Chemical characterization and source apportionment estimates of particulate matter collected within the framework of EU project HEPMEAP

H.J.T. Bloemen[1], M.E. Gerlofs-Nijland[2],
N.A.H. Janssen[2], T. Sandström[3], L. van Bree[4],
F.R. Cassee[2]

Contact:
F.R. Cassee
f.cassee@rivm.nl

1. Laboratory for Environmental Monitoring, Environment and Safety Division, RIVM
2. Centre for Environmental Health Research, Environment and Safety Division, RIVM
3. Department of Respiratory Medicine & Allergy, University Hospital, Umeå, Sweden
4. Quality of the Local Environment, Netherlands Environmental Assessment Agency, RIVM

Rapport in het kort

Chemische karakterisatie en bronbijdrageschattingen van fijn stof verzameld in het kader van het EU project HEPMEAP

In het kader van het project 'Health effects of particles from motor engine exhaust and ambient pollution – HEPMEAP', een unieke Europese samenwerking tussen toxicologen en epidemiologen, is buitenlucht fijn stof verzameld op diverse locaties in Europa gedurende de periode november 2001 – maart 2003. In het HEPMEAP project zijn relaties tussen de samenstelling van fijn stof en toxische en andere gezondheidseffecten bestudeerd. De chemische samenstelling van twee fracties (0.1 – 2.5 µm en 2.5 – 10 µm) is bepaald met aandacht voor specifieke verkeersindicatoren.

Een groot deel van de massa van het fijn stof bestaat uit anorganisch aërosol (34% nitraat, sulfaat en ammonium). Daarnaast bestaat circa 2% uit organisch materiaal afkomstig van verbrandingsprocessen. Ruwe schattingen van de verkeersbijdrage voor deze twee fracties variëren tussen 30% en 60%.

Behalve grote overeenkomsten in samenstelling van fijn stof op de verschillende locaties, zijn ook locatie-specifieke verschillen gevonden. Zo bleek op de locatie in Noord-Zweden relatief hoge concentraties organisch aërosol in fijn stof voor te komen, wat in een belangrijke mate afkomstig is van houtverbranding.
De gegevens in dit rapport worden gebruikt om de resultaten van experimenteel toxicologisch onderzoek wat ook is uitgevoerd in het kader van dit project, nader te verklaren.

Trefwoorden: fijn stof, chemie, bronherkenning, HEPMEAP

Abstract

Chemical characterization and source apportionment estimates of particulate matter collected within the framework of EU project HEPMEAP .

In the framework of the project 'Health effects of particles from motor engine exhaust and ambient pollution – HEPMEAP', a unique European collaboration between toxicologists and epidemiologists, ambient particulate matter (PM) was collected at various sites across Europe during the periods, November 2001 and March 2003. The HEPMEAP project studies the relation between the composition of particulate matter, and the toxicity and health effects.

The chemical composition of fine (0.1 – 2.5 μm) and coarse mode (2.5 – 10 μm) particulate matter is determined with specific attention paid to indicators of traffic emissions. Inorganic ions nitrate, sulphate and ammonium sum to 34% of PM mass and the measured organics from combustion processes up to 2%. Rough estimates of the traffic contributions of these two fractions vary from 30% to 60%.

Besides strong similarities, PM samples from these various locations/sources show substantial differences in chemical composition. For example, samples from the rural location in Northern Sweden were highly dominated by organic matter, most likely originating from wood combustion. The data presented in this report will provide valuable information for in vitro and in vivo toxicity studies performed within this European Union research project

Keywords: particulate matter, source apportionment, HEPMEAP, chemistry

Preface

The project 'Health effects of particles from motor engine exhaust and ambient pollution' (HEPMEAP) is a unique European collaboration between toxicologists and epidemiologists to collect and toxicologically examine ambient particulate matter (PM) fractions to study PM composition-toxicity-health effect relationships. The present project was set out to collect ambient PM fractions using high volume low cut-off inertial impactors at sites throughout Europe with established contrast in road traffic source types and traffic density.

The overall objective of the HEPMEAP initiative is to assess the inflammatory and toxicological potential of ambient suspended particles in comparison with freshly generated particles obtained from diesel and gasoline engines and to relate these observations to the effects of exhaust on human airways as well as to epidemiological findings of adverse PM health effects.

The results will be discussed also in relation to the physico-chemical characteristics of PM in order to explore the causal factor(s) responsible for the adverse health effects and to facilitate health risk assessment, standard setting as well as the application of cost-effective emission and risk control measurements. The outcomes of this European project are therefore of significant relevance both from the scientific as from a regulatory point of view.

Contents

Samenvatting

Dit rapport beschrijft de resultaten van een in Europa uitgevoerde fijnstofverzamelcampagne. Met behulp van een zogenaamde High-Volume Cascade Impactor (HVCI) werden twee fracties verzameld: grof (2,5-10 μm) en fijn (0,1-2,5 μm) stof. Dit is op locaties in Nederland, Duitsland, Zweden en Italië uitgevoerd. Daarnaast is ook rechtstreeks fijn stof verzameld vanuit de uitlaat van diesel en benzine gevoede automotoren. Alle fijn stof monsters zijn vervolgens chemisch gekarakteriseerd, waarmee ook een schatting is gemaakt van de bijdragen van emissies van verschillende bronnen.

De veldstudie is succesvol uitgevoerd in de periode tussen november 2001 en maart 2003. Alle veldlocaties zijn tenminste tweemaal bezocht gedurende verschillende seizoenen in het jaar. De massa van de gemeten parameters - elementen, ionen en organische verbindingen – bepalen samen 44% van de totale massa (25 en 75 percentiel: 36 en 53%). Hiervan is 34% nitraat, sulfaat en ammonium (25 en 75 percentiel: 18 en 44%) en de elementen vormen circa 8% (25 en 75 percentiel: 3 en 16%) van de massa. Verkeer lijkt de belangrijkste bron van PM te zijn. Schattingen van de verkeersbijdrage voor deze twee fracties varieert tussen 30% en 60%. Wel moet worden opgemerkt dat het aantal waarnemingen eigenlijk te beperkt is voor een betrouwbaar beeld over bronbijdragen

Naast sterke overeenkomsten blijken er tussen verschillende locaties aanzienlijke verschillen in samenstelling aanwezig te zijn. Zo werden bijvoorbeeld op een locatie in Noord-Zweden zeer hoge hoeveelheden organisch materiaal (polycyclische aromatische koolwaterstoffen) gemeten. Dit kon worden verklaard door grote bijdrage van houtverbranding.

De data die in dit rapport worden gepresenteerd vormen waardevolle informatie voor de interpretatie en evaluatie van de effecten die gevonden zijn in *in vitro* en *in vivo* toxiciteitsonderzoek, een ander onderdeel van dit EU project.

Summary

This report describes the results of a European-wide initiative for the collection of particulate matter samples. Using High-Volume Cascade Impactor (HVCI), coarse (2.5-10 μm) and fine (0.1-2.5 μm) particulate samples were collected in various locations in the Netherlands, Germany, Sweden and Italy. In addition, PM was also directly collected from diesel and petrol fuelled car engine exhaust. All PM samples were chemically characterized. This characterization was aimed at describing the PM in terms of composition as well as in contributions of main sources.

The sampling campaign has been successfully performed in the period between November 2001 and March 2003. All field locations were sampled at least twice, during different seasons of the year. The measured parameters - elements, ions and organic compounds - amount to 44% of the total PM mass (25 and 75 percentile: 36 and 53%, respectively) of which the ions nitrate, sulphate and ammonium sum to 34% (18 and 44%, 25 and 75 percentile) and the measured elements 8% (3 and 16%, 25 and 75 percentile). Traffic seems to be the major source and the contribution in the fine fraction is higher compared to the coarse fraction. Estimates of traffic contribution to these two fractions vary from 30% to 60%. It needs to be stated that the number of observations is insufficient for a reliable source apportionment assessment.

Besides strong similarities PM samples from these various locations/sources show substantial differences in chemical composition. For examples, samples from the rural location in Northern Sweden were highly dominated by organic matter, most likely originating from wood combustion.

The data presented in this report will provide valuable information for *in vitro* and *in vivo* toxicity studies performed within this European Union research project.

1. Introduction

There is increasing concern about the possible adverse effects of ambient particulate matter (PM) on human health and the specific role of traffic exhaust emissions like diesel exhaust (DE). Clean air legislation and the various abatement measures have resulted in the decline of the concentrations of the classic air pollutants. However, epidemiology data show adverse health effects at PM concentrations below national ambient air quality standards and health-based guidelines. An important source of air pollution is traffic the volume of which has increased substantially, and, despite improvements in engine technology, so has the amount of emissions from automobile engines. This change in the pattern of air pollution has been paralleled by a progressive increase in the proportion of children and adults suffering with asthma and other allergic diseases. In the literature it is shown that living close to major highways is associated with the development of allergies, and also that the adjuvant effect of diesel particulates on the development of specific IgE directed against airborne allergens is established. Furthermore, epidemiological studies have demonstrated a clear association between cardiovascular morbidity, decreased lung function, increased emergency room admissions and airborne concentrations of PM. Human exposure chamber studies have shown that exposure to diesel exhaust has an acute inflammatory effect on normal human airways.

Uncertainties about health effect-relevant PM characteristics and components and their respective sources seriously complicate the process of PM health risk assessment and standard setting and the application of cost-effective emission and risk control measures. Of eminent importance, both from the scientific and regulatory point of view, is whether the mass concentration of ambient PM and/or its composition is related to the biological activity and toxicity. From this perspective the new EU PM Daughter Directive will also be based on the consideration of controlling the fine fraction of PM_{10} (i.e. $PM_{2.5}$) or to relate to a source related PM fraction like traffic and motor vehicle exhaust emissions.

The pan-European research initiative Health effects of particles from motor engine exhaust and ambient pollution (HEPMEAP) focuses on the inflammatory and toxicological potential of ambient PM related with traffic. More detailed description of scope and overall objectives of the HEPMEAP study are published elsewhere (http://www.hepmeap.org). As part of this project ambient PM was collected at various sites in European countries as well as directly from diesel and petrol fuelled car engine exhaust and was characterized physically and chemically. The characterization is aimed at describing the PM in terms of elemental composition, acid aerosol related ions and a selection of organic compounds enabling largely the explanation of the found mass as well as in contributions of main sources.

Identical PM material, extracted from the collection medium is to be used for studying the inflammatory and toxicological potential in different *in vivo* and *in vitro* biological models by a number of European research groups. These investigations will be published elsewhere. In this report the collection, the chemical characterization and attributing to the main sources is described.

2.   Material and methods

2.1   Particle collection

A High Volume Cascade Impactor (HVCI) with a multi-stage round slit nozzle impactor was used to collect PM fractions on polyurethane foam (PUF) by impaction (Kavouras and Koutrakis, 2001; Demokritou et al., 2002). This instrument was developed by the Environmental Chemistry Laboratory at the Harvard School of Public Health. It can be used for the collection of samples for periods up to one week or longer (depending on the particle load) at a flow rate of 900 l/min. The impactor cut-points used are for the range 9.9, 2.46, and 0.12 µm for all the sites except Rome and Hendrik-Ido-Ambacht. For these sites the cut-points were 8.5, 2.35 and 0.12 µm. The cut-points were measured by the manufacturer of the slits. The design features round slit acceleration jets, with corresponding PUF rings for impaction substrates. The jets are mounted in modular cylindrical housings. The housings are stacked in sequence, with the selected stages in proper order (by descending size cut-offs). A removable rain cover is attached to the top stage. An option for the final stage, using a glass fiber filter to collect ultra-fine particles (below the lowest used impactor cut-point) was used in this project, however, ultra-fine particles were not extracted from the substrate and consequently not characterised chemically. The HVCI is shown in Figure 2.1 showing a typical configuration of impactor stages (size cut-offs of 10, 2.5, and 0.1 µm).

Figure 2.1   HEPMEAP PM collection device with the HVCI next or on top of a box with the pump to pull the air through the impactor (left two panels) and the inside of the HVCI showing the pink PUF with collected PM (black) of the fine mode stage (right panel).

2.2   Sampling locations and periods

The main objective of the HEPMEAP project is the overall analysis on composition-source-toxicity-health effect relationships. In the Dutch ISAAC-II (International Studies of Asthma

and Allergic disease in Childhood) study on respiratory health of children attending schools near highways health effects of ambient PM and the role of traffic emissions were determined. A close link to the epidemiological and human clinical studies would be beneficial to perform the above-mentioned overall analysis. Therefore, 4 sites in the Netherlands, characterized by differences in traffic density, were selected close to those used in the Dutch ISAAC-II study. Fine and coarse PM samples were collected for 4-5 two-week periods per site, spaced over a one-year period (November 2001-October 2002).

The Dutch sites are:
- *Netherlands – Amsterdam*: located at 50 meters from the road with high car and truck use
- *Netherlands – Dordrecht*: located at 300 meters from a road with moderate car and high truck density
- *Netherlands – Badhoevedorp*: located at 200 meters from the road with moderate car and truck use
- *Netherlands – Sassenheim*: located at 375 meters from a road with low car and truck densities.

The characteristics of the selected sites in the Netherlands are presented in table 1.

Table 1: Traffic characteristics of selected sites in the Netherlands during the HEPMEAP study

	HEPMEAP (2001/2002)			
City	Orientation[1]	Distance (m)	Traffic Intensity (vehicle/day - 2001)	
			Cars	Trucks
Amsterdam	270º	50	132,715	16,672
Dordrecht	268º	300	98,419	19,082
Badhoevedorp	215º	200	93,173	10,352
Sassenheim	148º	375	47,730	4,721

1 Geographical orientation relative to the road

Figure 2.2: Overview of HEPMEAP sampling sites

In Germany (Munich) the number of sampling sites was limited to two due to difficulties locating the collectors at or close to ISAAC-II sites. These two sites were chosen for maximum contrast in traffic density. Eight PM samples were collected over a fortnight at each of those two sites in Germany during 9-months.

- *Germany – Munich Ost Bahnhof*: located in customs centre Munich, east railway station, close to two major four-lane motorways with very high traffic density
- *Germany – Munich Grosshadern hospital*: located in a suburban area with university institutes in a residential area on the West side of Munich with low traffic density

Three sites were added to increase the contrast on source/composition/toxicological bioactivity:

- *Italy – Rome*: a representative Southern European site where the traffic situation is intense but there are differences in vehicle fleet and additional sources (2 fortnight's samples);
- *Netherlands – Hendrik-Ido-Ambacht*: a Dutch freeway tunnel which is mainly used by heavy diesel trucks is included in order to distil a diesel exposure atmosphere (2 fortnight's samples);
- *Sweden – Lycksele*: a small Scandinavian town of 15,000 citizens located in a rural area with sampling during a cold winter period with inversion pattern. Contribution was expected from the frequent use of wood burning for domestic heating. The area includes local traffic as well as thoroughfare of buses, trucks and other vehicles, but without any major highway in the area. Therefore, this site was included as a reference with little vehicle contribution to outdoor PM (4 collections; 1 collection of 4 weeks and 3 fortnight's samples).

In addition, PM fractions obtained from freshly generated diesel and gasoline exhaust were sampled in a special chamber as reference materials. The reference diesel PM was identical to that used in the human exposure studies (Frew et al., 2001; Salvi et al., 1999; Stenfors et al., 2004). Samples in the Dutch freeway tunnel and in Rome were collected according to the Standing Operation Procedure (SOP) published in Cassee et al. (2003). The sampling at the other sites was conducted according to the SOP from the Institute of Risk Assessment Science (IRAS) of the Utrecht University and is available on request.

2.3   Sample pre-treatment

PUF pieces used to collect particulate matter were cut to the correct sizes and cleaned before use. To this end, PUF pieces were sonicated for 30 minutes to 1 hour in an excessive amount water, ethanol (only for samples from the locations Rome and Hendrik-Ido-Ambacht), and 100% methanol respectively and dried. The weight of the foam was determined using an analytical balance. After sampling the foam was conditioned and weighed in the same way. A detailed description of the procedure is given in Cassee et al. (2003) for samples collected in

Rome and Hendrik-Ido-Ambacht. The procedure at the other sites was conducted according to the SOP from IRAS and is available on request.

The PM was extracted from the foam based on the procedure developed by Salonen et al. (2000): approximately 20 ml methanol was added to the tube containing the foam, stirred (vortex) violently and subsequently placed in an ultrasonic bath for 30 minutes after which the supernatant was decanted into a round-bottom flask. This was repeated once more and occasionally twice. The methanol was concentrated (rotary evaporator at 30 °C, low pressure, approximately 15 minutes) until about 1 ml suspension was left. This suspension was sonicated in the flask for several seconds to remove the PM from the wall of the flask and divided over weighed and labelled Eppendorf-tubes. The flask was rinsed with 1 ml methanol and sonicated again to remove all PM from the wall of the flask and this suspension was also divided over the Eppendorf tubes. If the flask was still containing PM the rins step was repeated once more. The Eppendorf tubes were transferred to an oven at 30 °C overnight and afterwards conditioned for 24 hrs. The amount of PM per Eppendorf tube was determined using an analytical balance. The tubes were stored at –20 °C until analysis.

2.4   Chemical characterization

The collected material was characterized by the analysis for an extended suite of elements and ions, organic traffic markers and polycyclic aromatic hydrocarbons (PAHs). The selection of these parameters was based on the notion that they would provide sufficient information to reconstruct the mass by using the parameters as proxies or tracers for the mass not measured. The amount of sample necessary for each analysis was determined based on the detection limits of the various analysis methods and data on the occurrences of the compounds, published in the literature. These assumptions were tested with a limit number of samples from other studies. Approximately 10 mg of the collected PM suspended in methanol was used for the characterization. The sample was divided over 4 tubes as methanol suspension, each for one type of analysis, in portions equivalent to 1 mg (twice), 6 mg and 0.1 mg. The sub-samples were dried under nitrogen and gentle heating (30 °C).

2.4.1   Elemental composition

The supplied methanol sample containing 0.1 mg was evaporated to dryness. The material was suspended with 0.5 ml water and transferred into a digestion vial of the microwave system. The sample cup was rinsed with subsequently 0.5 ml, twice with 1 ml water and thrice with the 1 ml digestion medium (diluted aqua regia:
1 ml 65% HNO_3 + 3.3 ml 37% HCl + 3 ml water) and the rinse solutions added to the digestion vial. The volume of the sample was made up to 10 ml. The sample was digested with the aid of microwave. Afterwards 5 ml water was added to the sample, mixed and the sample was transferred to autosampler vials for analyses with inductively coupled plasma mass spectrometry (ICPMS). Whenever necessary, the sample pre-treatment was extended by

centrifugation or filtration to avoid the transfer of particles into the sample introduction system of the ICPMS.

High sensitivity and the option to deal with many matrix- and plasma-related interferences are required whenever measuring an extended suite of elements. Therefore high resolution (HR)-ICPMS was preferred to quadrupol (Q-) ICPMS. Initially an existing multi-element method with HR-ICPMS was used as a screening method, which was, subsequently optimised and applied. This method includes the following elements: Li, Be, Br, Na, Mg, Si, Al, K, Ca, Sc, Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, As, Se, Sr, Mo, Cd, Sb, Ba, La, Ce, Nd, Hf, Hg, Sm, Tl, Pb, and U (see appendix 1 for explanation abbreviations). Rh was used as an overall internal standard. The samples were quantified with external 2-point calibration.

The used HR-ICPMS was an ELEMENT2 (ThermoFinnigan MAT, Bremen, Germany) equipped with 100 μl/min PFA nebulizer – used in pumped mode - with on-line spiking of the internal standard (1:1), a Scott-spray chamber, Quartz injector and Nickel cones. It was operated in the hot plasma mode (RF power = 1290 W). The runtime of the method (excluding take-up and wash time of the system) was approximately 3.5 min.

For quality control of the whole procedure and for controlling the completeness of digestion a standard reference material (0.01 g NIST 2710 'Montana soil') was treated in the same way. It was concluded that this was the most suitable reference material for this matrix. Each digestion run included a procedural blank, which was used for the calculation of detection limits. The analyses were performed under the QC/QA system of the laboratory.

2.4.2   Ionic species

Two of the supplied methanol samples, each containing 1 mg were evaporated to dryness, dissolved in water by sonification, filtered to remove remaining particles and analysed using ion-chromatography for chloride (Cl^-), nitrate (NO_3^-) and sulphate (SO_4^{2-}). These anions were analysed using a Dionex guard column (AG-4A), separation column (Dionex AS-4A) and pulsed electrochemical detector (Dionex-PED). Detection limits were 0.106, 0.124 and 0.096 mg/l for Cl^-, NO_3^- and SO_4^{2-}, respectively. Precision was better than 2%.

After two steps of derivation ammonium (NH_4^+) was analysed by photometry: at first ammonium was chlorinated and then derivatised into the blue complex of 5-aminosalicylate. The absorption of this complex is correlated to the quantitative abundance of ammonium and was measured at 660 nm using a continuous flow analyser system (CFA). The analyses were performed under the QA/QC system of the laboratory.

2.4.3   Polycyclic aromatic hydrocarbons (PAH) and traffic tracers

The supplied methanol sample containing approximately 6 mg was evaporated to dryness. An aliquot (50 μl) of internal standards (6 deuterated PAHs and d2-C29-α,α,α,(20R)-ethylcholestane) and 50 ml dichloromethane/isohexane (1:1) was added and the compounds were released by sonification. After filtration the extract was concentrated by evaporation to nearly dryness and mixed with 0.5 ml standard solution of 2.4-dichlorobenzyltetradecylether, which was used to correct for the variation of the injection

volume. 1 μl was injected (splitless mode) at 290 ^{o}C on a 30 m 0.25 mm WCOT DB-5MS column (film 0.25 μm) using a column temperature programmed from 90 – (ramp rate) - 160 – (ramp rate) – 290 ^{o}C in a Fisons 8000 series gaschromatograph equipped with an Interscience MD800 mass-spectrometer with EI in SIR mode. Detection limits were approximately 0.1 ng/extract. This method has been tested to give maximum yield for PAHs, as well as traffic markers. Occasionally the samples were loaded with other organic material that deteriorate the chromatographic separation which could be overcome by dissolving the sample in toluene, filtration over a low-binding Durapore PVDF membrane (0.22 μm) and evaporation again to the original volume. Comparison of the chromatograms of a number of samples before and after the clean-up showed no loss (less than 3%) of the PAHs and the selected traffic tracers

The reported PAHs include: naphthalene, acenaphthylene, acenaphthene, fluorene, phenanthrene, anthracene, fluoranthene, pyrene, benzo(a)anthracene, chrysene, benzo(b)fluoranthene, benzo(k)fluoranthene, benzo(a)pyrene, dibenzo(ah)anthracene, benzo(ghi)perylene en indeno(123cd)pyrene and the traffic markers: 17α(H)-22.29.30-trisnorhopane, 17α(H)-21β(H)-hopane, αββ-20R-cholestane, 5α-cholestane, αββ-20R-24S-methylcholestane, αββ-20R-24R-ethylcholestane. The analysis was performed under the QA/QC system of the laboratory.

2.4.4 Endotoxin

For the analysis of endotoxins, approximately 2 mg of PM was suspended in 1.2 ml pyrogen-free water with 0.05% Tween-20, and vortexed for 40 minutes. Endotoxin was measured in the extract with the kinetic Limulus Amebocyte Lysate (LAL) test, as described by Douwes et al. (1995). Extracts were tested at a 5 fold dilution. The assay was performed using LAL and Endotoxin Standard (BioWhittaker Lot 1L463F and Lot 1L4440, respectively), and the EL808 Ultra microplate reader/KC4 v3.0 software package assay system (Bio-Tek Instruments Inc.)

3.   Results and discussion

3.1   Introduction and aims

The analysis results are presented in Appendix 1 for all the samples identical as they are to be used in the in vivo and in vitro tests. The HEPMEAP samples mostly consist of 2 one-week ambient air samples and are analysed as the pooled samples. The detection limits are also given in Appendix 1 and used to calculate surrogate results (2/3 of detection limits) for sample set comparisons. Only those elements were included in the evaluation described below for which more than 50% had mass concentrations above the detection limit.

The results are expressed as mass by mass concentrations (ng or µg element or component by mg of PM mass) and this implies that when evaluating the results in the light of known compositions of ambient PM_{coarse} or PM_{fine} the ambient concentrations of each mode and hence their ratios are relevant. Furthermore, the sample pre-treatment (extraction and suspension handling) is not optimised or tested for maximum sample integrity and so discrimination of PM constituents might alter the patterns compared to those found in ambient air. However, the sample integrity is especially important to express the source contribution for each PM sample and is of less interest examining the relation between the chemical components and the toxicity of the same PM sample extracted from the collection substrate.

It is relevant to acknowledge that the composition, when expressed as mass by mass concentration, depends on the contributions of all sources to ambient PM and subsequently the relation between the found composition and the real world situation might not clearly be reflected. For example, during dry windy conditions wind-driven crustal material might be the major source although the sample is collected near a heavy traffic location. On the other hand, during wet conditions the contribution of tail-pipe emission might be the most relevant one although the sample is collected at a background location.

It is the objective of the evaluation of the analytical results to describe the composition of the analysed samples in general terms of elemental and compound composition. Although the number of collected samples is relatively small, a second aim was to quantify the contributions of the main sources for the samples collected at the different sites. This quantification was performed on PM already extracted from the collection substrate, thereby introducing artefacts that may have decreased the reliability of the assessment. The absence of good and solid source information as well as the limited databases on source profiles, and the limited number of samples collected at each site, do not enable the application of powerful source apportionment models (or receptor models) such as Chemical Mass Balance, Positive Matrix Factorisation or UNMIX. However, describing the found composition in terms of source contribution overcomes the lack of information on the molecular and crystal form in which the elements are present and so enables the distinction between the various forms based on known general composition of source emissions.

3.2   General profile

The measured parameters - elements, ions and organic compounds - amount to 44% of the total PM mass (25 and 75 percentile: 36 and 53% respectively) of which the ions nitrate, sulphate and ammonium sum to 34% (18 and 44%, 25 and 75 percentile) and the measured elements 8% (3 and 16%, 25 and 75 percentile). The measured organic compounds form only less than 2% of the total mass. The remaining part (median: 56%) consists of the non-measured elements of which oxygen and hydrogen are the most important ones. Another part, sometimes the main part, are the non-measured organic compounds – with common instrumentation maximum 20% of the organic compounds can be identified of which only a small portion can be quantified. Furthermore, any loss of material that occurred during the sample pre-treatment will add to the unidentified portion of the PM mass.

3.3   Specific chemical composition

3.3.1   Metal composition

An overview of key metals is provided in Figure 3.1. Significant location specific differences in metal composition were observed. For example, average total iron (Fe) and cupper (Cu) in the coarse fraction were almost three times higher at the Munich Ost Bahnhof location compared to all other locations. It seems likely that railway activities contributed substantially to these levels. This was also observed to a lesser extent, for the fine fraction. The highest aluminium (Al) content were observed in samples collected in Rome, irrespective the size fraction, whereas the zinc (Zn) content was at least twice as high at the motorway tunnel at Hendrik-Ido Ambacht compared to all other locations. Magnesium (Mg) was on average substantially higher in the coarse fraction, with slightly higher values for the Dutch locations compared to Munich and Lycksele. The latter are locations that are not influence by sea spray, whereas both the Dutch and Italian will be affected by sea salt. Influence of other sources is not excluded. Even though lead (Pb) is omitted from gasoline, this element is still present at substantial amounts in predominantly the fine fraction. Nickel (Ni) contents varied to a large extent, which highest levels observed in samples collected at Dordrecht and Rome. Vanadium (V), an element that can be associated with oil burning, was significantly higher at locations less than 25 kilometers from the sea or harbour, i.e. Dutch and Italian sites.

3.3.2   Inorganic composition

With the exception of sodium, and potassium, all other inorganic compounds are predominantly present in the fine fraction (Figure 3.2). Significant higher potassium (K) values were measured in Lycksele samples, but also in the fine fraction of samples taken in Sassenheim, the Netherlands. Wood combustion (see below) usually contributes substantially to K levels, but this can only be confirmed for Lycksele. Chloride levels are lower in Munich which is in line with the fact that PM in this city is not influenced by sea salt.

3.3.3   Organic composition

It is very clear that the levels of combustion related polycyclic hydrocarbons (PAHs) in Lycksele are at least an order of magnitude higher compared to all other sites and that this is related to wood burning (Figure 3.3). The levels of the other measured organic compounds are more comparable.

3.3.4   Endotoxin

Relatively low endotoxin levels were measured in all samples (Figure 3.4). The coarse fraction at the motorway tunnel near Hendrik-Ido Ambacht contained the highest levels of all samples, but the variation within the sample set of Hendrik-Ido Ambacht is also substantial. Endotoxin is likely derived from resuspended (road) dust.

3.4   Assessment of the extremes in the composition

To assess the extremes in the composition of the found patterns those mass/mass concentrations that are twice the average of the concentrations found at the sites or only one third are identified. Raw data used for this assessment is given in appendix 2.

- For Amsterdam high concentrations of La are found in both the fine and coarse fraction. In the fine fraction one PAH (acenaphtene) and one traffic tracer (abb-20R-cholestane) are higher than twice the average. All the measured average concentrations at the Badhoevedorp site are within the used limits (0.33 – 2.0 site average). For Sassenheim the elements Sr, Ba, Pb, Mg, Na and K and the PAH 2,3,5-trimethylnaphtalene are found to be high in the fine mode whereas NH_4 and Cl are high in the coarse mode.

- For the Dordrecht site only Ni and biphenyl are high in the coarse mode. For Hendrik-Ido-Ambacht Zn is higher than twice the average in both the fine and coarse mode.

- For the Ost Bahnhof site in Munich Mo is high whereas Sr, V and Cl are lower than 33% of the average in the fine mode. For the coarse mode the concentrations of the elements Mo, Sb, Cr, Fe and Cu are high. When the PAH concentrations of Swedish site Lycksele are excluded from the calculation of averages the PAHs – phenantrene, anthracene, 1-methylphenantrene, fluoranthene and pyrene are high in both the fine and coarse mode for the Ost Bahnhof site.

- For the Grosshadern hospital site in Munich the elements Cl, V, La, Ba and Sr are low in the fine mode and Ca as well as acenaphtene and anthracene are high in the coarse mode.

- Lycksele is characterised by extremely high concentrations of the nearly all PAHs in both the fine and coarse modes. Along high concentrations of K in the coarse mode the concentrations of Sb, La, Ca, V, Cr and Fe are low in the fine mode.

It is difficult to give some general conclusions from this data but some observations are obvious just by observing the data without using source apportionment methodologies.

- The frequent use of wood burning for domestic heating in the small town of Lycksele, during a period of cold weather with tendency to inversion, most likely caused the high concentrations of PAHs. The high concentration of K(a vegetation-burning tracer) supports the conclusion that particulate matter for a major part originates from vegetation burning.
- The high concentrations of some of the PAHs at the Amsterdam, Sassenheim and both Munich sites might be related to traffic. Other high elemental concentrations at these sites might be related to tail pipe emissions (V, Cr, Fe and possibly Sr, La, Ba).
- Noticeable are the high concentrations at the Munich Ost Bahnhof site for Mo, Cu, Cr, Sb and Fe. Based on the available data a rough indication for a source type can be given: railway activities are likely to contribute to these high metal levels, in particular Fe and Cu. It is also likely that these are all in the oxidized form (Fe_2O_3 etc.).
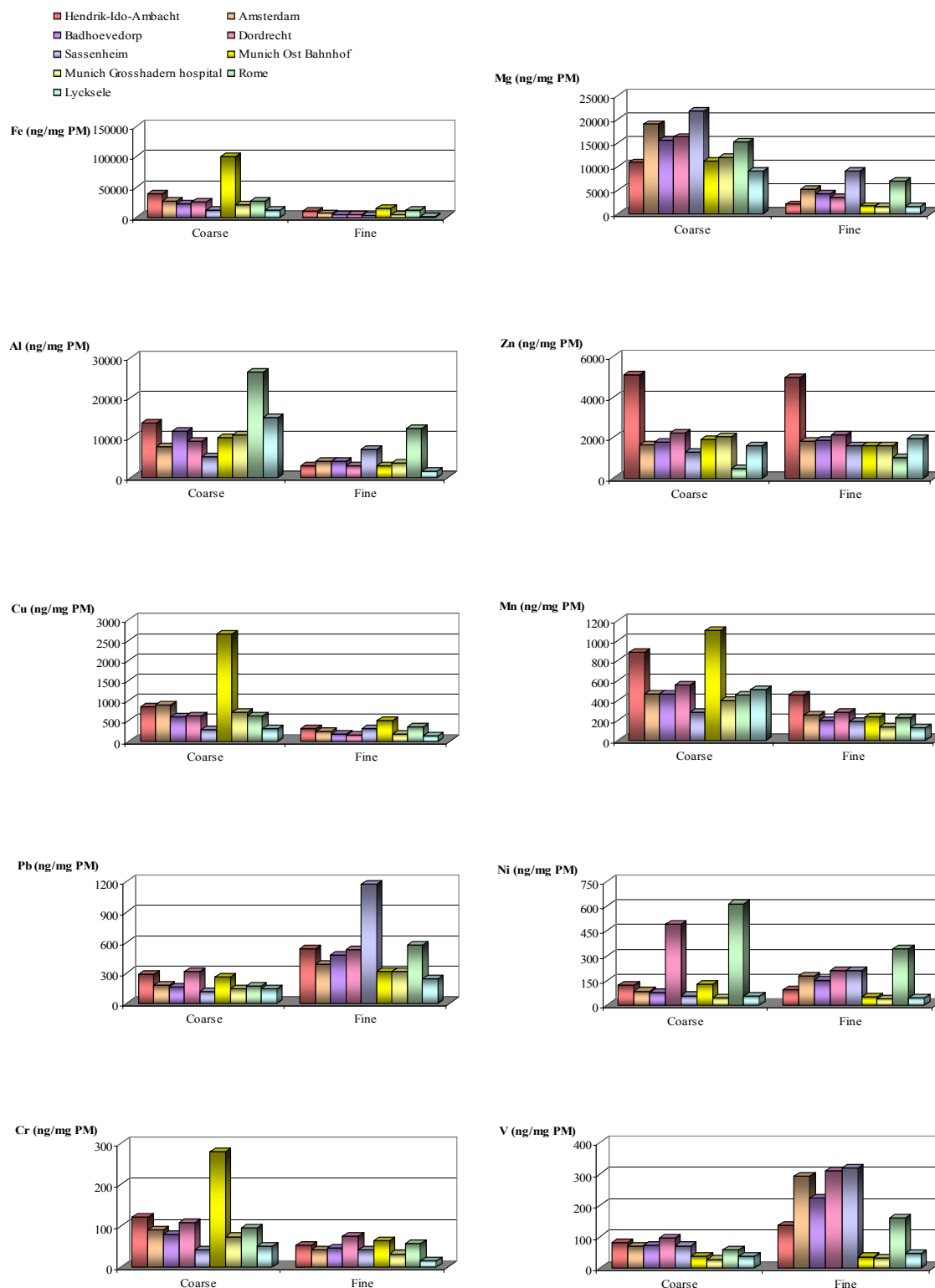
Figure 3.1 Average transition metal contents of PM per site from HEPMEAP locations.[1]

---

[1] Mean values for Zn, Ni and Cu include data below the detection limit and that are set as 2/3 of this limit see Appendix 2
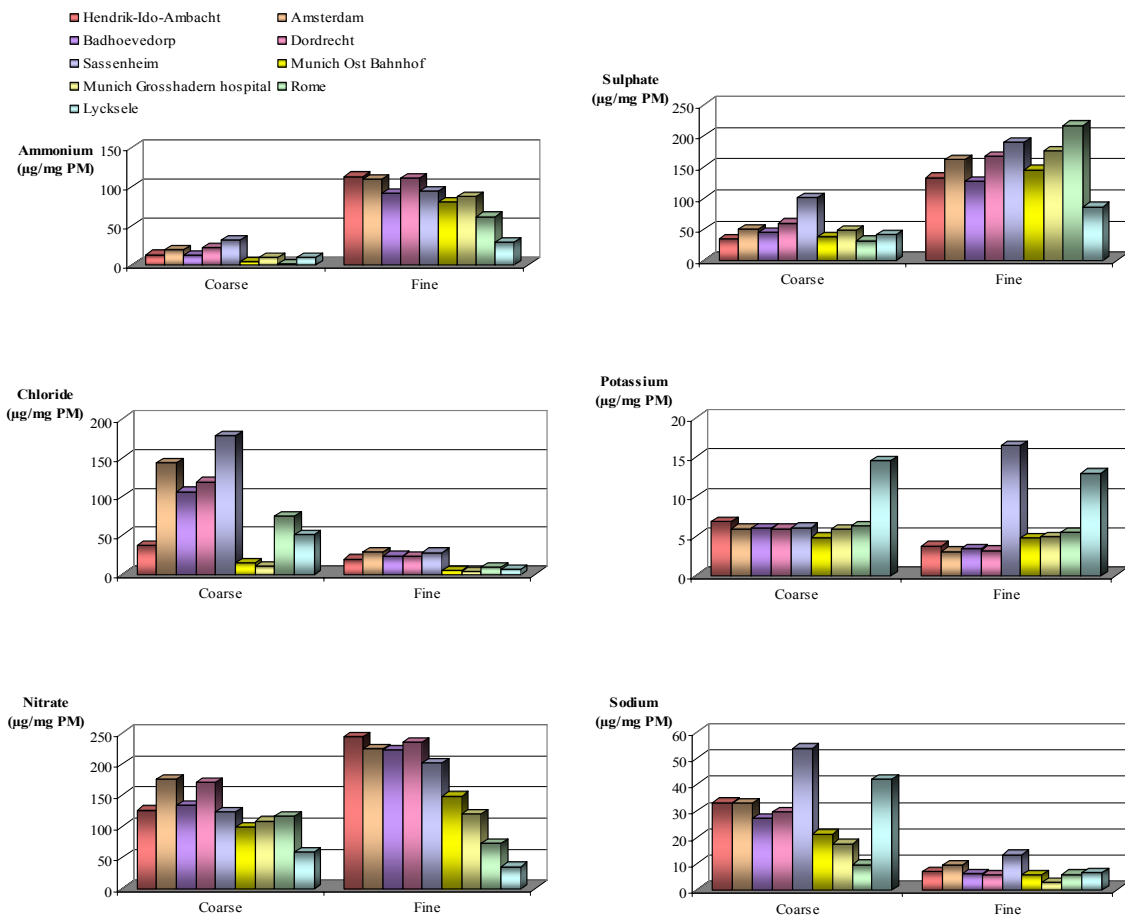
Figure 3.2 Average inorganic contents of PM per site from HEPMEAP locations.
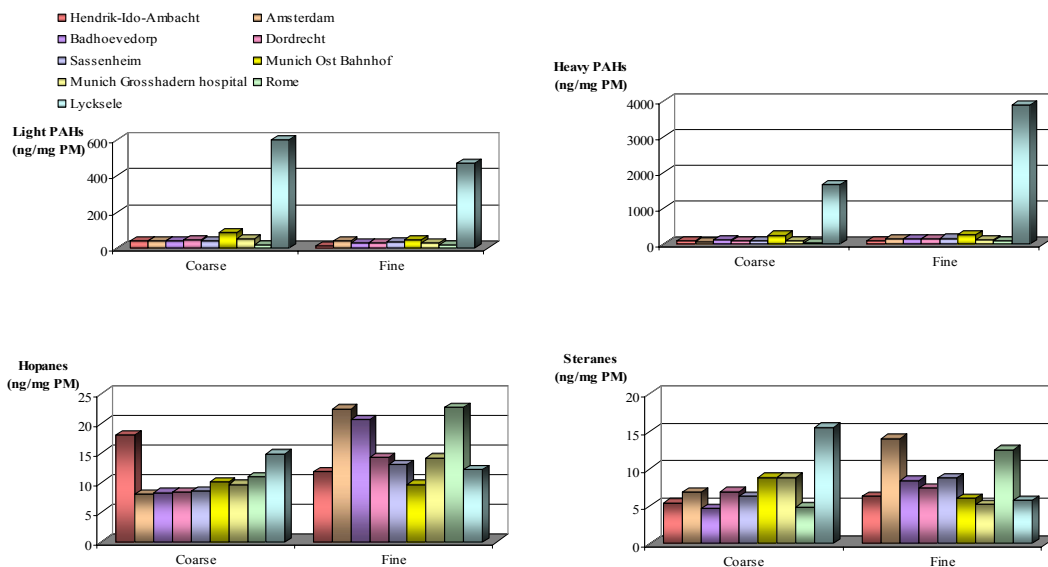
Figure 3.3 Average organic contents of PM per site from HEPMEAP locations[2].

---

[2] Mean values include data below the detection limit and that are set as 2/3 of this limit see Appendix 2.
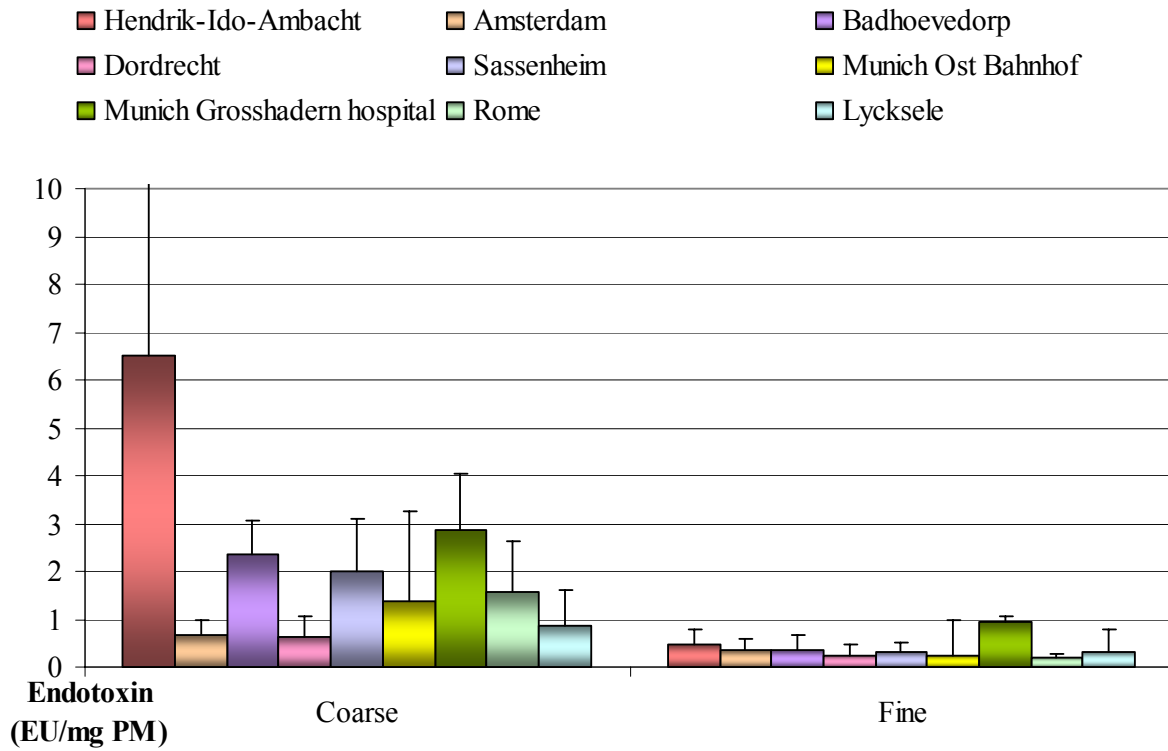
Figure 3.4 Average endotoxin contents of PM per site from HEPMEAP locations.

3.5   Source contributions

As mentioned before, the dataset of this project does not allow the use of source apportionment methodologies. To arrive at some indication of the contribution of the major sources the following approach is followed:

3.5.1   Secondary inorganic aerosol (SIA)

SIA consists of the mass of the ammonium sulphate and nitrate. In particular for ammonium nitrate the sample integrity when applying the pre-treatment procedure has not been optimized. Furthermore the amount of ammonium hydrogen sulphate compared to ammonium sulphate is not known and for assessing the relative contribution not relevant. Another relevant source for sulphate is sea spray salt, on mass base it contains 25% of the mass of Na. Hence:

$$SIA = NH_4 + [\, SO_4 - SO_{4,\,SS}\,] + NO_3$$

3.5.2   Sea Spray Salt (SS)

Assuming that SS is the only source for Na the total mass contribution of SS can be assessed. This assumption does not hold when de-icing salt is used. The mass contribution is based on the following composition (Na : Cl : SO_4 : Mg : K : Ca = 1 : 1.79 : 0.25 : 0.12 : 0.036 : 0.037) covering the major part of SS.

3.5.3   Crustal material (CRM)

CRM consists of Si , Al, Ca, Fe, K, Mn and a suite of other elements. Crustal material will vary in composition with the sites and so a single tracer not modified by other sources or activities needs to be used. As the sample has been in contact with glass the Si content might be overestimated. Ca might be added to enrich the soil at agricultural areas. Fe, K and Mn will also be part of profiles of other sources, in a mineral form or just as e.g. chloride. Hence Al is used as the tracer although this might also originate form traffic emissions but to a negligable rate. The following composition is used:

Al : Ca : Cl : Fe : K : Mn : Si : Ti = 1 : 0.38 : 0.01 : 0.65 : 0.15 : 0.01 : 2.95 : 0.06. This composition is derived from the source profiles published in the Speciate database of US.EPA. All these elements explain 42% of the total mass of CRM and a correction factor is applied to take into account the oxygen content.

3.5.4   Traffic (TR)

SIA, SS and CRM explain 46% (39% and 59%, 25 and 75 percentile) of the mass. It is assumed that the remaining part is due to the contribution of traffic and a number of other sources. If this assumption holds the regression graph of the remaining portion of the mass on a traffic tracer will give a scatter plot where a linear relation can be defined letting (most of) the data points having a positive addition to the explained part (SIA + SS + CRM). The regression coefficient is the multiplication factor for the tracer to arrive at the traffic

contribution. As the crustal material has already been defined, the traffic contribution does not include the resuspension of dust as far as this consists of crustal material like particles. The concentration of the hopanes and steranes is different for the fine and the coarse mode and so is the optimum use of the concentration data of each of the traffic tracers in order to minimize the uncertainty.

For the coarse mode the compound with the highest concentration (hopane :17a(H)-21b(H)-Hopane) is used . For the fine mode the sum of the six traffic tracers (HS) is used. Using the regression graph as described above the equation for the traffic contribution to the coarse mode is $TR_{coarse} = 36000$ x hopane + 14800. For the fine mode this equation is $TR_{fine} = 5600$ x HS + 30000. This report will not discuss traffic contributions in more details. This is the topic of a paper entitled 'High and low volume sampling of particulate matter at sites with different traffic profiles in the Netherlands and Germany: results from the HEPMEAP study' (Janssen et al, 2005).

3.5.5 Others (including wood smoke)

The limited number of samples, the applied assumptions and the uncertainty in the used profiles does not permit more apportionment and hence the remaining part (1 – [SIA + SS + CRM + TR) is the sum of all the other source contributions. The average source contribution calculated with the above-described procedures is given in Figure 3.5 and 3.6 (pie-charts). The calculation included correction for deviation from 100%, including proportional reduction of all source contributions if the sum of all except 'Others' exceeded already 100%.

For some (mostly the Dutch sites) the sum of the contributions exceeded the total mass. This might be caused by the overestimation of the assumed profiles. In the pie-charts this is corrected for proportionally over the contributions. The raw data per collected PM samples (coarse, fine) from each site are listed in Appendix 3.

3.5.6 Synthesis

High contributions of one source will automatically reduce the percentage contribution of other sources. The source estimates should be judged with this comment in mind.

The composition of the coarse mode collected at urban sites in the Netherlands and in Germany shows only moderate variation. At the Dutch sites the contribution of secondary inorganic aerosol and sea salt are slightly higher than at the German sites whereas the contribution of traffic and other sources are slightly higher at the German sites. The contribution of crustal material is more or less the same at all urban sites (12%). The contribution of traffic in the Hendrik-Ido-Ambacht samples and Lycksele samples are higher than at the urban sites, 60% and 46% due to the nearby traffic tunnel and the low impact of other sources, respectively.

The fine mode shows more variation for some of the source contributions. Sea salt is for obvious reason (proximity to the sea) less in the German samples (averages of 9 and 3% respectively for the Dutch and German samples), which is a larger difference than for the coarse mode (15% and 12%, respectively). As argued before, this comparison should also take into account the absolute contribution of other sources. The relative contribution of traffic is higher in the Netherlands samples than in the German ones whereas the contribution of other sources in the Dutch samples is almost negligible (2%) and in the German sample account for a quarter (26%). In particular the Ost Bahnhof site is also dominated by railway activities which partially are included in the traffic source estimate. In the Dutch samples no contribution of other sources could be calculated due to the overestimation of one or more of the named sources, possibly traffic.
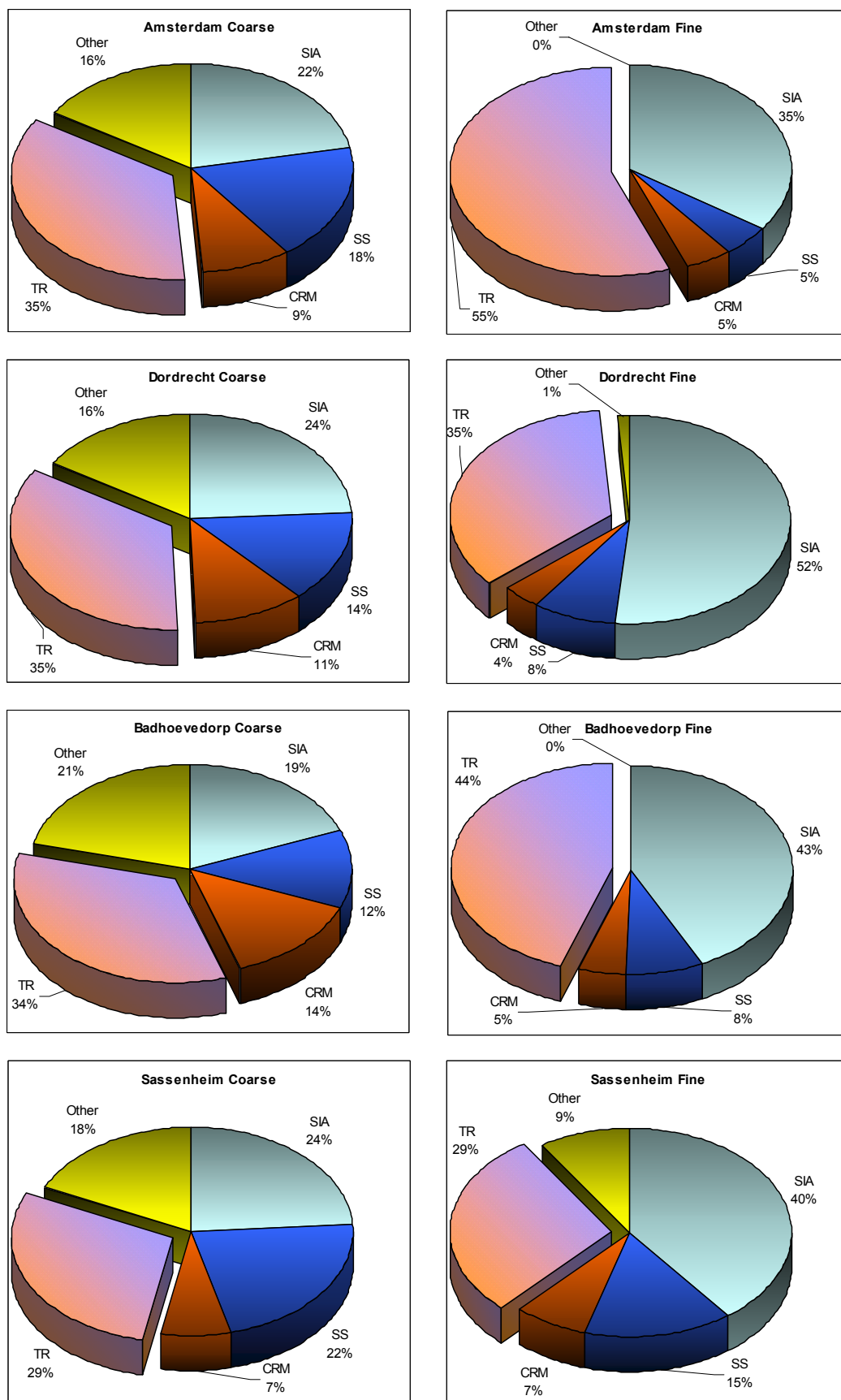
Figure 3.5 Average source contributions for the Dutch HEPMEAP sites
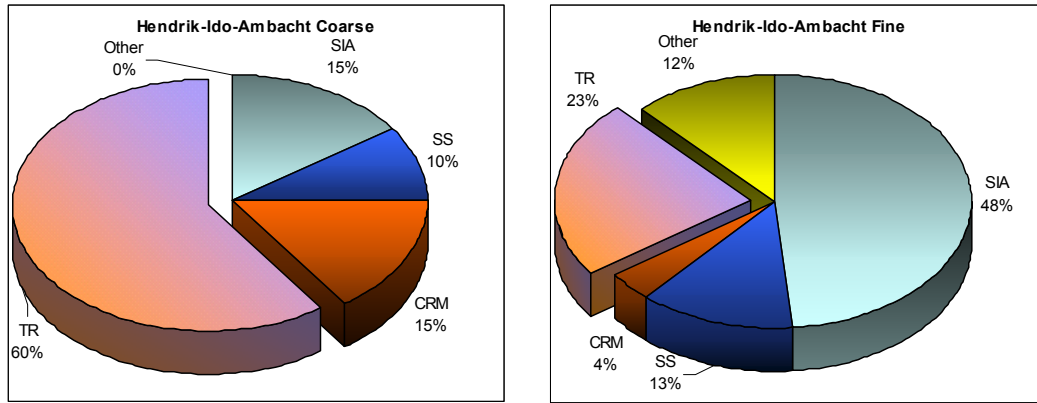
Figure 3.5 Average source contributions for the Dutch HEPMEAP sites (continued)
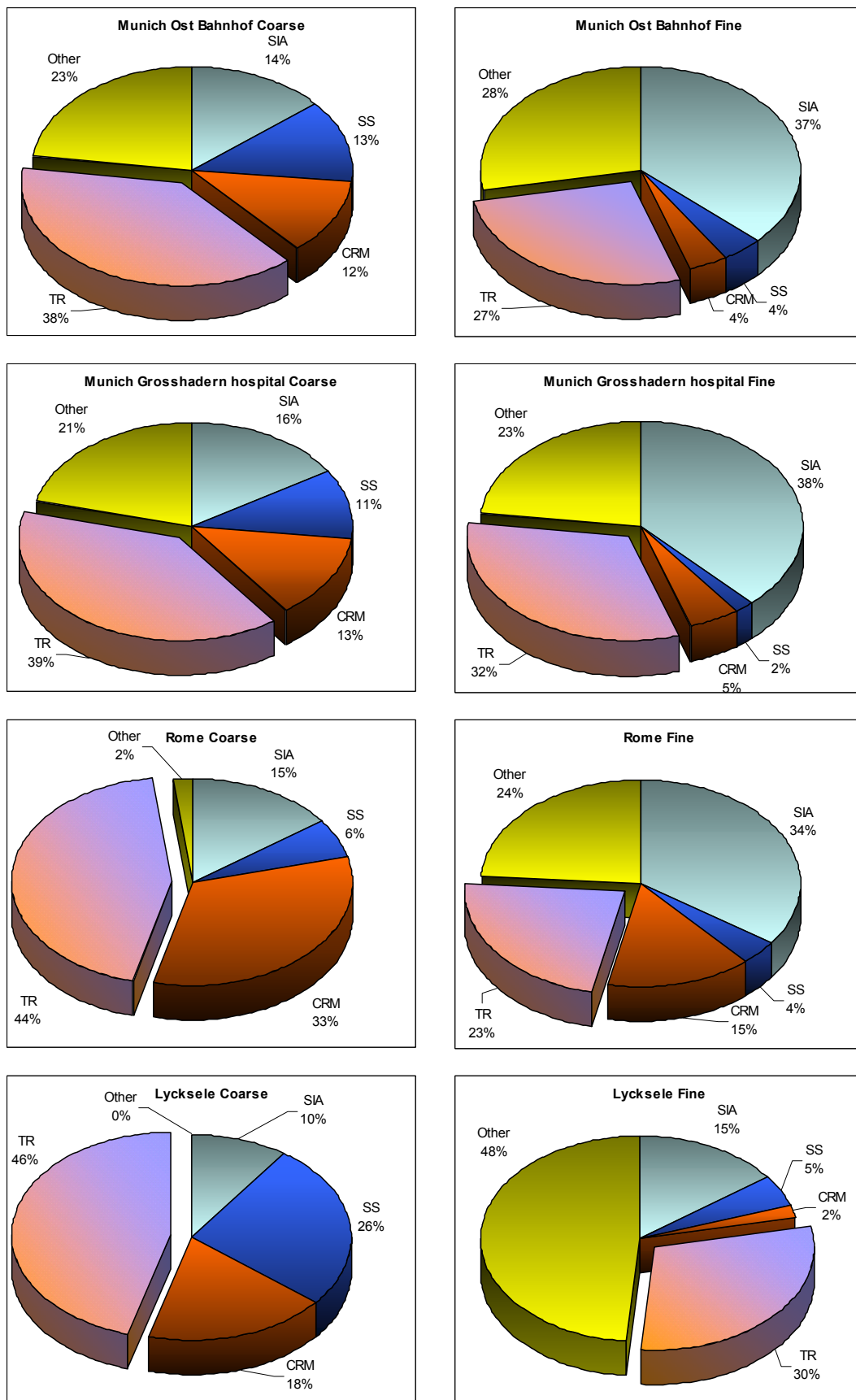
Figure 3.6 Average source contributions HEPMEAP sites in Germany, Italy and Sweden

4.   Conclusions

Over a period of approximately one year samples of ambient particulate matter were successfully collected at a number of sites. This material was collected to test its toxicological potential in a number of *in vitro* and *in vivo* bioassays. In this report, we focus on the chemical composition. A large number of elements and a more limited number of organic compounds were measured along with ions originating from atmospheric reactions and sea spray material.

The main observation is the close resemblance of the composition of material collected at the various sites that are different in terms of traffic intensity and other characteristics. Despite this, some sites (or samples) show distinct differences compared to other sites, for example:

- Samples taken at the Ost Bahnhof site in Munich appear to have much higher metal contents (Fe, Cu, Mn etc) than other locations.
- Potassium, an element that suggests high wood smoke contents was high in Lycksele.
- Typical sea spray elements as Na and Cl are higher in the Netherlands compared to the other locations.

In particular near traffic roads contributions from other sources than tailpipe emissions will vary in the coarse as well as in the fine mode. Nevertheless, the chemical characterization, different in some of the relative concentrations of some parameters (elements, organics or ions) is expected to further the understanding of sources that cause the effects to be found in the suite of biological tests. By the rough estimations of source contributions we could confirm that traffic was often a major contributor to the collected PM and that this effect was by percentage more present in the fine compared to the coarse fraction. The analysis also revealed that in line with the expectations, crustal material is present in the coarse fraction, whereas it is only a minimal fraction in the fine part of PM. It is very likely that the large portion of 'Other' fraction in Lycksele is dominated by PM originating from wood combustion as it was a major source of emissions during the collection campaign.

References

Cassee FR, Fokkens PHB, Leseman DLAC, Bloemen HJTh, Boere AJF (2003)**.** Respiratory Allergy and Inflammation Due to Ambient Particles (RAIAP) Collection of Particulate Matter samples from 5 European sites with High Volume Cascade Impactors - Onderzoeksrapport - RIVM rapport 863001001**.** http://www.rivm.nl/bibliotheek/rapporten/863001001.pdf

Demokritou P, Gupta T, Ferguson S, Koutrakis P (2002). Development and laboratory performance evaluation of a personal cascade impactor. *J Air Waste Manag Assoc* 52: 1230-1237.

Douwes J, Versloot P, Hollander A, Heederik D, Doekes G (1995). Influence of various dust sampling and extraction methods on the measurement of airborne endotoxin. *Appl Environ Microbiol* 61: 1763-1769.

Frew AJ, Salvi S, Holgate ST, Kelly F, Stenfors N, Nordenhäll C, Blomberg A, Sandström T (2001). Low concentrations of diesel exhaust induce a neutrophilic response and upregulate IL-8 mRNA in healthy subjects but not in asthmatic volunteers. *Int Arch Allegry Immunol* 124 (1-3): 324-325.

Janssen NAH, Meliefste K, Fuchs O, Weiland SK, Cassee FR, Brunekreef B, Sandström T. High and low volume sampling of particulate matter at sites with different traffic profiles in The Netherlands and Germany: Results from the HEPMEAP study. In preparation.

Kavouras IG and Koutrakis P (2001). Use of polyurethane foam as impaction substrate/collection medium in conventional inertial impactors. *Aerosol Sci Technol* 34: 46–56.

Salonen RO, Pennanen AS, Halinen AI, Hirvonen M-R, Sillanpaa M, Hillamo R, Karlsson V, Koskentalo T, Aarnio P, Ferguson ST, Koutrakis P (2000). A chemical and toxicological comparison of urban air PM10 collected during winter and spring in Finland. *Inhal Toxicol* 12:95–104.

Salvi S, Blomberg A, Rudell B, Kelly FJ, Sandström T, Holgate ST, Frew AJ (1999). Acute inflammatory response in the airways and peripheral blood following short term exposure to diesel exhaust in healthy human volunteers. *Am J Respir Crit Care Med* 159:702-709.

Stenfors N, Nordenhall C, Salvi SS, Mudway I, Soderberg M, Blomberg A, Helleday R, Levin JO, Holgate ST, Kelly FJ, Frew AJ, Sandström T (2004). Different airway inflammatory responses in asthmatic and healthy humans exposed to diesel. *Eur Respir J* 23: 82-86.

Acknowledgement

Appendices

Appendix 1 Abbreviations elements

Abbreviation	Full name	Abbreviation	Full name
Li	lithium	Sc	scandium
Be	beryllium	Ti	titanium
Sr	strontium	V	vanadium
Mo	molybdenum	Cr	chromium
Cd	cadmium	Mn	manganese
Sb	antimony	Fe	iron
Ba	barium	Co	cobalt
La	lanthanum	Ni	nickel
Ce	cerium	Cu	copper
Nd	neodymium	Zn	zinc
Sm	samarium	Na	sodium
Hf	hafnium	K	potassium
Hg	mercury	As	arsenic
Tl	thallium	Se	selenium
Pb	lead	NH4	ammonium
U	uranium	Cl	chloride
Mg	magnesium	NO3	nitrate
Al	aluminum	SO4	sulphate
Si	silicon	Br	bromide
Ca	calcium	Rh	rhodium

Appendix 2 Chemical composition data

NOTE:
1) All measurements are given in ng/mg of PM retrieved from the collection substrate, with the exception of endotoxin, which is listed as EU/mg PM.
2) For values lower than the detection limit, 2/3 (67%) of the detection limit is used as value. These values are printed in italics.
3) The values of the elements Be, Sm, Co, As, Se, and Br were substantial lower than the detection limit and were not reported.
4) 'Not determined' (ND) is noted whenever a component could not be measured due to resolution issues.

Table A Sample ID	Location City/site	Country	Period Start	Finish	Mode Coarse Fine	Mass (mg)	Time (days)	Volume (m3)
1	Munich, Grosshadern	Germany	19-Apr-02	03-May-02	C	75.3	12.96	16790
2	Munich, Grosshadern	Germany	19-Apr-02	03-May-02	F	88.1	12.96	16790
3	Munich, Grosshadern	Germany	03-May-02	17-May-02	C	106.7	13.40	17361
4	Munich, Grosshadern	Germany	03-May-02	17-May-02	F	80.9	13.40	17361
5	Munich, Grosshadern	Germany	14-Jun-02	28-Jun-02	C	159.9	11.70	15165
6	Munich, Grosshadern	Germany	14-Jun-02	28-Jun-02	F	124.8	11.70	15165
7	Munich, Grosshadern	Germany	28-Jun-02	12-Jul-02	C	57.3	11.78	15272
8	Munich, Grosshadern	Germany	28-Jun-02	12-Jul-02	F	65.0	11.78	15272
9	Munich, Grosshadern	Germany	16-Aug-02	30-Aug-02	C	72.7	14.00	18140
10	Munich, Grosshadern	Germany	16-Aug-02	30-Aug-02	F	98.0	14.00	18140
11	Munich, Grosshadern	Germany	30-Aug-02	13-Sep-02	C	76.8	14.01	18156
12	Munich, Grosshadern	Germany	30-Aug-02	13-Sep-02	F	107.8	14.01	18156
13	Munich, Grosshadern	Germany	18-Nov-02	02-Dec-02	C	62.2	13.79	17875
14	Munich, Grosshadern	Germany	18-Nov-02	02-Dec-02	F	103.1	13.79	17875
15	Munich, Grosshadern	Germany	02-Dec-02	16-Dec-02	C	94.4	13.94	18062
16	Munich, Grosshadern	Germany	02-Dec-02	16-Dec-02	F	209.8	13.94	18062
17	Munich, Ost Bahnhof	Germany	22-Mar-02	04-Apr-02	C	108.6	12.47	16165
18	Munich, Ost Bahnhof	Germany	22-Mar-02	04-Apr-02	F	208.1	12.47	16165
19	Munich, Ost Bahnhof	Germany	04-Apr-02	18-Apr-02	C	133.5	13.34	17288
20	Munich, Ost Bahnhof	Germany	04-Apr-02	18-Apr-02	F	208.2	13.34	17288
21	Munich, Ost Bahnhof	Germany	17-May-02	31-May-02	C	95.6	12.92	16748
22	Munich, Ost Bahnhof	Germany	17-May-02	31-May-02	F	82.7	12.92	16748
23	Munich, Ost Bahnhof	Germany	31-May-02	14-Jun-02	C	104.4	12.77	16553
24	Munich, Ost Bahnhof	Germany	31-May-02	14-Jun-02	F	84.3	12.77	16553
25	Munich, Ost Bahnhof	Germany	15-Jul-02	26-Jul-02	C	95.3	10.93	14165
26	Munich, Ost Bahnhof	Germany	15-Jul-02	26-Jul-02	F	90.6	10.93	14165
27	Munich, Ost Bahnhof	Germany	02-Aug-02	16-Aug-02	C	87.7	13.81	17899
28	Munich, Ost Bahnhof	Germany	02-Aug-02	16-Aug-02	F	90.5	13.81	17899
29	Munich, Ost Bahnhof	Germany	21-Oct-02	04-Nov-02	C	107.6	13.85	17954
30	Munich, Ost Bahnhof	Germany	21-Oct-02	04-Nov-02	F	95.5	13.85	17954
31	Munich, Ost Bahnhof	Germany	04-Nov-02	18-Nov-02	C	127.7	13.94	18060
32	Munich, Ost Bahnhof	Germany	04-Nov-02	18-Nov-02	F	112.5	13.94	18060
33	Lycksele	Sweden	23-Dec-02	27-Jan-03	C	44.3	19.81	25678
34	Lycksele	Sweden	23-Dec-02	27-Jan-03	F	133.0	19.81	25678
35	Lycksele	Sweden	02-Jan-03	17-Jan-03	C	33.2	14.86	19259
36	Lycksele	Sweden	02-Jan-03	17-Jan-03	F	113.9	14.86	19259
37	Lycksele	Sweden	27-Jan-03	12-Feb-03	C	41.9	16.04	20788
38	Lycksele	Sweden	27-Jan-03	12-Feb-03	F	108.9	16.04	20788
39	Lycksele	Sweden	28-Feb-02	27-Mar-02	C	62.9	26.74	34657
40	Lycksele	Sweden	28-Feb-02	27-Mar-02	F	118.5	26.74	34657
41	Rome	Italy	09-Jul-01	23-Jul-01	C	211.0	13.39	17351
42	Rome	Italy	09-Jul-01	23-Jul-01	F	163.5	13.39	17351
43	Rome	Italy	10-Apr-02	24-Apr-02	C	329.2	13.94	18068
44	Rome	Italy	10-Apr-02	24-Apr-02	F	268.8	13.94	18068

Table B Sample ID	Location City/site	Country	Period Start	Finish	Mode Coarse Fine	Mass (mg)	Time (days)	Volume (m3)
45	Amsterdam	The Netherlands	16-Nov-01	30-Nov-01	C	118.5	10.60	13742
46	Amsterdam	The Netherlands	16-Nov-01	30-Nov-01	F	99.9	10.60	13742
47	Amsterdam	The Netherlands	30-Nov-01	13-Dec-01	C	130.6	12.88	16690
48	Amsterdam	The Netherlands	30-Nov-01	13-Dec-01	F	139.8	12.88	16690
49	Amsterdam	The Netherlands	22-Feb-02	12-Mar-02	C	173.1	12.94	16772
50	Amsterdam	The Netherlands	22-Feb-02	12-Mar-02	F	99.4	12.94	16772
51	Amsterdam	The Netherlands	13-May-02	28-May-02	C	173.3	13.82	17912
52	Amsterdam	The Netherlands	13-May-02	28-May-02	F	95.6	13.82	17912
53	Amsterdam	The Netherlands	09-Jul-02	23-Jul-02	C	135.2	13.92	18045
54	Amsterdam	The Netherlands	09-Jul-02	23-Jul-02	F	96.4	13.92	18045
55	Badhoevedorp	The Netherlands	21-Jan-02	04-Feb-02	C	160.9	13.95	18085
56	Badhoevedorp	The Netherlands	21-Jan-02	04-Feb-02	F	94.1	13.95	18085
57	Badhoevedorp	The Netherlands	25-Mar-02	10-Apr-02	C	199.1	13.72	17782
58	Badhoevedorp	The Netherlands	25-Mar-02	10-Apr-02	F	278.2	13.72	17782
59	Badhoevedorp	The Netherlands	28-May-02	11-Jun-02	C	157.9	13.83	17919
60	Badhoevedorp	The Netherlands	28-May-02	11-Jun-02	F	104.1	13.83	17919
61	Badhoevedorp	The Netherlands	20-Sep-02	04-Oct-02	C	96.9	13.89	17998
62	Badhoevedorp	The Netherlands	20-Sep-02	04-Oct-02	F	107.0	13.89	17998
63	Dordrecht	The Netherlands	08-Feb-02	22-Feb-02	C	123.1	12.19	15804
64	Dordrecht	The Netherlands	08-Feb-02	22-Feb-02	F	86.8	12.19	15804
65	Dordrecht	The Netherlands	16-Apr-02	29-Apr-02	C	126.5	10.89	14118
66	Dordrecht	The Netherlands	16-Apr-02	29-Apr-02	F	157.5	10.89	14118
67	Dordrecht	The Netherlands	11-Jun-02	26-Jun-02	C	134.6	14.82	19206
68	Dordrecht	The Netherlands	11-Jun-02	26-Jun-02	F	113.5	14.82	19206
69	Dordrecht	The Netherlands	04-Oct-02	18-Oct-02	C	107.9	13.85	17954
70	Dordrecht	The Netherlands	04-Oct-02	18-Oct-02	F	138.9	13.85	17954
71	Hendrik-Ido-Ambacht	The Netherlands	27-Mar-02	11-Apr-02	C	184.0	14.81	19193
72	Hendrik-Ido-Ambacht	The Netherlands	27-Mar-02	11-Apr-02	F	477.5	14.81	19193
73	Hendrik-Ido-Ambacht	The Netherlands	04-Sep-02	18-Sep-02	C	113.6	13.96	18097
74	Hendrik-Ido-Ambacht	The Netherlands	04-Sep-02	18-Sep-02	F	181.6	13.96	18097
75	Sassenheim	The Netherlands	20-Dec-01	03-Jan-02	C	129.9	13.50	17494
76	Sassenheim	The Netherlands	20-Dec-01	03-Jan-02	F	85.4	13.50	17494
77	Sassenheim	The Netherlands	12-Mar-02	25-Mar-02	C	111.7	12.80	16583
78	Sassenheim	The Netherlands	12-Mar-02	25-Mar-02	F	130.6	12.80	16583
79	Sassenheim	The Netherlands	29-Apr-02	13-May-02	C	138.9	11.99	15535
80	Sassenheim	The Netherlands	29-Apr-02	13-May-02	F	130.6	11.99	15535
81	Sassenheim	The Netherlands	26-Jun-02	09-Jul-02	C	124.3	12.33	15983
82	Sassenheim	The Netherlands	26-Jun-02	09-Jul-02	F	69.1	12.33	15983
83	Diesel exhaust (chamber)	Sweden	01-Jul-02	02-Jul-02	F	37.1	0.37	481
84	Diesel exhaust (chamber)	Sweden	22-Nov-02	22-Nov-02	F	194.3	0.13	167
85	Diesel exhaust (chamber)	Sweden	25-Feb-03	26-Feb-03	C	114.8	0.92	1191
86	Diesel exhaust (chamber)	Sweden	25-Feb-03	26-Feb-03	F	801.2	0.92	1191
87	Gasoline exhaust (chamber)	Sweden	27-Feb-03	07-Mar-03	C	77.5	2.75	3559
88	Gasoline exhaust (chamber)	Sweden	27-Feb-03	07-Mar-03	F	123.9	2.75	3559

Table C Sample ID	Li	Sr	Mo	Cd	Sb	Ba	La	Ce	Nd	Hf	Hg	Tl	Pb	U
1	20.9	115.3	36.0	3.5	123.0	256.8	8.1	16.1	6.1	37.0	1.0	1.0	128.1	0.5
2	4.1	17.4	10.1	6.5	60.5	46.4	1.8	3.5	1.0	10.1	1.0	1.0	292.8	0.1
3	17.7	159.3	41.3	2.3	135.9	440.7	7.8	16.5	6.2	38.4	1.0	1.0	106.6	0.5
4	4.9	24.6	17.5	6.8	45.2	64.4	2.3	5.3	1.0	10.1	1.0	1.0	276.7	0.1
5	17.8	134.8	27.3	1.0	74.6	373.9	8.7	16.9	7.9	35.1	1.0	1.0	67.1	0.5
6	7.5	30.6	17.2	6.3	44.2	63.6	4.3	8.8	2.9	26.0	1.0	1.0	199.3	0.1
7	7.4	52.9	36.5	2.0	114.5	145.5	4.3	8.4	2.7	31.6	1.0	1.0	66.5	0.2
8	4.0	19.0	22.2	6.3	63.9	54.2	2.2	4.3	1.0	19.7	1.0	1.0	239.6	0.1
9	10.6	81.9	52.0	1.9	165.1	279.7	5.7	12.1	5.2	88.9	1.0	1.0	118.1	0.5
10	3.0	19.9	21.7	5.4	61.4	107.8	2.4	5.3	1.0	31.2	1.0	1.0	235.2	0.1
11	15.0	104.2	54.7	2.5	176.8	322.5	7.0	14.5	5.1	112.8	1.0	1.0	131.3	0.5
12	2.4	17.6	20.2	7.5	57.5	97.2	2.3	4.4	1.0	30.5	1.0	1.0	325.8	0.1
13	13.9	137.9	109.1	4.0	358.1	483.4	7.8	16.2	4.9	66.0	1.0	1.0	191.1	0.6
14	1.9	15.6	20.7	10.0	60.9	81.5	1.6	3.6	1.0	10.1	1.0	1.0	368.5	0.1
15	14.9	116.6	92.1	14.2	309.3	438.8	6.9	17.7	4.6	54.0	1.0	1.0	325.3	0.7
16	4.1	10.1	10.1	14.0	47.2	58.6	1.0	2.2	1.0	10.1	1.0	1.7	550.2	0.1
17	16.2	102.6	270.7	4.7	492.5	619.8	8.6	23.5	5.8	133.8	1.0	1.0	237.8	0.5
18	3.7	10.1	36.0	10.2	71.1	62.8	1.0	3.6	1.0	19.9	1.0	1.0	295.4	0.1
19	17.4	109.1	258.3	4.6	509.3	653.3	8.7	19.4	7.3	125.7	1.0	1.0	246.8	0.6
20	4.3	10.1	40.8	10.1	77.4	81.3	1.5	3.6	1.0	23.1	1.0	1.0	320.4	0.1
21	12.2	85.3	294.7	2.7	576.8	671.3	5.9	16.4	3.4	129.3	1.0	1.0	234.0	0.3
22	7.8	18.7	70.5	6.6	136.2	131.3	2.6	6.3	1.0	49.2	1.0	1.0	266.9	0.1
23	12.5	93.7	275.5	2.6	588.3	650.0	8.5	16.4	4.5	126.0	1.0	1.0	215.3	0.4
24	5.6	26.0	81.2	7.3	155.9	154.9	3.4	6.3	1.0	56.9	1.0	1.0	280.4	0.1
25	9.5	102.5	297.0	2.5	805.1	959.5	6.8	18.4	3.7	135.9	1.0	1.0	312.2	0.4
26	3.8	17.5	80.6	7.0	194.6	227.5	3.0	7.4	1.0	32.7	1.0	1.0	350.6	0.4
27	8.8	93.3	337.5	2.8	777.3	921.8	7.4	18.8	3.9	146.9	5.4	1.0	262.9	0.4
28	2.6	25.9	76.4	6.5	161.9	230.5	3.2	7.1	1.0	33.6	1.0	1.0	292.9	0.1
29	12.2	118.9	296.2	3.4	799.6	856.2	6.1	17.6	3.7	119.5	1.0	1.0	272.1	0.4
30	3.9	25.0	69.5	7.3	159.5	175.2	2.4	6.8	1.0	25.3	1.0	1.0	311.6	0.1
31	19.1	146.2	336.6	2.9	799.1	940.1	9.8	26.8	7.3	135.8	1.0	1.0	282.5	0.6
32	7.5	23.0	74.9	10.1	171.1	194.4	2.9	8.1	1.0	27.3	1.0	1.0	361.6	0.1
33	13.6	165.0	20.8	3.5	79.3	655.6	9.3	20.6	7.4	35.3	1.0	1.0	178.9	0.8
34	4.5	167.4	10.1	10.2	18.8	633.8	1.0	2.2	1.0	10.1	1.0	1.0	387.9	0.1
35	12.4	103.6	16.8	5.2	85.8	263.8	7.6	15.5	5.9	29.4	2.0	1.0	132.6	0.7
36	2.7	10.1	10.1	10.1	8.2	47.4	1.0	1.5	1.0	10.1	1.0	1.0	119.9	0.1
37	18.4	95.7	17.5	5.5	57.7	311.1	13.3	27.2	10.4	41.0	1.0	1.0	162.3	1.2
38	4.6	10.1	10.1	12.1	15.0	46.8	1.0	3.0	1.0	10.1	1.0	1.0	285.6	0.1
39	21.5	81.9	10.1	2.8	34.7	170.6	12.6	28.6	10.7	59.4	1.0	1.0	81.7	1.4
40	3.6	17.6	10.1	9.9	14.2	31.4	1.0	3.4	1.0	10.1	1.0	1.0	168.8	0.1
41	19.8	220.1	58.0	1.0	181.1	370.8	22.4	46.5	17.0	144.3	1.0	1.0	232.8	1.1
42	9.6	68.2	38.4	9.3	219.3	149.5	7.7	16.5	5.6	48.4	1.0	2.8	784.2	0.3
43	35.8	246.6	50.1	1.8	144.8	350.4	21.3	46.1	17.5	122.9	1.0	1.0	105.8	0.9
44	17.8	88.9	28.9	10.3	121.0	123.7	9.2	20.5	7.2	50.8	1.0	2.0	364.2	0.3

Elements

Table D Sample ID	Elements													
	Li	Sr	Mo	Cd	Sb	Ba	La	Ce	Nd	Hf	Hg	Tl	Pb	U
45	17.2	127.7	172.3	6.3	506.1	759.8	119.1	38.3	7.4	123.5	1.0	1.0	316.1	0.7
46	4.6	28.5	43.5	12.3	118.6	150.6	54.4	13.3	2.0	32.0	1.0	3.2	537.4	0.1
47	10.1	119.0	101.0	5.1	297.8	468.8	59.7	18.0	5.2	137.9	1.0	1.0	240.9	0.4
48	4.7	15.7	26.0	8.2	69.8	88.8	23.6	6.3	1.0	57.8	1.0	1.6	415.5	0.1
49	11.1	121.9	55.9	3.1	172.7	266.8	7.0	10.6	3.0	43.3	1.0	1.0	110.9	0.2
50	5.0	38.1	30.0	11.2	95.5	116.6	3.2	3.0	1.0	20.8	1.0	2.9	324.0	0.1
51	14.5	109.5	67.9	5.7	199.4	312.8	35.0	15.4	4.9	51.6	1.0	1.0	233.7	0.4
52	4.8	34.1	30.7	12.0	74.1	70.6	24.4	5.5	1.0	20.1	1.0	2.3	264.6	0.1
53	8.9	87.9	55.9	2.8	207.6	355.5	10.6	10.0	3.1	74.8	1.0	1.0	114.2	0.4
54	2.3	25.3	23.6	7.7	79.8	109.3	5.0	3.6	1.0	38.5	1.0	1.6	277.4	0.1
55	10.5	130.2	33.2	3.3	104.3	128.4	8.5	7.3	2.3	23.4	1.0	1.0	112.1	0.2
56	5.7	53.6	22.8	13.0	70.8	71.3	4.6	3.5	1.0	15.5	1.0	2.5	404.8	0.1
57	33.1	144.3	63.8	6.1	130.4	301.0	42.6	34.5	12.2	61.9	1.0	1.0	211.0	0.9
58	4.8	15.2	17.2	11.6	40.0	41.8	9.9	4.6	1.0	10.1	1.0	1.0	343.4	0.1
59	15.2	94.0	46.9	2.9	114.6	205.9	26.9	14.5	5.1	38.5	1.0	1.0	115.7	0.3
60	6.2	23.3	31.8	11.5	62.9	57.6	16.9	4.9	1.0	19.8	1.0	3.1	423.7	0.1
61	11.9	114.2	91.9	5.6	313.7	551.9	24.4	18.6	5.2	72.5	1.0	1.0	205.2	0.5
62	3.9	17.2	35.9	15.9	131.4	138.6	13.0	5.9	1.0	16.4	1.0	2.6	709.7	0.1
63	14.4	99.5	39.0	3.5	98.8	214.1	7.5	10.3	3.0	35.7	1.0	1.0	248.1	0.2
64	6.9	38.3	23.8	14.1	47.5	62.3	3.3	3.4	1.0	10.1	1.0	5.1	506.4	0.1
65	17.8	84.1	50.6	6.1	156.5	306.4	12.6	15.9	5.0	47.2	1.0	1.0	166.6	0.4
66	3.2	10.1	10.1	8.5	42.8	42.0	2.6	2.6	1.0	10.1	1.0	2.1	269.0	0.1
67	15.2	85.5	58.6	6.5	177.9	329.9	15.7	17.3	5.5	53.7	1.0	1.0	387.5	0.5
68	7.1	17.7	29.3	24.2	83.4	59.1	4.1	3.7	1.0	16.8	1.0	6.3	629.0	0.1
69	17.6	119.9	63.4	13.7	199.6	437.8	16.6	18.6	6.2	55.6	1.0	1.0	435.2	0.7
70	8.5	17.4	27.3	19.1	65.8	83.6	3.3	2.9	1.0	10.1	2.9	3.7	710.9	0.1
71	25.1	118.0	59.4	6.8	172.7	439.1	16.1	28.3	10.5	90.8	1.0	1.0	355.9	0.7
72	6.5	16.4	23.8	12.6	55.7	70.7	3.0	3.9	1.0	20.4	1.0	2.3	493.0	0.1
73	15.4	123.5	67.7	6.3	219.8	620.8	16.0	21.0	7.3	156.5	1.0	1.0	223.6	0.6
74	6.2	30.2	48.2	11.7	117.3	230.0	6.6	5.9	1.0	58.3	1.0	2.5	575.5	0.1
75	7.2	165.7	10.1	2.3	43.8	352.3	7.1	4.9	1.0	17.2	1.0	1.0	107.9	0.1
76	5.2	2,302.4	18.7	13.7	102.7	8,282.3	8.2	5.4	1.0	15.8	1.0	8.3	3,545.4	0.1
77	10.6	75.2	33.6	3.1	113.4	206.4	10.9	11.3	3.1	32.4	1.0	1.0	131.9	0.3
78	3.3	15.7	10.1	8.9	46.1	52.9	3.0	2.5	1.0	10.1	1.0	1.9	334.6	0.1
79	11.2	73.3	21.7	3.7	68.3	178.2	13.5	9.3	3.4	25.1	1.0	1.0	131.7	0.3
80	3.7	10.1	10.1	7.3	25.1	42.3	5.4	2.2	1.0	10.1	1.0	1.5	309.8	0.1
81	10.0	102.0	25.6	2.6	65.0	159.4	11.5	8.9	3.3	20.5	1.0	1.0	90.6	0.3
82	4.2	23.2	15.7	13.2	56.1	63.5	6.1	3.2	1.0	10.1	1.0	2.4	486.8	0.1
83	1.0	10.1	10.1	1.0	1.0	16.0	1.0	1.0	1.0	10.1	4.0	1.0	16.8	0.1
84	1.0	10.1	10.1	1.0	1.0	10.1	1.0	1.0	1.0	10.1	1.0	1.0	10.1	0.1
85	1.0	10.1	10.1	1.0	1.0	31.5	1.0	1.0	1.0	10.1	1.0	1.0	10.1	0.1
86	1.0	10.1	10.1	1.0	1.0	23.1	1.0	1.0	1.0	10.1	1.0	1.0	10.1	0.1
87	1.0	10.1	10.1	1.0	1.0	17.4	1.0	6.1	1.0	10.1	1.0	1.0	19.9	0.1
88	1.0	10.1	10.1	1.0	1.0	10.1	1.0	1.9	1.0	10.1	1.0	1.0	10.1	0.1

Table E Sample ID	Elements												
	Mg	Al	Si	Ca	Sc	Ti	V	Cr	Mn	Fe	Ni	Cu	Zn
1	13,717	13,799	25,672	52,171	23.4	390	32.1	60.3	376	16,341	54.0	296	2,021
2	1,989	3,669	5,756	3,105	4.2	76	36.5	28.7	117	3,423	46.6	101	1,872
3	18,971	14,457	24,866	96,468	24.0	361	27.6	67.0	448	19,129	51.7	371	1,417
4	2,160	4,432	7,015	8,017	6.2	95	27.7	33.4	156	4,991	52.5	101	1,793
5	17,111	15,384	24,423	94,462	36.4	340	36.3	54.4	503	19,747	44.9	294	996
6	2,529	7,390	13,707	6,737	10.5	169	56.2	31.2	169	6,249	57.0	101	1,200
7	6,756	6,564	12,163	27,051	12.1	183	17.5	52.6	270	12,558	25.1	477	2,754
8	1,544	3,274	4,885	3,713	2.3	61	34.1	34.1	135	4,360	45.4	176	1,413
9	7,180	7,563	20,740	42,557	14.1	196	18.4	52.2	276	18,370	25.1	786	1,281
10	994	3,312	6,745	4,008	1.6	47	24.6	23.2	110	5,174	25.1	241	1,115
11	9,354	8,844	25,517	53,200	15.6	283	22.1	63.9	311	21,271	25.1	742	2,012
12	1,192	3,268	6,695	4,568	1.0	50	25.5	25.3	139	4,743	25.1	205	1,447
13	12,278	9,734	28,496	84,496	15.9	343	27.8	114.3	535	30,396	72.0	1,456	3,411
14	866	2,635	6,417	4,496	1.0	25	15.0	50.8	130	4,055	25.1	264	2,310
15	10,086	9,687	27,939	67,106	15.5	332	41.4	126.7	506	29,223	74.1	1,185	2,441
16	503	1,892	2,513	2,623	1.0	25	32.1	28.9	130	3,063	42.6	198	1,639
17	12,415	13,546	26,445	45,418	22.5	470	47.5	281.1	1,402	115,096	156.3	1,983	1,956
18	947	2,075	2,513	2,091	2.6	50	30.6	34.1	194	9,921	44.6	200	1,501
19	12,975	12,408	22,635	54,779	25.7	419	46.9	257.1	1,263	107,338	142.2	1,921	1,577
20	1,099	2,659	4,458	2,877	3.8	81	42.6	40.2	203	11,408	43.3	268	1,342
21	9,647	7,646	17,382	36,179	11.7	250	32.7	275.0	1,021	99,365	137.7	2,386	1,828
22	1,478	1,761	5,240	3,223	1.8	52	26.7	60.6	240	15,920	59.6	457	1,711
23	11,774	9,167	18,416	43,771	15.8	291	37.7	286.7	1,121	107,074	139.8	2,540	1,862
24	2,282	2,909	5,912	4,563	3.5	66	33.3	84.9	313	20,477	76.4	526	2,067
25	8,990	6,697	23,304	49,196	11.4	262	32.4	296.7	1,002	95,959	115.2	3,130	2,138
26	1,234	1,909	6,177	4,390	1.0	63	43.8	68.9	253	16,569	42.9	645	1,952
27	7,886	7,495	22,556	45,114	12.0	262	34.6	301.5	1,085	107,013	122.8	3,156	2,105
28	1,090	3,465	6,787	4,058	1.0	67	48.6	58.8	216	16,298	37.9	585	1,280
29	11,827	7,251	22,346	46,554	10.9	229	32.1	241.5	829	75,923	99.4	2,959	2,044
30	3,076	4,928	7,866	5,222	1.0	53	39.2	68.7	214	12,681	49.9	605	1,464
31	13,527	15,753	43,062	71,082	25.2	445	42.8	294.3	1,091	97,498	116.5	3,175	1,907
32	1,875	4,434	8,786	6,230	2.8	93	29.1	96.9	254	16,088	46.0	734	1,601
33	9,155	11,388	36,308	11,276	17.1	517	31.8	44.0	618	11,807	48.1	432	839
34	1,795	1,512	3,998	1,005	1.0	54	41.0	19.1	114	1,340	25.1	210	1,935
35	11,414	11,177	36,826	12,767	15.1	471	25.9	48.9	561	10,468	43.1	339	3,847
36	1,151	831	2,513	1,005	1.0	42	16.8	10.1	67	875	25.1	101	1,854
37	5,730	18,096	57,614	13,843	27.6	795	62.8	55.4	483	14,982	51.7	273	758
38	865	1,779	6,598	1,005	1.0	55	91.3	20.0	145	2,127	78.5	101	1,925
39	9,676	19,342	39,788	10,739	26.7	783	35.6	54.7	389	14,501	74.7	170	944
40	2,227	2,466	5,747	2,405	2.7	74	42.4	16.0	182	2,455	62.5	101	2,212
41	14,798	20,170	35,332	36,608	27.3	633	57.8	95.0	462	25,144	52.4	710	503
42	7,046	8,675	15,182	9,505	11.4	220	208.5	57.1	208	10,784	137.7	416	1,120
43	15,581	32,534	59,812	47,683	48.1	760	59.4	93.4	440	28,820	46.7	518	503
44	6,936	15,764	28,108	13,370	23.2	344	108.8	56.2	243	12,880	81.6	272	924

Table F Sample ID	Mg	Al	Si	Ca	Sc	Ti	V	Cr	Mn	Fe	Ni	Cu	Zn
											Elements		
45	15,779	9,002	16,887	16,227	12.8	417	83.9	155.4	584	43,909	119.9	1,658	1,711
46	4,147	10,452	2,513	4,039	1.9	88	340.2	70.0	522	11,270	275.9	370	2,654
47	21,225	5,879	12,164	21,080	10.5	229	66.3	132.5	529	37,877	137.3	1,217	1,883
48	2,484	3,517	2,513	1,861	2.2	86	168.9	46.7	213	5,907	137.7	184	1,952
49	23,384	5,954	11,137	18,562	10.2	234	66.9	73.5	359	20,488	77.5	638	1,145
50	10,736	3,564	2,513	3,810	1.8	58	315.7	42.1	232	7,638	203.8	279	1,983
51	16,284	9,105	15,695	21,549	18.0	309	69.6	86.4	521	27,347	87.3	690	1,412
52	3,799	2,972	2,513	4,782	2.5	70	255.6	42.7	247	7,309	138.8	101	1,299
53	14,101	5,671	14,734	11,816	8.6	194	61.1	62.8	295	17,401	48.5	670	973
54	2,199	2,756	3,907	2,617	1.0	43	351.3	23.4	111	5,400	167.1	221	821
55	27,418	3,429	6,529	15,210	6.8	131	71.0	41.7	249	11,020	79.0	328	1,473
56	11,295	4,859	2,513	4,866	2.0	81	332.3	43.6	248	4,595	262.3	101	2,402
57	9,218	25,251	40,610	45,582	45.8	761	88.4	94.0	722	30,472	86.2	491	1,748
58	948	2,728	4,238	3,012	4.2	81	84.4	30.2	146	3,948	57.6	101	1,319
59	14,023	8,600	14,941	20,693	15.6	293	64.9	63.2	411	16,923	65.8	313	1,678
60	3,273	3,237	2,513	2,351	1.9	74	281.5	41.5	208	4,592	179.0	101	1,385
61	11,630	8,643	24,201	24,698	14.5	326	64.9	121.7	476	32,239	75.1	1,308	2,302
62	1,566	5,305	4,374	2,426	1.0	78	193.1	71.6	212	7,615	111.9	382	2,318
63	28,092	7,343	12,275	13,366	10.9	280	68.1	81.5	364	18,310	1263.3	350	2,091
64	9,085	5,162	2,513	4,506	1.9	108	351.1	153.9	389	7,757	273.9	101	3,398
65	13,641	9,221	16,880	19,592	16.9	361	124.2	107.2	575	27,367	331.7	522	2,062
66	1,757	2,202	2,513	1,875	1.0	50	323.2	37.0	168	3,537	219.3	101	1,374
67	11,970	9,734	15,728	22,370	19.9	355	108.4	112.8	753	26,416	228.8	670	2,274
68	1,815	1,873	2,513	2,200	1.6	71	411.1	42.4	282	5,310	221.6	169	1,816
69	11,335	10,197	25,679	25,751	17.9	461	81.0	128.9	517	28,750	131.2	913	2,579
70	1,322	2,403	2,513	2,759	1.0	49	151.5	69.7	300	5,362	117.9	228	1,947
71	9,378	16,967	31,769	36,866	34.1	592	89.7	137.2	1,098	41,640	165.9	741	6,152
72	1,546	2,879	4,818	2,967	3.6	94	80.4	44.9	414	6,950	65.6	166	5,237
73	12,355	10,260	29,574	29,970	20.3	413	74.3	104.7	663	37,322	77.1	970	4,064
74	2,506	2,871	6,407	4,605	2.2	117	192.2	61.4	491	15,338	125.1	449	4,738
75	37,128	2,843	5,586	8,211	3.3	109	48.3	26.4	162	8,638	59.3	313	1,011
76	27,820	19,767	2,513	7,942	2.1	321	404.5	73.6	387	6,136	312.3	905	2,200
77	18,527	5,770	10,973	11,987	10.6	210	83.8	63.1	311	15,175	83.9	341	2,060
78	3,224	2,880	2,513	1,828	1.0	48	237.5	35.6	147	2,979	165.5	101	2,083
79	13,479	7,021	12,660	12,511	12.9	247	86.6	43.9	314	13,189	68.8	202	1,014
80	1,918	2,781	2,513	1,623	2.5	54	252.4	27.0	92	2,652	170.8	101	1,049
81	17,981	5,326	15,556	16,566	10.2	252	66.7	36.5	340	10,645	25.1	300	1,009
82	3,380	3,106	2,513	2,390	1.0	49	377.4	30.6	138	3,092	193.1	101	1,033
83	251	251	3,934	1,005	1.0	25	1.0	15.3	25	151	25.1	101	2,274
84	251	251	2,513	1,005	1.0	25	1.0	10.1	25	101	25.1	101	503
85	251	408	2,513	1,005	1.0	25	1.0	10.1	25	101	25.1	101	503
86	251	386	2,513	1,005	1.0	25	1.0	10.1	25	101	25.1	101	503
87	251	573	2,513	1,005	1.0	25	1.0	26.0	25	8,103	25.1	101	1,858
88	251	251	2,513	1,005	1.0	25	1.0	63.3	25	1,003	25.1	101	503

Table G Sample ID			Ions				
	Na	K	Ammonium	Chloride	Nitrate	Sulphate	Endotoxin
1	4,120	4,793	14,716	19,318	147,617	45,612	0.06
2	1,068	2,690	91,827	3,386	205,415	121,905	0.12
3	1,527	4,335	5,953	4,539	87,026	22,441	0.52
4	732	4,154	115,157	2,970	100,843	282,897	0.70
5	3,770	4,500	1,547	6,411	77,721	27,699	1.07
6	2,775	3,329	75,349	4,605	35,295	224,784	1.38
7	7,620	4,394	1,557	10,683	109,105	47,826	2.30
8	5,417	2,429	59,891	5,603	55,889	194,572	1.45
9	41,046	6,522	3,580	10,616	108,298	40,910	
10	2,864	4,703	106,928	764	75,050	242,150	
11	54,919	6,534	3,567	12,722	106,856	64,044	2.36
12	3,749	4,391	72,816	1,152	113,507	123,991	3.65
13	13,293	7,498	3,907	8,108	105,001	44,643	5.96
14	3,584	8,705	80,689	4,489	193,512	84,884	3.30
15	13,233	8,176	38,044	13,409	125,664	89,674	1.01
16	3,372	8,853	100,437	6,293	180,626	126,051	0.93
17	1,749	3,799	8,927	9,515	85,930	29,648	0.13
18	404	5,440	138,740	3,384	187,855	263,400	0.24
19	812	3,003	4,075	7,819	100,196	57,568	0.34
20	464	3,907	123,295	4,393	215,821	189,210	0.39
21	5,916	3,321	3,263	9,628	117,686	36,528	0.33
22	4,205	2,413	55,655	6,263	109,361	152,008	0.28
23	6,639	3,163	2,054	12,228	129,180	35,312	0.09
24	6,499	2,829	56,489	5,009	71,771	194,166	0.11
25	43,485	5,664	3,998	10,385	106,985	42,045	0.86
26	5,938	4,254	57,882	2,132	102,147	92,146	3.56
27	47,573	5,870	3,690	10,004	96,480	49,053	1.21
28	4,105	4,500	59,387	1,314	112,321	88,507	2.12
29	47,403	6,794	6,503	51,432	89,066	31,864	0.53
30	18,446	7,220	71,441	14,217	177,970	92,984	2.21
31	15,199	7,093	2,798	8,245	62,816	21,879	0.28
32	5,636	7,824	85,332	6,472	209,873	86,946	0.31
33	52,217	27,715	5,587	40,367	55,055	46,418	1.05
34	8,961	25,452	22,325	7,881	31,118	76,555	0.11
35	71,068	12,658	5,045	82,872	46,034	35,277	0.04
36	7,913	10,076	16,578	7,035	26,863	44,365	0.03
37	38,170	12,355	20,354	21,865	87,886	48,934	0.46
38	6,848	9,653	46,362	2,817	44,638	119,631	0.07
39	6,283	5,257	6,547	58,282	46,700	33,577	1.73
40	2,246	6,594	32,254	7,388	39,143	103,507	1.17
41	12,275	5,646	1,934	87,153	149,435	31,159	0.26
42	9,254	5,823	60,491	6,653	38,050	256,585	0.11
43	7,031	6,878	1,268	62,009	82,060	32,355	0.86
44	2,540	5,190	62,992	12,648	106,243	176,162	2.31

Table H Sample ID	Na	K	Ammonium	Chloride	Nitrate	Sulphate	Endotoxin
45	14,634	4,404	32,593	119,058	165,633	62,682	0.22
46	2,528	3,525	98,407	34,723	205,101	145,596	0.22
47	13,294	4,621	24,143	85,672	114,887	55,889	0.72
48	1,894	2,232	101,425	28,680	236,442	128,534	0.50
49	22,517	4,687	12,594	239,522	120,693	52,329	0.07
50	7,007	2,837	85,824	62,889	221,493	132,598	1.00
51	20,846	4,516	13,290	144,610	174,647	57,084	0.89
52	14,863	2,705	80,606	13,448	170,523	196,914	0.46
53	135,754	6,715	18,289	102,449	195,507	52,596	0.22
54	35,806	2,667	90,091	8,717	157,969	169,059	0.68
55	26,259	5,163	12,047	244,933	128,240	57,588	0.10
56	7,893	4,716	62,954	62,337	149,094	157,567	0.10
57	2,031	5,569	12,466	13,042	95,126	28,909	0.58
58	484	2,879	123,937	8,339	310,665	119,089	0.65
59	14,339	4,372	10,463	90,075	169,256	61,453	1.94
60	4,009	1,730	85,369	16,120	206,904	131,687	1.62
61	65,996	8,985	15,503	76,803	143,219	31,195	3.14
62	12,248	4,450	92,296	9,833	223,017	99,752	2.72
63	24,964	5,707	14,456	264,824	125,377	50,351	0.17
64	6,687	3,631	87,068	61,459	230,109	140,679	0.14
65	10,750	4,251	33,018	83,927	222,211	47,159	0.57
66	1,482	1,642	128,527	14,582	338,771	123,145	0.13
67	13,182	4,593	11,235	41,055	212,778	71,829	1.25
68	4,223	1,988	111,653	4,136	130,991	276,097	0.61
69	69,743	9,269	27,500	86,297	122,245	68,726	0.24
70	10,300	5,642	116,678	13,247	238,641	129,161	0.33
71	1,995	4,014	12,920	13,985	104,461	29,937	0.21
72	493	2,678	133,563	30,023	295,704	138,134	0.70
73	64,234	9,732	12,918	59,905	147,472	38,002	2.23
74	13,316	4,865	93,074	9,182	192,270	127,970	10.82
75	29,151	8,762	25,221	312,848	105,477	103,756	0.18
76	8,420	58,449	64,145	49,995	118,219	294,220	0.52
77	16,077	4,514	24,410	144,322	18,445	41,083	0.47
78	2,588	2,650	115,059	27,420	253,167	158,041	0.15
79	11,970	3,487	67,407	114,187	199,342	189,638	2.50
80	3,481	1,496	114,517	18,620	266,857	154,333	0.49
81	157,308	7,582	11,990	140,815	171,180	65,656	3.08
82	38,954	3,159	85,585	16,332	169,446	151,111	1.94
83	49,350	702	270	9,964	32,858	39,620	0.03
84	2,195	683	1,426	917	8,158	3,261	0.03
85	3,073	1,501	8,503	982	30,084	7,660	0.16
86	2,067	251	1,187	422	3,429	1,899	0.03
87	3,920	1,703	11,468	2,235	3,660	19,738	0.03
88	2,876	1,821	1,599	3,108	3,675	4,952	0.09

Table I Sample ID	Light Polycyclic Aromatic Hydrocarbons										Heavy Polycyclic Aromatic Hydrocarbons				
	Naphtalene	1-Methyl-naphtalene	Bifenyl	2,6-Dimethyl-naphtalene	Acenaphtylene	Acenaphtene	2,3,5-Trimethyl-naphtalene	Fluorene	Phenantrene	Anthracene	1-Methyl-phenantrene	Fluoranthene	Pyrene	Benz[a]anthracene	Chrysene
1	2.4	0.6	1.1	4.4	7.5	5.1	2.6	5.7	18.3	0.1	1.6	20.1	16.2	3.7	6.4
2	3.9	0.1	1.1	4.3	4.1	10.6	1.9	5.3	9.7	2.1	1.1	17.7	16.2	8.1	16.4
3	3.6	0.4	1.8	8.9	21.2	17.8	3.1	10.7	11.8	0.1	1.1	12.6	11.3	2.7	4.7
4	3.7	0.8	1.6	3.5	3.4	9.1	1.1	7.1	7.5	1.5	0.8	10.2	9.7	3.6	9.5
5	2.7	0.1	0.4	3.8	0.1	4.2	0.5	3.9	5.6	0.4	0.6	6.9	5.6	3.1	8.2
6	3.2	1.1	2.4	3.3	1.3	0.1	0.8	0.1	4.8	0.7	0.1	5.3	4.5	2.6	9.5
7	4.0	0.1	1.5	4.4	9.4	8.5	0.9	8.1	10.3	0.1	0.7	11.7	7.7	3.0	4.2
8	0.1	0.1	6.5	6.9	0.1	0.1	0.1	0.1	8.7	0.6	0.1	8.2	6.9	2.3	6.6
9	2.3	0.8	1.6	0.9	0.1	ND	0.7	ND	22.5	0.9	2.2	40.5	29.5	14.2	19.1
10	2.0	1.0	1.9	0.6	0.6	ND	0.4	ND	13.2	0.7	1.3	16.8	13.4	7.2	13.9
11	2.8	0.7	1.3	0.8	0.1	ND	0.6	ND	26.9	0.5	2.4	31.9	22.7	7.3	12.2
12	2.1	0.8	2.0	0.4	0.6	ND	0.6	ND	13.9	0.5	1.2	18.5	15.2	6.8	15.2
13	1.4	0.3	0.4	0.4	0.4	0.1	1.3	1.4	40.8	1.5	26.8	53.1	43.3	5.4	7.5
14	1.4	0.4	0.7	0.3	0.4	0.4	0.7	0.6	14.0	0.7	9.9	30.4	31.1	19.0	21.4
15	1.7	0.8	0.9	0.5	1.9	1.6	0.9	8.6	92.9	90.9	10.8	68.2	13.1	11.5	11.1
16	1.5	0.8	1.5	0.5	4.9	0.1	1.0	2.3	43.4	44.4	7.4	51.9	12.9	23.4	28.1
17	1.8	0.4	0.7	3.1	0.7	3.9	6.0	5.5	76.4	1.9	7.7	108.8	76.7	4.4	9.9
18	2.4	0.9	1.5	1.4	0.9	0.1	0.1	1.0	24.4	2.0	0.1	38.9	35.9	12.2	11.6
19	3.0	0.6	1.1	6.6	1.4	8.0	8.7	7.3	60.9	1.9	5.9	96.7	61.2	4.0	8.8
20	1.7	0.7	0.8	2.6	2.8	5.9	2.7	4.2	27.4	2.6	3.2	66.2	46.8	9.9	19.7
21	2.0	0.4	0.6	2.0	4.5	3.4	1.4	6.8	101.7	2.5	6.0	181.0	117.9	3.5	9.2
22	3.9	0.1	1.4	4.1	5.3	14.7	1.7	7.3	31.8	2.4	3.1	197.2	101.1	5.7	13.7
23	2.8	0.5	1.0	5.1	13.5	7.7	1.5	7.6	71.2	2.2	4.7	145.1	105.2	3.5	10.0
24	5.5	0.1	1.0	2.9	4.0	9.4	1.3	6.4	33.5	2.7	3.1	162.8	80.9	4.2	13.2
25	1.1	0.8	0.5	0.6	0.2	0.9	0.2	0.8	17.8	23.0	4.4	89.3	46.1	0.9	2.4
26	3.2	1.1	1.3	3.2	0.1	6.8	1.0	8.8	20.6	18.2	7.2	88.1	48.7	2.9	2.9
27	2.6	1.4	2.1	2.6	0.1	4.5	0.1	11.0	118.8	74.6	9.1	239.8	114.4	2.9	2.9
28	1.5	0.6	1.6	2.0	0.2	4.8	0.9	7.7	40.4	45.9	4.5	137.1	81.7	2.9	2.9
29	1.4	0.3	0.5	0.7	0.4	0.3	0.7	1.1	18.5	0.7	9.9	71.0	43.3	2.6	4.1
30	2.4	0.5	0.8	0.6	0.5	0.4	0.7	0.5	14.4	0.7	12.0	63.9	45.1	13.9	17.7
31	1.4	0.3	0.5	0.5	0.9	0.6	1.5	3.0	45.3	2.2	29.9	78.4	55.6	4.5	6.1
32	1.5	0.5	0.8	0.6	0.8	0.4	1.2	1.6	29.7	1.6	21.4	65.2	58.7	24.2	27.7
33	7.9	3.6	19.0	5.5	75.9	5.4	10.5	262.8	460.6	87.2	187.5	411.5	407.7	48.7	53.5
34	4.7	1.5	2.0	1.1	15.6	10.0	2.4	74.5	408.5	158.1	373.9	854.6	602.1	530.9	219.5
35	1.7	1.2	2.5	0.9	6.7	16.7	1.9	56.5	549.3	103.9	298.9	602.3	545.5	138.0	81.4
36	2.5	1.1	4.9	1.5	19.3	8.8	0.6	32.0	644.1	97.9	437.3	1294.0	1019.4	735.4	313.8
37	1.8	0.9	3.8	0.7	1.7	21.5	1.2	39.9	570.6	1323.2	172.3	497.2	416.1	59.6	43.5
38	2.1	0.8	4.3	0.6	14.2	12.2	ND	26.2	465.2	1027.9	231.1	889.8	883.7	296.7	284.1
39	5.3	0.7	0.0	17.0	2.3	4.2	5.6	20.8	199.6	31.5	21.2	202.7	161.8	9.8	21.2
40	7.1	1.1	2.8	13.4	40.3	0.1	0.1	0.1	43.2	24.4	0.2	81.4	72.7	ND	0.1
41	1.7	0.4	0.4	3.3	0.1	1.8	0.1	2.0	2.7	0.5	0.7	6.8	6.9	1.0	2.8
42	2.1	1.2	4.9	6.2	0.1	0.1	0.1	0.1	2.8	1.2	0.1	4.2	4.9	2.5	4.6
43	2.2	0.3	0.5	3.1	0.1	4.0	2.4	2.6	9.3	0.8	2.0	14.6	14.2	1.5	3.3
44	2.4	1.0	6.1	4.4	0.1	0.1	0.1	0.1	7.6	1.7	0.1	12.7	13.6	7.4	13.6

Table J Sample ID	Light Polycyclic Aromatic Hydrocarbons										Heavy Polycyclic Aromatic Hydrocarbons				
	Naphtalene	1-Methyl-naphtalene	Bifenyl	2,6-Dimethyl-naphtalene	Acenaphtylene	Acenaphtene	2,3,5-Trimethyl-naphtalene	Fluorene	Phenantrene	Anthracene	1-Methyl-phenantrene	Fluoranthene	Pyrene	Benz[a]anthracene	Chrysene
45	6.5	1.3	2.0	1.3	0.7	9.7	3.3	11.8	39.4	4.3	10.7	49.5	43.2	2.8	5.0
46	4.6	1.4	2.0	5.4	0.1	10.8	5.4	9.6	23.5	2.7	3.9	46.5	43.8	12.1	21.5
47	5.0	0.8	15.4	5.9	0.1	0.1	0.1	0.2	22.2	3.9	0.1	35.4	33.2	3.5	5.8
48	4.6	0.8	1.5	4.2	0.1	9.7	5.0	4.0	14.1	0.1	3.1	49.4	46.2	10.7	34.6
49	5.4	1.5	2.0	4.9	1.1	15.2	0.8	8.5	21.4	1.3	4.6	24.5	18.5	1.6	3.5
50	2.3	1.1	2.7	2.7	0.9	0.1	0.1	0.8	22.1	3.1	0.1	44.8	38.8	8.6	20.7
51	1.3	0.3	0.4	3.2	0.1	2.6	0.6	2.7	10.0	0.2	0.9	17.5	11.9	1.3	2.6
52	3.0	0.6	0.8	2.8	3.3	6.8	0.6	5.5	8.3	1.8	1.0	18.0	13.0	3.1	7.1
53	1.3	0.6	0.9	0.3	0.3	1.0	0.2	0.5	3.9	5.5	1.0	12.1	2.0	0.6	1.7
54	1.7	0.7	0.5	0.3	0.3	0.9	0.2	0.4	3.7	4.6	0.6	8.6	1.6	1.6	2.8
55	3.5	0.8	0.8	1.8	0.6	8.7	5.2	6.2	15.7	0.4	3.5	42.3	46.1	6.1	12.5
56	10.3	1.2	1.4	6.7	0.1	ND	ND	5.9	12.5	1.9	2.6	47.7	48.8	12.7	35.8
57	2.5	0.6	1.6	2.5	0.1	16.0	5.9	10.2	20.8	1.3	2.0	57.2	29.8	3.3	7.4
58	2.2	0.6	1.9	3.2	1.5	13.7	2.2	7.1	9.8	1.5	1.1	30.8	17.5	3.8	11.0
59	2.5	0.6	1.0	2.8	5.3	6.0	1.2	6.0	17.5	0.2	1.6	63.9	31.5	2.5	5.6
60	2.1	1.0	2.3	6.9	0.1	0.1	0.1	0.7	14.3	1.5	0.1	41.2	28.1	7.9	14.0
61	0.9	0.3	0.4	0.3	0.1	0.4	0.2	0.8	16.0	0.5	0.1	49.9	33.6	6.0	9.4
62	1.3	0.5	0.6	0.3	0.3	0.1	0.1	0.5	9.4	0.4	9.2	37.4	24.8	10.0	14.6
63	6.6	1.0	30.0	14.5	0.1	0.1	0.1	0.1	28.5	4.2	0.1	36.5	27.3	2.5	5.5
64	2.9	0.9	2.4	5.1	0.9	0.1	0.1	0.8	22.7	2.7	0.1	47.7	40.6	12.7	20.1
65	1.8	0.4	0.6	1.5	0.1	2.9	1.8	3.3	20.4	0.3	2.9	39.9	25.5	2.4	4.9
66	5.5	0.8	1.2	3.9	0.1	12.6	2.7	5.4	8.5	1.3	1.4	25.2	17.0	3.4	9.8
67	3.8	0.5	0.7	4.3	0.1	8.6	1.0	5.2	22.6	1.3	2.2	47.1	25.9	2.3	7.0
68	2.6	1.3	3.2	3.4	0.3	0.1	0.3	0.7	13.2	1.7	0.1	32.1	20.1	4.2	12.5
69	1.0	0.3	0.5	0.5	0.2	0.4	0.8	1.7	20.3	0.9	0.1	43.0	30.5	6.1	7.4
70	0.8	0.3	0.5	0.2	0.4	ND	0.3	0.8	10.7	0.5	8.5	26.6	22.7	9.1	12.4
71	2.0	0.5	0.5	1.9	1.3	3.4	1.3	4.2	34.3	0.1	2.7	43.7	25.1	4.7	12.6
72	2.0	0.6	0.9	1.2	0.3	0.1	0.1	0.2	9.4	1.0	0.1	17.1	13.0	6.2	13.7
73	1.7	0.7	0.8	0.5	0.3	ND	0.3	ND	24.4	0.5	3.5	47.5	28.6	1.8	3.3
74	1.3	0.8	1.2	0.4	0.6	ND	0.3	ND	11.5	0.5	1.6	25.1	18.6	4.9	9.8
75	1.4	0.4	0.4	1.4	0.6	3.3	3.2	5.5	51.2	3.7	3.7	51.6	29.5	3.3	6.1
76	5.5	0.9	0.7	4.6	0.1	5.9	6.1	4.3	42.5	4.0	3.4	71.3	56.7	14.4	41.7
77	1.2	0.7	1.9	3.8	0.1	0.1	0.1	0.9	26.4	2.0	0.1	53.6	44.2	6.2	13.2
78	2.4	0.7	2.7	4.6	0.4	0.1	0.1	8.0	12.9	1.4	0.1	40.3	30.1	10.6	14.9
79	3.1	0.7	1.1	6.6	0.1	8.9	2.0	7.1	13.8	0.1	1.7	25.4	17.7	3.2	6.6
80	2.2	0.6	0.6	4.2	3.4	6.8	1.0	4.8	7.5	1.5	0.8	21.3	15.7	4.4	10.9
81	1.0	0.6	0.4	0.2	0.4	0.7	0.3	1.6	17.5	ND	2.6	34.7	4.1	0.6	1.8
82	1.5	0.7	0.5	0.3	0.9	0.9	0.3	1.4	5.9	11.7	1.6	30.9	4.0	1.4	4.4
83	2.2	2.0	1.8	10.5	0.9	ND	3.5	6.1	235.9	ND	215.9	19.1	24.4	5.2	7.5
84	5.1	ND	22.5	ND	ND	ND	3035.5	ND	ND	ND	1006.0	ND	18.4	20.1	21.4
85	5.2	5.4	7.3	1.0	19.8	19.5	31.4	283.1	709.5	1547.0	1167.9	181.6	187.7	3.7	5.5
86	2.5	2.1	2.6	0.4	3.6	11.2	2.0	43.8	299.7	630.3	600.5	173.2	233.3	28.7	35.1
87	8.8	8.3	24.4	ND	67.4	ND	58.2	1090.5	894.0	2089.8	3650.4	1281.6	1515.3	38.4	56.2
88	4.7	3.0	4.8	7.3	15.5	ND	21.2	36.8	ND	ND	ND	84.1	110.3	0.3	3.6

Table K Sample ID	Heavy Polycyclic Aromatic Hydrocarbons								Hopanes and steranes					
	Benzo[b]fluoranthene	Benzo[k]fluoranthene	Benzo(e)pyrene	Benzo[a]pyrene	Perylene	Indeno[1,2,3-cd]pyrene	Dibenzo[a,h]antracene	Benzo[g,h,i]perylene	17a(H)-22,29,30-Trisnorhopane	17a(H)-21b(H)-Hopane	b-20R-Cholestane	5a-Cholestane	abb-20R-24S-Methylcholestane	abb-20R-24R-Ethylcholestane
1	2.0	1.0	1.4	0.9	0.3	1.1	0.4	1.2	5.4	6.0	0.6	4.1	0.5	1.5
2	14.1	10.7	7.7	7.8	2.3	11.3	1.7	10.7	12.6	36.2	1.3	3.7	1.1	2.9
3	1.0	0.5	1.0	0.4	0.2	0.7	0.3	1.0	4.2	9.6	1.0	3.6	1.1	2.1
4	6.6	6.6	4.4	3.8	1.5	6.4	0.9	7.0	8.9	12.8	1.2	3.3	0.9	2.8
5	0.4	0.3	0.3	0.1	0.3	0.3	0.1	0.4	2.4	14.5	1.1	3.8	1.1	2.6
6	2.5	0.5	1.1	0.6	0.4	1.0	0.4	1.7	2.2	6.5	0.8	0.3	0.9	1.4
7	0.4	0.2	0.4	0.3	0.7	0.3	0.1	0.5	2.7	6.4	0.8	2.9	0.3	1.6
8	5.9	1.0	2.3	1.7	1.1	2.7	0.8	4.1	2.7	5.4	0.8	0.2	0.7	1.1
9	0.7	0.7	0.5	0.6	0.2	0.3	0.1	0.4	4.5	6.3	0.8	0.1	1.3	3.1
10	1.7	1.7	ND	3.0	0.2	1.7	0.1	2.4	3.9	5.4	0.7	ND	1.1	2.8
11	0.7	0.7	ND	1.8	0.3	0.4	0.1	0.5	3.2	5.4	0.7	0.1	1.0	2.0
12	2.7	2.7	ND	4.2	0.6	2.6	0.2	3.8	5.4	6.0	0.8	0.1	1.2	3.0
13	4.7	1.5	2.2	2.1	0.5	3.3	0.2	2.3	1.5	4.1	1.3	0.8	0.6	0.7
14	32.8	8.2	15.1	16.6	3.4	17.9	1.8	18.5	1.5	2.9	1.0	0.7	0.6	0.9
15	11.9	3.8	5.2	4.1	0.5	1.6	0.3	2.9	0.4	0.8	8.5	7.7	0.1	13.9
16	57.8	9.6	16.3	11.0	1.6	8.6	0.1	9.2	0.2	0.5	1.9	1.4	0.2	2.3
17	3.6	1.8	3.1	1.8	0.6	2.0	0.4	2.8	7.4	9.2	1.2	2.4	0.9	6.4
18	16.4	4.0	9.9	10.4	2.8	14.4	2.5	16.2	0.1	3.9	0.8	0.2	0.8	0.8
19	3.7	1.4	2.9	2.0	0.5	2.0	0.3	2.5	5.1	8.7	1.2	1.6	1.0	5.0
20	16.2	11.6	8.1	9.0	2.7	12.3	1.6	11.7	5.6	5.5	1.0	1.4	0.7	2.5
21	1.3	0.5	1.1	0.5	0.2	0.6	0.1	1.2	3.7	10.8	1.2	1.6	0.9	2.8
22	6.1	5.5	4.7	3.6	1.5	4.0	0.7	6.9	4.7	22.6	2.6	2.3	1.9	5.9
23	1.1	0.5	1.1	0.5	0.4	0.6	0.1	1.1	3.0	9.6	1.2	2.1	0.9	2.2
24	5.0	4.1	3.7	2.7	1.2	3.2	0.5	5.4	2.5	11.9	1.6	2.7	1.1	3.4
25	1.2	0.7	0.5	ND	0.1	0.1	0.1	0.1	0.6	1.5	9.3	8.2	0.5	2.0
26	1.5	1.5	1.3	1.3	ND	1.3	0.3	3.1	2.7	1.0	0.5	1.7	0.6	2.2
27	0.4	0.4	1.3	1.3	0.2	0.2	0.1	0.7	3.5	0.9	0.2	3.4	0.4	1.8
28	1.7	1.7	1.3	1.3	ND	1.6	0.2	3.6	2.4	0.6	0.3	1.4	0.3	1.2
29	2.2	0.4	1.0	0.7	0.2	1.5	0.1	1.2	1.8	5.3	1.1	1.6	0.6	0.9
30	26.0	6.0	11.6	10.4	2.2	13.3	1.3	15.2	2.3	5.1	1.3	1.2	0.9	1.6
31	3.8	1.1	1.9	1.8	0.5	2.3	0.2	2.3	2.3	7.1	2.2	2.6	1.3	2.0
32	39.8	9.3	17.0	18.8	3.9	16.9	1.9	21.0	2.3	4.4	1.4	1.2	1.0	1.6
33	59.7	38.4	23.0	26.4	4.1	20.3	2.5	18.9	2.8	9.4	0.8	3.5	1.2	2.6
34	490.7	114.0	163.4	232.9	37.2	133.0	23.7	169.4	2.6	4.0	1.8	0.9	0.8	1.8
35	108.3	31.5	36.6	51.2	8.5	34.6	5.2	34.5	2.9	7.6	3.4	1.6	2.1	2.8
36	645.6	165.4	196.5	349.2	59.6	170.2	28.0	207.8	3.0	6.2	1.2	1.5	1.0	2.6
37	47.4	20.3	19.2	18.5	2.9	18.1	3.3	16.2	4.2	9.9	3.4	2.8	3.6	6.1
38	466.5	131.3	138.2	203.7	33.2	136.7	20.4	153.4	3.0	5.4	1.3	1.2	1.2	2.0
39	9.6	8.4	4.9	7.4	2.4	6.8	1.0	6.8	13.5	8.7	1.5	16.2	1.6	8.8
40	55.0	14.2	72.8	101.2	33.0	147.0	17.9	158.7	11.8	12.4	2.0	0.4	1.6	2.1
41	1.0	0.6	0.7	0.3	0.2	0.6	0.1	0.9	2.5	7.7	1.1	0.8	0.8	1.9
42	11.0	1.6	7.9	2.0	0.7	5.3	1.0	9.8	3.4	17.3	2.2	0.9	2.2	5.2
43	1.2	0.9	0.9	0.5	0.3	0.7	0.1	1.3	2.8	8.8	1.4	0.7	1.0	2.1
44	26.2	4.8	13.3	6.5	1.8	10.5	1.7	17.8	4.7	19.7	3.4	0.9	3.4	6.8

Table L Sample ID	Heavy Polycyclic Aromatic Hydrocarbons								Hopanes and steranes					
	Benzo[b]fluoranthene	Benzo[k]fluoranthene	Benzo(e)pyrene	Benzo[a]pyrene	Perylene	Indeno[1,2,3-cd]pyrene	Dibenzo[a,h]antracene	Benzo[g,h,i]perylene	17a(H)-22,29,30-Trisnorhopane	17a(H)-21b(H)-Hopane	b-20R-Cholestane	5a-Cholestane	abb-20R-24S-Methylcholestane	abb-20R-24R-Ethylcholestane
45	3.0	1.6	2.1	2.0	0.6	1.7	0.7	2.4	6.0	8.4	1.7	1.8	1.1	3.2
46	16.9	8.4	14.7	12.9	3.7	11.3	2.3	18.5	15.9	24.1	6.4	2.8	4.1	9.9
47	5.0	1.3	3.0	1.5	0.4	2.4	0.7	3.5	4.0	4.9	1.3	0.6	2.3	1.2
48	26.1	19.1	14.7	15.5	4.9	19.9	2.8	23.2	12.7	52.8	5.8	3.6	4.1	10.0
49	1.9	0.9	2.4	0.9	0.4	0.8	0.2	1.0	4.7	4.7	1.0	1.1	0.6	5.4
50	24.2	6.2	10.3	7.1	2.1	9.3	2.2	13.8	7.4	12.7	3.2	0.9	2.3	3.5
51	1.1	0.5	0.8	0.5	0.3	0.6	0.1	0.8	3.1	7.4	1.0	1.1	1.0	2.2
52	4.4	2.9	3.3	1.9	1.0	2.4	0.5	3.6	3.8	14.3	2.6	2.8	1.9	4.9
53	1.9	0.4	0.5	0.2	0.1	0.2	0.1	0.2	1.2	3.0	8.5	6.8	0.7	0.8
54	2.1	0.3	1.2	0.6	0.1	0.4	0.1	0.7	0.7	2.4	5.5	4.1	0.8	2.3
55	2.1	1.2	1.3	1.2	0.3	1.0	0.3	1.2	3.1	5.5	0.8	2.2	0.5	1.6
56	22.6	15.0	12.0	11.4	3.7	15.2	3.1	15.5	13.8	14.1	3.0	2.8	2.3	5.7
57	4.3	2.4	3.0	2.1	0.7	2.4	0.6	2.4	4.8	6.2	1.1	1.7	0.8	2.4
58	8.8	6.7	4.8	4.2	1.3	6.6	1.1	6.6	3.5	28.9	1.7	1.7	1.1	3.5
59	1.4	0.7	1.1	0.7	0.4	0.8	0.3	1.0	2.6	7.4	1.0	1.7	0.6	1.9
60	14.5	3.8	5.7	4.2	2.0	5.3	1.5	6.6	2.9	10.0	1.6	0.4	1.6	2.4
61	2.4	0.6	1.3	1.0	0.2	0.9	0.2	1.1	1.2	2.3	0.9	0.6	0.4	0.7
62	12.4	2.6	6.4	4.4	1.0	6.1	0.9	7.0	2.0	6.9	1.5	0.9	1.2	2.4
63	3.4	1.0	2.9	0.8	0.3	1.4	0.4	1.9	2.6	4.2	0.9	0.7	2.1	0.9
64	27.5	7.7	11.4	10.9	3.3	15.8	3.2	20.6	8.7	10.4	2.3	0.7	2.2	2.6
65	2.3	1.2	1.9	1.4	0.7	1.5	0.3	1.5	4.8	7.9	1.3	2.3	0.9	5.1
66	6.2	4.4	4.0	2.9	1.1	4.2	0.8	5.1	7.9	12.4	2.2	1.6	1.4	5.4
67	2.5	1.9	1.4	0.9	1.3	1.4	0.3	1.4	3.1	7.0	1.6	2.6	1.1	4.3
68	10.7	2.4	4.5	2.3	1.0	3.8	0.9	5.5	4.0	8.7	1.9	0.6	1.8	2.7
69	7.1	1.9	3.6	3.6	1.0	3.2	0.6	3.5	1.4	2.5	1.0	1.6	0.5	0.8
70	17.6	3.9	7.8	5.9	1.1	8.1	1.0	8.2	1.4	3.5	1.1	0.6	0.8	1.5
71	6.4	4.7	2.5	1.8	0.9	2.5	0.7	2.6	2.6	24.4	1.8	1.3	1.2	3.1
72	19.6	3.8	6.9	4.9	1.3	6.4	1.4	7.6	2.1	11.5	1.9	0.6	1.7	3.5
73	0.8	0.8	ND	1.3	0.1	0.5	0.1	0.8	4.4	4.5	0.5	0.1	0.8	2.1
74	2.9	2.9	ND	4.4	0.7	2.0	0.2	3.4	4.5	5.5	1.0	0.1	1.1	2.9
75	3.7	2.0	2.0	1.8	0.4	1.5	0.4	1.8	5.3	4.7	0.4	2.0	0.6	1.8
76	33.6	26.2	17.2	19.5	5.7	22.0	3.8	23.1	11.2	11.7	2.2	2.0	1.9	4.0
77	7.1	0.1	1.4	1.1	1.1	1.5	0.5	2.4	8.5	4.0	0.7	0.2	0.6	0.6
78	15.5	3.9	8.4	7.5	2.4	10.5	2.5	13.6	6.1	6.4	1.2	0.3	1.3	1.5
79	1.2	0.6	1.0	0.7	0.3	0.7	0.2	0.8	3.2	6.6	0.7	2.4	0.5	1.6
80	4.3	4.2	2.9	2.0	0.8	2.6	0.6	3.3	4.4	9.1	1.3	2.3	0.8	2.6
81	1.7	0.5	0.4	ND	0.1	0.1	0.1	0.2	0.9	1.0	6.5	5.4	0.2	1.3
82	3.0	0.5	1.3	0.0	0.1	0.5	0.1	0.8	1.3	2.0	6.8	5.4	0.5	0.9
83	1.6	ND	3.2	0.5	0.2	1.4	0.2	2.0	24.7	33.4	17.5	8.0	10.2	15.0
84	27.6	16.5	5.1	1.7	ND	0.4	ND	0.2	11.2	6.5	34.3	13.1	5.8	23.1
85	1.8	1.7	1.6	1.8	0.6	1.0	ND	1.0	14.7	23.9	7.4	4.4	5.3	11.9
86	23.4	7.6	7.9	5.9	1.5	8.4	0.7	9.1	23.9	35.7	12.8	6.3	8.5	18.5
87	6.8	3.3	2.4	4.5	2.7	0.3	0.3	1.4	43.2	82.5	17.1	21.0	37.5	49.7
88	0.4	0.3	0.8	0.4	0.9	0.6	0.4	0.2	3.3	3.9	27.3	11.3	61.4	35.2

Appendix 3 Source contribution data

Table M Sample ID	Secondary inorganic aerosol (SIA)	Sea spray salt (SS)	Crustal material (CRM)	Traffic (TR)	Other	Sample ID	Secondary inorganic aerosol (SIA)	Sea spray salt (SS)	Crustal material (CRM)	Traffic (TR)	Other
1	0.2	0.0	0.2	0.4	0.2	45	0.3	0.1	0.1	0.5	0.1
2	0.4	0.0	0.0	0.4	0.2	46	0.4	0.1	0.1	0.4	0.0
3	0.1	0.0	0.2	0.5	0.2	47	0.2	0.1	0.1	0.3	0.4
4	0.5	0.0	0.1	0.2	0.2	48	0.5	0.0	0.0	0.5	-0.1
5	0.1	0.0	0.2	0.7	0.0	49	0.2	0.1	0.1	0.3	0.3
6	0.3	0.0	0.1	0.1	0.5	50	0.4	0.1	0.0	0.2	0.2
7	0.2	0.0	0.1	0.4	0.4	51	0.2	0.1	0.1	0.4	0.1
8	0.3	0.0	0.0	0.1	0.5	52	0.4	0.1	0.0	0.2	0.2
9	0.1	0.2	0.1	0.4	0.2	53	0.2	0.5	0.1	0.3	0.0
10	0.4	0.1	0.0	0.1	0.3	54	0.4	0.6	0.0	0.1	-0.1
11	0.2	0.2	0.1	0.3	0.2	55	0.2	0.2	0.0	0.3	0.2
12	0.3	0.2	0.0	0.1	0.3	56	0.4	0.1	0.1	0.3	0.2
13	0.2	0.1	0.1	0.3	0.4	57	0.1	0.0	0.3	0.4	0.1
14	0.4	0.1	0.0	0.1	0.5	58	0.6	0.0	0.0	0.3	0.1
15	0.3	0.1	0.1	0.2	0.4	59	0.2	0.0	0.1	0.4	0.2
16	0.4	0.1	0.0	0.1	0.4	60	0.4	0.1	0.0	0.1	0.3
17	0.1	0.0	0.2	0.5	0.2	61	0.2	0.2	0.1	0.2	0.3
18	0.6	0.0	0.0	0.1	0.3	62	0.4	0.3	0.1	0.1	0.2
19	0.2	0.0	0.2	0.5	0.2	63	0.2	0.1	0.1	0.3	0.3
20	0.5	0.0	0.0	0.1	0.3	64	0.5	0.1	0.1	0.2	0.2
21	0.2	0.0	0.1	0.5	0.2	65	0.3	0.1	0.1	0.4	0.1
22	0.3	0.0	0.0	0.3	0.4	66	0.6	0.0	0.0	0.2	0.1
23	0.2	0.0	0.1	0.5	0.2	67	0.3	0.0	0.1	0.4	0.1
24	0.3	0.0	0.0	0.2	0.4	68	0.5	0.1	0.0	0.1	0.3
25	0.1	0.2	0.1	0.2	0.4	69	0.2	0.2	0.1	0.2	0.2
26	0.3	0.2	0.0	0.1	0.5	70	0.5	0.3	0.0	0.1	0.1
27	0.1	0.2	0.1	0.2	0.4	71	0.1	0.0	0.2	1.0	0.0
28	0.3	0.2	0.0	0.1	0.5	72	0.6	0.0	0.0	0.1	0.2
29	0.1	0.2	0.1	0.3	0.3	73	0.2	0.2	0.1	0.3	0.2
30	0.3	0.2	0.1	0.1	0.3	74	0.4	0.3	0.0	0.1	0.2
31	0.1	0.1	0.2	0.4	0.2	75	0.2	0.1	0.0	0.3	0.3
32	0.4	0.1	0.1	0.1	0.4	76	0.5	0.1	0.2	0.2	-0.1
33	0.1	0.2	0.1	0.5	0.1	77	0.1	0.1	0.1	0.3	0.5
34	0.1	0.2	0.0	0.1	0.6	78	0.5	0.1	0.0	0.1	0.3
35	0.1	0.3	0.1	0.4	0.1	79	0.5	0.0	0.1	0.4	0.0
36	0.1	0.3	0.0	0.1	0.5	80	0.5	0.0	0.0	0.1	0.2
37	0.1	0.1	0.2	0.5	0.0	81	0.2	0.5	0.1	0.2	0.0
38	0.2	0.1	0.0	0.1	0.5	82	0.4	0.6	0.0	0.1	-0.2
39	0.1	0.0	0.2	0.5	0.2	83	0.1	0.3	0.0	1.7	-1.0
40	0.2	0.0	0.0	0.2	0.6	84	0.0	0.2	0.0	1.4	-0.6
41	0.2	0.1	0.3	0.4	0.1	85	0.0	0.0	0.0	1.0	-0.1
42	0.4	0.0	0.1	0.2	0.3	86	0.0	0.0	0.0	1.6	-0.6
43	0.1	0.1	0.4	0.5	0.0	87	0.0	0.0	0.0	3.1	0.0
44	0.3	0.0	0.2	0.2	0.2	88	0.0	0.0	0.0	2.2	-1.2

Note: Data are presented as % x 100.