts.

Finally some of the analysed 24-hours sample volumes were reduced from about 300 µl to 50 µl for analysis in a full scan GC-MS mode to get an estimate on other compounds present in the tyre and not only the 26 PAH selected in SIM mode. One sample, the extract form the Bridgestone tyre, was reanalysed in the full-scan mode after a clean-up procedure using a LC-back-flush technique [41]. This clean-up procedure eliminated the alkanes from the sample.

3.Results

3.1 Descriptive Statistics

Descriptive statistics for the PAH data from Kista, Enskede and Hornsgatan is listed in Appendix 1 together with descriptive statistics for elemental data from Gubbängen and hydrocarbon- and PAH-data from the Söderledstunnel. The PAH-data from the Söderledstunnel is preliminary and small adjustments will be made. The statistics include mean, standard deviation, maximum and minimum.

A raw data plot including PAH data from the three monitoring sites Hornsgatan, Kista and Enskede is also shown in Appendix 1. Figure 3.1 shows the annual mean values of 14 PAH and the partitioning between gas and particulate phase for 1991 and 1994-98 at Hornsgatan. No obvious trend can be seen from this data, but except for 1997 there seems to be a decline in the PAH levels at Hornsgatan 1994-1998. Comparing this data with the traffic frequency on Hornsgatan the same years (see figure 3.2) the high PAH levels measured in 1997 can be explained by relatively more vehicles/24h this year. However, despite these facts there is no clear correlation between traffic measurements and PAH level in Hornsgatan. The number of cars equipped with catalyst and the increased use of MK I diesel fuel of course also play parts.

If taking the ratio of methylphenanthrenes to phenanthrenes for particulate associated PAH as Nielsen 1996 (see introduction) proposed Hornsgatan has the highest mean value of 2.2. Corresponding value for Enskede is only 0.8 and for Kista 1.1. The value for Enskede and Kista are close to the value for gasoline vehicles of 0.8 and the value for Hornsgatan indicate some diesel vehicle influence [14].
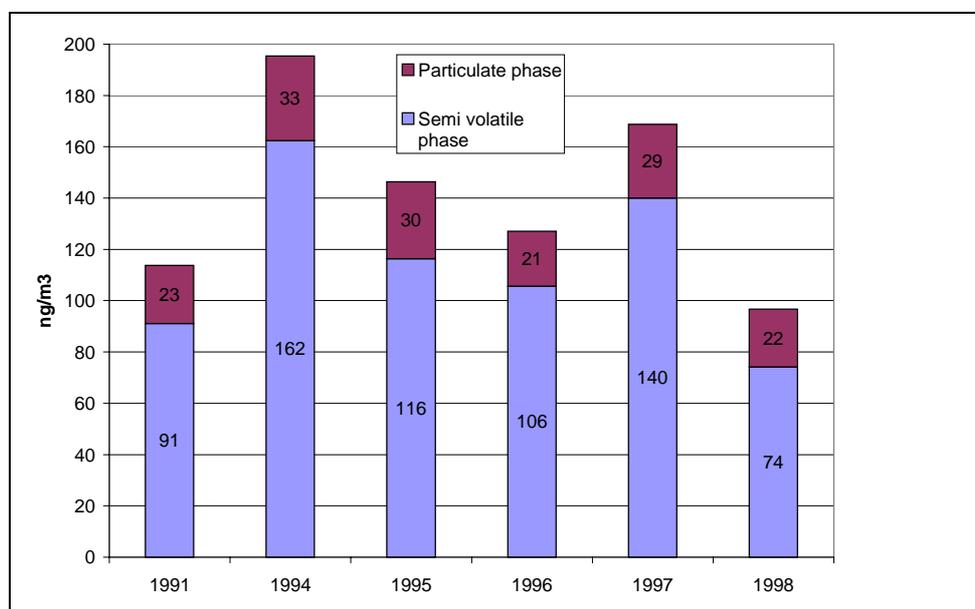
3.1 Annual mean values and partitioning between particulate and semi-volatile phase in Hornsgatan 1991, 1994-98.
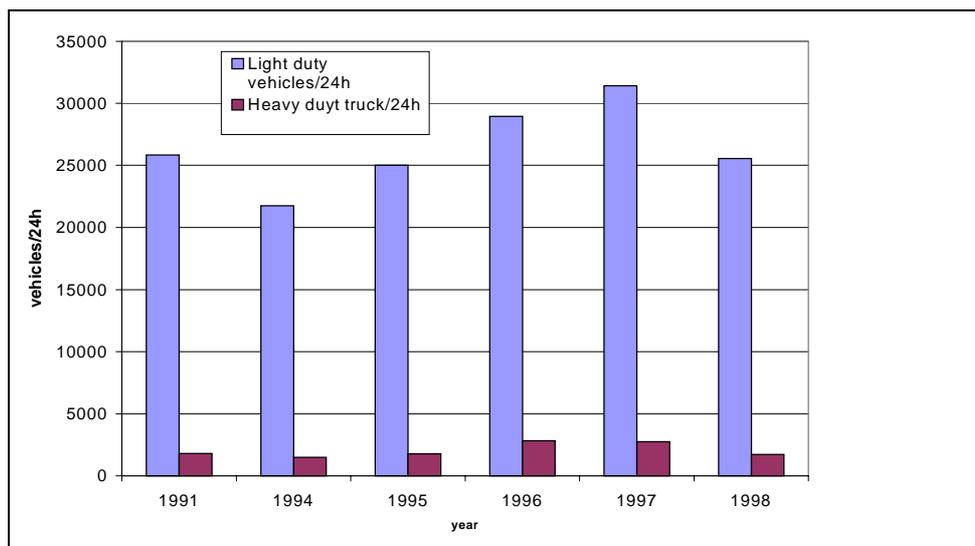
Figure 3.2 Frequency of light-duty vehicles and heavy-duty truck at Hornsgatan 1991 and 1994-98.

As obvious from the descriptive statistics in Appendix 1 there are a lot of missing values in the elemental data from Gubbängen. Because of missing data it is difficult to see trends but there seems to be a decline in the ambient metal particulate concentrations, at least for some metals. Lead decreases with 75% during 1989-96. Because sulphur, silicon, potassium, calcium and iron have considerably higher concentrations raw data for these elements are shown in a separate plot in Appendix 1.

Descriptive statistics and raw data plots are shown in Appendix 1, both for the alkane- and naphtalene-data from Åsö separately and for the Åsö subtracted from Noa data. Descriptive statistics for the PAH data is also included in Appendix 1. Bar plots of the mean values for the six alkanes and the three naphtalenes at Åsö and Noa-Åsö is shown in figure 3.3. Outliers are not included in the mean values.
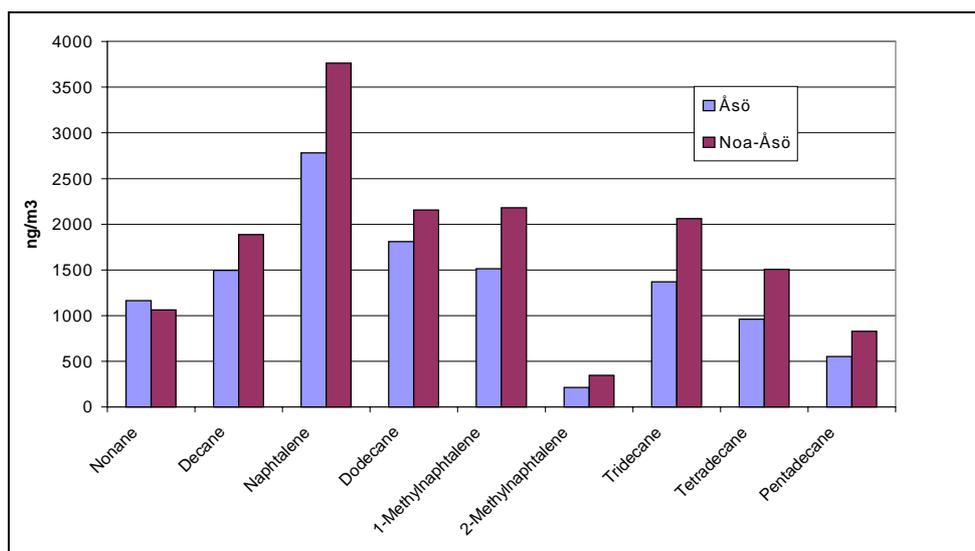
Figure 3.3 Mean values of the alkanes and naphtalenes at Åsö and Noa-Åsö.

3.2 Varimax Rotated Principal Component Analysis

3.2.1 The Hornsgatan-model

Sample number 10 from 1998 has strong influence on the third component and looks like an outlier in the scores plots (figure 3.4). But in the data plot sample number 10 does not differ from the other objects. Samples number 10 and 11 are from 1998 and are not analysed by the same laboratory as samples from 1991 and 1994-97. In sample 10 benzo(a)pyrene is 2% of the total PAH and in sample 11 benzo(a)pyrene constitute only 1.4%. In all the other samples it is about 1%, and benzo(a)pyrene has high loadings in the third component (see table 3.1).

However, if samples 10 and 11 are excluded from the further analysis for example sample number 8 and 9 seems to be outliers in the third PC. In raw-data plot it is observed that these samples have high values in 1-Methylphenanthrene which is the variable that now has the highest loadings in the third PC. Because of the few samples it is not justified to exclude any of the samples from the model.
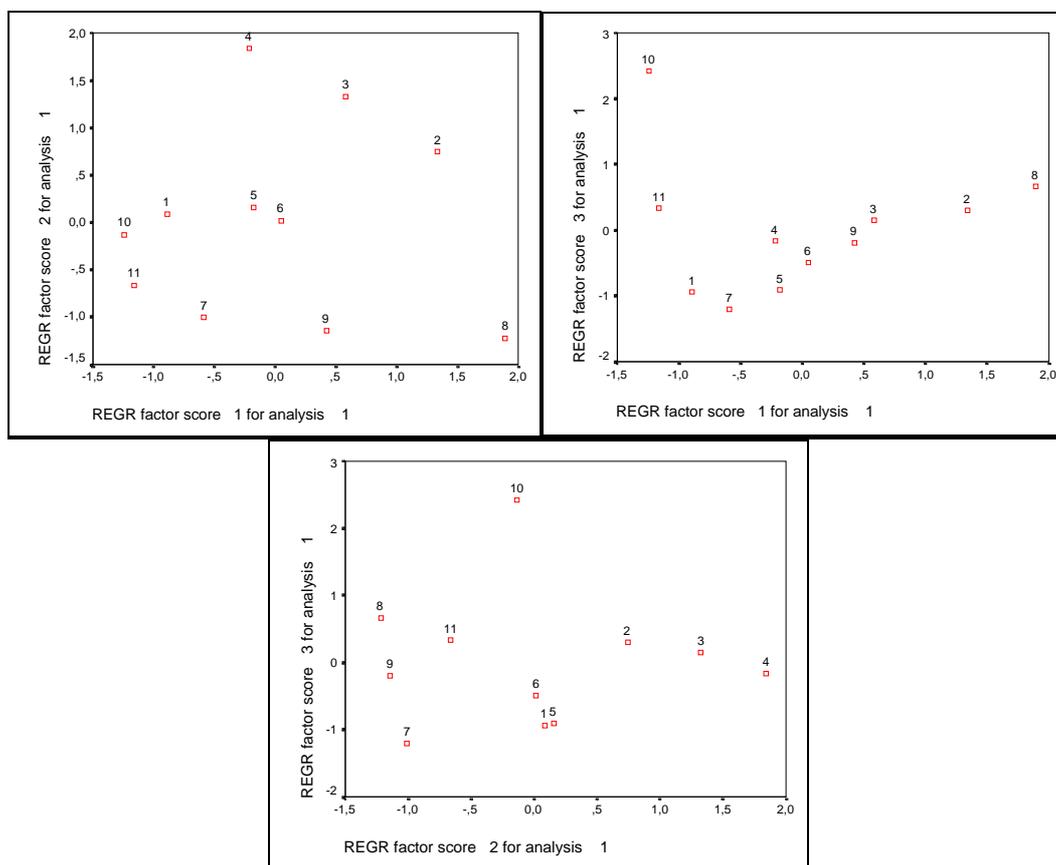
Figure 3.4 Scores plots of all objects in the Hornsgatan-model, PC 1 vs. PC 2, PC 1 vs. PC 3 and PC 2 vs. PC 3.

The first component explains 42% of the variance and has high loadings in phenanthrene, fluoranthene and pyrene, which are characteristic for diesel vehicle emissions [13]. In the second component coronene and benzo(ghi)perylene, which are characteristic for gasoline vehicle emissions, have high loadings. This second component explains 40% of the variance. It's more difficult to interpret the sources of

the third component it can be a mixture of several sources or just the background level. Three PC explain 95% of the variance.

Table 3.1 Loadings for all variables and all objects in Hornsgatan.

Rotated Component Matrix[a]

	Rescaled		
	Component		
	1	2	3
Phenanthrene	**,96**	,21	-,06
1-Methylphenanthrene	**,90**	-,21	,01
Anthracene	**,90**	,34	,16
Fluoranthene	**,87**	,42	,03
Pyrene	**,84**	,50	,03
Benzo(e)pyrene	**,77**	,60	-,19
Coronene	,10	**,98**	,08
Indeno(cd)pyrene	,10	**,97**	,07
Benzo(gih)perylene	,26	**,93**	,21
Benzo(a)anthracene	,59	**,78**	,08
Chrysene	,59	**,76**	-,08
Benzofluoranthenes	,17	**,71**	,58
Perylene	-,47	-,09	**,85**
Benzo(a)pyrene	,43	,35	**,83**

Extraction Method: Principal Component Analysis.
Rotation Method: Varimax with Kaiser Normalization.
a. Rotation converged in 5 iterations.

3.2.2 The Kista-model

In raw data plot samples number 6, 9, 10, 12 and 13 differ from the other and they are also suspicious outliers in the scores plot (figure 3.5). But when excluding these samples, for example sample number 1 is an obvious outlier and excluding as much as 40% of the samples do not seem realistic. These deviations are probably due to natural variation and not measure- or analytical errors, at least in sample 9 and 10 because the high levels of fluoranthene and pyrene coincide with high levels in Enskede samples from the same days.

Three components explain almost 93% of the variance. The first component (49 %) seems to correspond to gasoline vehicle emissions of PAH, this can be seen from the loadings in table 3.2 where for example coronene has high loadings. The second component explains 33% of the variance and seems to be influenced by diesel vehicle emissions. Pyrene, fluoranthene, phenanthrene and methylphenanthrenes all have high loadings in this component. It's more difficult to interpret the sources of the third component it can be a mixture of several sources or just the background level.
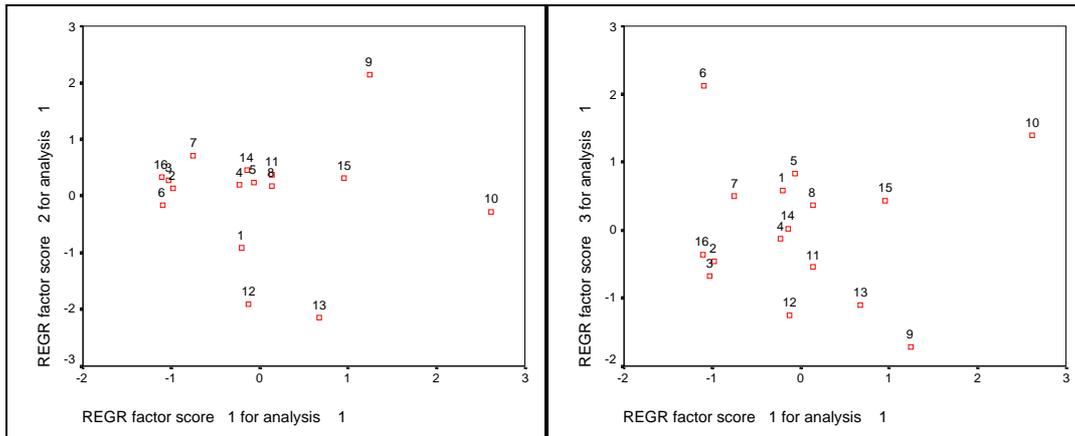
Figure 3.5 Scores plots of all objects in the Kista-model, PC 1 vs. PC 2 and PC 1 vs. PC 3.

Table 3.2 Loadings for all variables and all objects in Kista.

Rotated Component Matrix[a]

	Rescaled		
	Component		
	1	2	3
Benzo(a)anthracene	**,92**	,35	,10
Benzofluoranthenes	**,91**	,35	,16
Benzo(ghi)perylene	**,91**	,26	,29
Perylene	**,91**	,32	,07
Benzo(a)pyrene	**,91**	,37	,10
Benzo(e)pyrene	**,91**	,34	,23
Chrysene	**,89**	,28	,20
Coronene	**,89**	,25	,31
Benzo(a)fluorene	**,88**	,38	,05
Indeno(1,2,3-cd)pyrene	**,81**	,36	,02
9+4-Methylphenanthrene	,34	**,90**	,14
3-Methylphenanthrene	,39	**,85**	,29
2-Methylphenanthrene	,33	**,85**	,40
2-Methylanthracene	,54	**,79**	,15
Phenanthrene	,38	**,78**	,45
1-Methylphenanthrene	,33	**,77**	,52
Pyrene	,59	**,76**	,26
Fluoranthene	,63	**,73**	,19
Anthracene	,42	,36	**,71**
2-Phenylnaphtalene	-,04	,45	**,69**

Extraction Method: Principal Component Analysis.
Rotation Method: Varimax with Kaiser Normalization.

a. Rotation converged in 8 iterations.

3.2.3 The Enskede-model

Sample number 6 and 9 were identified as outliers both in the data plot and in scores plots (figure 3.6) and these samples were excluded from the PCA-model. The new model with 14 samples has no obvious outlier, see figure 3.7.
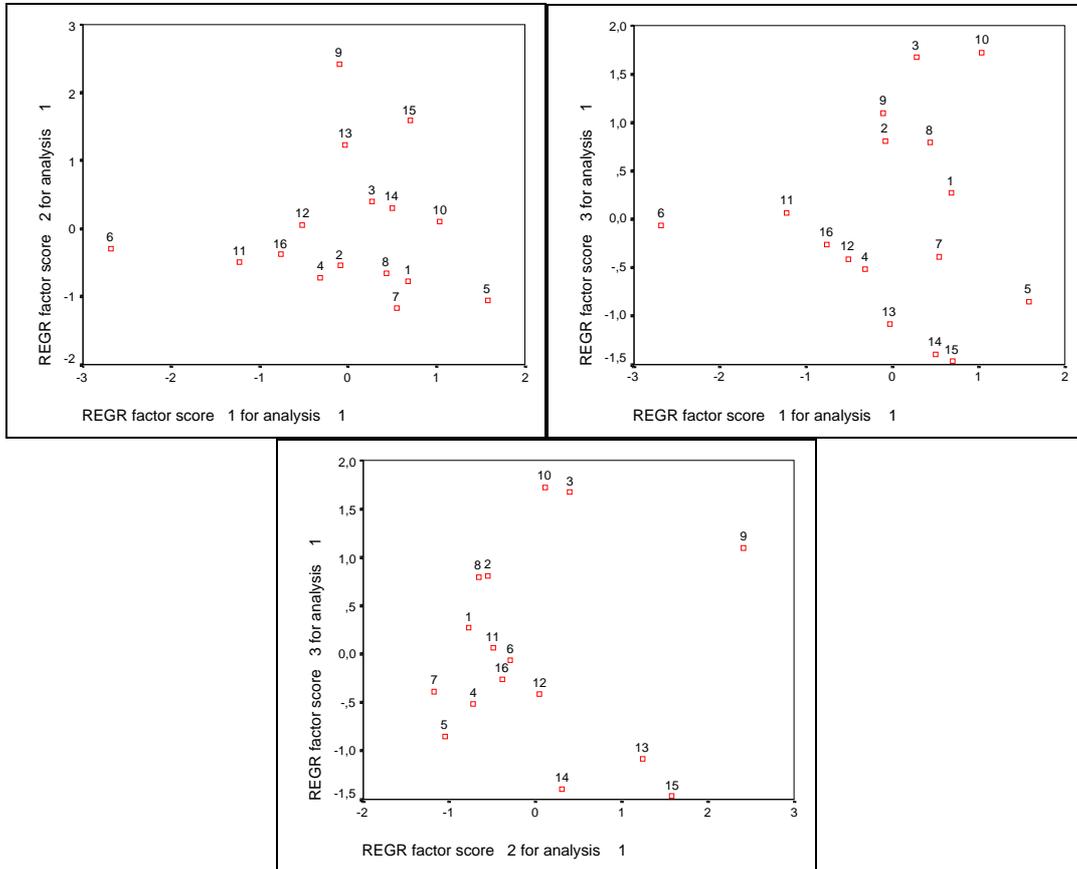
Figure 3.6 Scores plots of all objects in the Enskede-model, PC 1 vs. PC 2, PC 1 vs. PC 3 and PC 2 vs. PC 3.
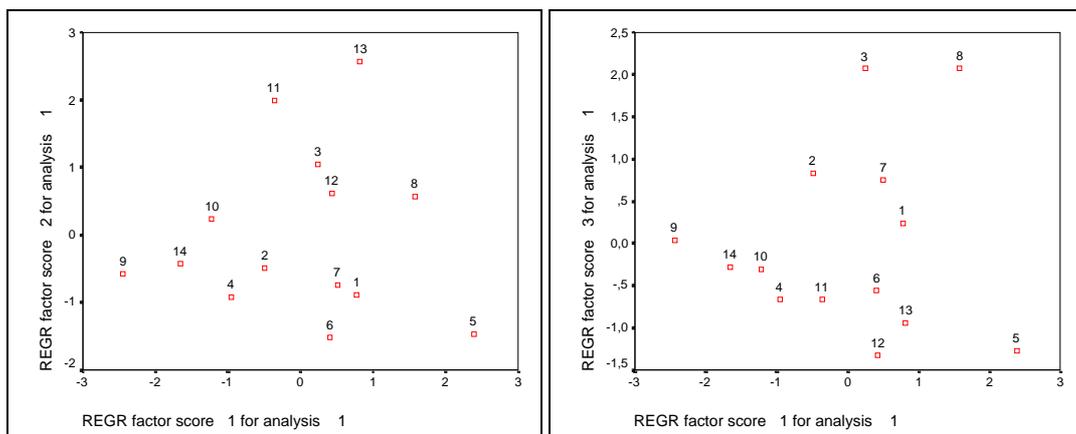
Figure 3.7 Scores plots of 14 objects in the Enskede-model, PC 1 vs. PC 2 and PC 1 vs. PC 3

Three principal components explain 94% of the variance. The first PC is due to diesel vehicle emissions and is responsible for almost 42% of the variance. Domestic wood burning may also influences the first component. Pyrene, fluoranthene, phenanthrene

and methylphenanthrenes, all typical in diesel exhaust, have high loadings in this first component, see table 3.3. The second component (40 %) correspond to gasoline exhaust emissions, here coronene has high loadings. The third component is difficult to interpret. In order to identify domestic wood burning retene could be measured, because it is a potential marker for wood burning [42].

Table 3.3 Loadings for all variables and 14 objects in Enskede

Rotated Component Matrix[a]

	Rescaled		
	Component		
	1	2	3
Phenanthrene	**,93**	,26	,20
2-Phenylnaphtalene	**,92**	,04	,19
Anthracene	**,90**	,28	-,21
1-Methylphenanthrene	**,90**	,36	,18
2-Methylanthracene	**,89**	,27	,28
2-Methylphenanthrene	**,86**	,47	,13
3-Methylphenanthrene	**,79**	,46	,30
9+4-Methylphenanthrene	**,78**	,55	,19
Pyrene	**,75**	,42	,43
Fluoranthene	**,73**	,33	,56
Perylene	,03	**,95**	,15
Benzo(a)anthracene	,25	**,93**	,14
Benzo(a)pyrene	,35	**,93**	-,01
Benzo(e)pyrene	,31	**,93**	,18
Coronene	,37	**,89**	-,05
Benzo(ghi)perylene	,37	**,89**	,07
Benzofluoranthenes	,29	**,76**	,41
Chrysene	,56	**,73**	,17
Benzo(a)fluorene	,41	**,71**	,47
Indeno(cd)pyrene	,24	,11	**,93**

Extraction Method: Principal Component Analysis.
Rotation Method: Varimax with Kaiser Normalization.
a. Rotation converged in 5 iterations.

3.2.4 Hornsgatan, Enskede and Kista-model

Eleven samples from Hornsgatan, Enskede and Kista were used in the same model. Sample number 9, 10, 12, 13, 15 in Kista and sample number 6, 9, 13, 14, 15 in Enskede have been excluded. The excluded samples are identified as outliers in separate models from Enskede and Kista with 14 different PAH as variables. In the separate Kista-model with 20 variables sample number 6 was suspicious. Excluding sample number 6 instead of 15 gave an identical model, because all Enskede and Kista samples form a cluster near the origin. Even if using 16 samples from Enskede and Kista and only 11 from Hornsgatan the model does not change much.
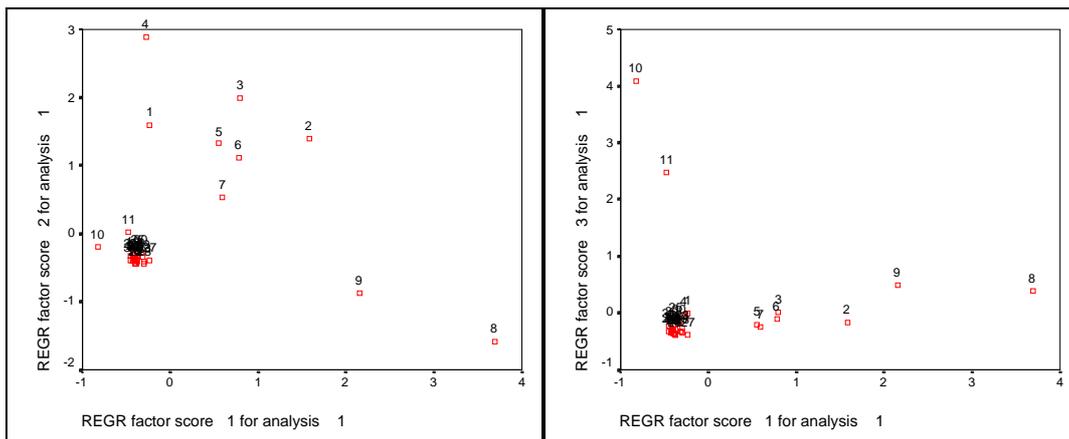
Figure 3.8 Scores plots of 11 objects from Hornsgatan, Enskede and Kista PC 1 vs. PC 2 and PC 1 vs. PC 3

It is obvious from the scores plots (figure 3.8) that sample number 8 and 9 from Hornsgatan1997 have high scores in the first PC. The first component corresponds to diesel vehicle emission and a comparison with traffic data from 1997 confirms that heavy traffic was frequent. However, 1996 has the highest per cent of heavy traffic, and sample 6 and 7 do not have exceptionally high scores in PC 1. The raw data plot (see Appendix 1) explains this incongruity because sample 8 and 9 have high values in 1-methylphenanthrene. 1-methylphenanthrene has the highest loadings in PC 1 (see table 3.4) because it is characteristic for diesel traffic. Sample number 10 and 11 again have high scores in PC 3 and the explanation is the high values of benzo(a)pyrene as in the separate Hornsgatan-model.

Table 3.4 Loadings for all variables and 11 objects from each of the three places.

Rotated Component Matrix[a]

	Rescaled		
	Component		
	1	2	3
1-Methylphenanthrene	**,89**	,35	,27
Phenanthrene	**,78**	,55	,27
Anthracene	**,74**	,57	,34
Fluoranthene	**,71**	,61	,33
Pyrene	**,69**	,63	,36
Benzo(e)pyrene	**,68**	**,68**	,27
Benzo(a)pyrene	**,60**	,53	,58
Coronene	,48	**,77**	,42
Indeno(cd)pyrene	,49	**,76**	,42
Benzo(gih)perylene	,53	**,72**	,45
Benz(a)anthracene	,61	**,71**	,34
Chrysene	,62	**,70**	,34
Benzofluoranthenes	,52	**,65**	,53
Perylene	,22	,28	**,93**

Extraction Method: Principal Component Analysis.
Rotation Method: Varimax with Kaiser Normalization.
a. Rotation converged in 7 iterations.

The diesel component explains 40% and the gasoline component explains almost as much of the variance (39%). The third background or mixed component explains 20% and the three components together explain almost all variance 99%.

3.2.5 Elemental model from Gubbängen

Sample 166 is an obvious outlier in PC5 as can be seen from the scores plot PC1 vs. PC5 (see figure 3.9). PC5 has high loadings only in potassium and this is consistent with high potassium concentrations for sample 166 in raw data. Eliminating this sample reduce the number of significant principal components from five to four and the suspicious outliers sample number 4 and 172 from the scores plot PC1 vs. PC2 (see figure 3.9) become more obvious. Sample number 4 is an outlier in PC1 which has high loadings for titanium, manganese and lead. The same elements show high concentrations in raw data for this sample. Sample 172 has high concentration in copper and is an outlier in PC2 where copper has high loadings.
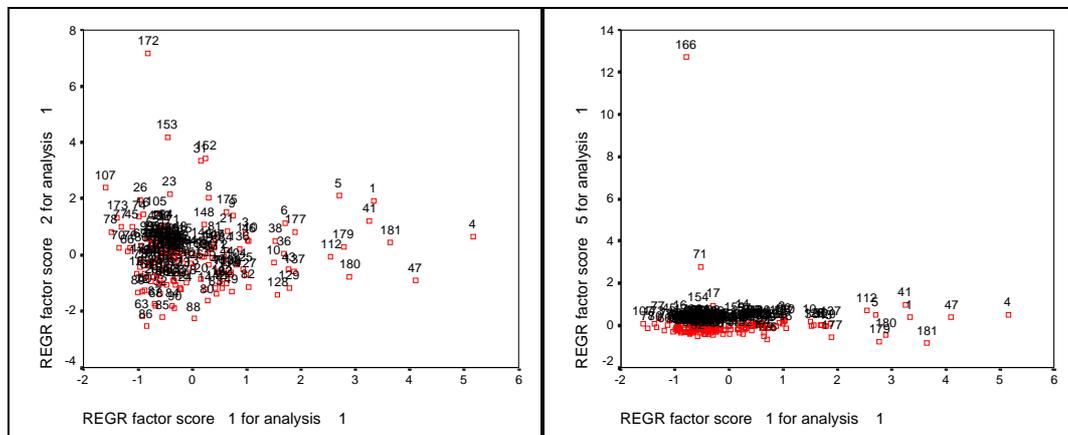
Figure 3.9 Scores plots PC1 vs. PC2 and PC1 vs. PC5 for all objects.

Excluding these three samples yield a model with four principal components and no obvious outlier as can be seen in scores plots in figure 3.10. Possible outliers from scores plot do not coincide with deviations in raw data.
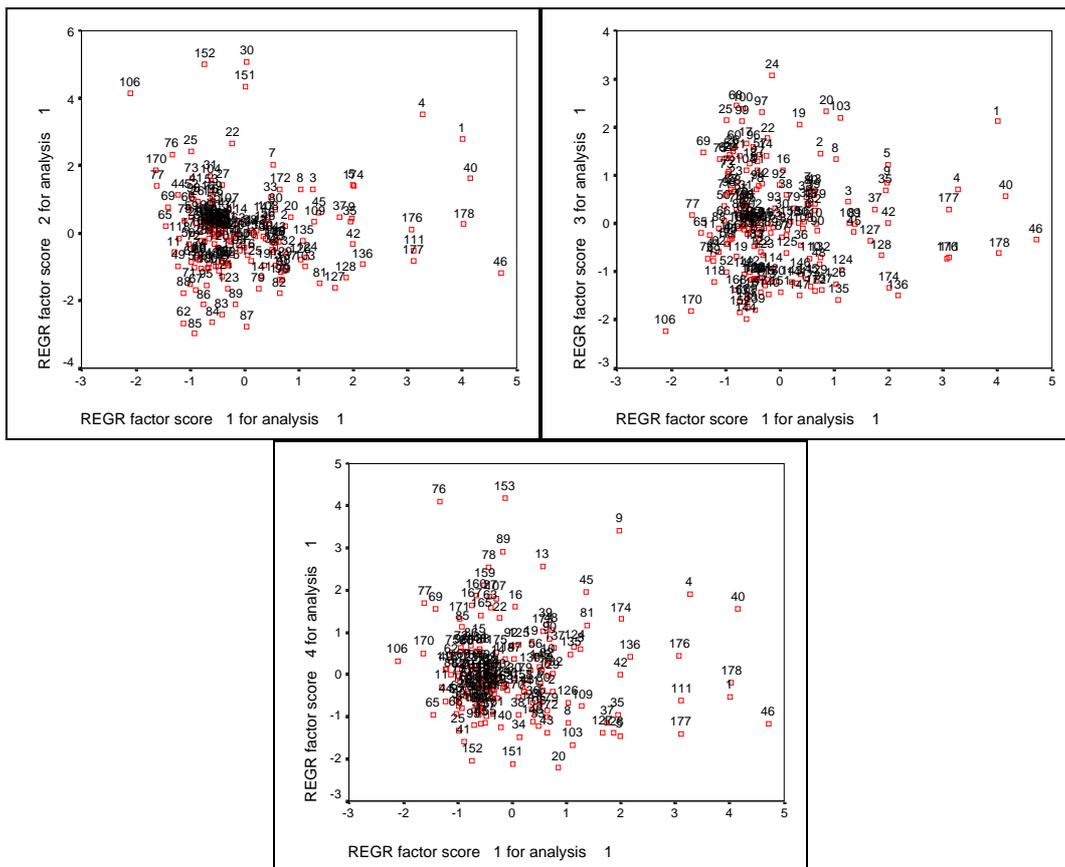
Figure 3.10 Scores plots PC1 vs. PC2, PC1 vs. PC3 and PC1 vs. PC4, sample 4, 166 and 172 are excluded.

The first component corresponds to resusupended road dust because of high loadings in silicon, titanium, iron, calcium, manganese and potassium see table 3.5. The second component with high loadings in nickel, zinc, copper, chromium, arsenic and selenium is probably a mixture of different coal- and oil-combustion sources. The third PC has high loadings in lead and bromine, which are typical of gasoline traffic. The decline of lead is obvious during the period because of the successive elimination from gasoline. The last component has only high loadings in sulphur and is due to secondary sulphate. This source type does not represent any real source of emissions but is the result of continues oxidation of gaseous SO_2 to particulate sulphate [21] during long range transport. The four components explain 63% all together. The first PC is responsible for almost 30% and the others for 16%, 11% and 6%, respectively.

Table 3.5 Loadings for 179 object (sample 4, 166 and 172 is eliminated).

Rotated Component Matrix[a]

	Rescaled			
	Component			
	1	2	3	4
Si	**,93**	,08	-,02	-,06
Ti	**,92**	,11	,07	-,07
Fe	**,89**	,31	,01	-,08
Ca	**,86**	,12	,00	,23
Mn	**,81**	,36	,08	,14
K	**,63**	,18	,15	,21
Ni	-,06	**,80**	,05	,15
Zn	,40	**,70**	,20	,04
Cu	,26	**,62**	,17	-,14
Cr	,20	**,50**	,14	-,12
As	,09	**,48**	,19	,09
Se	,23	**,33**	,15	,11
Br	,01	,22	**,88**	,17
Pb	,08	,31	**,84**	-,10
S	,36	,26	,09	**,86**
Sr	,04	,14	,00	-,16

Extraction Method: Principal Component Analysis.
Rotation Method: Varimax with Kaiser Normalization.
a. Rotation converged in 6 iterations.

3.2.6. Söderledstunneln alkanes (Åsö)

The first model of the Söderledstunnel-data initially includes104 samples and nine variables from the monitoring site Åsö 100 m from the tunnel entrance. In the scores plot (figure 3.11) sample number 33, 36, 37 and 38 are obvious outliers. These samples also differ in raw data Appendix 1. Eliminating these four samples give a model without outliers see scores plot in figure 3.11.
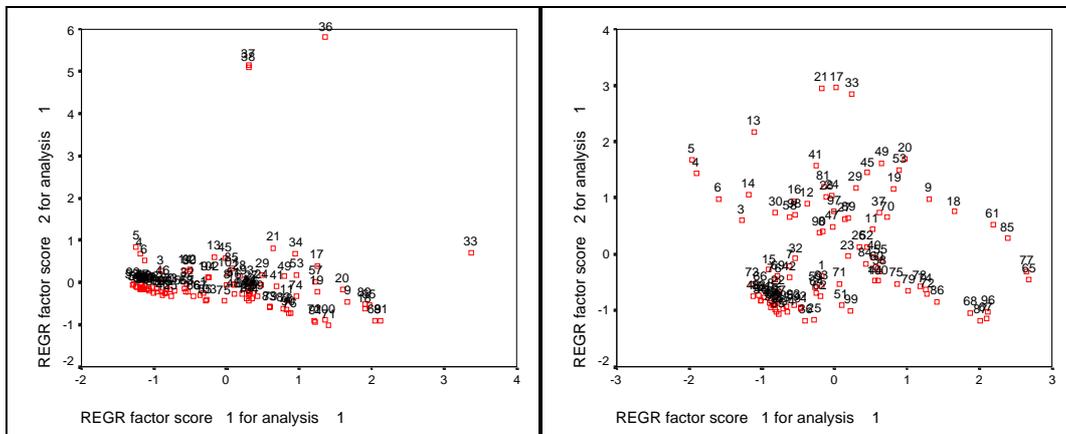
Figure 3.11 Scores plot with all samples to the left and without outliers to the right.

The first PC has high loadings in pentadecane, tridecane, tetradecane, dodecane and decane (see table 3.6) and is responsible for 48% of the variance. The latent variable is

probably diesel vehicle emissions, because *n*-paraffines with more than 10 carbons have together with naphtalene and methylnaphtalene isomers much higher emission rates for diesel vehicles than for gasoline vehicles [3].

The second component explains 47% and has high loadings in nonane, naphtalene, 1-methylnaphtalene and 2-methylnaphtalene. This PC is probably due to gasoline vehicle emissions, despite the high loadings in naphtalenes, which according to Zielinska *et al.* 1995 should be mainly coming from diesel exhaust. However, there may be differences in traffic emission profiles between Sweden and U.S.A. Two principal components explain 95% of the variance after varimax rotation.

Table 3.6 Loadings for the nine variables used in the PCA-model.

Rotated Component Matrix[a]

	Rescaled	
	Component	
	1	2
Pentadecane	**.88**	.43
Tridecane	**.80**	.58
Tetradecane	**.80**	.58
Dodecane	**.77**	.61
Decane	**.72**	.61
Naphtalene	.48	**.86**
1-Methylnaphtalene	.54	**.83**
Nonane	.50	**.80**
2-Methylnaphtalene	.61	**.74**

Extraction Method: Principal Component Analysis.
Rotation Method: Varimax with Kaiser Normalization.
a. Rotation converged in 3 iterations.

3.2.7 Söderledstunneln alkanes (Noa-Åsö)

The second model of data from the Söderledstunnel where Åsö samples are subtracted from Noa include 49 samples and 9 variables. In the scores plot (figure 3.12) sample number 4 and 26 are obvious outliers this is also consistent with the raw data plot. Eliminating these samples give several more suspicious ouliers. Three of this sample 12, 20 and 47 are also outlier in raw data and are these samples are also excluded in the final model see figure 3.12.

Figure 3.12 Scores plot with all objects to the left and without outliers to the right.

The first PC has high loadings in the *n*-alkanes decane to pentadecane as in the model for Åsö. This PC explains 46% of the variance in the data matrix. The second PC explains 41% and has high loadings in nonane and the naphtalenes (see table 3.7) and is probably due to gasoline vehicle emissions.

Table 3.7 Loadings for the nine variables used in the Noa-Åsö model.

Rotated Component Matrix[a]

	Rescaled	
	Component	
	1	2
Pentadecane	**.91**	.27
Tetradecane	**.90**	.36
Tridecane	**.90**	.42
Dodecane	**.82**	.49
Decane	**.71**	.27
Naphtalene	.26	**.95**
1-Methylnaphtalene	.36	**.91**
2-Methylnaphtalene	.44	**.87**
Nonane	.35	**.72**

Extraction Method: Principal Component Analysis.
Rotation Method: Varimax with Kaiser Normalization.

a. Rotation converged in 3 iterations.

Including 13 aldehydes and ketones to the Åsö data give no further information, because aldehydes and ketones form one PC and alkanes and naphtalenes form one. A model Noa-Åsö including alkanes, aldehydes, ketones and naphtalenes is not possible to made because too few samples remain.

3.2.8 Söderledstunneln PAH

Because of only nine samples available for the varimax rotated PCA it was difficult to make an interpretable model. Initially four components were extracted but one sample was an obvious outlier see the left scores plot in figure 3. 13. Eliminating this sample result in a model with three PC but with some more suspicious outliers. The three components with high eigenvalues received were not easy to interpret. Therefore number of PC were set to two, giving one diesel (PC1) and one gasoline (PC2) component.
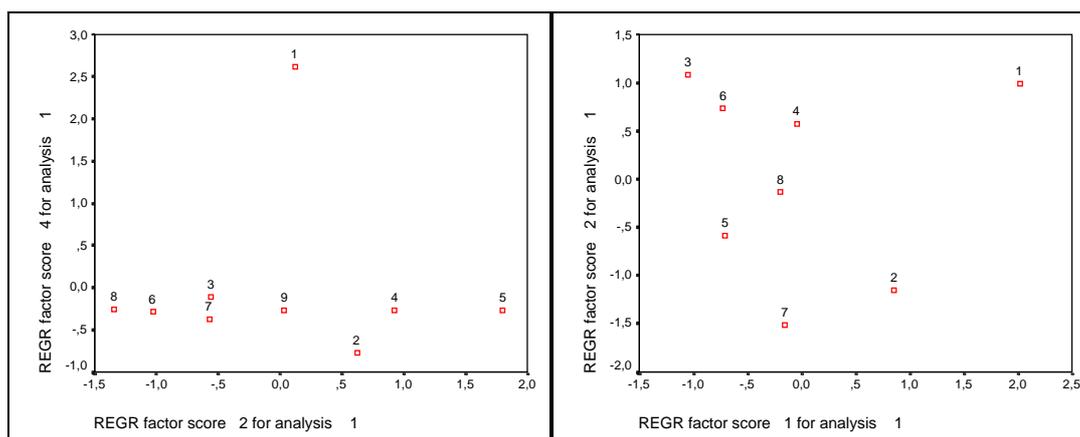
Figure 3.13 Scoresplot with all objects to the left and without sample number 1 to the right.

From the scores plot without sample number 1 (figure 3.13 to the right) it can be seen that one sample (new number 1) have high scores values in both the diesel and the gasoline component. This sample has highest concentrations in all PAH and is from a Monday morning between 8 and 9 am.

As can be seen from the loadings in table 3.8 anthracene, phenanhtrene, pyrene, fluorantnene and metylated PAH have high loadings in the diesel component. The gasoline component have high loadings in coronene, benz(ghi)perylene, chrysene, benzofluoranthenes and indeno(cd)pyrene. The result is in consistent with the other models done and the literature [13, 40]. The diesel component explains 57% of the variance and the gasoline component 32%.

Table 3.8 Loadings for the PAH from the Söderledstunnel

Rotated Component Matrix[a]

| | Rescaled | |
| | Component | |
	1	2
Anthracene	**,96**	,22
Phenanthrene	**,96**	,17
2-Phenylnaphtalene	**,95**	,23
3,6-Dimethylphenanthrene	**,94**	,29
3-Methylphenanthrene	**,94**	,31
2-Methylflourene	**,94**	,24
2-Methylphenanthrene	**,93**	,35
1-Methylphenanthrene	**,93**	,35
3,9-Dimethylphenanthrene	**,92**	,36
4H-Cyclopenta(def)phenanthrene	**,91**	,35
2-Methylanthracene	**,91**	,38
9-Methylanthracene	**,89**	,37
Fluoranthene	**,85**	,51
9-Methylphenanthrene	**,85**	,42
1-Methylfluoranthene	**,84**	,46
4-Methylpyrene	**,83**	,55
Pyrene	**,82**	,56
3-Methylchrysene	**,82**	,56
Sum Methylchrysene	**,81**	,56
2-Methylpyrene	**,81**	,59
1-Methylpyrene	**,80**	,59
Fluorene	**,79**	,40
Dibenzothiophene	**,78**	,18
Benz(a)fluorene	**,76**	,63
Retene	**,72**	-,41
Benz(b)fluorene	,71	,69
Benzo(a)anthracene	,70	,67
Benzo(b)naphto(1,2-d)thiop	-,49	-,26
Indeno(cd)pyrene	-,03	**,84**
Perylene	,50	**,83**
Benzo(k)fluoranthene	,20	**,82**
Benzo(a)pyrene	,55	**,80**
Benzo(ghi)perylene	,00	**,79**
Benzo(e)pyrene	,57	**,78**
Coronene	,20	**,78**
Benzo(b)fluoranthene	,46	**,76**
Benzo(ghi)fluoranthene	,66	**,75**
Benzo(c)phenanthrene	,56	**,75**
Cyclopenta(cd)pyrene	,60	**,73**
Chrysene	,53	**,71**

Extraction Method: Principal Component Analysis.
Rotation Method: Varimax with Kaiser Normalization.

a. Rotation converged in 3 iterations.

3.3 Cluster Analysis

Hierarchical cluster analysis were made on the same data as the varimax rotated PCA to complete the information about groupings. The dendrograms are shown in Appendix 4. For Enskede and Kista the cluster analysis gave almost identical result as the PCA, but for Hornsgatan and the combined model with the three places in one, the results differ somewhat.

The cluster analysis of the elemental data from Gubbängen gave a result difficult to interpret because of several small clusters and is omitted from the report.

3.4 Chemical Mass Balance Model

3.4.1 CMB Hornsgatan

Table B in Appendix 3 gives the source contribution estimates (SCE) in ng/m^3 and their standard errors for 1991, both periods 1994-97 and a mean value for all years and periods in Hornsgatan. Table D in Appendix 3 gives the SCE for the model with 13 different PAH for 1997. Figure 3.14 shows annual mean values for SCE 1991, 1994-97 and the mean of the all the years. In figure 3.15 the SCE for 1997 using 13 variables in the model is plotted.

	1991	1994	1995	1996	1997	mean
gasoline	34,3	110,7	69,8	76,1	121,6	82,5
diesel	37,1	46,4	29,5	24,9	28,1	33,2
background	29,5	20,8	30,8	14,6	5,2	20,2
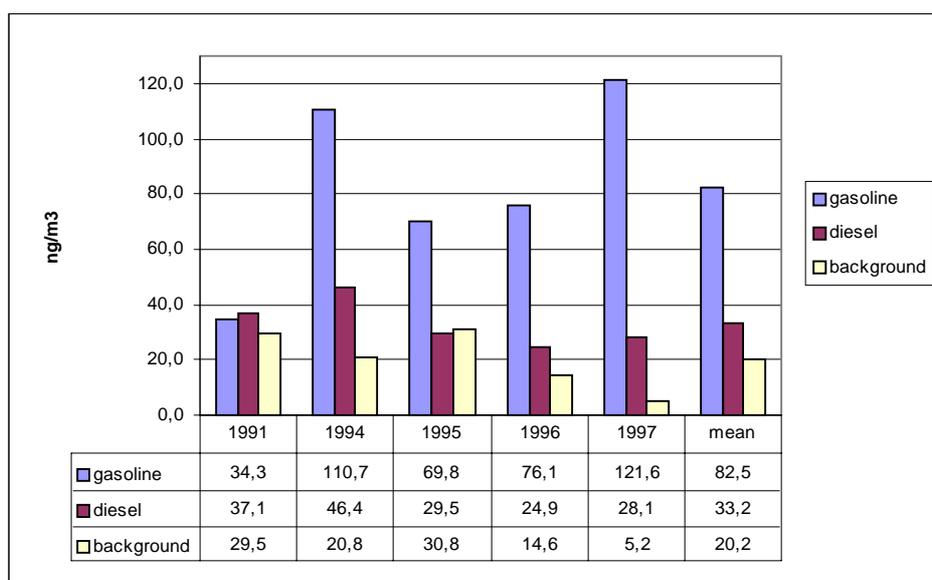
Figure 3.14 Annually mean- values of SCE 1991 and 1994-97.

The contribution from background seems to be comparatively high in 1995 even though the high March sample has been excluded (see Experimental). In 1991 all sources contribute by approximately the same amount, this can perhaps be explained by the fact that MK I diesel was not available and background source is from Rörvik 1994.

The CMB output for 1991 and 1994-96 indicates a contribution from the background much higher (14.6-30.8ng/m^3) than the concentrations measured in Rörvik (<5ng/m^3). The SCE for the background is the contribution from the surroundings, the level of PAH that always is present apart from the traffic at the monitoring site. Therefore would it probably be more relevant to use background profiles from the vicinity of Stockholm for the same periods. Unfortunately were no background profiles from Stockholm

available for 1991 and 1994-96. Using Enskede /Kista as background profile is possible for 1997 but for the other years the result is not satisfying.
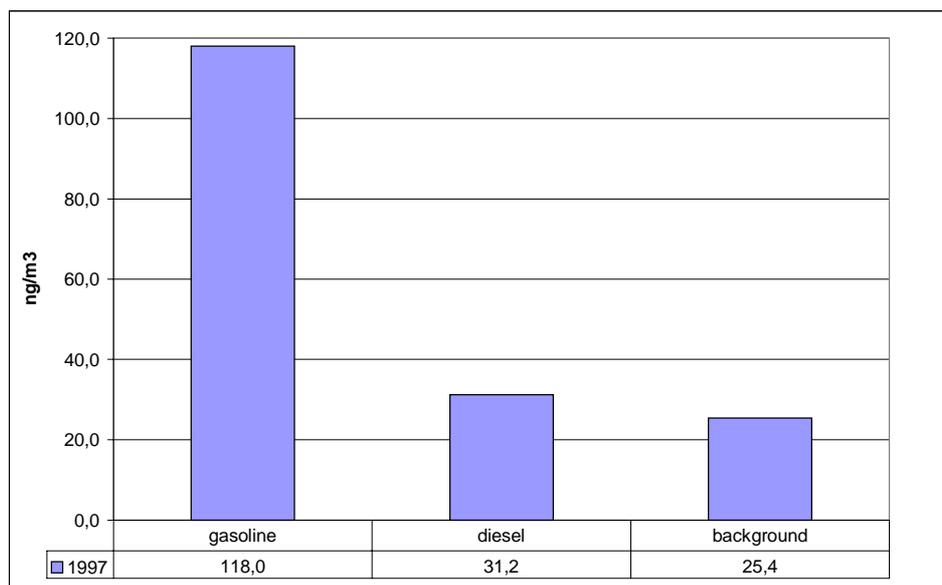
Figure 3.15 SCE mean- value 1997, 13 different PAH used in the model.

A TSTAT-value greater than 2.0 in table B and D in Appendix 3 shows that the relative precision of the source contribution estimates (also given in figure 3.14) is high and that the source is significant. A TSTAT smaller then 2.0 means that a source contribution is not present at a level, which exceeds two times standard error. Such sources may be omitted from the CMB or retained to provide an upper limit, if they are not collinear with the other sources since then they elevate the standard errors of other SCE [28].

For the years 1991 and 1994-96 only three of the TSTAT –values for the background are smaller than 2.0. For the period mean value all TSTAT are greater than 2.0. But including 1997 reduce the background TSTAT to 1.5 because of very low TSTAT for both periods in 1997. In 1997 the standard error of the SCE even exceeds the SCE for the background source.

Using 13 different PAH in CMB for 1997 give a somewhat better model. The background TSTAT-values do not exceed 2.0 but are considerably higher and the SCE standard errors do not exceed the source contributions. The background source is not omitted because these models give a much higher ratio of calculated to measured for the total concentration and the standard error of the other sources is not elevated.

For 1998 no background source was available and when using data from Enskede and Kista both TSTAT-values for diesel vehicle and background source are smaller than 2.0. A model with only one significant source does not make any sense and is therefore not included in the report.

From table B in Appendix 3 the conclusion is that gasoline exhaust account for 73% and diesel exhaust for 27% of the contributions to the traffic related PAH concentrations at Hornsgatan 1991 and 1994-97. In 1996 the corresponding values are 75% from gasoline and 25% from diesel.

For comparison the PAH emissions in Stockholm from gasoline vehicles is about 830 kg/year and from diesel vehicles 103 kg/year. This corresponds to 89% and 11% respectively [39]. The corresponding relative values for Hornsgatan April to May 1996, estimated based on measured traffic flow and composition and emission factors for different vehicles in Stockholm, are 79% to 88% for gasoline vehicles and 21% for diesel vehicles. If cold start effects are included the value for gasoline is 88%. This is in good agreement with the CMB- result [11, 39].
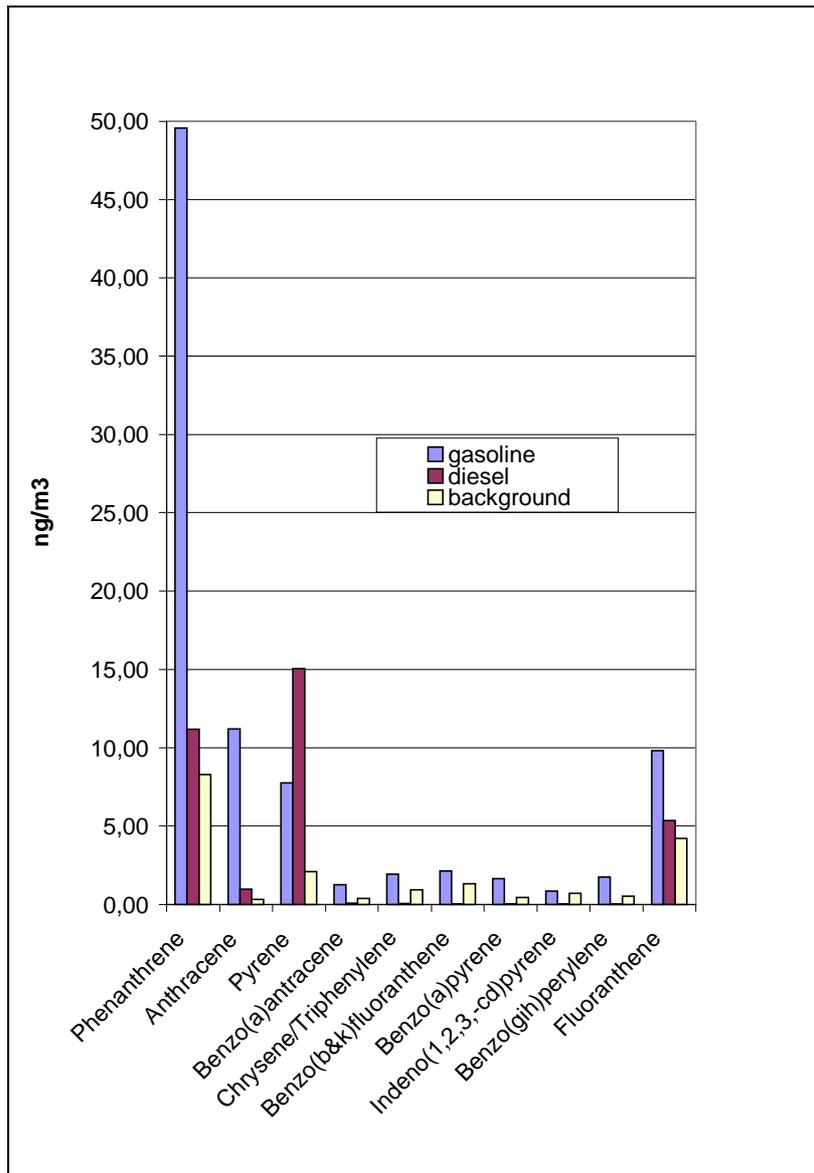
Figure 3.16 Mean values for the 10 different PAH from the three sources at Hornsgatan 1991 and 1994-97.

In Appendix 3 (table A and C) the contributions for the 10 or 13 different PAH in ng/m^3 for the three sources are listed. Mean values for the periods are also included in Appendix 3 and are summarised in figure 3.16. Figure 3.17 shows the mean of 13 PAH in 1997. The last column in Appendix 3 shows the ratio of calculated to measured concentration, the ratio should be near 1.00 if the model has accurately explained measured concentrations [28]. For the total mass this quotient vary from 0.98 to 1.10 in

1991 and 1994-97, the mean is 1.02. For the individual PAH the ratio of calculated to measured show larger deviations. In the CMB-model with 13 PAH the mean value for total mass calculated to measured ratio is 1.04 but for the other model with 10 PAH the mean for 1997 is 1.07.
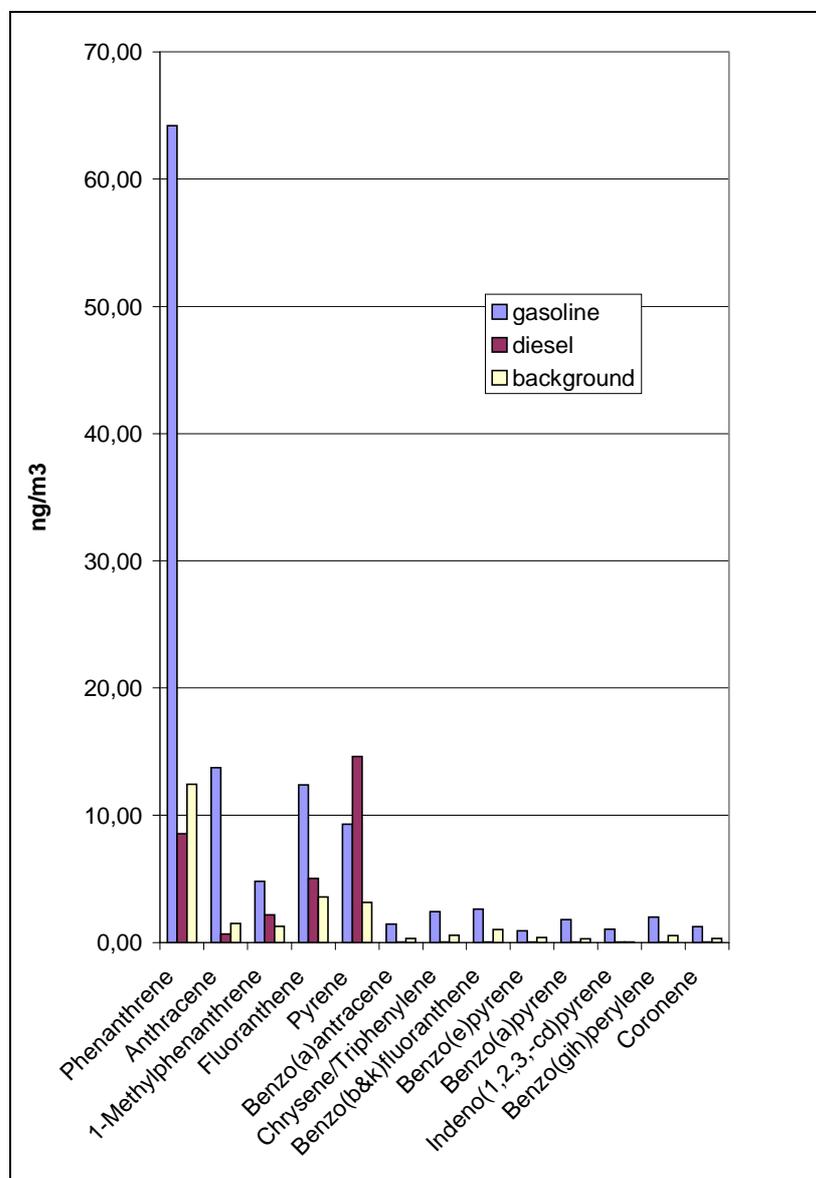
Figure 3.17 Mean values for the 13 different PAH from the three sources at Hornsgatan 1997.

3.4.2 CMB Kista

None of the attempts to make CMB models with three sources for Enskede and Kista were successful and are not included in the report. For most of the samples the background source gave negative SCE. For other samples all TSTAT-values were smaller than two. For the model with two sources for Kista three samples number 10, 12 and 13 gave negative source contributions for diesel emissions and are excluded from the average. These samples are also suspicious outliers in varimax rotated PCA. Samples numbers12 and 13 have low PAH levels and number10 have high. Only one of the remaining TSTAT-values is smaller than 2.0 and the ratios of calculated to measured concentrations differ more than 20% from 1.0 only in three cases (see table E

and G in Appendix 3). The mean calculated to measured value is 1.04 and the TSTAT mean values are 14 for gasoline emissions and 5 for diesel indicating that these two sources are significant.

3.4.3 CMB Enskede
Only sample number 6 has negative source contributions for the model with two sources for Enskede. However sample number 9 is identified as an outlier in the varimax rotated PCA, in CMB TSTAT-value is almost zero for the diesel source and the calculated total concentration exceeds the measured by 40%. Sample number 6 and 9 are both outliers and are therefore eliminated from average. Four of the remaining TSTAT- values are smaller than 2.0 and the mean TSTAT- value are 14 for gasoline emissions and 3 for diesel. In three cases the ratio of calculated to measured differ more than 20% from 1.0 and the mean value is 1.05 (see table F and H in Appendix 3).

The mean SCE for Enskede and Kista are visualised in figure 3.18. In Enskede 87% of the emission of 13 PAH came from gasoline vehicles and 13% from diesel vehicles (the diesel source maybe also include wood burning emissions). The corresponding values for Kista are 71% from gasoline vehicles and 29% from heavy-duty diesel trucks.

	Enskede	Kista
gasoline	12,6	5,46
diesel	1,9	2,21
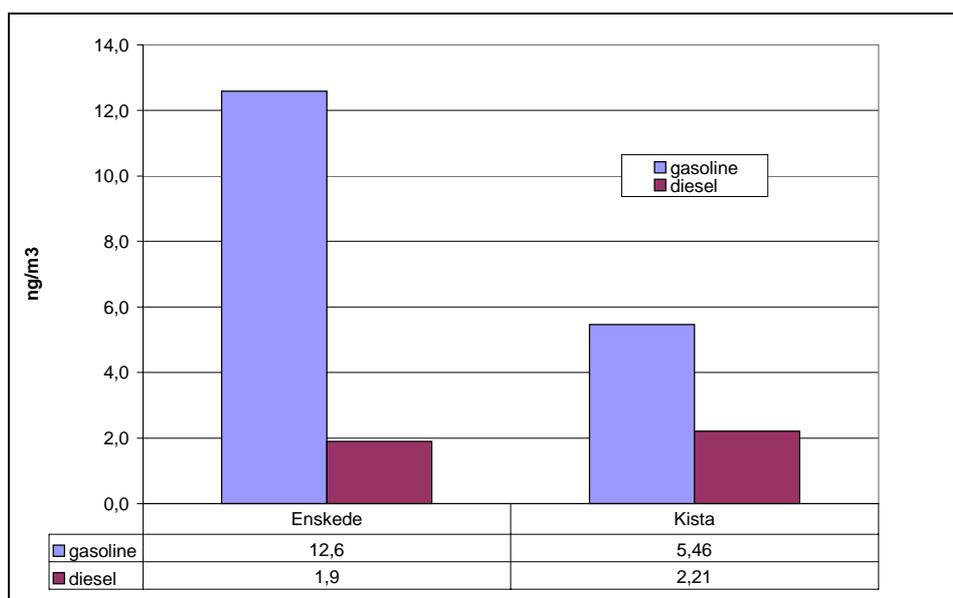
Figure 3.18 SCE mean values for Enskede and Kista

Tables E and F in Appendix 3 show the SCE for individual samples and in table G and H are the mean values for individual PAH in both Kista and Enskede. The standard deviations are also given. Averages of the 13 PAH are also plotted in figure 3.19 for Enskede and 3.20 for Kista.

The diesel contributions are small in Kista and especially in Enskede, but the shift to low molecular PAH for diesel emissions is obvious. In Kista the diesel contribution of pyrene exceed that of gasoline, but not in Enskede.
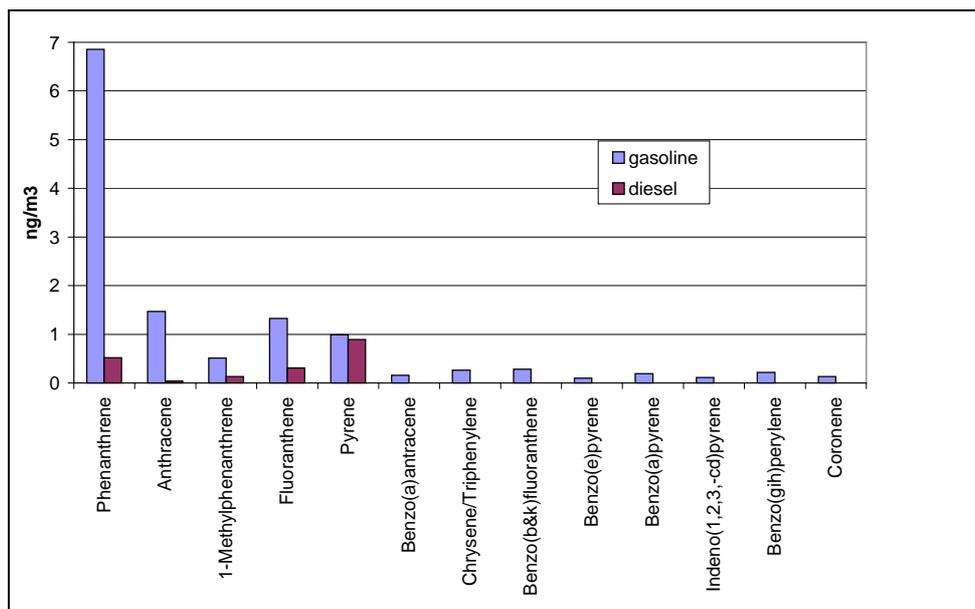
Figure 3.19 Average of the individual PAH (in ng/m^3) due to CMB results in Enskede 1997.
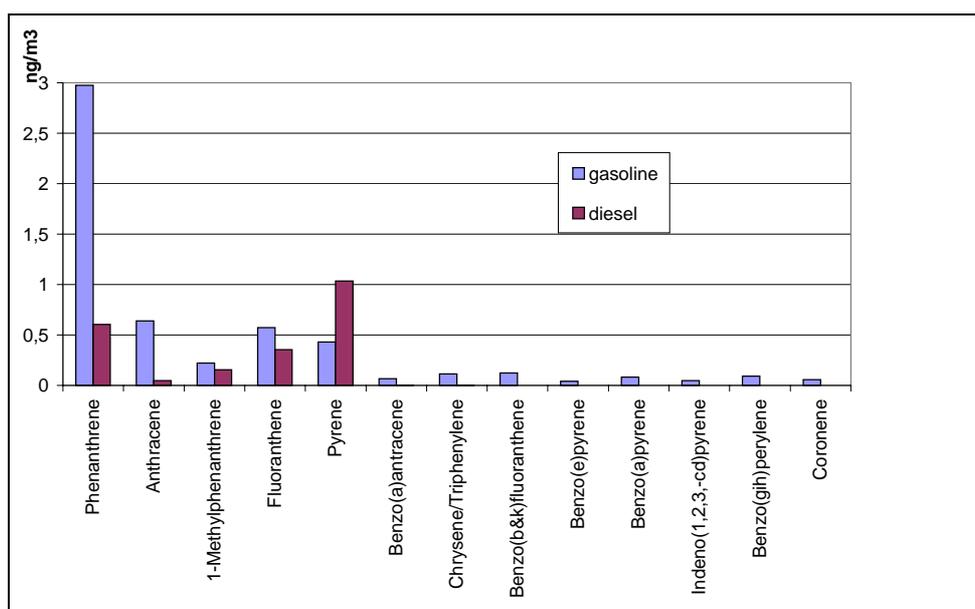
Figure 3.20 Average of the individual PAH (in ng/m^3) due to CMB results in Kista 1997.

3.4.4 CMB Gubbängen

With the source profiles available it was not possible to make any CMB model for the elemental data from Gubbängen. SCE became negative or the mass recoveries were very low. This was also true for the models using PCA loadings as source profiles.

3.5 Absolute Principal Component Analysis

None of the attempts using Thurston's APCA to calculate the absolute contributions from gasoline and diesel exhaust at Hornsgatan succeeded. Using three PC from the principal component analysis resulted in negative source contributions from the third component. If using only two PC the diesel or gasoline contributions became negative. The analysis is based only on 11 samples and this can be one reason for the failure. To derive a stable result there should be 50 more objects than variables [32], which in this case would require 64 samples.

The alkane- and naphtalene-data from Noa-Åsö (Söderledstunneln) were chosen for APCA calculations because this model have two principal components with eigenvalues one time over the mean eigenvalue and this was not true for the Åsö model. Source contributions for the six alkanes and three naphtalenes were 7500 ng/m^3 or 47% for the diesel source and 8500ng/m^3 or 53% for the gasoline source. Because of a big negative offset (-240 ng/m^3) in the first regression step the contributions of the individual compounds always became negative for one of the sources. The big offset could be due to problems in sampling and/or chemical analysis. More samples would probably also give a better model.

The APCA-analysis according to Swietlicki using PAH-data from Hornsgatan gave a quite different result comparing to the CMB results. Mean values for the years 1991 and 1994-97 are 61% from gasoline vehicles, 24% from diesel vehicles and 15 % from background sources for the sum of 10 PAH used in the CMB. The corresponding values for the APCA output is 30%, 68% and 2% for the sum of 14 different PAH. The source contributions for the individual PAH are shown in figure 3.21. The diesel contributions of phenanthrene, anthracene, 1-methylphenanthrene, pyrene and fluoranthene all exceed the gasoline contributions. In the CMB results only the pyrene diesel contribution exceeded the contribution for gasoline.
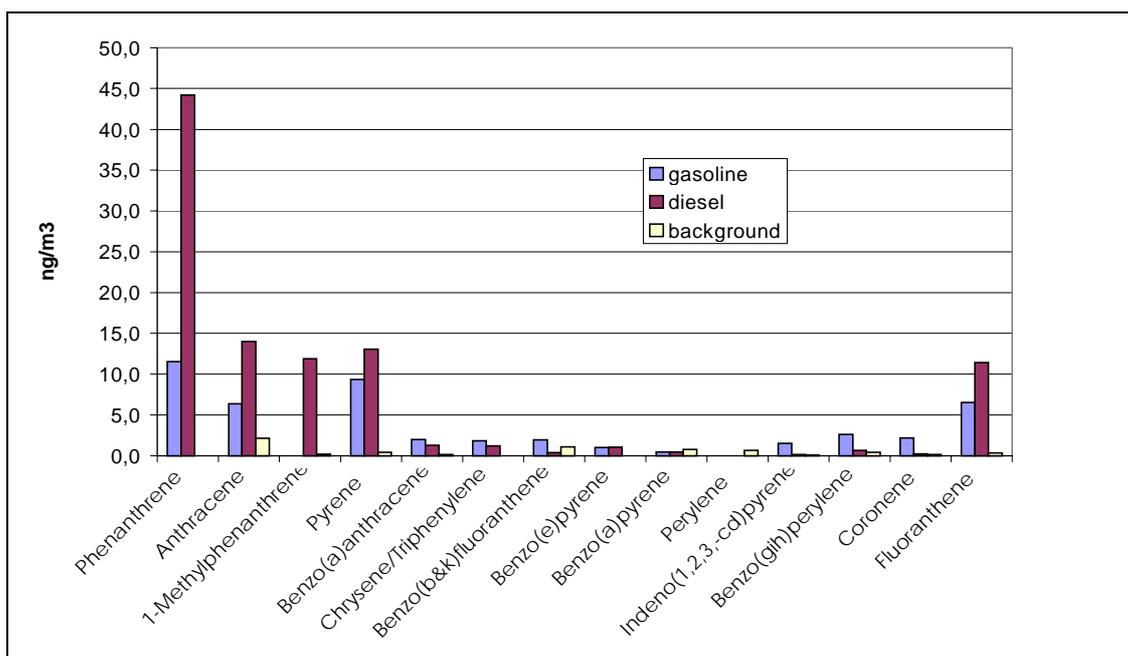
Figure 3.21 The mean source contributions of 14 PAH at Hornsgatan 1991, 1994-97.

3.6 PAH content in tyres

The results from the selected ion monitoring GC-MS analysis are shown in a line plot in figure 3.22. PAH concentrations are in μg/g (ppm) and it is obvious that concentrations of PAH differ between different tyres and makes. None of the analysed tyres have detectable concentrations of perylene, benz(a)anthracene or indeno(cd)pyrene. The profiles are similar (i. e. the relative amount of the individual PAH are about the same) but the Bridgestone tyre from week 25 1993, the Michelin tyre from week 53 1998 and the Gislaved tyre from week 15 1999 have markedly higher concentrations than the other tyres. In all tyres, except Michelin 9853, where coronene has the highest concentration, pyrene is the dominating PAH.

In table 3.9 the sum of the 26 analysed PAH are listed for all 24-hour extracts of the eight tyres. The individual PAH concentrations are listed in Appendix 5. Extracting the tyre crumb for 24 hours at least result in a 98% recovery. Only for three of the tyres the 48- and 72-hours extracts have detectable concentrations of PAH. In the Bridgestone tyre the 48- and 72 hours extract together account for 0,5% of the total PAH concentration and the corresponding value for the Michelin tyre from week 53 1998 are 1,8%. For the Gislaved tyre the 48- hour extract counts for about 0,9% of the extracted PAH. This tyre was not extracted for 72 hours.

For a more exact quantification the analysis could be repeated with smaller amount of internal standard. To the 24 hours sample about 200 μg/g of internal standard was added, the highest concentration of an individual PAH was about 130 μg/g.
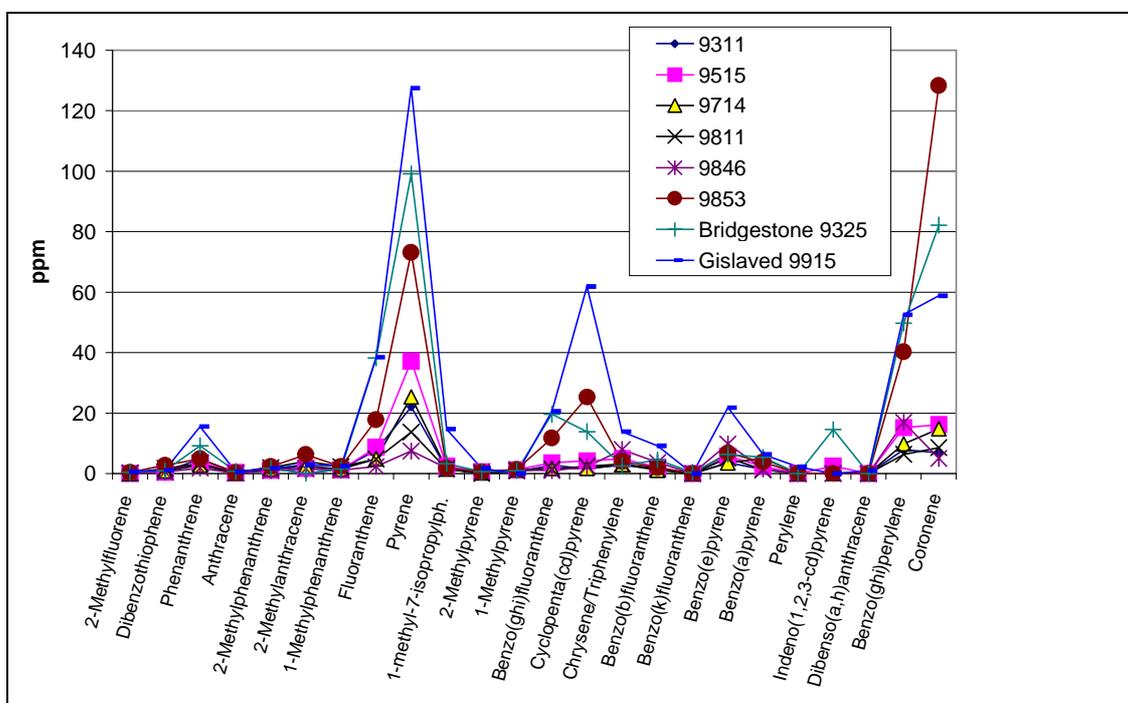
Figure 3.22 PAH concentrations in eight analysed tyres.

Table 3.9 Sum of PAH in the analysed tyres.

tyre,year, week	ug/g
Michelin 9311	70,0
Michelin 9515	115,1
Michelin 9714	82,8
Michelin 9811	64,4
Michelin 9846	68,0
Michelin 9853	335,7
Bridgestone 9325	356,0
Gislaved 9915	455,4
Mean value	193,4

In two of the tyres with higher PAH concentrations; Michelin 9853 and Bridgestone 9325 were fluoranthene, pyrene, benzo(ghi)fluoranthene, cyclopenta(cd)pyrene, benzo(ghi)perylene, indeno(cd)pyrene and coronene also identified in the chromatograms from the full-scan GC-MS analysis mode. Some phthalates and alkanes were also present in the extracts. For the tyres with lower concentrations of PAH (Michelin 9311, 9515, 9714 and 9811) only fluoranthene, pyrene and coronene were identified in the full-scan mode chromatograms together with some phthalates and alkanes. In all full-scan mode chromatograms some other PAH, not included in standard are present but not identified. In Appendix 5 examples of mass spectra for two possible but not identified PAH are shown. The relative retention times compared to the internal standard (2, 2'-binaphtyl) are 1.10 for the compound with molecular weight 272 and 1.14 for the compound with molecular weight 286. The LC-clean-up procedure did eliminate the alkanes from the sample of the Bridgestone tyre but no more compounds were identified from the chromatogram.

4. Discussion

4.1 PCA

In the four PCA-models made on the PAH-data from Hornsgatan, obvious diesel and gasoline contributions are revealed. In the Kista model the gasoline-PC explains most of the variance, but in the other models the diesel-component explain most of the variance. However, after varimax rotation the gasoline and diesel component in all models explain approximately equal parts of the variance.

Coronene, benzo(*ghi*)perylene, benzofluoranthenes, benzo(*a*)anthracene and chrysene all have their highest loadings in the gasoline-component in all models. Corresponding substances for the diesel-component are phenanthrene, 1-methylphenanthrene, fluoranthene and pyrene.

It is more difficult to interpret the sources of the third component, because only one or two PAH have their highest loadings in this component and not the same PAH in all models. The third PC can be due to background contributions, tyres or maybe high emitting vehicles. In Hornsgatan the third component has high loadings in perylene. Perylene is not found in the analysed tyres which indicates that tyre wear is not the probable explanation for the third component at Hornsgatan.

Because of little variation and lower concentrations compared to Hornsgatan, PAH samples from Kista and Enskede form a cluster of their own. Enskede and Kista represent a stable background level of the measured PAH. The PAH-contribution in all three places is mainly from traffic, the differences are that in Enskede and Kista the contributions has been diluted.

To make a more relevant model more samples from high traffic areas must be included. More background samples are also needed and to interpret contributions from domestic wood burning retene could be measured and analysed.

The varimax rotated PCA of elemental data from Gubbängen indicate that four sources are responsible for 63% of the variance. The four sources are resuspended road dust, oil- and coal-combustion, gasoline vehicles and secondary sulphate. The elements that have high loadings in the different sources are consistent with other results e.g. Swietlicki *et al.* 1996 [21].

The varimax rotated PCA on volatile organic compounds from the Söderledstunnel indicate that nonane and the naphtalenes are characteristic for gasoline emissions and the heavier alkanes for diesel vehicle emissions. This is not fully consistent with studies in the U.S.A. [3] but there could be differences between fuel composition and vehicle exhaust in different countries.

The PCA on PAH-data from the Söderledstunnel gave the same indication of characteristic PAH for diesel and gasoline emissions as the PCA on Hornsgatan, Kista and Enskede. To make a better model more samples must be included. More samples for PAH-analysis are collected in the tunnel and will be analysed in the future.

4.2 CMB

The chemical mass balance model suggest that the contribution to PAH concentrations from gasoline vehicles is higher than diesel vehicles and background contributions together in Hornsgatan 1994-97. However in 1991 all three source contributed by approximately the same. For all individual PAH, gasoline vehicles give highest contributions except for pyrene, which is emitted from diesel vehicles to a greater extent. On average 7.4% of the total traffic flow at Hornsgatan are diesel vehicles during the campaign period and this part is responsible for about twice as much of the concentrations of pyrene as the gasoline vehicles.

The calculated total PAH concentration is in excellent agreement with the measured concentration at Hornsgatan. The last period 1997, the agreement was not as good as the other periods.

The mean ratio of calculated to measured concentration in the CMB for Enskede and Kista with two sources are 1,05 and 1,04 and suggest a good model fit. The background sources in Enskede and Kista may mainly consist of diluted traffic contributions from Stockholm, which can be the reason for the failure of making a CMB model with three sources. This can also be the reason for the very low backgrounds contributions when using Enskede/Kista as background profile in the Hornsgatan model. Due to the CMB result the emissions from diesel vehicles seems to be a larger part of the total PAH concentrations in Kista than in Enskede

The expected decline in PAH concentrations due to the introduction of environmental classified diesel fuel and increased number of cars equipped with catalysts, is not obvious either in the data or in the CMB results. In the data there seems to be a decline in the PAH concentrations except for 1997. This also true for the CMB output for the diesel vehicle source but for the gasoline vehicle source no trend can be seen.

The lack of consistence between the CMB and APCA result of the PAH-data from Hornsgatan is difficult to explain. Calculations using emission factors indicate that the CMB results are most relevant.

4.3 PAH concentrations in tyres

The analyses of PAH in tyres show substantial amounts of PAH in tyres. The concentrations of PAH show variations between tyres from different years and tyres of different makes. The mean sum PAH content in the analysed tyres is 193 µg/g. Assuming 0.2 g tyre worn off every kilometre this gives an emission factor of 39 µg/km This is in good agreement with the factor (28 µg/km) calculated by Ahlbom and Duus. The relative amount of individual PAH reported by Ahlbom and Duus are not the same as reported in this report. Chrysene and benzo(e)pyrene are the PAH with highest concentration in the analysis of HA-oil [16]. From the analyses of tyre crumbs coronene, pyrene and cyclopenta(cd)pyrene seems to be the PAH with highest concentrations. The PAH profile from the analysed tyre crumbs are different to the source profiles for gasoline and diesel vehicle exhaust and can perhaps be used in a CMB model (see figure 4.1). To make such a CMB model or some other statistical model it is important to know the particle size of the worn of tyre. The particles may be too large to be collected in the high volume sampler, used for ambient air measurements.
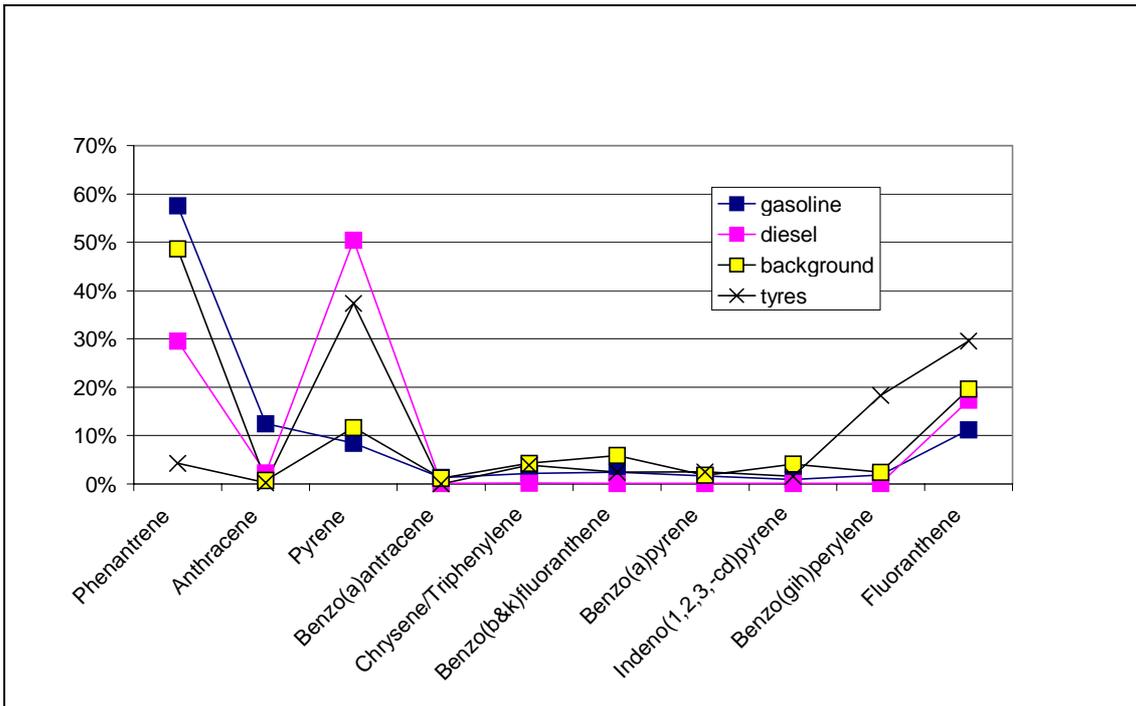
Figure 4.1 Source profiles of gasoline, diesel and background from 1997compared to a tyre profile

5. Conclusions

Future measurements

To make a better PCA model on the PAH data from Hornsgatan and the Söderledstunnel more samples are necessary. This is also true for the separate models from Kista and Enskede. To make better multivariate models considerations of seasonal and diurnal variation should be taken. To distinguish between diesel exhaust and emissions from domestic wood burning in Enskede retene and possibly other PAH in wood smoke should also be analysed. It seems like coronene, benzo(ghi)perylene, benzofluoranthenes, benzo(a)anthracene and chrysene are important to measure for identifying gasoline exhaust emissions. Pyrene, phenanthrene, fluoranthene and methylphenanthrenes are appropriate for diesel exhaust identification.

Concerning the CMB it seems to be very important to have relevant source profiles, this is probably the reason for the failure of the CMB calculations using PAH data from Hornsgatan in 1998 and elemental data from Gubbängen. This can of course also have other reasons for example many missing values in the elemental data from Gubbängen. The PAH samples from 1998 at Hornsgatan differ from the other as outlined above but there was no relevant background profile from 1998. To see if domestic wood burning contribute to the PAH concentrations in Enskede both better source and receptor profiles are needed. As mentioned above retene and possibly other PAH should be included in the analysis and also more samples taken in wintertime when wood burning is frequent. It is not possible to distinguish contributions from wood smoke from diesel exhaust contributions in any of the models made.

The analyses of PAH in tyres indicate that this can be an environmental problem in the future. Fluoranthene, pyrene, benzo(ghi)fluoranthene, cyclopenta(cd)pyrene, benzo(ghi)perylene, indeno(cd)pyrene and coronene are identified in the tyres. Important in this discussion is the particle size of the worn of tyre. Are the particles capable of entering the human respiratory system and how fast are the chemical transformations of PAH on tyre particles. Several other questions remain to be answered about PAH in tyres for example variation between other types of tyres and manufacturers. From the analysis of tyres done in this thesis no conclusion about differences in PAH concentration between different makes and years can be made.

Acknowledgements

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Appendix 1: Descriptive Statistics and data plots.

Hornsgatan (ng/m³):

Descriptive Statistics

	N	Minimum	Maximum	Mean	Std. Deviation
Phenanthrene	11	29,55	81,48	52,77	17,04
Anthracene	11	11,70	26,93	17,84	5,77
1-Methylphenanthrene	11	4,72	21,10	10,62	4,89
Pyrene	11	17,50	34,46	24,01	5,74
Benzo(a)anthracene	11	1,60	3,67	2,43	,79
Chrysene	11	2,00	4,00	2,90	,74
Benzofluoranthenes	11	2,34	4,76	3,51	,86
Benzo(e)pyrene	11	,86	2,49	1,72	,52
Benzo(a)pyrene	11	,80	2,00	1,44	,40
Perylene	11	,20	1,30	,49	,33
Indeno(cd)pyrene	11	1,10	2,70	1,80	,48
Benzo(gih)perylene	11	2,70	5,30	3,95	,88
Coronene	11	1,80	3,70	2,54	,69
Fluoranthene	11	11,00	27,47	17,79	4,83
Valid N (listwise)	11				

Data plot of all samples in Hornsgatan, Kista and Enskede:
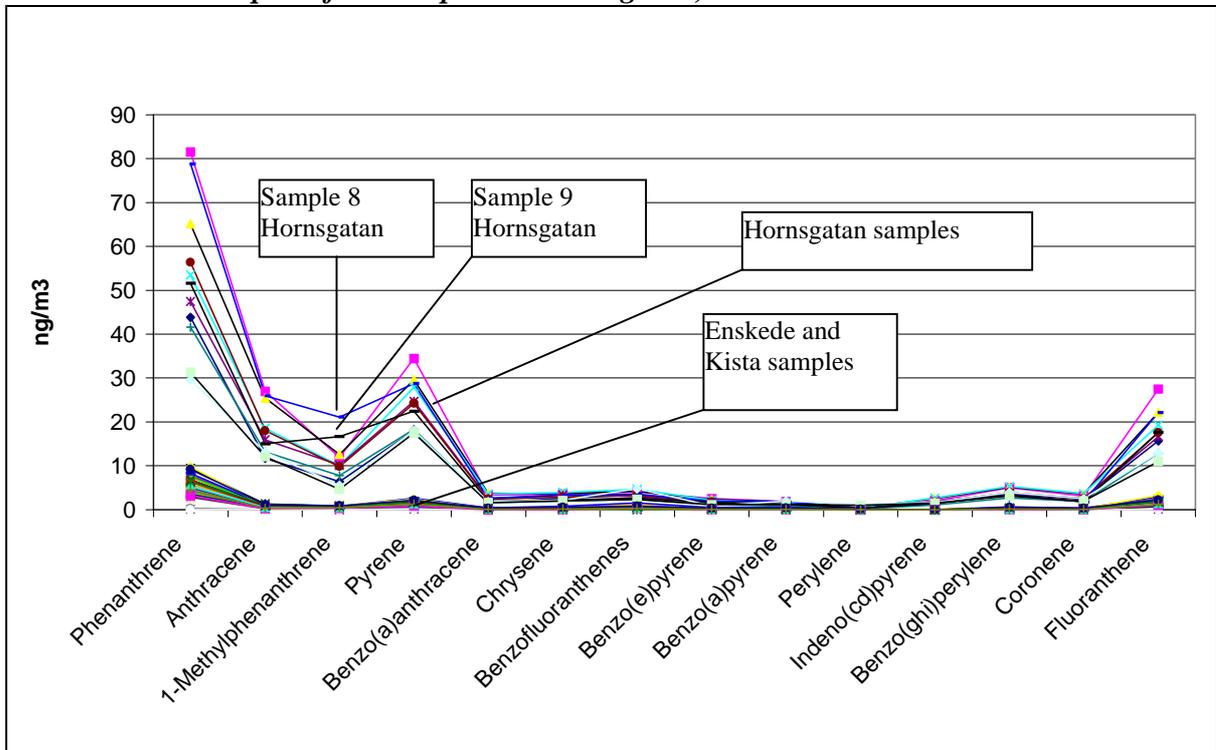
Kista (ng/m³):

Descriptive Statistics

	N	Minimum	Maximum	Mean	Std. Deviation
Phenanthrene	16	,13	5,88	3,45	1,53
Anthracene	16	,05	,85	,42	,22
3-Methylphenanthrene	16	,02	,66	,38	,17
2-Methylphenanthrene	16	,03	,79	,48	,21
2-Methylanthracene	16	,01	,78	,32	,19
9+4-Methylphenanthrene	16	,02	,60	,32	,14
1-Methylphenanthrene	16	,03	,56	,37	,15
2-Phenylnaphtalene	16	,00	,97	,36	,23
Fluoranthene	16	,06	2,30	1,03	,60
Pyrene	16	,05	1,78	,88	,45
Benzo(a)fluorene	16	,00	,14	3,93E-02	4,43E-02
Benzo(a)anthracene	16	,00	,27	7,36E-02	8,10E-02
Chrysene	16	,00	,62	,14	,17
Benzofluoranthenes	16	,00	,95	,24	,26
Benzo(e)pyrene	16	,00	,34	9,41E-02	9,28E-02
Benzo(a)pyrene	16	,00	,20	6,46E-02	6,54E-02
Perylene	16	,00	,05	1,60E-02	1,72E-02
Indeno(1,2,3-cd)pyrene	16	,00	,04	9,56E-03	1,58E-02
Benzo(ghi)perylene	16	,00	,47	,14	,13
Coronene	16	,00	,30	8,76E-02	8,30E-02
Valid N (listwise)	16				

Enskede without the outliers sample number 6 and 9 (ng/m³):

Descriptive Statistics

	N	Minimum	Maximum	Mean	Std. Deviation
Phenanthrene	14	3,20	9,85	6,84	1,93
Anthracene	14	,26	1,33	,82	,32
3-Methylphenanthrene	14	,33	1,00	,68	,18
2-Methylphenanthrene	14	,51	1,25	,88	,22
2-Methylanthracene	14	,27	1,13	,72	,24
9+4-Methylphenanthrene	14	,31	,63	,49	9,83E-02
1-Methylphenanthrene	14	,38	,91	,69	,17
2-Phenylnaphtalene	14	,35	,97	,58	,19
Fluoranthene	14	,99	3,22	1,87	,58
Pyrene	14	,82	2,42	1,70	,46
Benzo(a)fluorene	14	,00	,18	8,35E-02	4,87E-02
Benzo(a)anthracene	14	,04	,39	,17	,11
Chrysene	14	,08	,56	,29	,15
Benzofluoranthenes	14	,23	,88	,54	,21
Benzo(e)pyrene	14	,10	,38	,20	8,71E-02
Benzo(a)pyrene	14	,04	,41	,17	,11
Perylene	14	,00	,11	4,38E-02	3,14E-02
Indeno(1,2,3-cd)pyrene	14	,00	,06	1,34E-02	2,15E-02
Benzo(ghi)perylene	14	,07	,53	,28	,14
Coronene	14	,04	,34	,16	9,41E-02
Valid N (listwise)	14				

Gubbängen without the outliers sample number 4, 166 and 172 (ng/m³):

Descriptive Statistics

	N	Minimum	Maximum	Mean	Std. Deviation
S	179	148,3	2892,1	856,1	516,1
As	35	,6	6,0	2,3	1,2
Br	164	,5	9,5	4,2	2,2
Ca	177	-29,5	822,0	145,8	117,4
Cr	46	,2	4,2	1,7	1,0
Cu	152	,4	6,7	3,4	1,2
Fe	160	62,0	661,7	235,7	122,3
K	178	20,8	572,6	126,3	76,1
Mn	162	,7	14,2	5,0	2,5
Ni	136	,1	6,0	1,3	,9
Pb	159	3,7	57,1	20,5	11,7
Se	33	,1	2,3	,9	,5
S	36	,2	16,7	2,9	3,8
Si	165	30,4	1720,0	411,9	338,8
Zn	165	2,5	52,6	15,8	9,4
Ti	142	3,7	54,1	16,1	10,0
Valid N (listwise)	7				

Data plot for S, Si, K, Ca and Fe for all samples in Gubbängen:
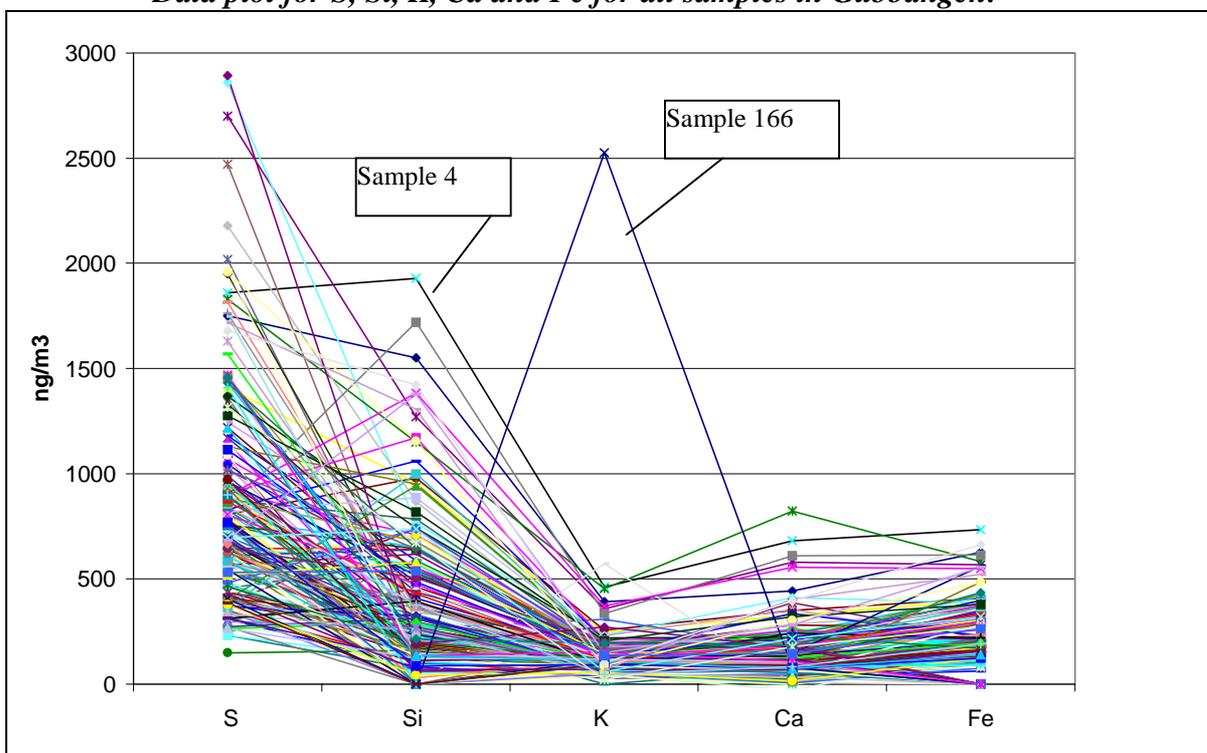
Data plot for the rest of the analysed elements for all samples in Gubbängen:
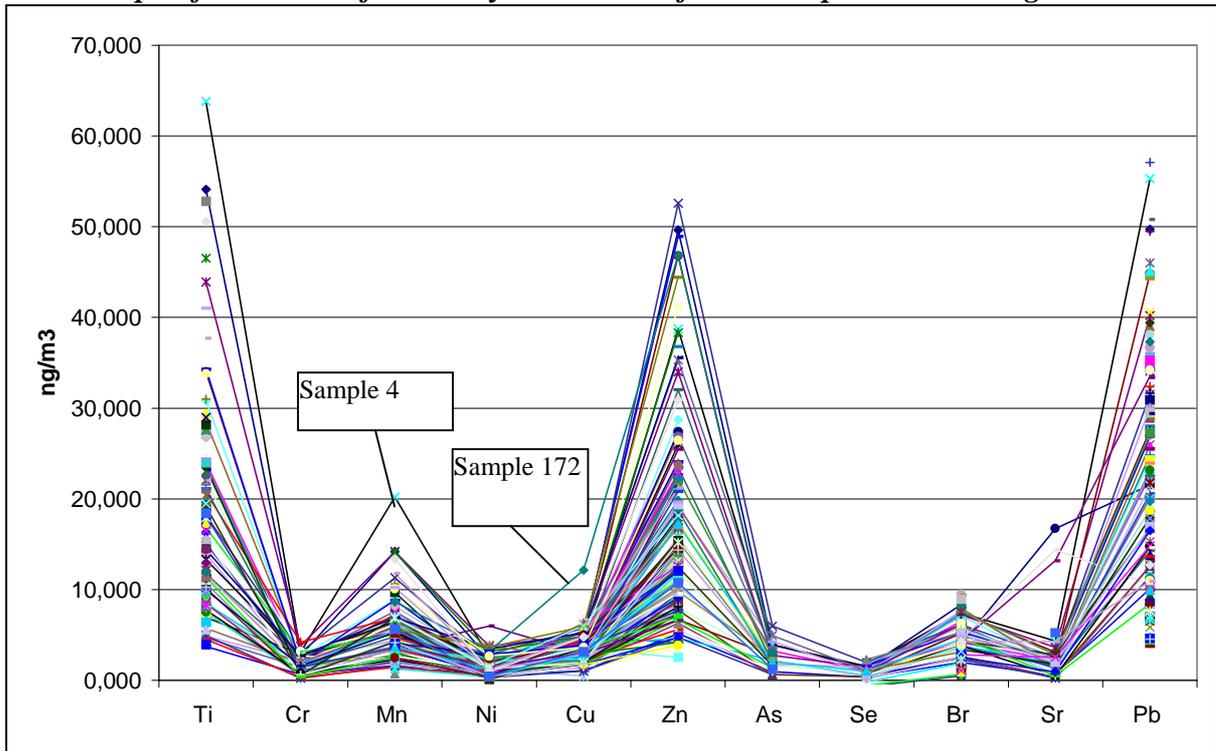
Söderledstunneln:

Alkanes and naphtalenes

Åsö-monitoring site without the outliers; sample number 33,36, 37 and 38 (ng/m³):
(The negative minimum value for pentadecane is because of a value lower than the
average of three blank samples)

Descriptive Statistics

	N	Minimum	Maximum	Mean	Std. Deviation
Nonane	100	60	3623	1162	794
Decane	100	136	4085	1495	1040
Naphtalene	100	219	8712	2782	2071
Dodecane	100	235	4617	1807	1207
1-Methylnaphtalene	100	119	4493	1513	1111
2-Methylnaphtalene	100	0	704	213	176
Tridecane	100	41	3729	1371	1034
Tetradecane	100	41	2486	961	699
Pentadecane	100	-24	1462	550	393
Valid N (listwise)	100				

Data plot for all samples Åsö:
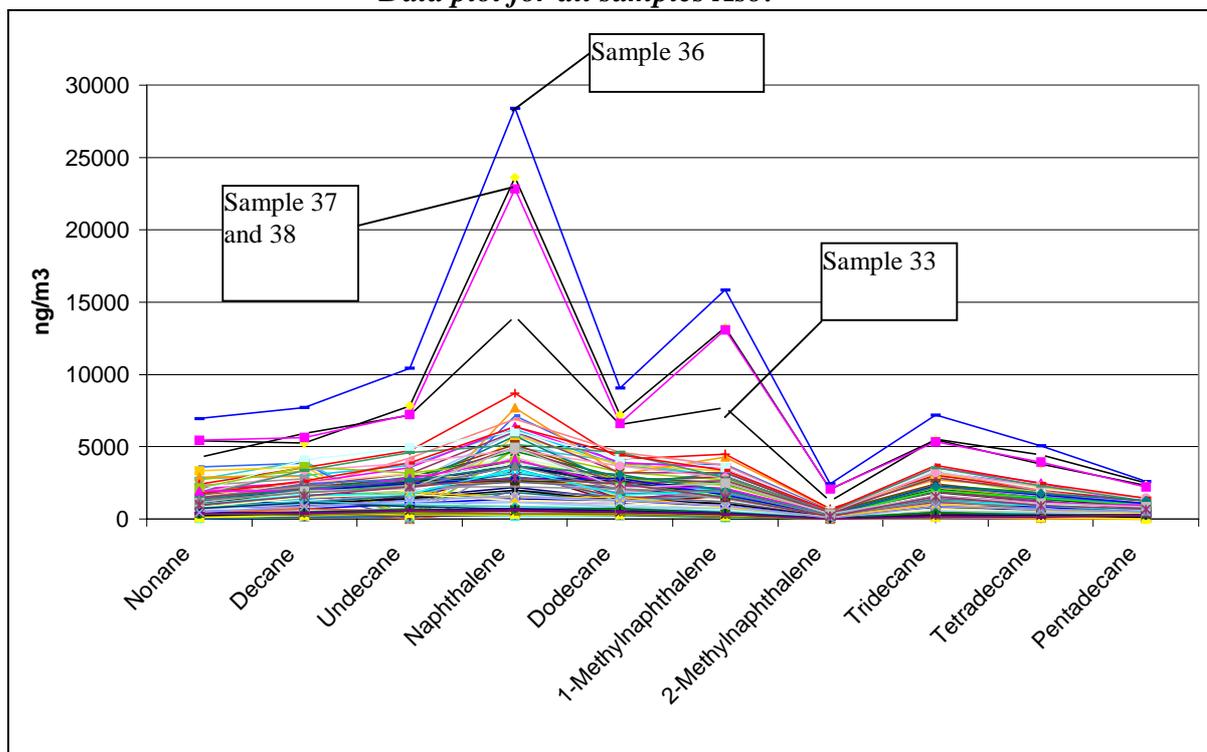
Noa-Åsö without the outliers sample number 4, 12, 20, 26 and 47 (ng/m^3):

Descriptive Statistics

	N	Minimum	Maximum	Mean	Std. Deviation
Nonane	44	95	2676	1062	676
Decane	44	204	5860	1886	1417
Naphtalene	44	787	7814	3764	1629
Dodecane	44	347	4944	2154	1147
1-Methylnaphtalene	44	469	4268	2181	901
2-Methylnaphtalene	44	41	675	346	144
Tridecane	44	355	4304	2060	994
Tetradecane	44	249	3155	1505	712
Pentadecane	44	89	1850	828	433
Valid N (listwise)	44				

Data plot with all samples Noa-Åsö:
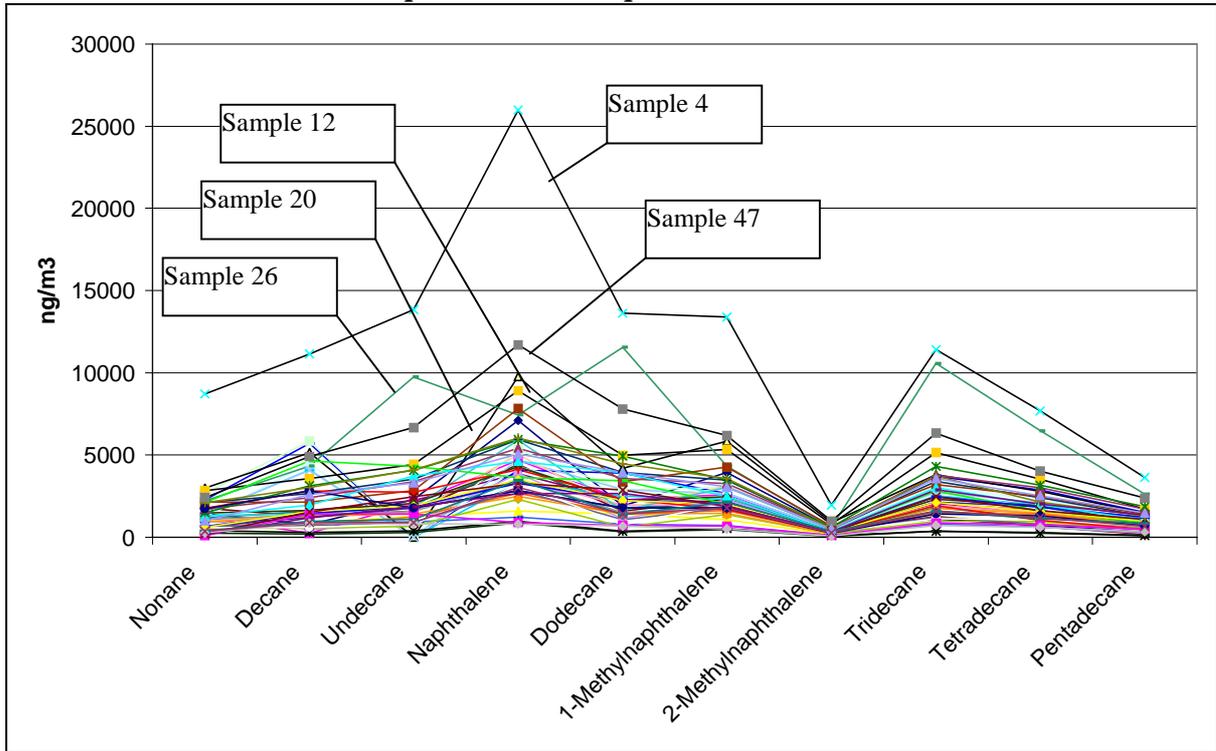
PAH

Data plot of all samples:
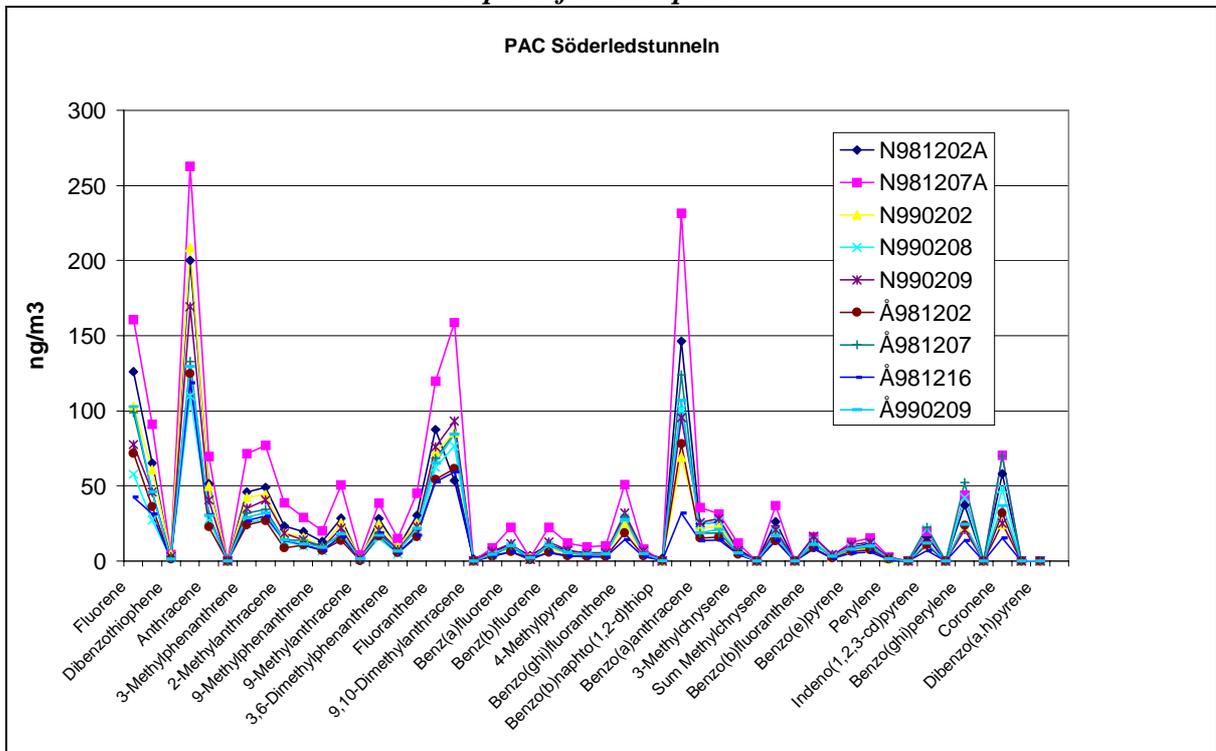
PAH-data without the outlier sample 1 (ng/m³):

Descriptive Statistics

	N	Minimum	Maximum	Mean	Std. Deviation
Fluorene	8	42,40	160,90	89,36	36,32
2-Methylflourene	8	27,10	91,00	48,03	20,30
Dibenzothiophene	8	1,00	4,60	2,41	1,36
Phenanthrene	8	110,00	262,70	157,08	53,55
Anthracene	8	22,60	69,70	37,79	15,35
3-Methylphenanthrene	8	24,10	71,40	35,76	15,60
2-Methphenanthrene	8	27,00	77,10	39,23	16,43
2-Methanthracene	8	8,80	38,70	17,40	9,15
4H-Cyclopenta(def)phenanthrene	8	10,00	29,10	14,40	6,27
9-Methphenanthrene	8	6,90	20,10	9,80	4,33
1-Methylphenanthrene	8	13,70	50,70	22,43	11,99
9-Methanthracene	8	,20	3,90	1,61	1,06
2-Phenylnaphtalene	8	15,10	38,60	21,28	7,54
3,6-Dimethylphenanthrene	8	4,80	15,10	7,53	3,35
3,9-Dimethylphenanthrene	8	16,00	45,20	23,24	9,51
Fluoranthene	8	52,60	119,70	71,49	21,12
Pyrene	8	59,20	158,60	87,86	30,98
1-Methylfluoranthene	8	2,80	8,80	4,76	1,96
Benz(a)fluorene	8	6,00	22,30	10,63	5,13
Retene	8	,70	2,40	1,49	,63
Benz(b)fluorene	8	5,60	22,50	10,71	5,34
2-Methylpyrene	8	3,20	11,90	5,88	2,73
4-Methylpyrene	8	2,80	9,40	4,78	2,05
1-Methylpyrene	8	2,70	10,10	4,89	2,30
Benzo(ghi)fluoranthene	8	14,20	50,90	28,20	10,91
Benzo(c)phenanthrene	8	2,80	7,80	5,15	1,63
Benzo(b)naphto(1,2-d)thiop	8	,00	,30	,11	,12
Cyclopenta(cd)pyrene	8	31,80	231,40	104,68	58,33
Benzo(a)anthracene	8	13,40	35,50	21,64	6,99
Chrysene	8	14,00	31,30	22,35	6,11
3-Methylchrysene	8	4,40	11,80	6,36	2,37
Sum Methylchrysene	8	13,50	37,00	19,61	7,47
Benzo(b)fluoranthene	8	7,80	16,30	11,94	3,11
Benzo(k)fluoranthene	8	1,60	4,10	2,85	,85
Benzo(e)pyrene	8	5,20	12,40	8,30	2,33
Benzo(a)pyrene	8	5,90	15,30	9,90	2,97
Perylene	8	1,10	2,60	1,68	,51
Indeno(cd)pyrene	8	6,80	22,30	14,16	5,86
Benzo(ghi)perylene	8	13,70	52,30	30,34	13,71
Coronene	8	15,30	70,40	40,19	20,84
Valid N (listwise)	8				

Appendix 2: Source profiles for Chemical Mass Balance

1991	gasoline	diesel	background
Phenanthrene	0,539	0,448	0,414
Anthracene	0,133	0,047	0,015
Pyrene	0,097	0,356	0,072
Benzo(a)anthracene	0,016	0,007	0,022
Chrysene/Triphenylene	0,022	0,002	0,052
Benzo(b&k)fluoranthene	0,025	0,001	0,084
Benzo(a)pyrene	0,024	0,000	0,025
Indeno(1,2,3,-cd)pyrene	0,010	0,000	0,026
Benz(gih)perylene	0,023	0,000	0,027
Fluoranthene	0,111	0,139	0,262

1994	gasoline	diesel	background
Phenanthrene	0,554	0,369	0,414
Anthracene	0,130	0,034	0,015
Pyrene	0,092	0,432	0,072
Benzo(a)anthracene	0,015	0,004	0,022
Chrysene/Triphenylene	0,022	0,002	0,052
Benzo(b&k)fluoranthene	0,024	0,001	0,084
Benzo(a)pyrene	0,021	0,001	0,025
Indeno(1,2,3,-cd)pyrene	0,010	0,000	0,026
Benz(gih)perylene	0,021	0,000	0,027
Fluoranthene	0,111	0,157	0,262

1995	gasoline	diesel	background
Phenanthrene	0,561	0,306	0,402
Anthracene	0,128	0,024	0,029
Pyrene	0,089	0,493	0,201
Benzo(a)anthracene	0,014	0,001	0,023
Chrysene/Triphenylene	0,022	0,001	0,048
Benzo(b&k)fluoranthene	0,024	0,001	0,045
Benzo(a)pyrene	0,019	0,001	0,023
Indeno(1,2,3,-cd)pyrene	0,010	0,001	0,036
Benz(gih)perylene	0,020	0,001	0,029
Fluoranthene	0,112	0,171	0,164

1996	gasoline	diesel	background
Phenanthrene	0,569	0,302	0,486
Anthracene	0,126	0,024	0,007
Pyrene	0,087	0,498	0,117
Benzo(a)anthracene	0,014	0,001	0,012
Chrysene/Triphenylene	0,022	0,001	0,042
Benzo(b&k)fluoranthene	0,024	0,001	0,058
Benzo(a)pyrene	0,018	0,001	0,018
Indeno(1,2,3,-cd)pyrene	0,010	0,001	0,041
Benz(gih)perylene	0,019	0,001	0,024
Fluoranthene	0,112	0,172	0,196

1997	gasoline	diesel	background
Phenanthrene	0,576	0,295	0,530
Anthracene	0,125	0,023	0,064
Pyrene	0,084	0,504	0,135
Benzo(a)anthracene	0,013	0,001	0,013
Chrysene/Triphenylene	0,022	0,001	0,024
Benzo(b&k)fluoranthene	0,024	0,001	0,044
Benzo(a)pyrene	0,017	0,001	0,013
Indeno(1,2,3,-cd)pyrene	0,010	0,001	0,001
Benz(gih)perylene	0,018	0,001	0,023
Fluoranthene	0,112	0,173	0,153

Sourceprofile with 13 different PAH			
1997	gasoline	diesel	background
Phenanthrene	0,544	0,274	0,489
Anthracene	0,117	0,021	0,059
1-MethylPhenanthrene	0,041	0,07	0,05
Fluoranthene	0,105	0,161	0,141
Pyrene	0,079	0,468	0,125
Benz(a)antracene	0,012	0,001	0,012
Chrysene/Triphenylene	0,021	0,001	0,022
Benzo(b&k)fluoranthene	0,022	0,001	0,04
Benzo(e)pyrene	0,008	0,001	0,015
Benzo(a)pyrene	0,015	0,001	0,012
Indeno(1,2,3,-cd)pyrene	0,009	0,001	0,001
Benzo(gih)perylene	0,017	0,001	0,021
Coronene	0,01	0,001	0,013

The first two columns in this source profile were used in CMB models for Enskede and Kista.

Appendix 3: Result from Chemical Mass Balance

Table A: SCE of 10 individual PAH and their standard errors at Hornsgatan 1991, 1994-97.

year	period	ng/m3	gasoline	STDERR	diesel	STDERR	background	STDERR	calculated mass	measured mass	calculated/ measured
1991		Phenanthrene	18,50	6,71	16,63	4,44	12,23	3,33	47,35	43,8	1,08
		Anthracene	4,58	1,66	1,74	0,47	0,45	0,12	6,77	11,7	0,58
		Pyrene	3,31	1,20	13,20	3,52	2,14	0,58	18,65	18	1,04
		Benzo(a)anthracene	0,56	0,20	0,25	0,07	0,66	0,18	1,47	1,6	0,92
		Chrysene/Triphenylene	0,74	0,27	0,06	0,02	1,53	0,42	2,33	2,6	0,90
		Benzo(b&k)fluoranthene	0,85	0,31	0,03	0,01	2,49	0,68	3,37	3,3	1,02
		Benzo(a)pyrene	0,81	0,29	0,01	0,00	0,73	0,20	1,56	1	1,56
		Indeno(1,2,3,-cd)pyrene	0,34	0,12	0,01	0,00	0,76	0,21	1,11	1,9	0,58
		Benzo(gih)perylene	0,81	0,29	0,01	0,00	0,81	0,22	1,62	3,6	0,45
		Fluoranthene	3,82	1,39	5,17	1,38	7,75	2,11	16,73	15,7	1,07
									100,96	103,2	**0,98**
1994	1	Phenanthrene	66,63	14,00	19,86	5,99	6,96	5,32	93,46	81,48	1,15
		Anthracene	15,63	3,28	1,85	0,56	0,26	0,20	17,73	26,93	0,66
		Pyrene	11,03	2,32	23,24	7,01	1,22	0,93	35,49	34,46	1,03
		Benzo(a)anthracene	1,81	0,38	0,20	0,06	0,38	0,29	2,39	3,32	0,72
		Chrysene/Triphenylene	2,62	0,55	0,08	0,03	0,87	0,67	3,57	3,64	0,98
		Benzo(b&k)fluoranthene	2,93	0,62	0,04	0,01	1,42	1,08	4,39	4,07	1,08
		Benzo(a)pyrene	2,50	0,53	0,03	0,01	0,42	0,32	2,94	1,9	1,55
		Indeno(1,2,3,-cd)pyrene	1,17	0,25	0,02	0,01	0,44	0,33	1,63	2,1	0,78
		Benzo(gih)perylene	2,58	0,54	0,02	0,01	0,46	0,35	3,06	5,09	0,60
		Fluoranthene	13,41	2,82	8,43	2,54	4,41	3,37	26,25	27,47	0,96
									190,92	190,46	**1,00**
1994	2	Phenanthrene	55,99	12,84	14,40	5,10	10,27	5,16	80,66	65,07	1,24
		Anthracene	13,13	3,01	1,34	0,47	0,38	0,19	14,85	25,45	0,58
		Pyrene	9,26	2,13	16,85	5,96	1,80	0,90	27,91	29,57	0,94
		Benzo(a)anthracene	1,52	0,35	0,15	0,05	0,56	0,28	2,22	3,67	0,61
		Chrysene/Triphenylene	2,20	0,50	0,06	0,02	1,28	0,65	3,54	3,74	0,95
		Benzo(b&k)fluoranthene	2,47	0,57	0,03	0,01	2,09	1,05	4,58	4,25	1,08
		Benzo(a)pyrene	2,10	0,48	0,02	0,01	0,62	0,31	2,74	1,78	1,54
		Indeno(1,2,3,-cd)pyrene	0,99	0,23	0,02	0,01	0,64	0,32	1,65	2,51	0,66
		Benzo(gih)perylene	2,17	0,50	0,02	0,01	0,68	0,34	2,86	5,15	0,56
		Fluoranthene	11,26	2,58	6,12	2,16	6,50	3,27	23,88	22,14	1,08
									164,90	163,33	**1,01**
1995	1	Phenanthrene	43,07	10,20	8,47	3,45	15,84	4,46	67,37	53,5	1,26
		Anthracene	9,83	2,33	0,67	0,27	0,51	0,14	11,01	18,6	0,59
		Pyrene	6,85	1,62	13,63	5,56	5,44	1,53	25,92	28	0,93
		Benzo(a)anthracene	1,11	0,26	0,04	0,01	0,82	0,23	1,97	3,6	0,55
		Chrysene/Triphenylene	1,67	0,40	0,04	0,02	1,98	0,56	3,69	4	0,92
		Benzo(b&k)fluoranthene	1,86	0,44	0,02	0,01	2,27	0,64	4,15	4,7	0,88
		Benzo(a)pyrene	1,49	0,35	0,02	0,01	0,89	0,25	2,40	1,6	1,50
		Indeno(1,2,3,-cd)pyrene	0,74	0,18	0,02	0,01	1,97	0,56	2,73	2,7	1,01
		Benzo(gih)perylene	1,57	0,37	0,02	0,01	1,13	0,32	2,72	5,3	0,51
		Fluoranthene	8,56	2,03	4,72	1,93	7,35	2,07	20,63	19,3	1,07
									142,59	141,3	**1,01**
1995	2	Phenanthrene	35,29	7,94	9,61	3,01	9,67	3,23	54,57	47,4	1,15
		Anthracene	8,05	1,81	0,76	0,24	0,31	0,10	9,13	16	0,57
		Pyrene	5,61	1,26	15,47	4,84	3,32	1,11	24,40	24,7	0,99
		Benzo(a)anthracene	0,91	0,20	0,04	0,01	0,50	0,17	1,45	2,5	0,58
		Chrysene/Triphenylene	1,37	0,31	0,05	0,01	1,21	0,40	2,63	3,3	0,80
		Benzo(b&k)fluoranthene	1,52	0,34	0,02	0,01	1,39	0,46	2,93	3,1	0,95
		Benzo(a)pyrene	1,22	0,27	0,02	0,01	0,54	0,18	1,78	1,1	1,62
		Indeno(1,2,3,-cd)pyrene	0,61	0,14	0,02	0,01	1,20	0,40	1,83	1,8	1,02
		Benzo(gih)perylene	1,28	0,29	0,02	0,01	0,69	0,23	2,00	3,8	0,53
		Fluoranthene	7,01	1,58	5,36	1,68	4,49	1,50	16,86	16,7	1,01
									117,58	120,4	**0,98**
1996	1	Phenanthrene	52,09	9,29	8,04	2,95	8,52	4,62	68,64	56,4	1,22
		Anthracene	11,57	2,06	0,63	0,23	0,12	0,06	12,32	18	0,68
		Pyrene	7,95	1,42	13,26	4,87	2,04	1,11	23,26	24,3	0,96
		Benzo(a)anthracene	1,27	0,23	0,03	0,01	0,20	0,11	1,50	2,4	0,62
		Chrysene/Triphenylene	2,01	0,36	0,04	0,01	0,74	0,40	2,79	2,9	0,96
		Benzo(b&k)fluoranthene	2,20	0,39	0,02	0,01	1,02	0,55	3,24	3,4	0,95
		Benzo(a)pyrene	1,65	0,29	0,02	0,01	0,31	0,17	1,97	1,3	1,52
		Indeno(1,2,3,-cd)pyrene	0,88	0,16	0,02	0,01	0,72	0,39	1,62	1,7	0,95
		Benzo(gih)perylene	1,78	0,32	0,02	0,01	0,42	0,23	2,21	4	0,55
		Fluoranthene	10,22	1,82	4,58	1,68	3,43	1,86	18,23	17,6	1,04
									135,76	132	**1,03**

year	period	ng/m3	gasoline	STDERR	diesel	STDERR	background	STDERR	calculated mass	measured mass	calculated/ measured
1996	2	Phenanthrene	34,44	6,29	6,97	2,20	5,69	3,10	47,10	41,6	1,13
		Anthracene	7,65	1,40	0,54	0,17	0,08	0,04	8,28	13,2	0,63
		Pyrene	5,26	0,96	11,50	3,63	1,37	0,75	18,12	18,3	0,99
		Benzo(a)anthracene	0,84	0,15	0,03	0,01	0,14	0,07	1,00	1,6	0,62
		Chrysene/Triphenylene	1,33	0,24	0,03	0,01	0,50	0,27	1,86	2	0,93
		Benzo(b&k)fluoranthene	1,45	0,27	0,02	0,01	0,68	0,37	2,15	2,4	0,90
		Benzo(a)pyrene	1,09	0,20	0,02	0,01	0,21	0,11	1,31	0,8	1,64
		Indeno(1,2,3,-cd)pyrene	0,58	0,11	0,02	0,01	0,48	0,26	1,08	1,1	0,98
		Benzo(gih)perylene	1,17	0,21	0,02	0,01	0,28	0,15	1,47	2,7	0,54
		Fluoranthene	6,76	1,23	3,97	1,25	2,29	1,25	13,02	12,9	1,01
									95,38	96,60	**0,99**
1997	1	Phenanthrene	80,16	15,08	9,13	3,56	4,02	13,24	93,30	78,8	1,18
		Anthracene	17,33	3,26	0,70	0,27	0,48	1,59	18,51	26	0,71
		Pyrene	11,73	2,21	15,57	6,07	1,03	3,38	28,33	28,8	0,98
		Benzo(a)anthracene	1,84	0,35	0,03	0,01	0,10	0,33	1,97	2,6	0,76
		Chrysene/Triphenylene	3,06	0,57	0,05	0,02	0,18	0,60	3,28	3,3	0,99
		Benzo(b&k)fluoranthene	3,31	0,62	0,02	0,01	0,33	1,09	3,67	3,6	1,02
		Benzo(a)pyrene	2,30	0,43	0,02	0,01	0,10	0,32	2,42	1,8	1,35
		Indeno(1,2,3,-cd)pyrene	1,32	0,25	0,02	0,01	0,01	0,03	1,36	1,4	0,97
		Benzo(gih)perylene	2,56	0,48	0,02	0,01	0,17	0,56	2,75	3,3	0,83
		Fluoranthene	15,53	2,92	5,36	2,09	1,16	3,81	22,05	22,2	0,99
									177,64	171,8	**1,03**
1997	2	Phenanthrene	59,92	12,04	7,45	2,77	1,54	10,61	68,91	51,6	1,34
		Anthracene	12,96	2,60	0,57	0,21	0,19	1,28	13,71	15,1	0,91
		Pyrene	8,77	1,76	12,72	4,73	0,39	2,71	21,88	22,5	0,97
		Benzo(a)anthracene	1,37	0,28	0,02	0,01	0,04	0,27	1,44	2	0,72
		Chrysene/Triphenylene	2,28	0,46	0,04	0,01	0,07	0,48	2,39	2,2	1,09
		Benzo(b&k)fluoranthene	2,48	0,50	0,02	0,01	0,13	0,87	2,62	2,7	0,97
		Benzo(a)pyrene	1,72	0,35	0,02	0,01	0,04	0,26	1,78	1,3	1,37
		Indeno(1,2,3,-cd)pyrene	0,99	0,20	0,02	0,01	0,00	0,03	1,01	1,4	0,72
		Benzo(gih)perylene	1,91	0,38	0,02	0,01	0,07	0,45	1,99	3,3	0,60
		Fluoranthene	11,61	2,33	4,37	1,63	0,44	3,05	16,43	17,7	0,93
									132,17	119,8	**1,10**
Mean value 1991, 1994-97 ng/m3											
		Phenanthrene	49,56	10,49	11,17	3,72	8,30	5,90	69,04	57,74	1,20
		Anthracene	11,19	2,38	0,98	0,32	0,31	0,41	12,48	19,00	0,66
		Pyrene	7,75	1,65	15,05	5,13	2,08	1,44	24,89	25,40	0,98
		Benzo(a)anthracene	1,25	0,27	0,09	0,03	0,38	0,21	1,71	2,59	0,66
		Chrysene/Triphenylene	1,92	0,41	0,05	0,02	0,93	0,49	2,90	3,08	0,94
		Benzo(b&k)fluoranthene	2,12	0,45	0,02	0,01	1,31	0,76	3,46	3,50	0,99
		Benzo(a)pyrene	1,65	0,36	0,02	0,01	0,43	0,24	2,10	1,40	1,50
		Indeno(1,2,3,-cd)pyrene	0,85	0,18	0,02	0,01	0,69	0,28	1,56	1,85	0,84
		Benzo(gih)perylene	1,76	0,38	0,02	0,01	0,52	0,32	2,30	4,03	0,57
		Fluoranthene	9,80	2,08	5,34	1,82	4,20	2,48	19,34	19,08	1,01
		toal mass	87,85		32,76		19,16		139,77	137,65	**1,02**

Table B: SCE for the sources and their standard errors at Hornsgatan 1991, 1994-97.

year		SCE ng/m3		STDERR	TSTAT (SCE/ STDERR)	measured mass
1991	gasoline	34,3	+ / -	12,4	2,8	
	diesel	37,1	+ / -	9,9	3,7	
	background	29,5	+ / -	8,1	3,7	
	calculated mass	101,0				103,2
1994	gasoline	120,3	+ / -	25,3	4,8	
period 1	diesel	53,8	+ / -	16,2	3,3	
	background	16,8	+ / -	12,9	1,3	
	calculated mass	190,9				190,5
1994	gasoline	101,1	+ / -	23,2	4,4	
period 2	diesel	39,0	+ / -	13,8	2,8	
	background	24,8	+ / -	12,5	2,0	
	calculated mass	164,9				163,3
1995	gasoline	76,7	+ / -	18,2	4,2	
period 1	diesel	27,6	+ / -	11,3	2,5	
	background	38,2	+ / -	10,8	3,5	
	calculated mass	142,6				141,3
1995	gasoline	62,9	+ / -	14,1	4,4	
period 2	diesel	31,4	+ / -	9,8	3,2	
	background	23,3	+ / -	7,8	3,0	
	calculated mass	117,6				120,4
1996	gasoline	91,6	+ / -	16,3	5,6	
period 1	diesel	26,7	+ / -	9,8	2,7	
	background	17,5	+ / -	9,5	1,8	
	calculated mass	135,8				132,0
1996	gasoline	60,6	+ / -	11,1	5,5	
period 2	diesel	23,1	+ / -	7,3	3,2	
	background	11,7	+ / -	6,4	1,8	
	calculated mass	95,4				96,6
1997	gasoline	139,1	+ / -	26,2	5,3	
period 1	diesel	30,9	+ / -	12,0	2,6	
	background	7,6	+ / -	25,0	0,3	171,8
	calculated mass	177,6				
1997	gasoline	104,0	+ / -	20,9	5,0	
period 2	diesel	25,2	+ / -	9,4	2,7	
	background	2,9	+ / -	20,0	0,1	
	calculated mass	132,2				119,8
mean	gasoline	87,8	+ / -	18,6	4,7	
	diesel	32,8	+ / -	11,1	3,0	
	background	19,2	+ / -	12,5	1,5	
	calculated mass	139,8				137,7

Table C: SCE of 13 individual PAH and their standard errors at Hornsgatan 1997.

year	period	ng/m3	gasoline	STDERR	diesel	STDERR	background	STDERR	calculated mass	measured mass	calculated/ measured
1997	1	Phenanthrene	74,82	14,40	9,64	3,43	13,06	11,63	97,52	78,80	1,24
		Anthracene	16,04	3,09	0,73	0,26	1,57	1,40	18,35	26,00	0,71
		1-Methylphenanthrene	5,58	1,08	2,46	0,87	1,34	1,20	9,39	21,10	0,44
		Fluoranthene	14,45	2,78	5,66	2,02	3,76	3,35	23,87	22,20	1,08
		Pyrene	10,81	2,08	16,48	5,86	3,33	2,97	30,62	28,80	1,06
		Benzo(a)anthracene	1,69	0,32	0,03	0,01	0,33	0,29	2,04	2,60	0,79
		Chrysene/Triphenylene	2,84	0,55	0,05	0,02	0,59	0,53	3,49	3,30	1,06
		Benzo(b&k)fluoranthene	3,07	0,59	0,02	0,01	1,07	0,96	4,17	3,60	1,16
		Benzo(e)pyrene	1,07	0,21	0,02	0,01	0,40	0,36	1,50	2,00	0,75
		Benzo(a)pyrene	2,09	0,40	0,02	0,01	0,31	0,28	2,42	1,80	1,35
		Indeno(1,2,3,-cd)pyrene	1,23	0,24	0,02	0,01	0,03	0,03	1,28	1,40	0,92
		Benzo(gih)perylene	2,34	0,45	0,02	0,01	0,56	0,50	2,92	3,30	0,88
		Coronene	1,42	0,27	0,02	0,01	0,34	0,30	1,78	1,80	0,99
		total mass	137,45						199,35	196,70	**1,01**
1997	2	Phenanthrene	53,59	11,41	7,45	2,68	11,78	9,36	72,82	51,60	1,41
		Anthracene	11,49	2,45	0,57	0,20	1,42	1,13	13,48	15,10	0,89
		1-Methylphenanthrene	4,00	0,85	1,90	0,68	1,21	0,96	7,11	16,70	0,43
		Fluoranthene	10,35	2,20	4,38	1,57	3,39	2,69	18,11	17,70	1,02
		Pyrene	7,75	1,65	12,73	4,57	3,01	2,39	23,48	22,50	1,04
		Benzo(a)anthracene	1,21	0,26	0,02	0,01	0,30	0,24	1,53	2,00	0,76
		Chrysene/Triphenylene	2,04	0,43	0,04	0,01	0,54	0,43	2,61	2,20	1,19
		Benzo(b&k)fluoranthene	2,20	0,47	0,02	0,01	0,97	0,77	3,19	2,70	1,18
		Benzo(e)pyrene	0,77	0,16	0,02	0,01	0,37	0,29	1,15	1,60	0,72
		Benzo(a)pyrene	1,49	0,32	0,02	0,01	0,28	0,23	1,80	1,30	1,38
		Indeno(1,2,3,-cd)pyrene	0,88	0,19	0,02	0,01	0,03	0,02	0,93	1,40	0,66
		Benzo(gih)perylene	1,67	0,36	0,02	0,01	0,50	0,40	2,19	3,30	0,66
		Coronene	1,02	0,22	0,02	0,01	0,31	0,24	1,34	1,80	0,75
		total mass	98,46						149,74	139,90	**1,07**
mean		Phenanthrene	64,21	12,91	8,54	3,05	12,42	10,49	85,17	65,20	1,31
		Anthracene	13,77	2,77	0,65	0,23	1,49	1,26	15,91	20,55	0,77
		1-Methylphenanthrene	4,79	0,96	2,18	0,78	1,28	1,08	8,25	18,90	0,44
		Fluoranthene	12,40	2,49	5,02	1,79	3,57	3,02	20,99	19,95	1,05
		Pyrene	9,28	1,87	14,60	5,22	3,17	2,68	27,05	25,65	1,05
		Benzo(a)anthracene	1,45	0,29	0,03	0,01	0,31	0,26	1,78	2,30	0,78
		Chrysene/Triphenylene	2,44	0,49	0,04	0,02	0,57	0,48	3,05	2,75	1,11
		Benzo(b&k)fluoranthene	2,64	0,53	0,02	0,01	1,02	0,86	3,68	3,15	1,17
		Benzo(e)pyrene	0,92	0,18	0,02	0,01	0,38	0,33	1,32	1,80	0,74
		Benzo(a)pyrene	1,79	0,36	0,02	0,01	0,30	0,25	2,11	1,55	1,36
		Indeno(1,2,3,-cd)pyrene	1,05	0,21	0,02	0,01	0,03	0,03	1,10	1,40	0,79
		Benzo(gih)perylene	2,00	0,40	0,02	0,01	0,53	0,45	2,55	3,30	0,77
		Coronene	1,22	0,25	0,02	0,01	0,32	0,27	1,56	1,80	0,87
		total mass	117,95						174,54	168,30	**1,04**

Table D: SCE and their standard errors at Hornsgatan 1997 (13 different PAH).

year			SCE ng/m3		STDERR	TSTAT (SCE/ STDERR)	measured mass
1997		gasoline	137,5	+ / -	26,5	5,2	
period 1		diesel	35,2	+ / -	12,5	2,8	
		background	26,7	+ / -	23,8	1,1	
		calculated mass	199,3				196,7
1997		gasoline	98,5	+ / -	21,0	4,7	
period 2		diesel	27,2	+ / -	9,8	2,8	
		background	24,1	+ / -	19,1	1,3	
		calculated mass	149,7				139,9
mean		gasoline	118,0	+ / -	23,7	5,0	
		diesel	31,2	+ / -	11,1	2,8	
		background	25,4	+ / -	21,5	1,2	
		calculated mass	174,5				168,3

Table E: SCE for the two sources and their standard errors in Kista.

sample		SCE ng/m3		STDERR	TSTAT (SCE/ STDERR)	measured mass
1	gasoline	3,8	+/-	0,3	13,6	
	diesel	1,1	+/-	0,3	4,1	
	calculated mass	4,9				5,5
2	gasoline	0,5	+/-	0,1	8,8	
	diesel	4,5	+/-	0,5	8,7	
	calculated mass	5,0				5,0
3	gasoline	0,5	+/-	0,1	9,2	
	diesel	4,2	+/-	0,5	8,6	
	calculated mass	4,7				4,8
4	gasoline	4,9	+/-	0,4	13,5	
	diesel	1,4	+/-	0,3	4,1	
	calculated mass	6,3				6,7
5	gasoline	7,7	+/-	0,6	13,8	
	diesel	1,2	+/-	0,4	2,9	
	calculated mass	8,9				9,2
6	gasoline	2,2	+/-	0,2	12,2	
	diesel	3,6	+/-	0,5	7,1	
	calculated mass	5,8				6,5
7	gasoline	4,3	+/-	0,3	13,2	
	diesel	2,5	+/-	0,5	5,5	
	calculated mass	6,9				7,9
8	gasoline	8,1	+/-	0,6	13,8	
	diesel	1,0	+/-	0,4	2,5	
	calculated mass	9,2				8,1
9	gasoline	13,7	+/-	1,0	13,8	
	diesel	1,4	+/-	0,7	2,1	
	calculated mass	15,1				12,4
11	gasoline	6,7	+/-	0,5	13,9	
	diesel	1,2	+/-	0,4	3,3	
	calculated mass	7,9				8,2
14	gasoline	6,6	+/-	0,5	13,7	
	diesel	1,3	+/-	0,4	3,3	
	calculated mass	7,8				7,4
15	gasoline	11,5	+/-	0,8	14,0	
	diesel	0,7	+/-	0,5	1,3	
	calculated mass	12,2				9,6
16	gasoline	0,5	+/-	0,1	8,7	
	diesel	4,6	+/-	0,5	8,7	
	calculated mass	5,1				4,9
mean	gasoline	5,46	+ / -	0,402	13,6	
	diesel	2,21	+ / -	0,451	4,9	
	calculated mass	7,67				7,4

Table F: SCE for the two sources and their standard errors in Enskede.

sample		SCE ng/m3		STDERR	TSTAT (SCE/ STDERR)	measured mass
1	gasoline	10,2	+/-	0,8	13,5	
	diesel	3,5	+/-	0,8	4,4	
	calculated mass	13,7				14,9
2	gasoline	10,8	+/-	0,8	13,9	
	diesel	1,7	+/-	0,6	2,9	
	calculated mass	12,5				12,2
3	gasoline	19,3	+/-	1,4	14,0	
	diesel	1,5	+/-	0,9	1,7	
	calculated mass	20,8				17,3
4	gasoline	7,7	+/-	0,6	13,7	
	diesel	1,8	+/-	0,5	3,6	
	calculated mass	9,5				9,7
5	gasoline	11,7	+/-	0,8	13,8	
	diesel	2,7	+/-	0,7	3,7	
	calculated mass	14,3				16,8
7	gasoline	6,0	+/-	0,5	13,1	
	diesel	4,2	+/-	0,7	5,8	
	calculated mass	10,1				12,2
8	gasoline	11,1	+/-	0,8	13,6	
	diesel	3,1	+/-	0,8	4,1	
	calculated mass	14,3				14,9
10	gasoline	19,7	+/-	1,4	13,9	
	diesel	2,1	+/-	0,9	2,2	
	calculated mass	21,7				20,1
11	gasoline	3,8	+/-	0,3	12,7	
	diesel	1,9	+/-	0,4	5,1	
	calculated mass	5,7				6,6
12	gasoline	10,9	+/-	0,8	13,9	
	diesel	1,0	+/-	0,5	2,0	
	calculated mass	12,0				10,8
13	gasoline	19,0	+/-	1,4	13,9	
	diesel	0,3	+/-	0,8	0,4	
	calculated mass	19,3				14,9
14	gasoline	15,2	+/-	1,1	13,9	
	diesel	1,0	+/-	0,7	1,4	
	calculated mass	16,2				13,9
15	gasoline	23,5	+/-	1,7	14,0	
	diesel	0,2	+/-	0,9	0,2	
	calculated mass	23,7				19,0
16	gasoline	7,5	+/-	0,5	13,7	
	diesel	1,6	+/-	0,5	3,4	
	calculated mass	9,1				8,8
mean	gasoline	12,6	+/-	0,9	13,8	
	diesel	1,9	+/-	0,7	2,8	
	calculated mass	14,5				13,7

Table G: SCE of 13 individual PAH and their standard errors in Kista 1997.

	ng/m3	gasoline	STDERR	diesel	STDERR	calculated mass	measured mass	calculated/ measured
Mean	Phenanthrene	2,97	0,22	0,61	0,12	3,58	3,76	0,95
value	Anthracene	0,64	0,05	0,05	0,01	0,68	0,44	1,55
	1-Methylphenanthrene	0,22	0,02	0,15	0,03	0,38	0,40	0,93
	Fluoranthene	0,57	0,04	0,36	0,07	0,93	1,08	0,86
	Pyrene	0,43	0,03	1,03	0,21	1,46	0,95	1,55
	Benzo(a)antracene	0,07	0,00	0,00	0,00	0,07	0,07	1,03
	Chrysene/Triphenylene	0,11	0,01	0,00	0,00	0,12	0,12	0,97
	Benzo(b&k)fluoranthene	0,12	0,01	0,00	0,00	0,12	0,22	0,57
	Benzo(e)pyrene	0,04	0,00	0,00	0,00	0,04	0,09	0,50
	Benzo(a)pyrene	0,08	0,01	0,00	0,00	0,08	0,06	1,35
	Indeno(1,2,3,-cd)pyrene	0,05	0,00	0,00	0,00	0,05	0,02	3,27
	Benzo(gih)perylene	0,09	0,01	0,00	0,00	0,09	0,12	0,76
	Coronene	0,06	0,00	0,00	0,00	0,06	0,08	0,71
		5,46		2,21		7,67	7,41	**1,04**

Table H: SCE of 13 individual PAH and their standard errors in Enskede 1997.

	ng/m3	gasoline	STDERR	diesel	STDERR	calculated mass	measured mass	calculated/ measured
mean	Phenanthrene	6,85	0,50	0,52	0,19	7,37	6,84	1,08
	Anthracene	1,47	0,11	0,04	0,01	1,51	0,82	1,84
	1-Methylphenanthrene	0,51	0,04	0,13	0,05	0,64	0,69	0,94
	Fluoranthene	1,32	0,10	0,31	0,11	1,63	1,87	0,87
	Pyrene	0,99	0,07	0,89	0,32	1,88	1,70	1,10
	Benzo(a)antracene	0,15	0,01	0,00	0,00	0,16	0,17	0,94
	Chrysene/Triphenylene	0,26	0,02	0,00	0,00	0,26	0,29	0,91
	Benzo(b&k)fluoranthene	0,28	0,02	0,00	0,00	0,28	0,54	0,53
	Benzo(e)pyrene	0,10	0,01	0,00	0,00	0,10	0,20	0,49
	Benzo(a)pyrene	0,19	0,01	0,00	0,00	0,19	0,17	1,15
	Indeno(1,2,3,-cd)pyrene	0,11	0,01	0,00	0,00	0,11	0,02	5,75
	Benzo(gih)perylene	0,21	0,02	0,00	0,00	0,22	0,28	0,77
	Coronene	0,13	0,01	0,00	0,00	0,13	0,16	0,80
		12,59		1,90		14,49	13,74	**1,05**

Appendix 4: Results from Cluster Analysis.

Hornsgatan:

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* * * * * * H I E R A R C H I C A L   C L U S T E R    A N A L Y S I S *
* * * * *


 Dendrogram using Average Linkage (Between Groups)

                      Rescaled Distance Cluster Combine

     C A S E      0         5        10        15        20        25
    Label    Num  +---------+---------+---------+---------+---------+

    B(ghi)p   12   -+
    Cor       13   -+------------+
    I(cd)p    11   -+              +---+
    Bfl        7   -------+-------+   I
    B(a)p      9   -------+           I
    Pyr        4   -+                 I
    Flu       14   -+---+             +---------------------------+
    Phe        1   -+   I             I                           I
    Ant        2   -+   +-----------+ I                           I
    B(a)a      5   -+-+ I           I I                           I
    Chr        6   -+ +-+           +-+                           I
    B(e)p      8   ---+             I                             I
    1-mphe     3   ----------------+                             I
    Per       10   --------------------------------------------+
```

Enskede:

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* * * * * * H I E R A R C H I C A L   C L U S T E R   A N A L Y S I S *
* * * * *


 Dendrogram using Average Linkage (Between Groups)

                     Rescaled Distance Cluster Combine

      C A S E        0         5        10        15        20        25
     Label     Num   +---------+---------+---------+---------+---------+

     2-mphe      4   -+
     1-mphe      7   -+
     Phe         1   -+-+
     3-mphe      3   -+ +-+
     9+4-mphe    6   ---+ +---+
     Flu         9   -+-+ I   I
     Pyr        10   -+ +-+   +---+
     2-mant      5   ---+     I   +------------------+
     2-phena     8   --------+  I                    I
     Ant         2   ------------+                   I
     B(a)fl     11   -----+-+                         +--------------+
     Chr        13   -----+ +-+                       I              I
     Bfl        14   -------+ I                        I              I
     B(a)a      12   -+-+     +----------------------+ I              I
     B(e)p      15   -+ +---+ I                        I              I
     B(ghi)p    19   -+ I   I I                        I              I
     Cor        20   -+-+   +-+                        I              I
     B(a)p      16   -+     I                          I              I
     Per        17   -------+                          I              I
     I(cd)p     18   -------------------------------------------------+
```

Kista:

```
* * * * * * H I E R A R C H I C A L   C L U S T E R    A N A L Y S I S *
* * * * *


 Dendrogram using Average Linkage (Between Groups)

                    Rescaled Distance Cluster Combine

    C A S E      0         5        10        15        20        25
   Label    Num  +---------+---------+---------+---------+---------+

   Bfl       14  -+-+
   B(e)p     15  -+ I
   Chr       13  ---+-+
   B(ghi)p   19  -+-+ I
   Cor       20  -+   I
   B(a)a     12  -+-+ I
   Per       17  -+ +-+-------+
   B(a)p     16  ---+ I       +---------+
   B(a)fl    11  -----+       I         I
   I(cd)p    18  -------------+         I
   Flu        9  -+-+                   +-----+
   Pyr       10  -+ +---+              I     I
   2-mant     5  ---+   I              I     I
   3-mphe     3  -+-+   +--------------+     I
   2-mphe     4  -+ +---+              +-----------------+
   Phe        1  ---+   I              I                 I
   1-mphe     7  ---+   I              I                 I
   9+4-mphe   6  -------+              I                 I
   Ant        2  ---------------------------+            I
   2-phena    8  ----------------------------------------------+
```

Kista, Enskede and Hornsgatan model:

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* * * * * * H I E R A R C H I C A L   C L U S T E R   A N A L Y S I S *
* * * * *


 Dendrogram using Average Linkage (Between Groups)

                    Rescaled Distance Cluster Combine

    C A S E       0         5        10        15        20        25
  Label     Num   +---------+---------+---------+---------+---------+

  I(cd)p     11   -+
  Cor        13   -+-+
  B(ghi)p    12   -+ +-+
  B(a)a       5   -+-+ I
  Chr         6   -+   +-+
  Pyr         4   -+   I I
  Flu        14   -+   I I
  B(e)p       8   -+---+ +---------+
  Phe         1   -+     I         I
  Ant         2   -+     I         +-----------------------------+
  Bfl         7   ---+---+         I                             I
  B(a)p       9   ---+             I                             I
  1-mphe      3   ----------------+                              I
  Per        10   ----------------------------------------------+
```
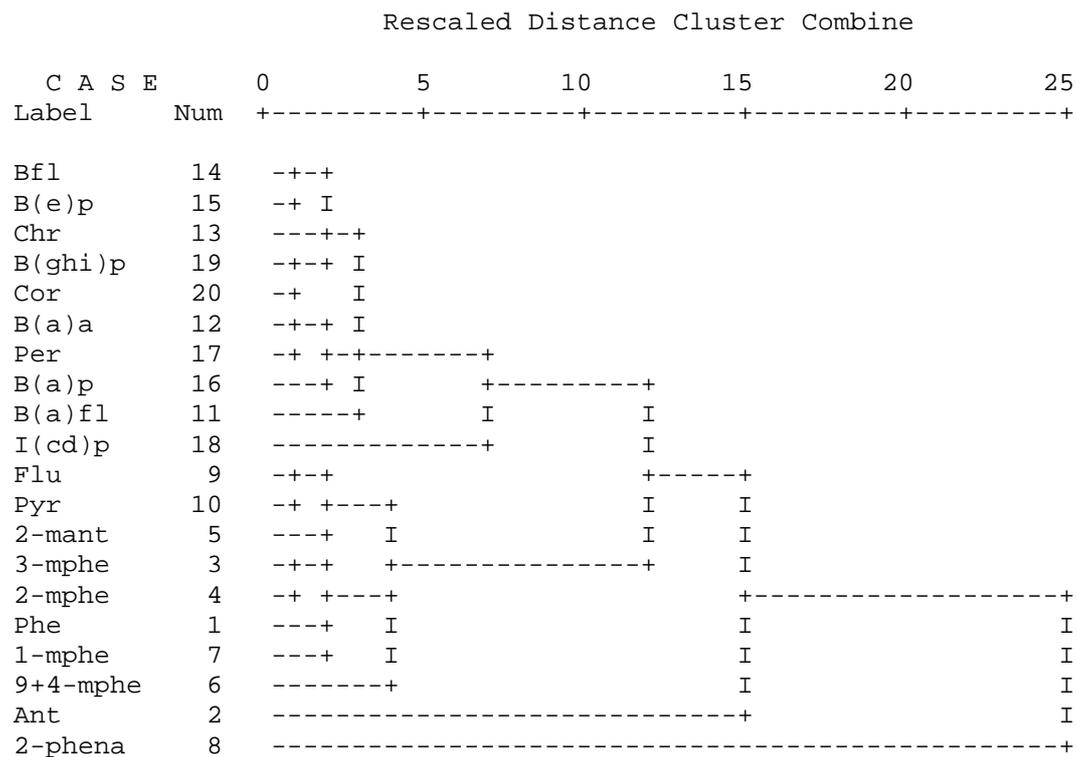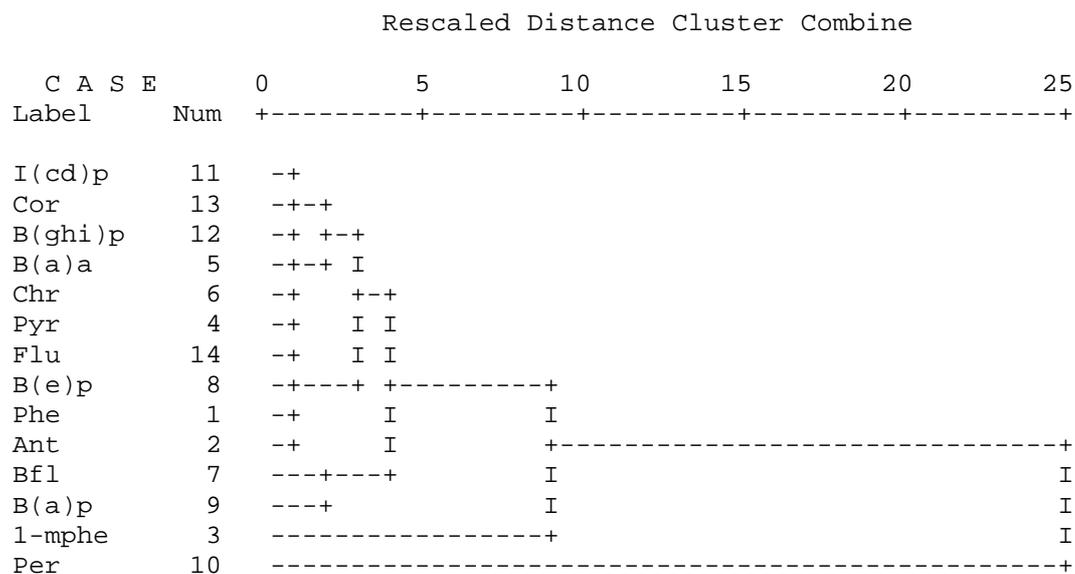
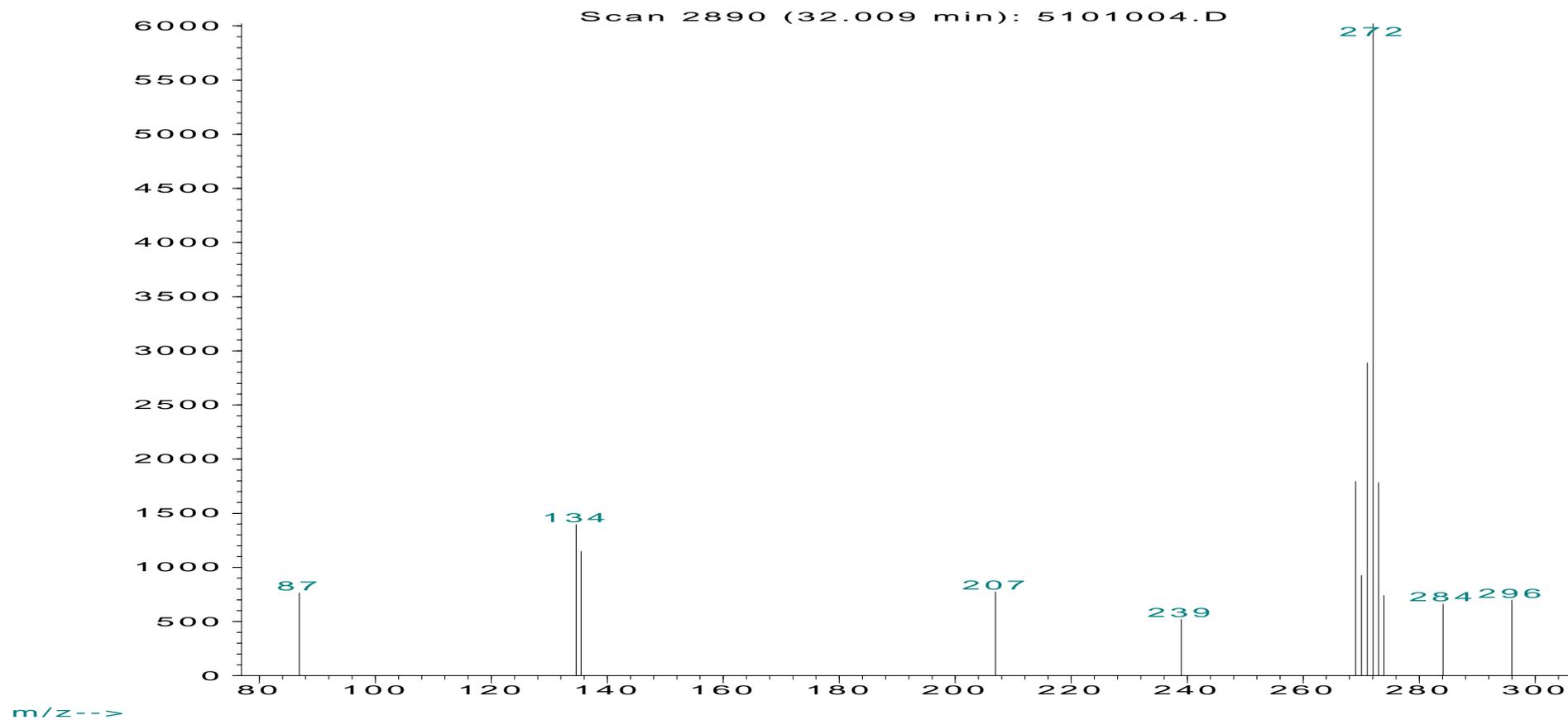| Abbreviations:	
Bfl	Benzofluoranthenes
B(e)p	Benzo(e)pyrene
B(a)p	Benzo(a)pyrene
Chr	Chrysene
B(ghi)p	Benzo(ghi)perylene
Cor	Coronene
Per	Perylene
B(a)a	Benzo(a)anthracene
B(a)fl	Benzo(a)fluorene
I(cd)p	Indeno(cd)pyrene
Flu	Fluoranthene
Pyr	Pyrene
2-mant	2-Methylanthracene
3-mphe	3-Methylphenanthrene
2-mphe	2-Methylphenanthrene
1-mphe	1-Methylphenanthrene
9+4-mphe	9+4-Methylphenanthrene
Phe	Phenanthrene
Ant	Anthracene
2-phena	2-phenylnaphtalene

Appendix 5: Results from analysis of PAH in tyres and Mass Spectra.

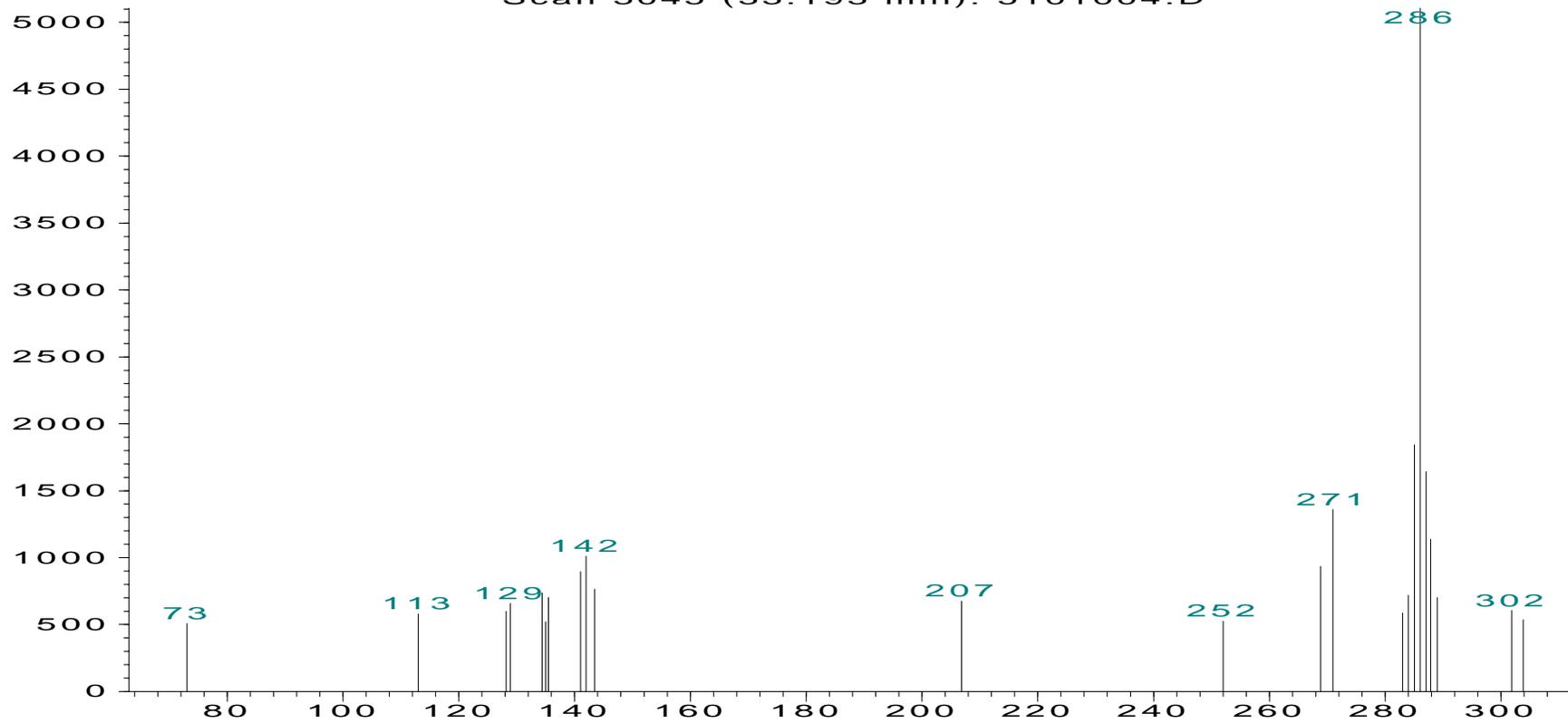| ug/g, ppm PAH	Michelin 9311	Michelin 9515	Michelin 9714	Michelin 9811	Michelin 9846	Michelin 9853	Bridgestone 1993	Gislaved 9915	mean value	Std dev
2-Methylfluorene	0,0	0,0	0,0	0,2	0,3	0,4	0,3	0,6	0,2	0,2
Dibenzothiophene	0,8	0,5	0,8	1,8	0,5	2,6	1,0	1,1	1,1	0,7
Phenanthrene	4,7	3,7	2,7	3,4	1,9	4,8	9,2	15,5	5,7	4,5
Anthracene	0,3	0,3	0,1	0,1	0,1	0,3	0,8	0,6	0,3	0,2
2-Methylphenanthrene	1,8	1,1	1,4	2,0	0,9	2,3	1,7	1,7	1,6	0,4
2-Methylanthracene	0,0	1,7	2,5	4,0	1,5	6,2	0,2	2,9	2,4	2,0
1-Methylphenanthrene	1,5	1,2	1,4	2,4	1,1	2,3	1,5	2,5	1,7	0,6
Fluoranthene	7,7	8,7	4,9	4,8	2,4	17,8	38,3	38,5	15,4	14,9
Pyrene	22,1	37,2	25,4	13,7	7,5	73,2	99,1	127,5	50,7	44,1
1-methyl-7-isopropylphen.	1,4	2,4	1,5	1,4	1,9	1,9	3,3	14,7	3,6	4,6
2-Methylpyrene	0,3	0,6	0,2	0,0	0,6	0,5	0,6	1,7	0,6	0,5
1-Methylpyrene	0,7	1,3	1,2	0,9	1,4	1,4	1,0	0,0	1,0	0,5
Benzo(ghi)fluoranthene	2,7	3,6	1,7	1,5	1,0	11,8	19,6	20,5	7,8	8,3
Cyclopenta(cd)pyrene	1,6	4,1	1,7	2,5	2,2	25,2	13,9	61,9	14,1	21,0
Chrysene/Triphenylene	2,9	4,9	2,9	3,2	7,9	3,9	2,5	13,8	5,3	3,9
Benzo(b)fluoranthene	1,8	2,1	1,1	1,4	3,7	2,0	4,6	9,1	3,2	2,7
Benzo(k)fluoranthene	0,0	0,0	0,0	0,0	0,0	0,0	0,3	0,0	0,0	0,1
Benzo(e)pyrene	3,6	5,7	3,5	5,1	9,8	6,7	6,4	21,8	7,8	6,0
Benzo(a)pyrene	1,3	2,3	5,0	1,2	1,5	3,8	5,4	6,4	3,4	2,0
Perylene	0,0	0,0	0,0	0,0	0,0	0,0	0,0	2,2	0,3	0,8
Indeno(1,2,3-cd)pyrene	0,0	2,4	0,0	0,0	0,0	0,0	14,6	0,0	2,1	5,1
Dibenso(a,h)anthracene	0,0	0,0	0,0	0,0	0,0	0,0	0,0	1,0	0,1	0,4
Benzo(ghi)perylene	8,0	15,2	9,9	6,4	16,9	40,3	49,7	52,5	24,9	19,4
Coronene	6,9	16,1	14,8	8,6	5,0	128,4	82,1	58,8	40,1	45,4
Summa	70,0	115,1	82,8	64,4	68,0	335,7	356,0	455,4	193,4	160,9

9311 mean made week 11 in 1993.

Mass spectra of possible but not identified PAH:

Abundance

Scan 2890 (32.009 min): 5101004.D

6000
5500
5000
4500
4000
3500
3000
2500
2000
1500
1000
500
0

87   134   207   239   272   284 296

m/z-->

80   100   120   140   160   180   200   220   240   260   280   300

Scan 3045 (33.193 min): 5101004.D