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Respiratory Allergy and Inflammation Due to Ambient Particles (RAIAP)

Collection and characterisation of particulate matter samples from 5 European sites

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Preface

Respiratory Allergy and Inflammation Due to Ambient Particles (RAIAP) is a European-wide assessment to study adverse and adjuvant effects of ambient particulate matter (PM) using a range of toxicological *in vitro* and *in vivo* studies.
This project was set out to collect ambient PM in European metropolitan and rural areas using both high and low PM sampling techniques. The overall objective is to assess the role of ambient suspended particles in causing local inflammation in the respiratory tract and induction and elicitation of respiratory allergies, in order to understand the underlying mechanisms for an involvement of particles in the development of these diseases. Specific objectives are:

- To characterise representative particulate samples from a western, a central, a northern and a southern European city and a sea-side site by physical, chemical and immunological methods,
- To screen the samples for allergenic and inflammatory potential; to verify findings from the screens in in vivo inhalation model, and
- To study mechanisms underlying the allergic and inflammatory effects.

The establishment of a role of ambient particulate matter in respiratory allergy and asthma is of clear public health importance, as on such a link preventive measures can be taken to improve the quality of life and health of individuals living in European cities.

Contents

Abstract

The aim of this part of the RAIAP project was to carry out a European-wide collection of particulate matter (PM) samples, with the aid of two High-Volume Cascade impactors (HVCIs), and to subsequently provide a description of the chemical composition. Coarse (2.5-10 μm) and fine (0.1-2.5 μm) samples were collected in Amsterdam, Lodz, Oslo, Rome and on the Dutch coast (De Zilk) during 3 periods of 4 to 6 weeks during the Spring, Summer and Winter of 2001-2002. PM was extracted from the collection substrate using methanol and sonication. After evaporation of the methanol in the suspensions, the PM samples were chemically characterised.
The sampling campaign was successfully performed in the period from March to April 2002. Yields were usually higher in Winter compared to the other two seasons, which may reflect contributions of combustion processes for heating purposes. Higher PM concentrations were also observed in Lodz and Rome than in Oslo and Amsterdam. In general, less secondary aerosol was measured in the coarse fraction than in the fine fraction. The contrast in chemical composition observed was considerable. Metal concentrations, with the exception of zinc, were high in Rome and zinc was high in Lodz. The Amsterdam location is characterised by relatively high magnesium (Mg) and vanadium (V) levels. As expected, sea-spray aerosol levels were significant in samples taken in Amsterdam and De Zilk. Relatively high levels of PAHs were measured in Lodz, in particular, during Winter. A more diverse pattern was found for the traffic markers,hopanes and steranes. Although generally higher amounts are found in the fine fraction, relatively high levels of steranes were observed in both Winter and Summer samples from the Oslo location, in the Winter sample from Rome and the Summer sample from Lodz. This pattern is not reflected in the hopane levels, which seem to be more dominant in both the Spring and Winter in samples from Lodz, Oslo and Rome. In conclusion, the sufficient amounts of PM have been collected and the chemical characterization of these samples is expected to provide valuable information for in vitro and in vivo toxicity studies performed within this project.

Samenvatting

Het doel van deze studie was het uitvoeren van een Europese fijn stof (PM) verzamelcampagne en de stofmonsters vervolgens uitgebreid chemisch te karakteriseren. De campagne is uitgevoerd met behulp van twee 'High-Volume Cascade impactor' (HVCI), waarbij zowel 'coarse' (2.5-10 µm) en 'fine' (0.1-2.5 µm) PM werd opgevangen op locaties in Amsterdam, Lodz, Oslo, Rome en De Zilk gedurende 3 perioden (zomer, winter en lente) van 4 a 6 weken in 2001-2002. Er werden groteverschillen in dechemische samenstelling waargenomen. In Rome werden hoge metaalconcentraties gemeten, behalvevoor zink, wat juist hoog was in Lodz. De locatie in Amsterdam wordt gekenmerkt door relatief hoge gehaltes aan magnesium en vanadium. Zoals verwacht zat in de monsters van Amsterdam en Lodzeen relatief groot aandeel zeezouten. De concentraties PAKs was relatief hoog in Lodz, in het bijzonder in de winterperiode. Het patroon van de verkeersgerelateerde stoffen (hopanen en steranen) wasmeer variabel. In het algemeen worden hogere gehaltes in de 'fine' fractie waargenomen en zijn de steraangehaltes hoog in de winter- en zomerperiode van de locatie in Oslo, alsmede in de winterperiode in Rome en in de zomerperiode in Lodz. Dit patroonreflecteert niet de hopaangehaltes, die meer dominant zijn in zowel het voorjaar als in de winter in Lodz, Oslo and Rome. Deze gegevens leveren waardevolle informatie voor in vitro en in vivo toxiciteitsonderzoeken die in dit project worden uitgevoerd.

1. Introduction

Inhaled ambient air particles have been found to be associated with adverse short-term health effects, such as an increased cardiopulmonary mortality in elderly individuals and the exacerbation of asthma in all age groups. These observations on asthmatics are supported by numerous laboratory studies, demonstrating an inflammatory effect from some types of particles, and an aggravation of allergic reactions in man by diesel exhaust particles. With regard to long-term health effects, in particular the development of allergy and asthma, evidence for an adverse effect from particulate exposure is less abundant, but some epidemiological studies have reported an association between the prevalence of asthma and allergy or pulmonary function and road traffic pollution. In contrast, in other studies such differences were not observed. In laboratory studies in man and animals, diesel exhaust particulate matter, but also other particles, have convincingly been demonstrated to enhance the development of allergic immune responses. Qualitative differences with regard to ambient air particle pollution, is the key element in one common hypothesis to explain the observed differences. Such differences may be related to adjuvant activity of the particles, to allergens being attached to the particles or to inflammatory effects caused by the particles. A European dimension is necessary because of the regional differences in disease prevalence and sources of particulate matter

Three broad classes of exogenous factors, in addition to allergens, have been proposed as underlying causative or regulating factors for the induction and elicitation of respiratory allergies, namely dietary factors, early childhood microbial exposure and air pollutants. The present research proposal focuses on one specific type of air pollutant, namely ambient suspended particles. Given that there are widely different prevalence rates of respiratory allergies and asthma between the countries of Europe and that exposure to ambient particles is substantial in urban environments throughout Europe, the RAIAP project will address the following research question:

May qualitative differences in particulate air pollution at different locations in part explain differences in prevalence or severity of respiratory allergies throughout Europe?

Quantitative variations in exposure to ambient particles across Europe are associated with different prevalence rates in short-term health outcomes. The difference in particle exposure is one of the leading hypotheses to explain the difference in prevalence of respiratory allergies and asthma between the formerly East Bloc countries and Western Europe. However, the noted differences in symptoms and diseases are not always readily explained by variations in exposure levels, but could also be envisioned to be due to regional differences in particle composition. Experimentally, there is substantial evidence that particles may differ qualitatively not only in relation to the induction of inflammatory responses, but also in relation to the elicitation of allergy. Thus, to enable the European Community to take effective and cost-efficient actions with regard to particulate air pollution, a better understanding of possible qualitative differences between air pollution in relation to inflammation and asthma is needed. The best way to obtain particle samples with qualitative differences relevant for the European community, obviously is to sample particles at locations in Europe where there are indications from epidemiological studies that the relation between particle exposure and adverse health effects differs.

We have collected representative ambient particulate matter samples (PM2.5-10 and PM0.1-2.5) in 4 major European cities (Amsterdam, Lodz, Oslo and Rome) at locations dominated by traffic emissions. In addition, one seaside location (De Zilk) was used as a control situation. This report provides the outcomes of the sampling campaign, as well as detailed information on the chemical composition of the PM samples. In addition, the available air quality and useful meteorological data collected during the periods of sampling are provided.

2. Material and methods

2.1 Particle collection

A high-volume cascade impactor with a multi-stage round slit nozzle impactor has been used to collect PM fractions on polyurethane foam (PUF) by impaction (Kavouras et al., 2001; Demokritou, 2002). This instrument, developed by the Environmental Chemistry Laboratory at the Harvard School of Public Health, can be used to collect samples for periods up to one week or longer (depending on how much particle pollution exists in the ambient atmosphere) at a flow rate of 900 liters per minute. Theimpactor cut-points used are for the range 10, 2.5 and 0.1 µm.
The key feature of the Sampler is the ability to collect particles in different size ranges, using a selection of impactor stages with the appropriate size cut-offs. For the RAIAP project the selected stages have actual measured cutpoints at 9.9, 2.52, and 0.12 µm. There is also the option for a final stage, which uses a PUF filter to collect ultrafine particles (below the lowest used impactorcutpoint). This final stage has not been used in the RAIAP project.
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 can be attached to the top stage.

Figure 2.1 RAIAP PM collection device with the HVCI on top of a box with the pump to pull the air trough the impactor (left panel) 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 seasons

A previous report "Description of sampling framework and the precise locations in four cities and a seaside site" (Cassee and Boere, 2001) has extensively described the selection procedure of the five locations in Europe as well as the sampling periods (see Appendix 1, Figure 1).

- The sampling site in Oslo (see Appendix 1, figure 2) is located along a throughway called Ring 2 (section Kirkeveien /Griffenfeldts gate) and placed approximately 20 meters from the kerb side of the road.
- The monitoring site in Lodz (see Appendix 1, figures 3 and 4) is situated in downtown (Srodmiescie) Lodz (15, Wieckowskiego str) near the theatre (Teatr Nowy). The sampling site is 30 meters from Zachodnia str. with heavy traffic, however without a significant contribution of heavy trucks but with a lot of busses and near a traffic light.
- The monitoring site in Rome (see Appendix 1, figures 7 and 8) is situated at Viale Regina Elena nr 299, Northeast of the Termini railway station and the centre of Rome. The proprietor of the sampling site is the Instituto Superiore di Sanita (ISS). The ISS site is located in an area where various public buildings are present (hospitals, university, administrative centre of the National Research Council, and other public or private office buildings. Viale Regina Elena is a large street and the monitor is positioned at a distance of about 8/10-m from the vehicle flux.
- The monitoring site in Amsterdam (IJsbaanpad, see Appendix 1, figures 5 and 6) is situated nearby the Olympic, south of the centre and north-east of a busy motorway (Ring South). In addition, a busy city street (Amstelveense weg) is located 100 meters eastward of the site.
- With a prevailing westerly wind, De Zilk is selected as a control site with low traffic emissions and natural allergens such as pollen. The site is only about 800 meters away from the sea and surrounded with sand dunes and fields. The nearest traffic route is 500 meters eastward.

PM was sampled on PUF foams that were cleaned as described in Appendix 2. PM was collected according to the procedure described in Appendix 3

2.3 Particle extraction from substrate

To conduct experiments with and/or to perform chemical composition analysis of the collected PM, the PM has to be extracted from the PUF. This was done by methanol-extraction based on a method described by Salonen et al. (2000). About 20-ml methanol was added to the tube containing the foam. This mixture was vortexed violently and put in a sonicate-bath for 30 minutes for sonication. The supernatant was decanted into a round-bottom flask. The steps above were repeated twice. Then the suspension was evaporated down under vacuum by using a rotary evaporator at 25 ºC for about 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. The suspension was transferred and divided over weighed and labelled Eppendorf-tubes (3 per extraction). The flask was washed with 1-ml fresh methanol andsonicated 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 wash-step as described above was repeated once more. The Eppendorf tubes were transferred to a vacuum-centrifuge and spun down for about 4 hrs. Afterwards the open tubes were put in the conditioned room for 24 hrs.

The next day the dried PM samples were weighed on the analytical balance to measure the PM yield. Finally they were stored at -20º C to prevent changes of the composition of PM due to evaporation or chemcial reactions.

2.4 Characterisation

The characterisation of the extract was performed by analysis of the collected material for an extended suite of elements, organic markers and polycyclic aromatic hydrocarbons (PAH). The amount of sample necessary for each analysis was determined based on the detection limits of the various analysis methods and the data on the occurrences of the compounds published in the literature. These assumptions were tested with a limit number of samples from other studies.

2.4.1 Pretreatment of samples

Approximately 10 mg of the collected particulate matter suspended in methanol was used for the characterisation. The sample was divided over 4 tubes as methanol suspension, each for one type of analysis, in portions equivalent to
1 (twice), 6 and 0.1 mg. The sample was dried under nitrogen and gentle warming (30^{o}C).

2.4.2 Chemical analysis

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 ICPMS. Whenever necessary, the samplepretreatment was extended by centrifugation or filtration to avoid the transfer of particles into the sample introduction system of the ICPMS.
When measuring an extended suite of elements high sensitivity and the option to separate many matrix- and plasma-related interference is required. 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 optimized and applied. This method included the following elements: Li, Be, B, Na, Mg, Al, K, Ca, Ti, V, Cr, Mn , Fe, Co, Ni, Cu, Zn, As, Se, Sr, Mo ,Cd ,Sn ,Sb ,Ba ,Ce ,Nd ,Sm , Au, Hg, Tl, Pb ,Bi and U. Hg was not analysed due to losses during digestion caused by its volatility. Si is determined in all samples although the background Si (using glass containers) might be large. The calibration ofSi was carried out as a one-point-calibration. Rh was used as an overall internal standard. The samples were quantified with external 2-point calibration.
The instrument was a ThermoFinniganMAT 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 is difficult to find an ideal 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.

Secondary aerosol

Two of the supplied methanol samples, each containing 1 mg were evaporated to dryness, dissolved in water by sonication filtered to remove remaining particles and analysed using ion-chromatography (Cl, NO_3 and SO_4) or photometry (NH_4). The anions were analysed using a Dionex guard column (AG-4A), separation column (Dionex AS-4A) and pulsed electrochemical detector (Dionex-PED). Detection limits were 0.003, 0.002 and 0.001 mmol/l for Cl, NO_3 and SO_4, respectively. Precision was better than 2%. The analyses were performed under the QA/QC system of the laboratory.

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 deuteratedPAHs and d2-C29- aaa(20R)-ethylcholestane) and 50 ml dichloromethane/isohexane (1:1) was added and the compounds were released by ultrasonic extraction. After filtration the extract was concentrated by evaporation to nearly dryness and mixed with 0.5-ml standard solution of 2,4-dichlorobenzyl-tetradecylether, which was used to correct for the variation of the injected volume. 1 µl was inject (splitless mode) at 290^{o}C on a 30 m 0.25 mmWCOT DB-5MS column (film 0.25 µm) using a column temperature programmed from 90 – 160 – 290 ^{o}C in a Fisons 8000 series gaschromatograph equipped with an Interscience MD800 massspectrometer with EI in SIR mode. Detection limits are approximately 0.1 ng/extract.
This method has been proven to give maximum yield for PAHs, as well as traffic markers. 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 and indeno(123cd)pyrene and the traffic markers:17a(H)-22.29.30-trisnorhopane, 17a(H)-21b(H)-hopane, abb-20R-cholestane, 5a-cholestane, abb-20R-24S-methylcholestane, abb-20R-24R-ethylcholestane. The analysis was performed under the QA/QC system of the laboratory.
The concentration of the traffic markers could be compared with the concentration in samples collected at a traffic tunnel in Hendrik-Ido Ambacht, the Netherlands and related to the traffic emission (expressed as fine particulate matter mass - $PM_{2.5}$) measured with co-located $PM_{2.5}$ monitors.

Endotoxins

Endotoxin concentrations were determined in suspension that were used in the in vivo allergy studies at the RIVM using a Limulus amebocyte lysate (LAL) test (Limusate, Sigma Aldrich Chemie BV, Zwijndrecht, The Netherlands) as described by the manufacturer, detection level (<0.125 ng endotoxin/ml. Endotoxin was determined in suspension that stirred or sonicated. The LAL test may be substituted for the U.S. Pharmacopeia (USP)Endotoxin Pyrogen Test (EPT) and is recommended for the quantitation of endotoxin in raw materials. The USP Bacterial Endotoxins Test is the official LAL test referenced in specific USP monographs(Bacterial Endotoxins Test, p. 1696-1697. USP 23 NF 18. 1994. U.S. Pharmacopeial Convention, Inc., Rockville, MD) and has been applied to PM samples used in the RAIAP*in vitro* inflammation studies. The samples were only stirred prior to the assay. The method is based on cleavage by endotoxin of pyrochrome into p-nitroaninline, which

absorbs at 540 nm and can be read in an ELISA-reader using microplates. It is more quantitative than the LAL-test. For more information:
http://www.acciusa.com/pdf/PyrochromeEnglish.pdf

3. Results and discussion

3.1 Particle collection

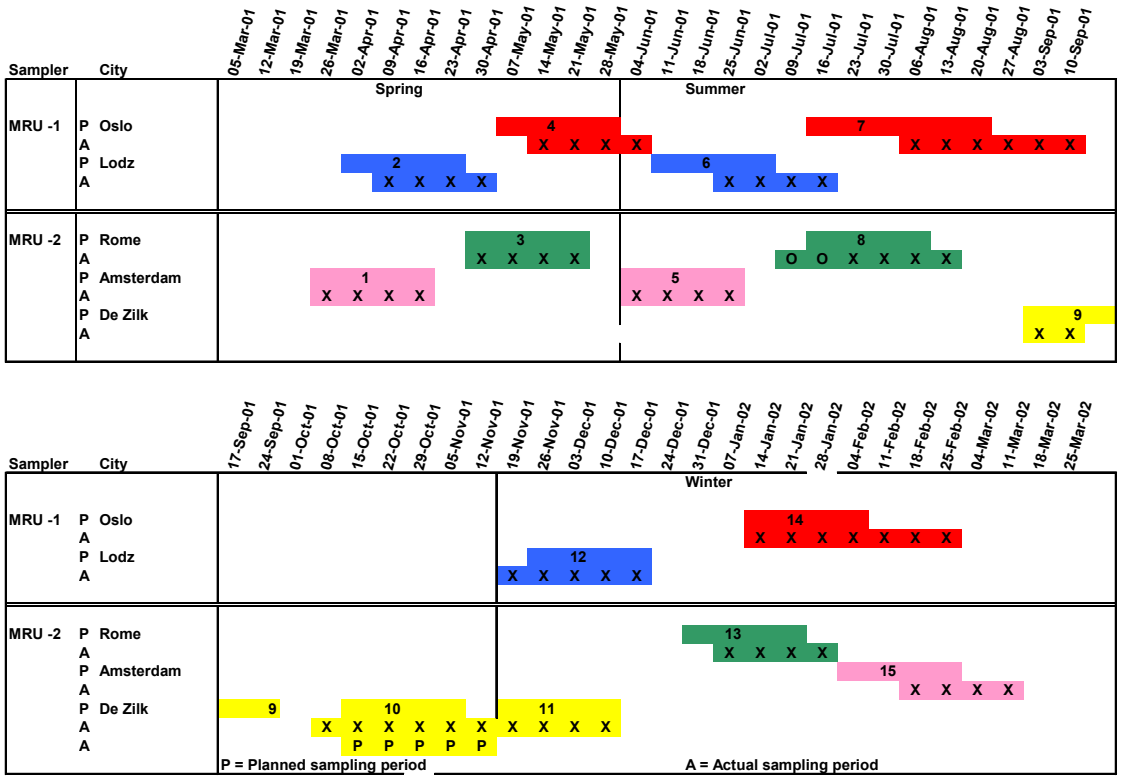

Figure 3.1: Schedule of the RAIAP sampling campaign. By using two identical samplers two parallel campaigns were set up. The boxes marked with X are used within RAIAP.

The sampling campaign was performed according to the schedule presented in figure 3.1. Slight deviations from the intended schedule were caused by delays during transport (e.g. due to Foot and Mouth disease epidemic in the Netherlands), but were not expected to affect the objectives of the project.
The collected masses of the particle collection campaign are listed in table 3.1. In general, the masses in Oslo were lower than expected. Furthermore, the “pollen” peak was also missed during the first Spring period. These two facts were the reason for sampling twice in Oslo during the Spring. Collected masses of the Amsterdam samples were also slightly lower compared to Rome and Lodz. The explanation could be the distance to the nearest street: a busy motorway dominates the location in Amsterdam and the distance is approximately 200 meters and the nearest busy street was approximately 100 meters away mostly downwind of the sampler. Dilution of the motorway emissions has probably caused the lower collected masses. Collected masses were usually higher in Winter compared to the other two seasons, which might be caused by contributions of combustion processes for heating purposes as well as the generally lower inversion layers during the Winter season.

Table 3.1: Summary of PM collection campaign. Oslo was sampled twice due to low collected masses and apparent lack of pollen in the air.

Spring

City	Start date	End date	Coarse fraction mass (mg)	Fine fraction mass (mg)	Volume sampled (m3)
Amsterdam	March 26, 2001	April 23, 2001	229	277	36201
Lodz	April 10, 2001	May 7, 2001	399	560	34830
Oslo	May 16, 2001	June 13, 2001	149	112	36036
Oslo 2	May 8, 2002	June 26, 2002	274	294	63069
Rome	May 2, 2001	May 30, 2001	442	508	36392

Summer

City	Start date	End date	Coarse fraction mass (mg)	Fine fraction mass (mg)	Volume sampled (m3)
Amsterdam.	June 8, 2001	July 6, 2001	204	301	36140
Lodz	June 25, 2001	July 30, 2001	331	401	45383
Oslo	August 8, 2001	September 19, 2001	139	212	53795
Rome	July 23, 2001	August 20, 2002	368	397	35769

Winter

City	Start date	End date	Coarse fraction mass (mg)	Fine fraction mass (mg)	Volume sampled (m3)
Amsterdam.	February 20, 2002	March 27, 2002	324	406	45188
Lodz	November 16, 2001	December 21, 2001	432	1476	44996
Oslo	January 9, 2002	February 27, 2002	360	377	63008
Rome	January 2, 2002	January 29, 2002	455	989	33449

Background

City	Start date	End date	Coarse fraction mass (mg)	Fine fraction mass (mg)	Volume sampled (m3)
De Zilk	September 5, 2001	December 7, 2001	1045	702	125020

* De Zilk (7 out of 12 weeks sampler A + 5 out of 7 weeks sampler B)

3.2 Chemical analysis

3.2.1 Overall composition

Figure 3.2 Overall composition of PM in Spring samples. Elements include all metals. secondary inorganics comprise sulphates. Nitrates and ammonia. whereas "others" include PAHs, hopanes and steranes.

The overall chemical composition of each main location is presented in figures 3.2 – 3.4 and the actual data are listed in Appendix 5. Although the values are projected as percentages. substantial differences were found among the locations in the Spring, whereas this was less evident for the Summer and the Winter. In general more secondary aerosol was measured in the fine fraction compared to the coarse fraction. The distribution of these four fractions across the three seasons seems rather stable for Amsterdam, highly variable for Rome whereas the other two locations (Lodz, Oslo) show moderate variability.

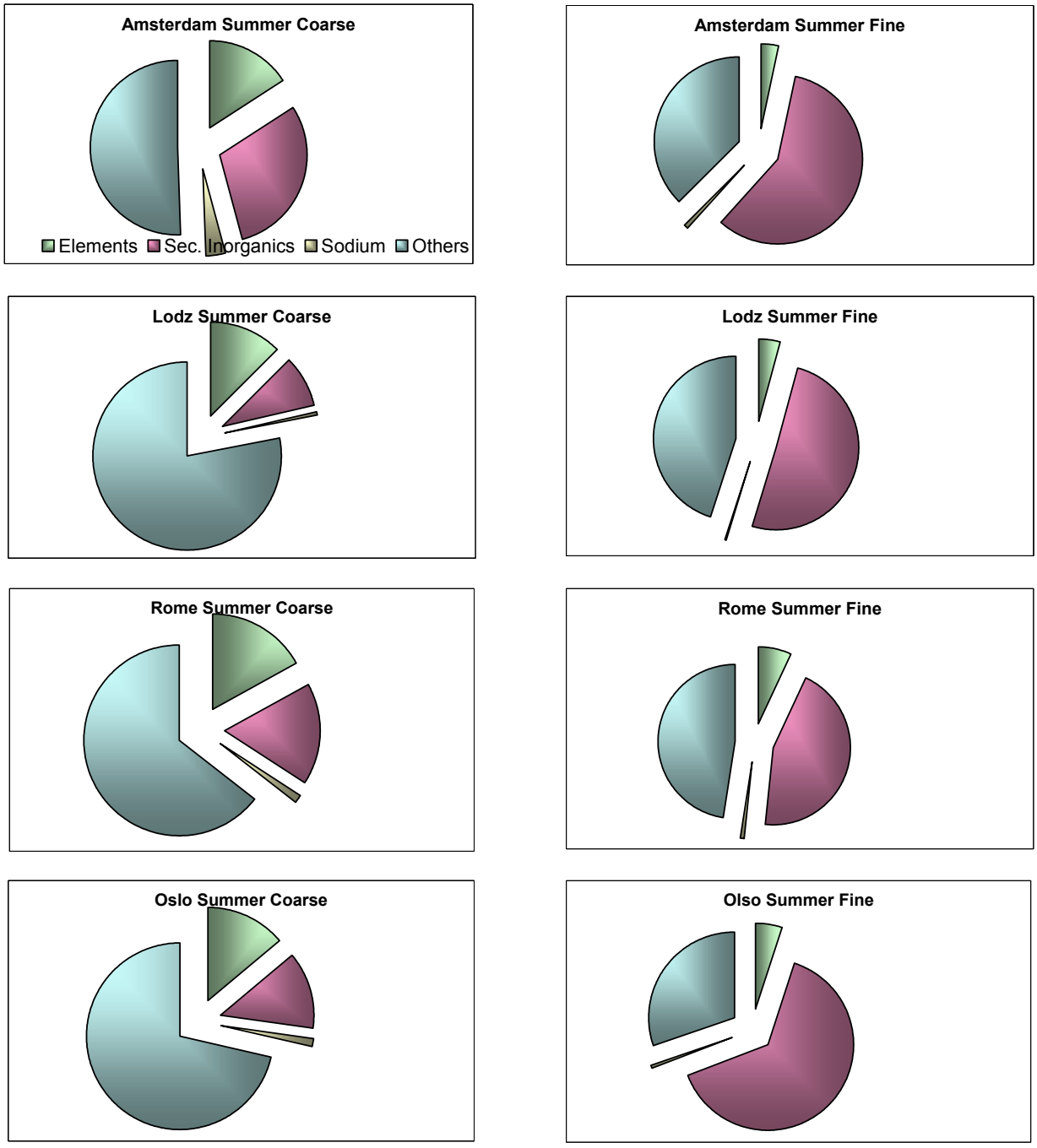

Figure 3.3 Overall composition of PM in Summer samples.

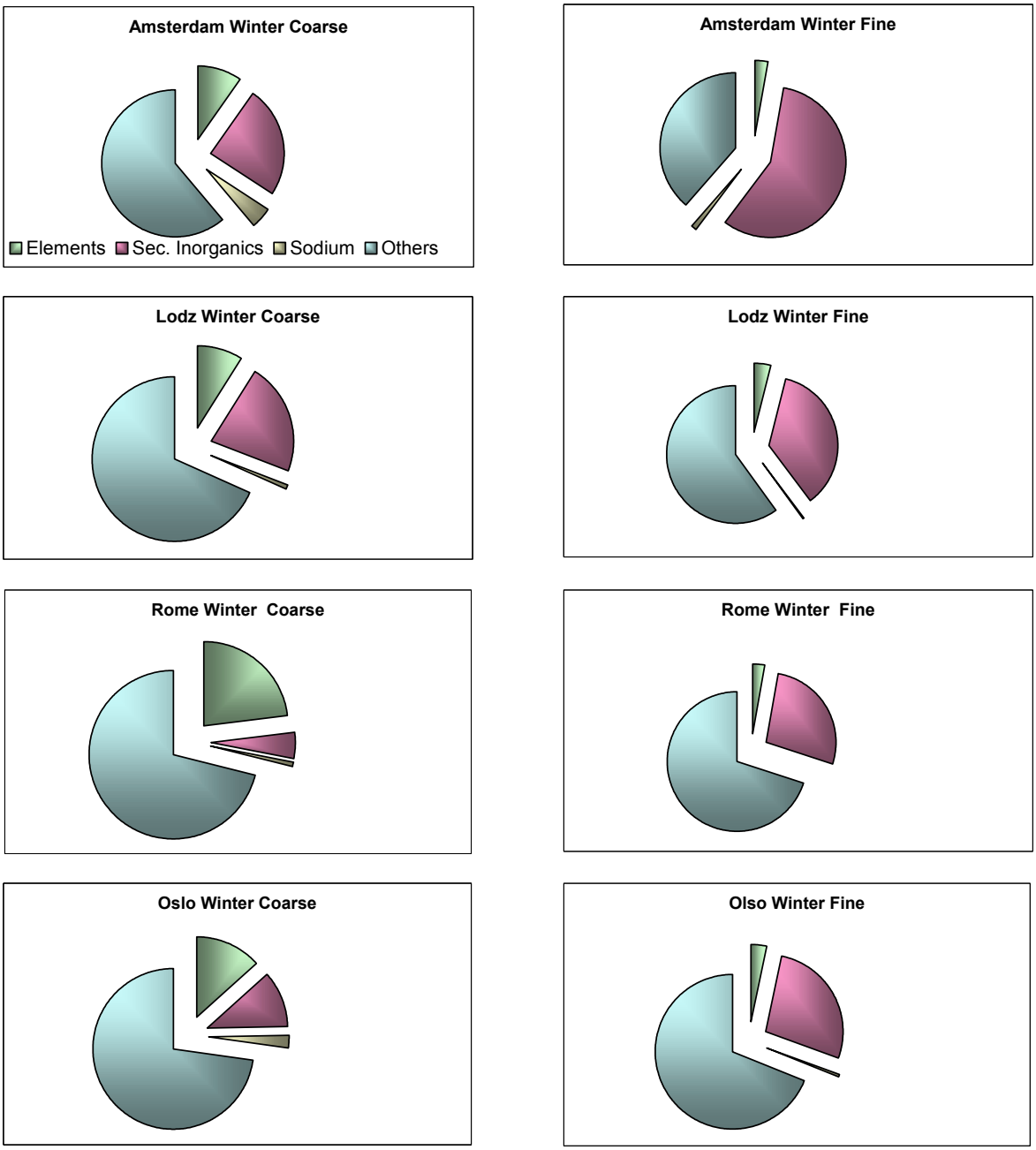

Figure 3.4 Overall composition of PM in Winter samples.

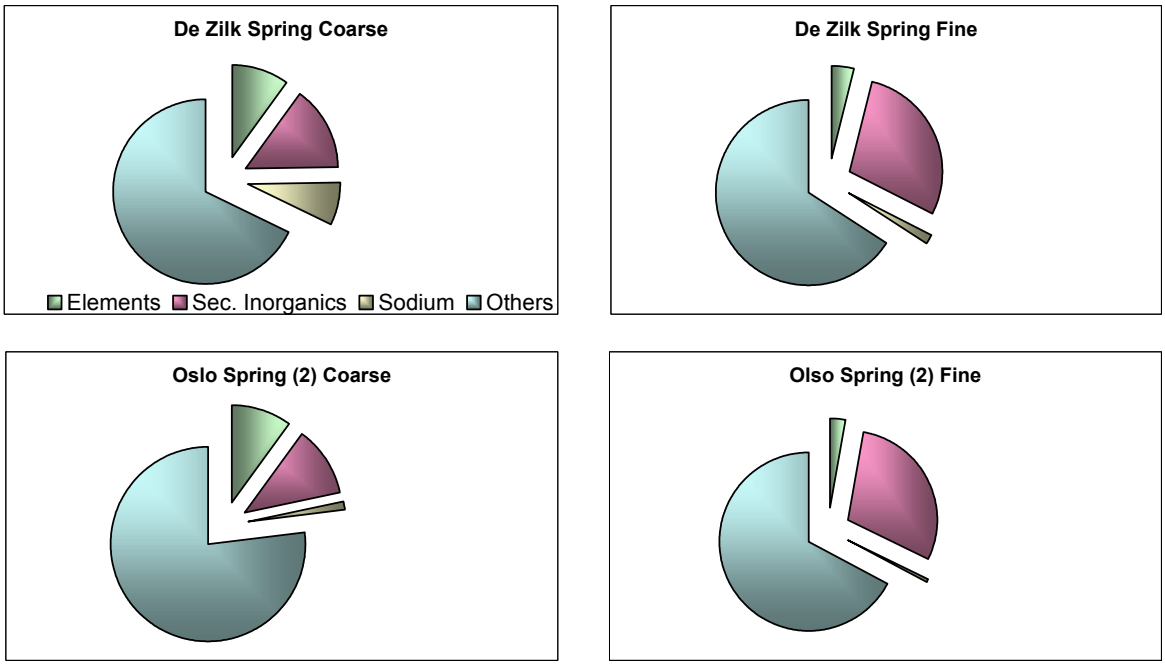

Figure 3.5 Overall composition of PM in the background location De Zilk as well as the second sampling in Oslo during Spring.

3.2.2 Elemental composition

Since a lot of emphasis is put on transition metals as (part of) the causal factors a selection of these constituents is presented in figure 3.6. See Appendix 6 for enlarged graphs. In general concentrations of metals were high in Rome with the exception of zinc. The location in Amsterdam is characterised by relatively high magnesium (Mg) and vanadium (V) levels in the coarse fraction during all three seasons. Lead (Pb) and zinc (Zn) where relatively high in the fine mode fraction in Lodz with the highest levels in the Winter. Iron (Fe), manganese (Mn), aluminium (Al), chromium (Cr) and copper (Cu) were usually higher in the coarse fraction, whereas Zn, Pb, nickel (Ni), vanadium (V) are higher in the fine mode of PM. The former set of elements is typical forcrustal material. The latter suite is often related to combustion processes such as traffic. There is no clear contrast in composition among the three seasons.

3.2.3 Inorganic constituents

Nitrate, sulphate, ammonia, chloride, sodium and potassium are the major constituents of the non-organic part of the collected PM (figures 3.7). The processing of the samples might cause losses of ammonium nitrate and as such the found levels might be low estimates. Sea-spray aerosol, containing sodium chloride is a substantial part of the samples collected at the sites in Amsterdam and De Zilk. Depending on the atmospheric aging of the particulate matter causing the depletion of chloride due to reaction with acids in the atmosphere the ratio of sodium and chloride might shift to higher values than expected based on the composition of sea spray. Ammonia and sulphate are predominantly found in the fine mode fraction, irrespective the sampling site or season. Nitrate is measured in both the fine and coarse mode fraction of PM, and the highest levels were observed for the Dutch locations. This observation complies with experiences in other studies. High levels of potassium were measured at the location in Rome.

3.2.4 Organic constituents

The amounts of light and heavy PAHs, as well as hopanes and steranes, are presented in figure 3.8 The highest yield ofPAHs are derived from the Lodz location, in particular during the Winter season. The PAHs are found in both size fractions. The PAHs may reflect the type of fossil fuel used for heating in Lodz, namely coal instead of natural gas or oil. A more diverse pattern is found for the traffic markers hopanes and steranes. Although generally higher amounts are found in the fine fraction, relatively high amounts of steranes were observed for both Winter and Summer samples of the location in Oslo, as well as the Winter samples from Rome and the Summer samples from Lodz. This pattern is not reflected in the hopane levels, which seem to be more dominant is both the Spring and Winter from Lodz, Oslo and Rome.

3.2.5 Traffic contribution

Although source apportionment is not an aim of the RAIAP project the organic constituents in combinations with elemental composition and site specific information will be used to estimate the contribution of traffic emissions to the total collected OM mass. The results will become available during a later stage in the RAIAP project.

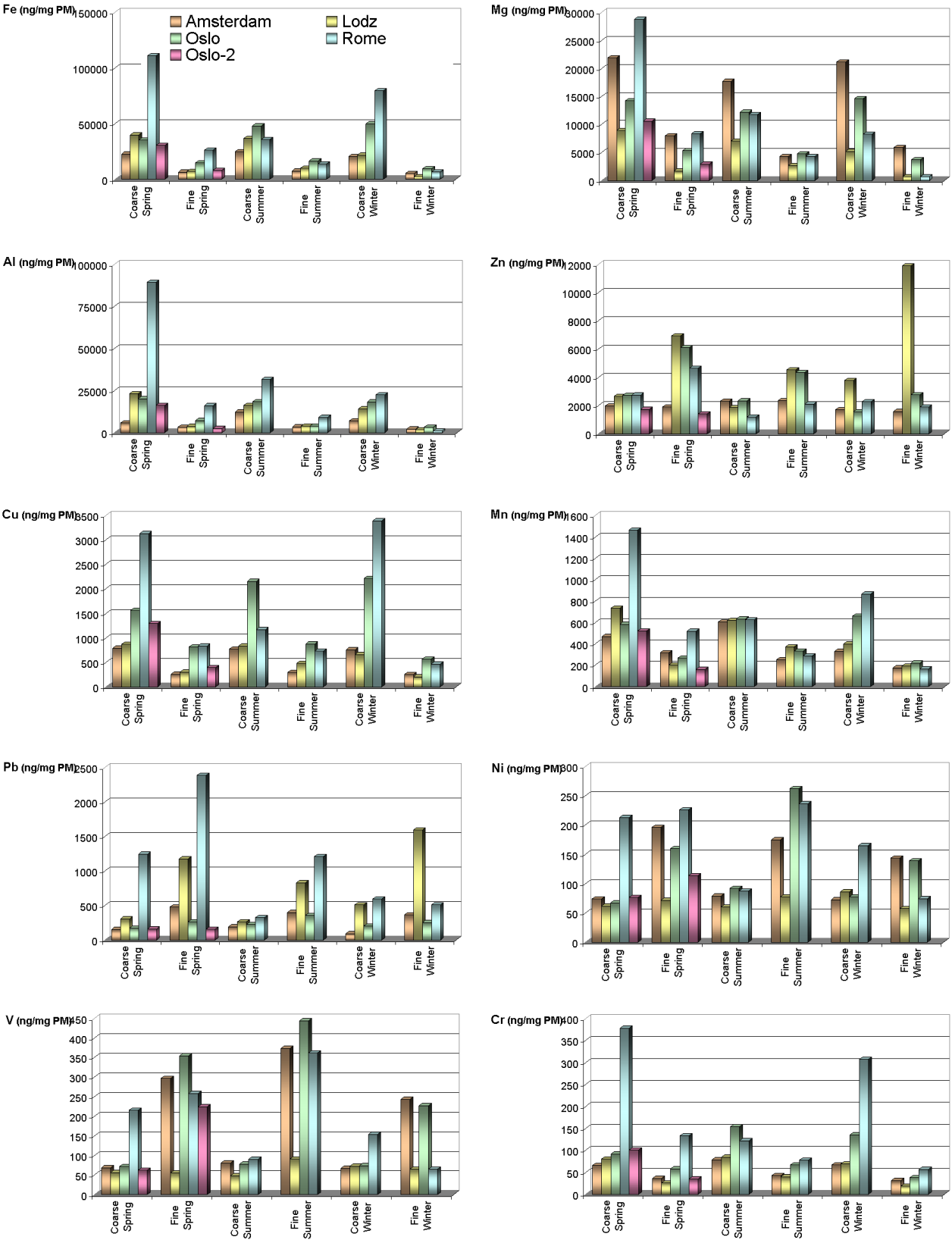

Figure 3.6 Transition metal contents of PM of Spring, Winter and Summer PM samples from Amsterdam, Lodz, Oslo and Rome. See Appendix 6

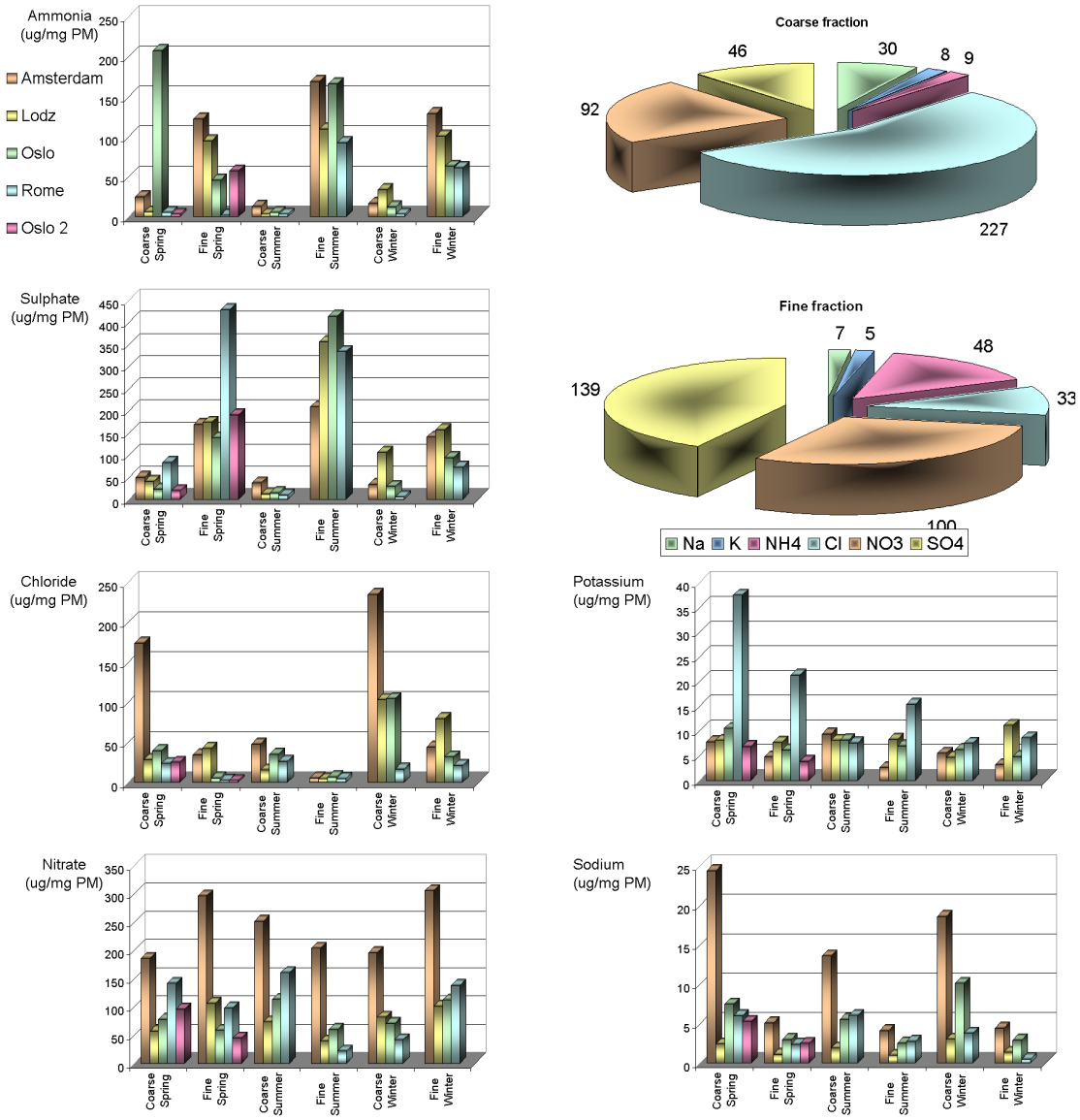

Figure 3.7 Inorganic contents of PM of Spring, Winter and Summer PM samples from Amsterdam, Lodz, Oslo and Rome. The pie charts are for De Zilk. See Appendix 6

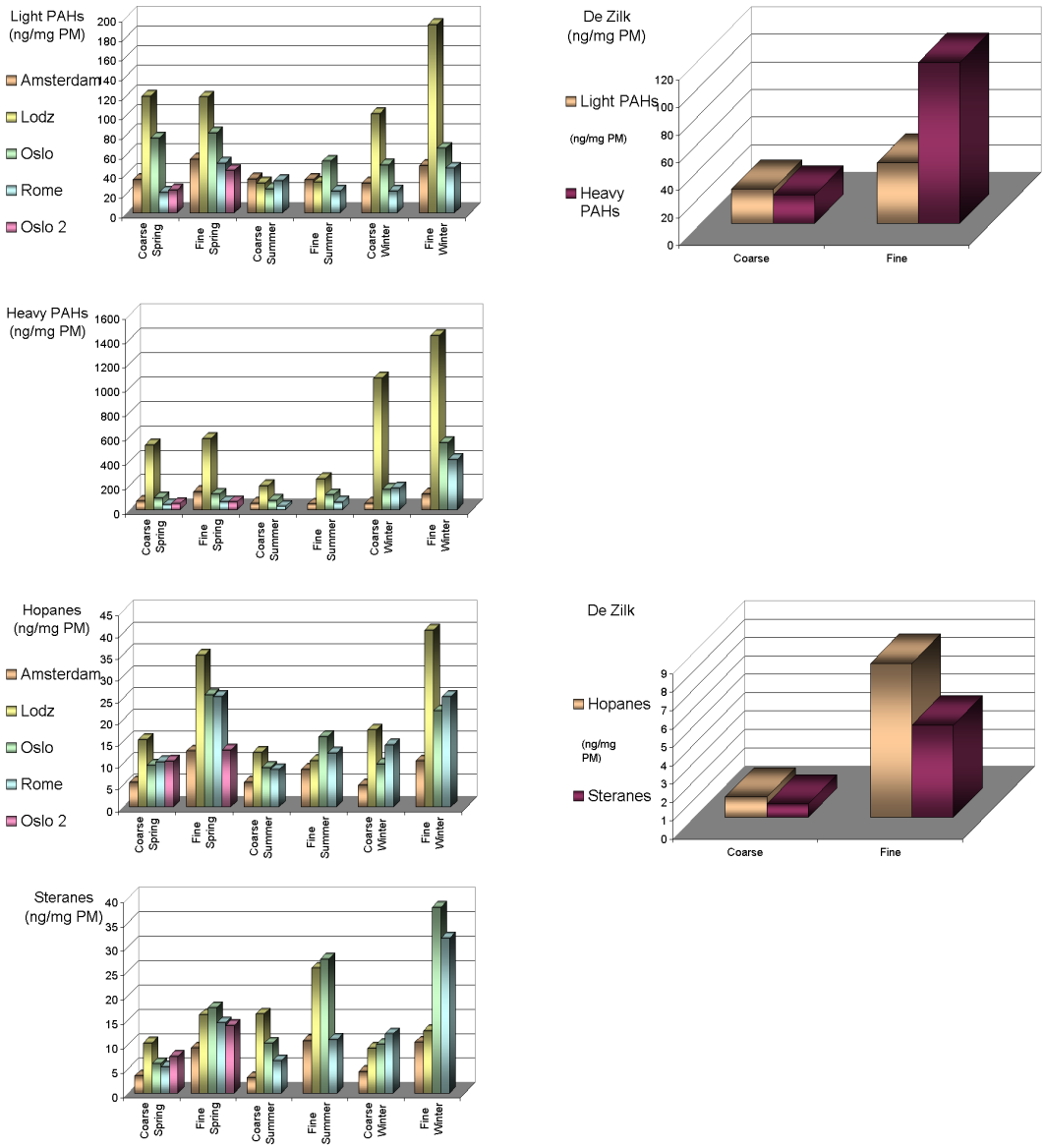

Figure 3.8 Organic contents of PM of Spring, Winter and Summer PM samples from Amsterdam, Lodz, Oslo and Rome. See Appendix 6

3.2.6 Endotoxins

The levels of endotoxins using the semi-quantative LAL assay were determined in suspensions of PM (figure 3.9). Clearly, coarse PM contains more endotoxin per mg PM compared to the fine fraction. The difference is 5-6 times for the Summer and Winter period and 13 times in the Spring. The levels of endotoxin in the coarse fraction are relatively low in the more polluted cities (Rome, Lodz) as well as in the seaside location (DeZilk) compared to the other cities in Spring. This pattern changes with season. See Appendix for full details.

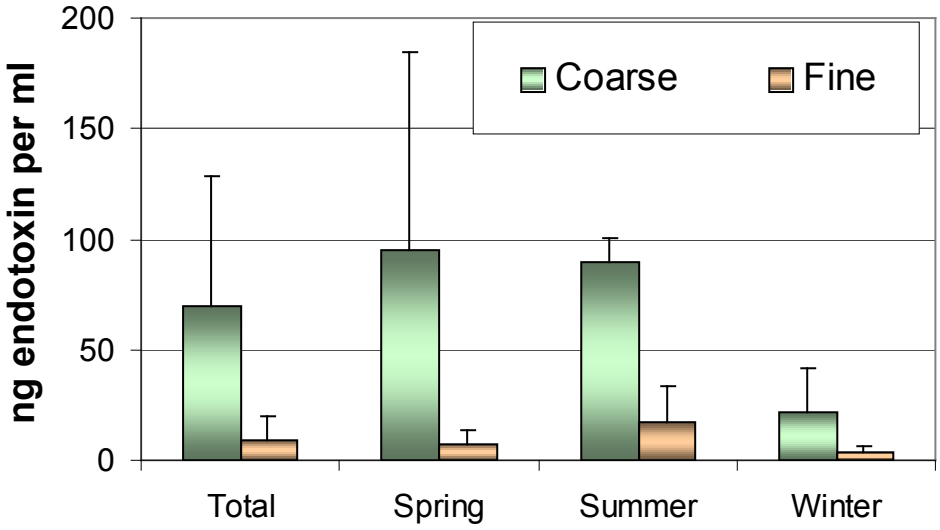

Figure 3.9 Endotoxin contents in suspensions of 6 mg PM per ml of PM samples. Values are averages from Amsterdam, Lodz, Oslo and Rome. See Appendix 6

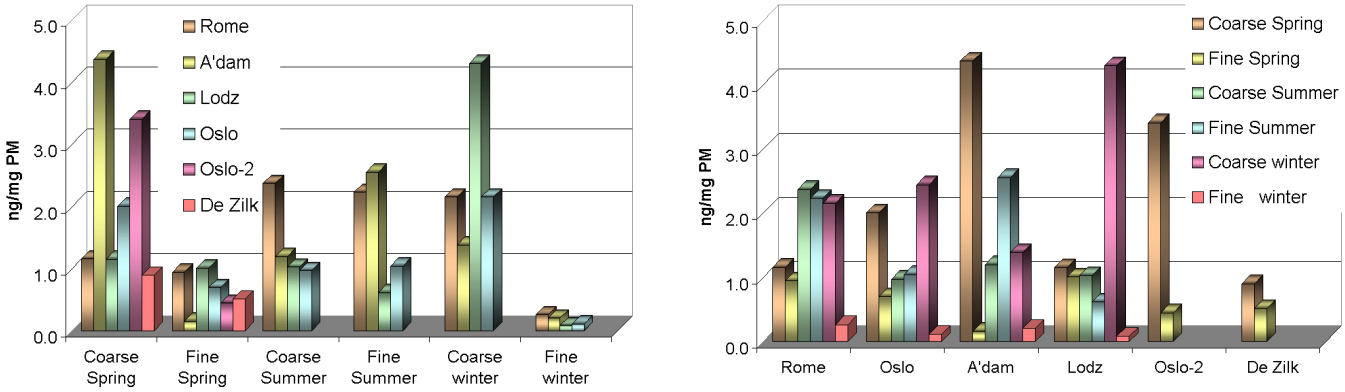

Figure 3.10 Total endotoxin contents in suspensions of PM samples. Values are averages from Amsterdam, Lodz, Oslo, Rome and De Zilk. See Appendix 6

4. Conclusions

A successful PM sampling campaign has been performed in the period of March 2001 – April 2002 in which four locations (Amsterdam, Lodz, Oslo, Rome) were visited three times (Spring, Summer and Winter). An additional background location (De Zilk) was sampled once. Most of the PM quantities were sufficient to use them for both chemical analysis and in vitro and in vivo studies in experimental animals. All promised constituents for the high volume samples were analysed. Endotoxins will be determined in the remainders of samples that are used for the in vivo or in vitro studies. In addition, estimations of the contribution of traffic emissions will be provides at a later stage.

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Oslo: Bjørn V.Johansen, Ellen Namork, Torunn Lővdal, Ragna Bogen Hetland (NIPH)
De Zilk: Dennis Vleeshouwer, Dick van Straalen (RIVM)

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Appendix 1 PM sampling locations

Figure 1 Map of Europe showing the sampling cities.

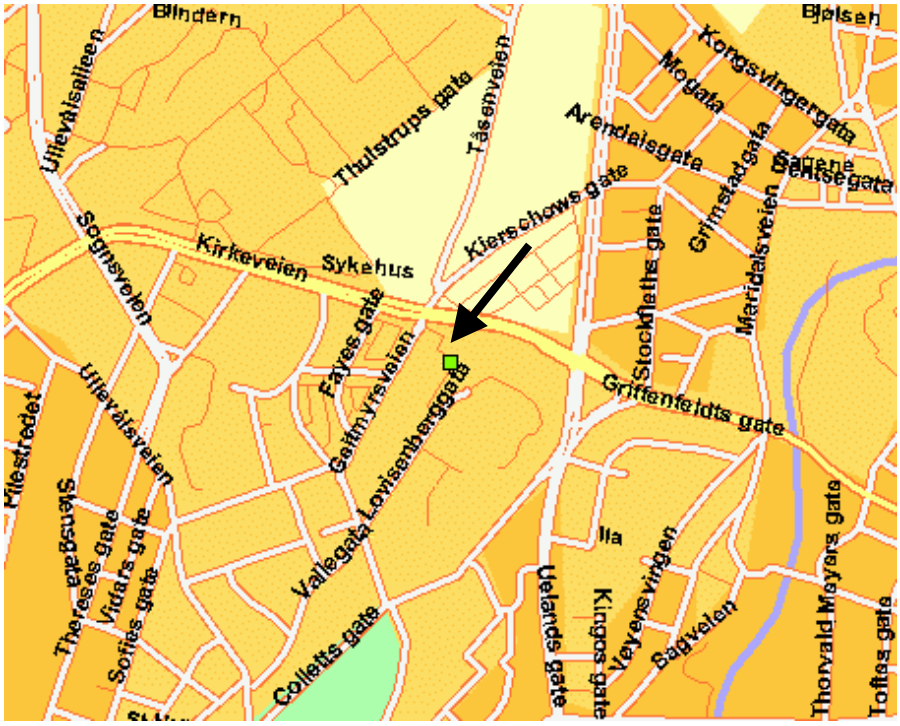


Figure 2. Location of PM sampling site in Oslo

Figure 3. Map of Lodz

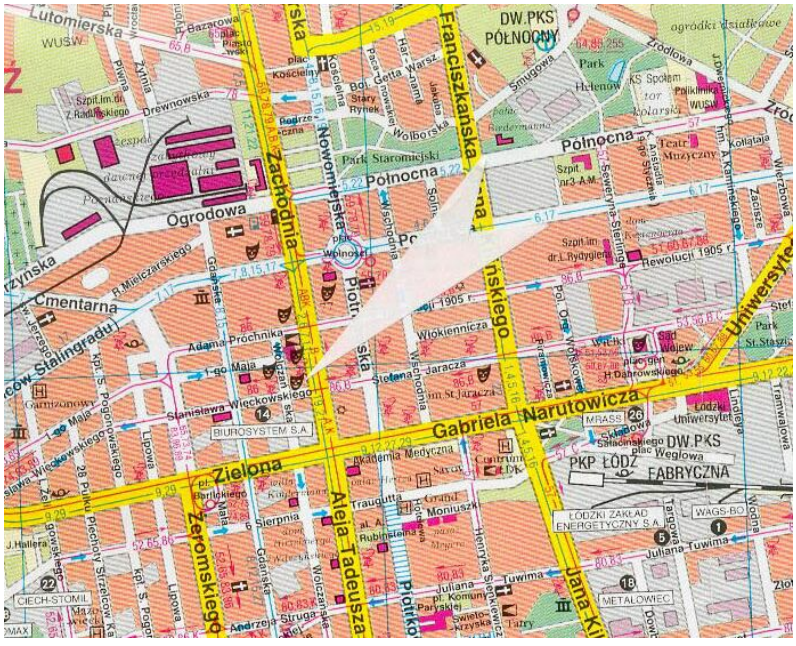


Figure 4 Location of PM sampling site in Lodz

Figure 5. Map of Rome.

Figure 6. Location of PM sampling site in Rome

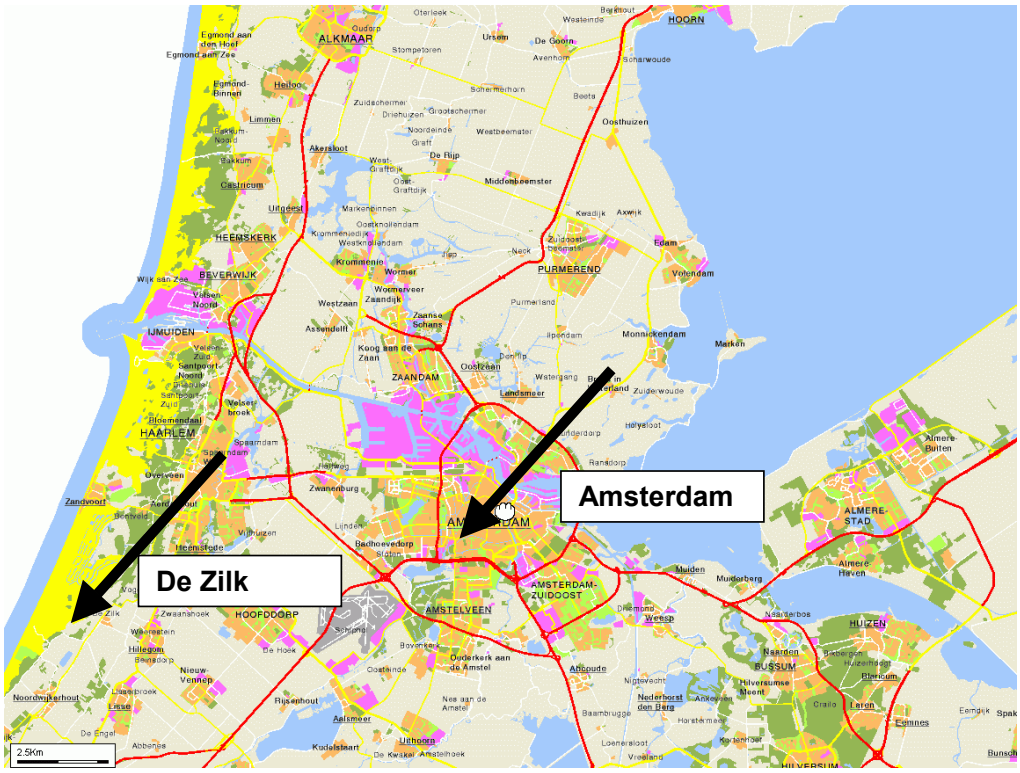


Figure 6: Overview of the two Dutch locations Amsterdam and De Zilk

Figure 7: Location of PM sampling site in Amsterdam

Appendix 2 Treatment of Polyurethane Foams (PUF)

1 Cutting the foams

In order to collect PM you will need the appropriate sized foams. We cut the foams on a glass subsoil from a standard piece of PUF, using a mould and a surgical scalpel. Take good care of your fingers! If you are not sure you can try to put the foams into the sampler-ring and see if it fits well. Be sure that you replace the scalpel frequently because they get blunt easily.

2 Cleaning the foams

To ensure that you use clean foams and that your extraction-pellet won't be comtaminated, you'll have to pretreat the foams. We wash them in a clean flask with an excessive amount of methanol (Methanol) and sonicate for 30 minutes in this Methanol in a sonicate-bath filled with water. Afterwards we decant the Methanol and refill the flask with fresh Methanol and repeat the steps as mentioned above. Finally we dry the foams in the flask covered with aluminum-foil in a stove at 70° C for about 2 hrs.

3 Weighing the unused foams and storage-tubes

To ensure that you weigh the "right" weight all the time you'll have to work under certain stable conditions. We put the dried foams and labeled 50ml tubes, with slightly opened screwcap, for 24 hrs in a conditioned room with a steady temperature and humidity. Then we weigh the empty tubes with screwcap on an analytical balance. Then we put the foam(s) into the appropriate tube and weight them again. From these figures we can calculate the foam-mass. (N.b. Weighing of foam itself fluctuated too much)

4 Using the foams

When PM is going to be collected the appropriate foams have to be installed into the rings of the RAIAP-sampler. This has to be done carefully to prevent contamination of the foams. Please wear pouder-free gloves and use non-sharp tweezers only. When the collection period is over the foams have to be transferred to the appropriate tube. Use pouder-free gloves and non-sharp tweezers again, and work carefully cause you might loose non-binding PM. Close the tubes firmly. Make sure you don't mix up the tubes, screwcaps and foams! Store cool (-20º C) to prevent degradation of the PM.

5 Weighing the used foams

After receiving/gathering the tubes containing the foams used for PM-collection, we put them with slightly unscrewed cap into the conditioned room for 24 hrs. Afterwards we weigh them on the same analytical balance as used previously. From the obtained values we can calculate

the amount of PM collected on the site per collection period and the amount of PM in the air (μg/m³) from the flowrate (900 l/min).

6 Extraction of the PM from the foam

To conduct experiments with and/or (chemical) composition analysis of the collected PM. The PM has to be extracted from the PUF. This is done by Methanol-extraction. About 20 ml Methanol was added to the tube containing the foam. This mixture was vortexed violently and put in a sonicate-bath for 30 minutes of sonication. The supernatant was decanted into a round-bottom flask. The steps above are repeated at least one time but preferrably twice. Then the suspension is boiled down under vacuum by using a rotary evaporator at 25º C for about 1- 5 minutes, until about 1 ml suspension is left. This suspension is sonicated in the flask for several seconds to remove the PM from the flask. The suspension is transferred and divided to preweighed and labelledEppendorf-tubes, 3 per extraction). The flask is washed with 1 ml fresh Methanol and sonicated again to remove all PM from the flaskwall and this suspension is also divided over the Eppendorf tubes. If the flask is still containing PM, the wash-step as described above is repeated once more. The Eppendorf tubes are transferred to a vacuum-centrifuge and spun down for about 4 hrs. Afterwards the open tubes are put in the conditioned room for 24 hrs. The next day they are weighed on the analytical balance to measure the PM yield. Finally the are stored at -20º C to prevent PM-degradation.

7 Data analysis

The amounts of PM collected and extracted are calculated and measured in 1/100-st of a milligram (5 decimal places of a gram) on an analytical balance and put in an excel-sheet for data processing. From the obtained values the amount of PM (coarse and fine) are calculated in μg/m³ to compare the different pollution-levels between the collection-sites. The extracted PM is used for composition-analysis and for animal-exposure and -instillation experiments.

Appendix 3 Procedure for changing foams of the RAIAP sampler

- Open the door of the electricity compartment.
- Take the logbook out of this compartment.
- Write down the date. time and location.
- Open the right door of the pump compartment.
- Check the pressure of the magnahelic and write it down in the logbook. (This pressure should be between 75 and 95 inches of water).
- Shut down the pump (switch to “zero”).
- Open the door of the electricity box (key is hanging on a short rope).
- Check and write down in the logbook the value of the “hour counter” and of the “energy consumption counter”.
- Close the door of the electricity box.
- Disassemble the black noise reduction ring around the sampler.
- Disassemble the sampler by disconnecting the lower stage of the sampler from the base plate.
- Place the sampler upside down (preferably on a table).
- Disassemble the lower stage “foam holding ring” and place the ring upside down (foam upwards).
- Now you can see the particles on the foam (as a black line).
- Write down unexpected events in the logbook (color. foam wet. fly’s etc).
- Take a pair of tweezers and take the foams out of the holding ring and put the foams in the 50 ml falcon tube with the right sample identification (“Fine”).
- Disassemble the lower stage from the two other stages.
- Disassemble the middle stage “foam holding ring” and place the ring upside down (foam upwards).
- Take the tweezers and take the foams out of the holding ring and put the foams in the 50 ml falcon tubes with the right sample identification. (“Coarse”) The middle stage foams are curved foams. Each foam will be placed in a falcon tube.
- Write down unexpected events in the logbook.
- Disassemble the middle stage from the upper stage.
- Disassemble the upper stage ring. This ring is filled with high vacuum grease. Inspect the ring and write down unexpected events (little flies in the grease etc.) in the logbook.
- With one of the feeler gauges you can scratch a small layer of the grease away. Clean the feeler with paper wipes.
- Fill the upper stage with new vacuum grease until the layer is flat and as high as the ring.
- Connect the upper stage ring back into the upper stage of the sampler and tighten the ring with the 3 butterfly nuts.
- Clean the middle stage slit first with soap. Then with water and finally with alcohol.
- The middle ring should also be cleaned with soap. Then water and finally with alcohol. Paper wipes or cotton pads can be used for this.
- Place the middle stage on top of the upper stage and re-connect it.
- Open a50 ml falcon tube with the new foam.
- With a pair of tweezers place the foam into the ring of the middle stage.
- Do this also for the two other foams with the same sample identification (“Coarse”).
- Do not touch the foams with your fingers!
- With the pair of tweezers guide the foams so that they are at the same height as the ring.

- Turn the ring around and assemble the ring into the middle stage with the 3 butterfly nuts.
- Clean the lower stage slit first with soap. Then with water and then with alcohol. The slit can be cleaned with the feeler gauge (0.006 inch). Be careful not to damage the slit.
- The lower ring should also be cleaned with soap. Then water and finally with alcohol. Paper wipes or cotton pads can be used for this.
- Place the lower stage on top of the middle stage and connect it.
- Open the 50 ml falcon tube with the new foam (“fine”).
- With the pair of tweezers place the foams into the ring of the lower stage.
- Do not touch the foams with your fingers!
- With the pair of tweezers guide the foams so that they are at the same height as the ring.
- Turn the ring around and assemble the ring into the lower stage with the 3 butterfly nuts.
- Turn the sampler 180 degrees and assemble it back on the base plate.
- Assemble the black noise reduction ring around the sampler.
- Start the pump (switch to “Two”).
- Check the pressure on the magnahelic in the pump compartment. should be 85 inch water (sampler MRU01 for collection in Rome. De Zilk and Amsterdam) or 80 inch water (MRU02 for collection in Lodz and Oslo)
- If pressure is lower or higher. Set to 80 inch using the valve.
- Close the door of the pump compartment and of the electricity compartment.

Appendix 4 Standard operating procedure for HVCI in RAIAP sampling campaign

Introduction

The Toxicological Sampler is a multi-stage round slit nozzleimpactor with Poly Urethane Foam (PUF) used for impaction substrates. This instrument, developed by the Environmental Chemistry Laboratory at the Harvard School of Public Health, can be used to collect samples for periods up to one week or longer (depending on how much particle pollution exists in the ambient atmosphere) at a flow rate of 900 liters per minute. The impactor cut-points are for the range used 10, 2.5 and 0.1 μm.

Material en Methods

Detailed Description of the Toxicological Sampler

A schematic diagram of the Toxicological Sampler is shown in Figure 1. This figure shows a typical configuration of impactor stages (size cut-offs of 10, 2.5, and 0.1 μm).

The key feature of the Sampler is the ability to collect particles in different size ranges, using a selection of impactor stages with the appropriate size cut-offs. For the RAIAP project the selected stages have actual measured cutpoints at 9.9, 2.52, and 0.12 μm. There is also the option for a final stage which uses a PUF filter to collect ultrafine particles (below the lowest used impactorcutpoint). This final stage will not be used in the RAIAP project.
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 raincover can be attached to the top stage.

The current design of the housings/stages are as follows:

- there is an “upper stage” housing that can hold any of the impactor; one or more upper stage housings can be used in series;
- there is a “lower stage” housing that can also hold any of the impactor stages, but has a sealed base with an outlet fitting to attach to the pumping system; so this housing must be used to be able to connect to the pump;
- only theimpactor stage for the 10 μm cutpoint (PM10) has the appropriate fittings to attach theraincover -- so to be able to use the raincover, the top stage has to be for PM.

Preparations of PUF’s at the Dutch laboratory.

Cutting andCleaning of PUF’s

The manufacturer of the sampler has provided 2 different metal pieces with the same dimensions as the foams that are needed. The technicians of the Dutch laboratory will cut

enough foams for all sampling weeks (3 (sampling periods) x 5 (sampling sites) x 5 (weeks per sampling period) x 3 (foams per stage) = 225 foams).
The pink PUF, used for impaction substrate has a density of 0.020 g/cc;

PUF color	Stage	Cutpoint µm	Label	Dimensions
pink	second impactor	2.52	P1	12x1.30x0.64cm(LxWxH)
pink	third impactor	0.12	P2	12x0.64x0.64cm(LxWxH)

The PUF substrate are provided (without cleaning) by the manufacturer. The following procedures will be used to cut and clean the pieces (handle PUF pieces only with clean unserrated forceps):

Method to cut substrate pieces:

required items:
unserrated stainless steel forceps
glass plate
scalpel
template for P1 (round, with curved rectangular slots)
template for P2 (rectangular, with straight slots)

P1 pink PUF directions:

lay out a piece of pink puff larger than the P1 template on the glass plate.
place the P1 template on top of the foam.
use the scalpel to cut out the P1 piece(s), following the template guidelines
each curved piece is about 13 cm long, in order to fit inside the slots in the substrate holder for the second stage.

P2 pink PUF directions:

lay out a piece of pink puff larger than the P2 template on the glass plate.
place the P2 template on top of the foam.
Put the rectangular template on top of the foam.
use the scalpel to cut out the P1 piece(s), following the template guidelines.

Method to clean PUF substrate pieces:

required items:
- large beakers (> 1 liter)
- unserrated stainless steel forceps
- ultrasonic bath large enough to hold the beaker
- ultrapure water (Milli-Q or equivalent)
- methanol (p.a.)

cleaning and drying procedure:

- put P1 and P2 pieces into the beaker(s).
- add the Milli-Q water to the beaker until it covers the foam pieces
- place beaker in the ultrasonic bath.
- place the bath in the clean air hood
- sonicate for 1 hour.
- repeat the same process for methanol (p.a.)
- repeat the same process another time with fresh methanol (p.a.)
- place the foam pieces in 50 ml Falcon tubes using tweezers.
- dry foams in tubes (disconnect the cap) in a stove for 12 hours at 70 ° Celsius.
- place the tubes with foams in a 20 ° Celsius, 50 %Rh room for 24 hours.
- close tubes.

method to store the clean, dry PUF pieces:

required items:
- for P1 and P2 pieces -- 50 ml Falcon tube with cap.
- aluminum foil

storing procedure:

- wrap the rack filled with the 50 ml tubes with aluminum foil (necessary to keep out light)
- store the wrapped racks in a refrigerator at + 4 °C
- estimated shelf life for cleaned PUF substrates is six months

Labeling of PUF's

- a label will be placed on the tube and for the "Fine"tube(s) an "F" will be writen on the cap of this tube.
- the following items will be present on each label:
- sampling city (Amsterdam, Lodz, Oslo, Rome, De Zilk)
- sampling period (Pollen, Summer, Winter)
- sampling week (number 1, 2, 3, 4, 5 and 6) some are reserve.
- sampling size: Coarse or Fine particles
- on the caps of Fine samples the letter "F" will be writen.

Operating Procedures

Preparation of impactor substrates holders (these procedures are performed in the laboratory):

Pre and post sampling weighing the tubes + PUF's.

Weighing should be performed in a temperature (20 °C) and relative humidity (50 %) controlled room (if available).
Before weighing of tubes (+ PUF's) can be performed the tubes must be put into the temperature/rH controlled room for at least 1 night. Tubes should be opened (cap loose, but on the tube) while adapting to the room temperature/rH. If a PUF sample is very wet at time of unloading, then a longer period should be used and the tube + PUF should be weighed more then once. A note should be written on the weighing datasheet.
All the PUF's are pre-packed in 50 ml polycarbonate tubes and are pre-labeled per week.

At the city where the sampling will be done they will be weighed again before and after sampling.
A analytical balance must be used with a minimum range of 50 gram and a readability of 0.1 mg (if possible 0.01 mg).
ThePUF's will be weighted inside and together with the tubes.
The difference between pre- and post weight of the tubes + foams is the mass of particles collected.
A reference tube with foam will be weighted also to check variances between days and balances.

Cleaning procedures for substrate holders:

* The substrate holder for size-selective inlet impactor stage (cutpoint 10 μm): remove the upper layer of the used grease from the collection substrate holder with a feeler gauge and paper wipes.
* The stages containing PUF: use cotton swabs moistened with (Milli-Q) water to wipe all surfaces that come in contact with the PUF pieces.

Preparation of the 10 μm substrate holder:

*fill the clean substrate holder with fresh grease (Dow Corning silicone high vacuum grease).
*using a metal straightedge, ensure that: a) the entire volume (except for 0.25 cm at each end of the cavity) is filled with grease; and b) the height of grease is level with the height of substrate holder.
Preparation of the PUF impactor substrate holders:

* There are two different substrate holders that should be filled with pink PUF.
The PUF for the substrate holder that will collect the "coarse particles"
(2.5 μm < particles < 10 μm) is 1.28 cm width and is cut as a part of a circle.
The PUF for the substrate holder that will collect the "fine"particles"
(0.12 μm < particles < 2.5 μm) is 0.64 cm width and is cut as a straight line.
*period. Remove the cover of the tube with the clean PUF piece(s). PS. never open two tubes at the same time since the pre-weight is performed with tube and cap. Switching caps give weighing faults!!
* Wear non-powdered handgloves during tube and foam handling.
* Use clean tweezers to take out the three pieces and insert them into the slot in the holder, spacing the pieces between the holes that are used to attach the substrate holder to the impactor stage
* The upper surface of each PUF piece must be flat with the surface of the holder

Installation of substrates into the sampler:

Assembly of sampler/installation of substrates
(this procedure is done indoors near or at the field sampling site):

* the installation of the sampling begins from the lower stage of the sampler to the top
* since the assembly of the sampler is from the bottom up, the stage with the substrate for the smallest cutpoint is attached first to the lower stage, with the other stages attached in the order of increasing cutpoints

* use the three screws for each stage to attach the substrate holders to the housings (stages)

Measurement/adjustment of gaps between acceleration jets and substrates:

After installation of the PUF substrates into the substrate holders of theimpaction stages, it is necessary to assure that the size of the gap between each jet and its corresponding substrate (see Figure 3.) is within the allowed tolerance (see table below). Each gap is measured with metal feeler gauges. If necessary, the substrate plate screws are adjusted to bring the gap to within the allowed tolerance. The gaps between holders and stages will be preset by the Dutch technicians, but should be checked at the installation of the sampler box at each sampling city.

Sampler stage	Gap between stage-holder	Used feeler gauge
> PM10	0.220 inch	0.215 inch
PM2.5-10	0.125 inch	0.120 inch
PM0.1-2.5	0.025 inch	0.023 inch

The correct feeler gauge (last columm) should be a composite of several gauges. It should be possible to move the gauge(s) freely between the holder and stage.

Set-up of the instrument on site:

A schematic diagram of the sampler is shown in Figure 2. The sampler, withraincover attached, is placed on top of the samplerbox (Figure 3). Between the pump and the sampler is a manually-adjusted flow control metering valve. A Magnahelic vacuum gage is connected to the outlet of the sampler to measure the total pressure drop of the system.
To set the flow through the sampler at 900 liter per minute (± 10 %), the vacuum gage should be set according to the calibration diagram. Adjustments should be made by opening/closing the valve.

The starting and ending flow, date, and time of day are recorded in the logbook. Depending on the duration of the sample collection, and on the stability of the sampling pump, it may be advisable to record the pressure at intermediate points of the sampling period.

Removal of PUF substrates:

Put the sampler upside down
Disconnect the “Fine” impactor stage
Unscrew the collection substrate holder of the second stage
Using two clean tweezers, remove each PUF piece from the holder and Place it in the 50 ml Falcon Tube with identification mark “Fine”.
Use the same tube for the remaining two pieces of foam substrate
Disconnect the “Coarse” stage
Unscrew the collection substrate holder of this stage
The 50 ml Falcon Tube with identification mark “Coarse”.
Use the two other tubes with the same identification mark for the Remaining two pieces of foam substrate
Disconnect the upper stage of the sampler.
Unscrew the collection substrate holder of this stage

Scrape a small bit of the grease layer away until the grease is “clean” again.
Add new grease on the substrate holder and using a small feeler gauge make the surface of the grease flat.
The holders should be cleaned with soap, water and alcohol before the new substrate PUF’s can be placed into the substrate holder.

Transportation of the sampler box

Packing the sampler box

Before each transport the sampler has to be disassembled, cleaned and placed inside the lower part of the electricity compartment of the sampler box.
Before the sampler can be taken off from the box, the quick connector has to be opened and the pressure tube disconnected. Then the sampler (including base plate) can be taken off the box.
There is a metal cap for the “sampler-opening” (on the roof of box). This cap is placed in the lower part of the electricity compartment during the sampling period.
The Low Volume Sampler connector on top of the box should be disconnected too. This connector should also be placed in the lower part of the electricity compartment.
There is also a small metal cap for the Low Volume Sampler opening (during sampling placed in the lower part of the electricity compartment
The electricity cord should also be placed in the lower part of the electricity compartment. In that compartment a jack is also present. (see page 11)

ATA carnet

For each transport the ATA carnet should be send with the sampler-box. The transportation company should handle the clearance at the borders. After arrival the RAIAP partner that receives the sampler-box should check if 2 forms are signed/stamped and the upper part has been torn of by the custom clearance. With the ATA carnet a set of keys will be available for the custom clearance to check the equipment.

Handling and transportation of the foams after sampling

After a sampling period ends and the sampler-box has been transported to the next sampling city, the foams of the sampling period can be shipped to the Dutch partner. All the tubes should be weighed before returning them.
The tubes with foams should be frozen at –20 ºC after weighing, and should be shipped frozen too. Preferable use a few kilo’s of dry ice for this (- 80 ºC).

Installing the sampler box

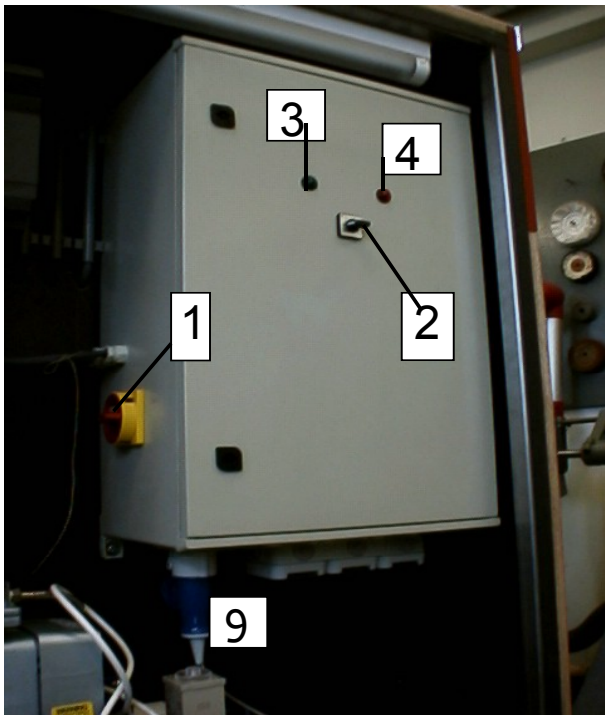


Figure 4 External components of the switchboard cabinet

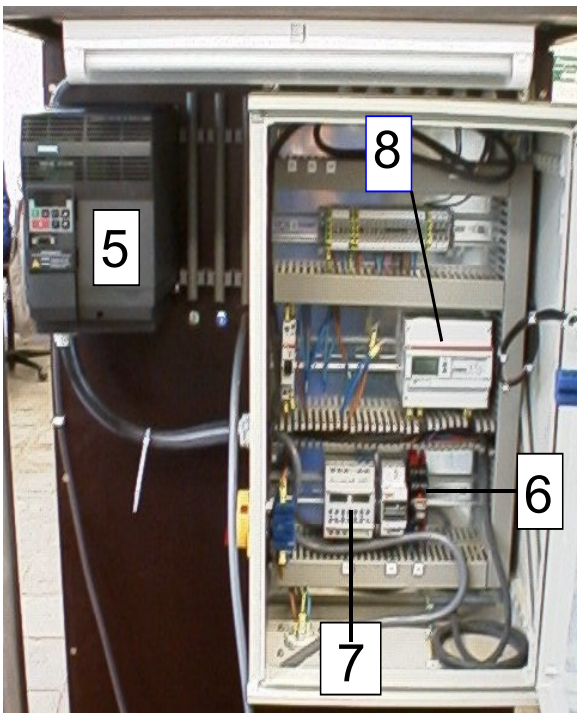


Figure 5 inside of the switchboard cabinet and a view of the motor control unit.

Main switch
On / Off switch for electrical installation.
Position “0” : Power Off
Position “1” : Power On
Switch must be Off before (dis)connecting the power to the mobile unit

Motor switch
“0” : Motor Off
Motor can be manually switched off. This switch position bypasses the clock but the clock remains running;
“1” : Motor On / Off by Clock. Motor is switched On/Off by a programmable clock. (will not be used in the RAIAP project);
“2” : Motor On. Motor can be manually switched on. This switch position bypasses the clock but the clock remains running.

Green light
Indicates that the motor in running or not.
Light Off: - No Power connected to the unit and main switch inOff position.
- Motor switch is in position “0” (Motor Off).
- When red light is On due to a fault detected by the Motor Control Unit.
Light On: - When motor is running with the motor switch in position “1” or “2” and

no MCU fault condition.

Red light
Indicates fault condition.
Light Off: - No Power connected to the unit and main switch inOff position.
- Motor switch is in position “0” (Motor Off).
- When motor runs correctly, Green light On and Motor switch in position “1” or “2”.

Light On: - Motor switch is in position “0” (Motor Off).
- When the motor stops running due to a failure encountered by the motor control unit.

Motor Control Unit (MCU)
The motor control unit is a frequency converter that converts asingle phase power supply into a three phase power supply for the motor.
N.P. The MCU is disabled as far as turning on/off and Log function are concerned. The keypad on the motor control is only to be used for changing the parameters.
N.P. The keypad should only be used by authorised personal only and when serious problems occur.
N.P. The default and user parameter settings are listed at the inside of the switchboard cabinet door.

Hour counter
Registers the time in hours that the pomp runs.
N.P. A complete instruction of this device can be found in the corresponding user manual.

Programmable Clock
Clock that switch the pomp on and off at predefined time intervals. These time intervals have to be programmed by the user. Using the keys at the front of the clock can alter the clock program. It is possible to program the clock a year in advance.
N.P. A complete instruction of the clock can be found in the corresponding user manual.

KWh meter
Measure the power consumption of the unit. Mobile RAIAP Unit 1 has a Reset button. This button should not be used. Mobile RAIAP Unit 2 has a meter without reset button.

Mains plug
Mains plug to which the mains cable has to connected to.
N.P. Make sure the main switch is switched off before disconnecting the main power.

Relais with uptime delay (not on the figure 5)
Mains plug to which the mains cable has to be connected.
N.P. Make sure the main switch is switched off before disconnecting the main power.

Operating the “Mobile RAIAP unit”

Precautions before operating the unit
Lock the wheels before connecting the unit to the main power.

Before connecting the power cable to the source make sure:
- the main switch is switched off
- the motor control switch is in the Motor Off position.
Make sure that the main power source has a 25 A fuse mounted.

Warning
When switching On the power for the first time it is possible the main fuse (25A) blows and has to be reset. The main fuse can be found either in the switch cabinet in the unit or in the location the main power is supplied from.
Do not use the keypad on the motor control unit to switch the motor On (Key“1”), Off (key “0”) or Log Key.

Warning
Parameters for the motor control unit (MCU) have to be set by a qualified person.
(A list with correct settings can be found at the inside of the switch cabinet)
To change the parameters settings of the motor control unit make sure the motor control switch is set to Motor Off (position “0”).

Running the unit
1 Connect power cable to the main supply somewhere near the unit (maximum cable length supplied with the unit 2 * 25 meter).
2Connect the power cable to switch cabinet.
3Check the display of the motor control unit that there’s no fault condition.
4 Set Main switch to “1”
5 For the RAIAP project the Clock control will not be used.
6Make sure the motor control unit is functioning properly. Changing the MCU settings see chapter 0.
7 Switch the motor control switch to “2”, green light should turn on.

Use of the adjustable Wheel base

The width of the unit can be adjusted to access doors up to 79 cm.
In normal use and during transportation the wheel-width should be set to maximum (approximately 125 cm) to gain better stability.

N.P. A small hydraulic jack is needed to lift the unit. It should be placed only at the long ends of the unit and under the jack mark between the two wheels.

Changing the wheel width

1 Place the jack at the marked position.
2Make sure the wheels that stay on the ground are blocked.
3Lift the unit to a heights that the wheels (max 2) can rotate freely. Make sure that you stop lifting the unit as soon as the wheels rotate freely.
4 remove the locking pin
5 widen or narrow the wheel width
6 put locking pin in place
7Lower the unit with the jack

Oil check, how often (once at arrival, once at depart)

Low volume sampler.

The Low Volume Sampler (LVS) is placed in the electricity room. It is fixed and should not be removed. The filters/samplers, supplied by the Norwegian partners, are placed on top of the sampler box using the support that is placed in the lower part of the electricity room when the sampler is transported. Place the support on the top of the box and fix the support with the butterfly nut. The cap should be placed inside the box since it will be needed again when the box it transported again. The filters should be connected to the support following the SOP of the LVS.

Maintenance

Roots blower

The oil of the “roots” blower (large pump) needs to be refilled after each month of continuous running. The oil needed is Tellus 100.
The “bottom” plug should be removed to empty the reservoir. Then place the plug back.
To fill the reservoir a volume of about 250 ml is needed. Filling should be performed with a 50 ml syringe through the upper plug (right side) while the lower (left side) plug is removed. Fill until oil starts draining from the lower plug. Then place both plugs back.
Pump
If the pump stops during a run it automaticly starts up again. If this happens frequently, the “leaking valve” can be opened a little more.
Sampler
The sampler needs to be cleaned every time thefaoms will be changed. Use mild soap, water and alcohol to clean the stages. Specially the slit of the lower stage (Fine) needs to be cleaned thoroughly.

Appendix 5: Chemical composition data

Concentrations of elements. (ng/mg collected PM)

Site season PMx	Amsterdam Spring Coarse	Amsterdam Spring Fine	Amsterdam Summer Coarse	Amsterdam Summer Fine	Amsterdam Winter Coarse	Amsterdam Winter Fine	De Zilk - Coarse	De Zilk - Fine	Lodz Spring Coarse	Lodz Spring Fine	Lodz Summer Coarse	Lodz Summer Fine	Lodz Winter Coarse	Lodz Winter Fine
Na	24,386	5,083	13,571	4,085	18,557	4,389	29,577	6,676	2,413	1,071	1,879	971	2,987	1,328
Fe	22,765	6,527	24,918	7,519	20,566	5,343	6,224	3,429	39,888	7,418	36,765	10,277	21,874	2,546
Mg	21,883	7,992	17,700	4,305	21,152	5,915	18,217	5,433	8,942	1,706	7,069	2,701	5,206	699
Ca	20,758	4,554	42,258	6,473	16,844	3,485	20,973	5,618	154,676	13,588	42,969	6,374	26,901	2,856
Si	14,148	4,134	32,665	1,315	2,898	705	11,266	5,089	55,503	8,810	6,309	1,613	4,821	3,882
K	7,764	4,749	9,386	2,568	5,430	3,151	7,541	4,946	8,098	7,693	8,100	8,273	4,668	11,122
Al	5,849	3,240	12,309	3,468	7,157	2,182	4,139	3,357	23,122	3,765	16,227	4,007	14,173	1,668
Zn	1,988	1,902	2,320	2,344	1,717	1,584	823	1,801	2,660	6,936	1,863	4,544	3,774	11,893
Cu	790	260	777	298	760	252	150	143	871	304	837	485	663	205
Mn	469	319	607	253	330	176	168	165	735	204	620	373	400	194
Ba	318	86	390	123	321	100	89	72	705	130	732	233	516	42
Ti	198	77	401	120	262	48	118	94	914	146	718	175	694	57
Sb	168	70	160	76	154	76	34	53	149	115	167	106	162	100
Pb	154	478	190	399	92	363	88	377	305	1,178	263	831	511	1,595
Sr	103	30	124	35	98	35	106	46	350	43	102	29	125	13
Ni	74	196	79	175	72	144	32	123	61	72	60	77	86	58
V	68	297	80	373	67	243	40	248	56	56	48	91	72	65
Cr	66	36	78	43	67	32	26	29	81	26	85	40	69	19
Mo	44	22	48	27	56	26	11	16	31	23	38	23	31	12
Hf	39	17	39	22	54	26	10	9	61	12	75	24	72	5
La	20	14	27	27	38	22	6	5	15	3	15	5	12	1
Ce	11.8	5.6	19.4	13.3	22.9	7.4	6.2	3.5	30.0	6.4	38.8	13.3	31.0	2.2
Li	11.8	5.4	17.5	5.7	10.7	3.9	8.2	5.3	26.5	19.0	18.6	12.3	27.3	23.8
Co	11.3	12.0	25.8	11.5	13.8	9.0	9.2	6.0	12.8	21.4	10.9	8.3	15.8	10.8
Sc	9.6	2.1	21.4	4.2	11.4	1.6	7.4	2.4	45.3	5.7	32.2	7.2	32.8	2.0
Cd	8.0	15.1	3.7	10.3	3.0	10.2	9.7	12.2	10.2	40.9	7.7	28.5	20.6	57.4
Nd	3.3	1.0	6.6	1.9	3.7	0.9	2.3	1.0	11.9	2.0	8.9	2.2	7.5	0.6
Tl	0.8	3.2	0.7	1.0	0.4	2.1	0.6	3.2	1.8	6.5	1.0	3.5	3.1	9.2
Hg	0.6	1.1	0.8	0.8	0.2	0.5	0.6	0.7	0.6	1.0	0.3	0.6	0.2	1.0
Sm	0.6	0.1	1.2	0.2	0.6	0.1	0.4	0.2	2.3	0.4	1.5	0.3	1.3	0.1
U	0.4	0.1	0.6	0.1	0.3	0.1	0.3	0.1	1.1	0.3	0.7	0.3	0.8	0.3
Be	0.1	0.1	0.6	0.2	0.5	0.1	0.1	0.2	2.2	0.3	1.6	0.6	2.7	0.3
As	56.0	41.1	29.7	35.7	13.6	33.7	19.1	42.3	38.4	81.1	23.4	42.6	70.6	102.7
Se	25.1	57.5	8.4	53.7	12.1	60.4	18.5	52.4	20.9	51.9	9.3	41.9	20.2	44.1

Concentrations of elements (ng/mg collected PM) (*continued*)

Site season PMx	Oslo Spring Coarse	Oslo Spring Fine	Oslo Summer Coarse	Oslo Summer Fine	Oslo Winter Coarse	Oslo Winter Fine	Oslo-2 Spring 2 Coarse	Oslo-2 Spring 2 Fine	Rome Spring Coarse	Rome Spring Fine	Rome Summer Coarse	Rome Summer Fine	Rome Winter Coarse	Rome Winter Fine
Na	7,454	2,967	5,546	2,501	10,071	2,872	5,264	2,474	5,992	2,341	6,019	2,719	3,746	472
Fe	35,380	14,953	48,110	16,590	49,977	9,569	30,619	8,146	111,239	26,431	35,885	14,122	79,819	6,805
Mg	14,252	5,373	12,221	4,782	14,604	3,716	10,600	2,924	28,782	8,360	11,764	4,329	8,249	739
Ca	27,176	8,893	29,756	6,819	18,686	3,437	16,577	3,882	180,772	27,125	57,836	13,018	86,424	4,321
Si	51,847	18,643	7,321	1,723	8,053	1,916	6,641	1,208	199,365	39,436	10,946	3,735	8,917	772
K	10,491	6,104	8,174	6,966	6,237	4,758	6,813	3,826	37,445	21,285	7,574	15,368	7,500	8,589
Al	20,211	7,260	18,408	3,938	18,252	3,253	16,138	2,480	89,338	16,042	31,618	9,141	22,646	1,089
Zn	2,733	6,115	2,336	4,353	1,576	2,765	1,730	1,406	2,754	4,652	1,193	2,105	2,273	1,899
Cu	1,564	822	2,155	878	2,215	570	1,296	396	3,133	836	1,170	735	3,390	467
Mn	583	269	633	334	662	222	521	162	1,464	520	627	289	867	166
Ba	677	329	957	605	879	199	532	168	2,159	621	778	312	1,528	136
Ti	1,439	376	1,167	203	1,934	214	1,228	161	2,334	343	1,065	340	871	51
Sb	310	186	466	232	487	115	254	89	665	403	225	239	620	136
Pb	172	264	224	355	205	252	160	159	1,247	2,391	328	1,213	597	510
Sr	97	41	106	66	123	26	80	24	749	169	281	82	345	23
Ni	67	160	92	262	77	139	77	114	213	226	88	237	165	74
V	72	354	78	444	74	227	62	225	216	258	90	362	154	65
Cr	92	58	154	67	135	38	101	35	378	134	122	78	307	57
Mo	63	39	105	48	111	29	64	25	232	76	70	51	240	40
Hf	75	37	129	42	141	29	95	26	326	57	194	77	272	24
La	16	6	16	6	22	3	16	3	79	12	45	12	40	2
Ce	36.7	14.4	47.1	13.3	70.0	12.1	46.1	7.2	159.3	26.0	113.8	32.7	112.9	6.8
Li	16.0	6.7	12.9	6.8	10.9	4.4	11.7	3.4	81.7	16.8	26.0	8.0	16.3	3.6
Co	13.8	7.0	13.9	9.5	13.5	9.6	15.6	7.3	39.8	11.9	14.4	23.6	15.6	6.4
Sc	39.6	10.9	34.7	6.0	35.1	4.2	31.0	4.1	121.9	26.2	38.3	10.6	28.0	1.4
Cd	1.9	11.9	3.4	14.3	1.9	10.9	1.8	5.6	4.3	24.5	5.8	17.0	3.8	11.0
Nd	13.6	4.0	10.5	2.5	15.3	1.7	11.6	1.6	60.9	8.9	26.7	6.6	23.1	1.1
Tl	0.3	1.5	0.4	2.8	0.3	1.3	0.4	0.7	2.9	7.5	1.0	4.0	1.8	3.8
Hg	0.5	0.9	0.1	0.3	0.2	0.2	0.4	0.2	1.5	1.3	0.5	0.9	0.1	0.3
Sm	2.3	0.6	1.6	0.3	2.2	0.2	1.7	0.3	10.1	1.5	3.7	0.9	3.2	0.1
U	0.7	0.3	0.5	0.1	0.5	0.1	0.5	0.1	4.1	0.6	1.5	0.4	1.6	0.1
Be	0.9	0.2	0.8	0.1	0.9	0.1	0.7	0.1	10.4	1.0	5.5	1.1	3.5	0.1
As	14.8	93.4	17.6	60.0	20.5	54.4	40.9	37.8	41.2	59.5	21.0	34.1	29.0	43.1
Se	3.3	39.3	8.4	32.3	11.1	22.4	10.5	18.3	11.9	51.0	13.2	40.8	7.7	20.4

Concentration of inorganics (ug/mg PM)

Site season PMx	Amsterdam Spring Coarse	Amsterdam Spring Fine	Amsterdam Summer Coarse	Amsterdam Summer Fine	Amsterdam Winter Coarse	Amsterdam Winter Fine	De Zilk - Coarse	De Zilk - Fine	Lodz Spring Coarse	Lodz Spring Fine	Lodz Summer Coarse	Lodz Summer Fine	Lodz Winter Coarse	Lodz Winter Fine
NH4	25	122	13	169	17	129	9	48	6	95	3	110	34	101
Cl	174	35	48	6	236	44	227	33	29	43	16	5	104	80
NO3	186	296	251	203	196	305	92	100	57	106	73	39	81	101
SO4	50	169	37	209	33	141	46	139	41	174	13	356	106	157
Br	-	-	-	-	-	-	-	-	-	-	-	-	-	-

Site season PMx	Oslo Spring Coarse	Oslo Spring Fine	Oslo Summer Coarse	Oslo Summer Fine	Oslo Winter Coarse	Oslo Winter Fine	Oslo-2 Spring 2 Coarse	Oslo-2 Spring 2 Fine	Rome Spring Coarse	Rome Spring Fine	Rome Summer Coarse	Rome Summer Fine	Rome Winter Coarse	Rome Winter Fine
NH4	208	46	5	166	13	63	3	57	5	2	3	93	3	61
Cl	40	6	35	7	105	32	25	2	24	3	27	5	17	21
NO3	78	58	113	60	70	112	96	45	141	98	160	22	41	138
SO4	23	139	15	413	29	94	20	191	84	428	10	334	6	73
Br	-	-	-	-	-	-	-	-	-	-	-	-	-	772

Concentration of PAHs (ng/mg PM)

Site	Amsterdam						De Zilk		Lodz					
season	Spring	Spring	Summer	Summer	Winter	Winter	-	-	Spring	Spring	Summer	Summer	Winter	Winter
PMx	Coarse	Fine	Coarse	Fine	Coarse	Fine	Coarse	Fine	Coarse	Fine	Coarse	Fine	Coarse	Fine
Naftalene	1.64	1.89	1.09	0.77	2.21	1.99	1.90	1.85	1.34	5.78	0.85	3.85	2.53	0.96
1-Methyl-naftalene	0.90	1.11	0.63	0.78	1.82	1.40	0.73	1.03	1.52	3.86	1.04	1.68	9.27	3.01
Bifenyl	2.04	2.88	1.90	0.02	0.19	0.03-	1.63	3.04	1.32	4.49	0.09	0.00	0.18	2.08
2,6-Dimethyl-naftalene	1.99	12.39	3.55	0.91	0.40	0.71	0.90	4.15	1.17	0.58	0.89	0.03	0.25	1.22
Acenaftylene	2.02	2.50	0.93	1.90	1.70	0.04	6.31	1.35	20.65	47.86	3.03	4.37	9.65	49.01
Acenaftene	14.22	21.57	16.04	27.79	23.38	42.02	7.80	24.95	10.81	25.07	15.34	18.21	15.39	4.84
2,3,5-Trimethyl-naftalene	0.02	0.18	0.02	0.01	0.01	0.01	0.02	0.04	0.53	0.35	0.02	0.01	0.19	1.78
Fluorene	0.70	2.76	1.57	1.86	0.80	1.69	0.34	1.92	8.73	2.90	1.08	1.06	0.71	17.78
Fenantrene	10.67	10.01	9.14	0.38	0.20	0.64	5.33	5.58	73.10	27.54	8.39	2.34	63.27	111.72
Anthracene	0.71	0.82	0.50	0.03	0.05	0.04	0.31	0.57	25.63	11.16	0.18	0.04	0.44	47.48
1-Methyl-fenantrene	2.96	1.86	1.69	0.16	0.01-	0.10	0.57	0.86	29.64	13.22	0.04	0.05	0.11	49.25
Fluorantene	25.95	24.71	23.56	8.22	22.08	18.27	9.14	13.29	85.90	40.41	38.79	9.83	114.44	151.93
Pyrene	22.91	20.70	14.88	6.84	16.90	16.63	5.52	10.16	80.54	54.36	44.30	11.24	136.17	159.32
Benz[a]antracene	2.69	8.94	1.16	3.59	1.67	11.51	0.59	6.99	55.61	70.20	28.25	23.34	195.57	161.25
Chrysene	3.70	12.09	2.34	3.82	2.84	10.85	1.12	9.65	45.56	46.00	25.02	11.61	83.67	110.89
Benzo[b]fluorantene	4.54	24.08	3.13	9.11	2.55	26.28	1.43	21.87	80.10	127.10	25.60	76.65	185.28	270.35
Benzo[k]fluorantene	0.86	4.05	0.48	1.01	0.66	4.36	0.29	3.84	18.07	36.83	4.84	8.49	36.64	80.00
Benzo(e)pyrene	2.05	14.86	1.90	4.73	1.37	10.98	0.54	14.79	23.72	43.53	9.98	38.21	67.78	96.93
Benzo[a]pyrene	1.38	6.95	0.82	2.04	1.19	8.59	0.36	6.28	28.59	60.52	7.09	29.26	100.66	143.37
Perylene	0.05	1.12	0.03-	0.63	0.16	2.06	0.44	0.92	6.01	14.51	1.98	7.76	25.28	30.70
Indeno[1,2,3-cd]-pyrene	1.39	13.22	1.56	2.26	1.23	8.84	0.23	13.96	25.73	2.09	6.18	18.03	71.84	5.38
Dibenzo[a,h]antracene	0.29-	0.18	0.32-	0.02	0.18	1.47	0.06-	0.29	1.60	4.37	0.17	0.55	2.96	10.12
Benzo[g,h,i]perylene	1.39	14.69	2.74	2.93	1.22	8.60	0.26	13.34	24.64	58.67	5.32	18.87	57.77	109.56

Concentration of PAHs (ng/mg PM) (*continued*)

Site	Oslo						Oslo-2		Rome					
season	Spring	Spring	Summer	Summer	Winter	Winter	Spring 2	Spring 2	Spring	Spring	Summer	Summer	Winter	Winter
PMx	Coarse	Fine	Coarse	Fine	Coarse	Fine	Coarse	Fine	Coarse	Fine	Coarse	Fine	Coarse	Fine
Naftalene	2.18	2.66	0.79	4.90	1.92	3.19	0.83	0.90	1.95	4.19	2.66	0.97	1.62	2.95
1-Methyl-naftalene	0.88	3.06	1.01	7.02	1.33	2.09	0.33	1.49	0.55	1.43	1.05	1.07	1.15	2.33
Bifenyl	4.07	5.88	0.05-	0.02-	0.05-	0.34	0.01	0.03	1.24	3.86	0.02-	0.04	0.05-	0.31
2,6-Dimethyl-naftalene	9.96	0.30-	0.70	0.02	1.18	0.35	0.39	1.68	1.08	0.06-	0.41	0.07	0.26	0.13
Acenaftylene	3.92	0.55-	3.75	1.65	16.46	18.72	0.10	0.55	0.44	1.34	0.20	0.04	4.12	10.25
Acenaftene	29.82	57.63	13.96	34.84	13.76	28.34	19.78	33.52	9.79	35.26	27.67	18.13	9.59	26.49
2,3,5-Trimethyl-naftalene	0.13	0.03	0.06	0.03	0.02	0.04	0.01-	0.04	0.04	0.06	0.01	0.01	0.04	0.08
Fluorene	2.48	3.36	1.16	2.48	0.62	1.95	2.49	4.46	1.56	2.47	1.02	1.81	0.65	0.99
Fenantrene	23.09	10.25	3.29	2.02	13.71	11.02	0.23-	0.78	4.52	2.29	0.17	0.38	4.95	2.34
Anthracene	2.63	1.58	0.28	0.17	0.80	0.64	0.07	0.05	0.40	0.34	0.02	0.05	0.43	0.31
1-Methyl-fenantrene	6.72	3.74	0.11	0.19	0.06	0.15	0.03	1.08	1.98	0.76	0.05	0.07	0.11	0.12
Fluorantene	34.08	24.83	23.44	14.49	52.81	44.22	16.92	9.91	12.04	6.01	5.99	3.59	45.98	20.91
Pyrene	37.92	29.58	30.94	17.65	67.65	53.35	20.62	14.02	15.06	7.54	6.59	4.51	59.79	25.60
Benz[a]antracene	3.28	9.57	5.89	16.06	11.54	86.52	3.50	5.76	1.41	4.09	1.75	4.58	16.94	59.87
Chrysene	4.28	11.18	3.97	9.72	7.45	43.74	2.75	4.68	2.82	5.71	2.92	5.32	12.49	30.15
Benzo[b]fluorantene	2.89	18.40	3.79	24.01	7.96	123.13	1.66	8.12	1.97	13.90	2.39	17.30	13.17	90.69
Benzo[k]fluorantene	0.35	3.03	0.74	2.52	1.50	14.60	0.55	2.20	0.28	1.81	0.76	1.96	2.58	12.91
Benzo(e)pyrene	1.34	6.51	2.24	13.82	3.73	48.91	1.41	5.67	1.48	7.89	1.45	8.99	5.77	46.35
Benzo[a]pyrene	0.62	4.58	1.44	7.05	3.84	52.46	0.94	3.56	0.56	2.56	1.16	3.81	5.59	50.16
Perylene	0.22-	0.59	0.31	2.28	0.79	12.37	0.49	0.37	0.00	0.44	0.14	1.12	1.20	13.91
Indeno[1,2,3-cd]-pyrene	0.33	4.92	1.06	5.24	3.66	29.62	1.18	3.86	1.35	5.28	2.17	5.33	5.34	29.04
Dibenzo[a,h]antracene	0.22-	0.81-	0.01-	0.06	0.50	0.65	0.07-	0.44	0.58	0.12-	0.29	0.05	0.04	0.93
Benzo[g,h,i]perylene	1.22	8.90	1.78	9.01	5.57	39.07	1.54	5.38	2.00	9.45	2.02	6.38	7.22	31.67

Concentration of traffic markers hopanes and steranes (ng/mg PM)

Site			Amsterdam				De Zilk		Lodz					
season	Spring	Spring	Summer	Summer	Winter	Winter	-	-	Spring	Spring	Summer	Summer	Winter	Winter
PMx	Coarse	Fine	Coarse	Fine	Coarse	Fine	Coarse	Fine	Coarse	Fine	Coarse	Fine	Coarse	Fine
17a(H)-22,29,30-Trisnorhopane	1.81	3.87	1.95	2.32	1.25	2.62	0.62	2.38	5.62	17.03	4.42	3.73	7.52	19.86
17a(H)-21b(H)-Hopane	3.91	8.99	3.79	6.35	3.77	7.98	0.48	6.00	9.83	17.84	8.10	6.90	10.16	20.77
	5.72	12.86	5.74	8.67	5.02	10.60	1.11	8.38	15.45	34.86	12.52	10.63	17.67	40.63
abb-20R-Cholestane	1.34	3.52	1.26	4.21	1.88	3.92	0.26	1.64	3.85	6.55	6.38	9.16	3.55	4.52
5a-Cholestane	0.48	1.08	0.35	1.59	0.66	1.59	0.12	0.61	1.73	2.41	2.54	3.88	1.30	3.07
abb-20R-24S-Methylcholestane	0.60	1.69	0.58	1.76	0.60	1.62	0.12	0.92	1.85	2.95	3.17	6.67	1.43	2.15
abb-20R-24R-Ethylcholestane	1.10	2.97	0.98	3.19	1.27	3.28	0.22	1.86	2.86	4.16	4.07	5.90	2.89	3.05

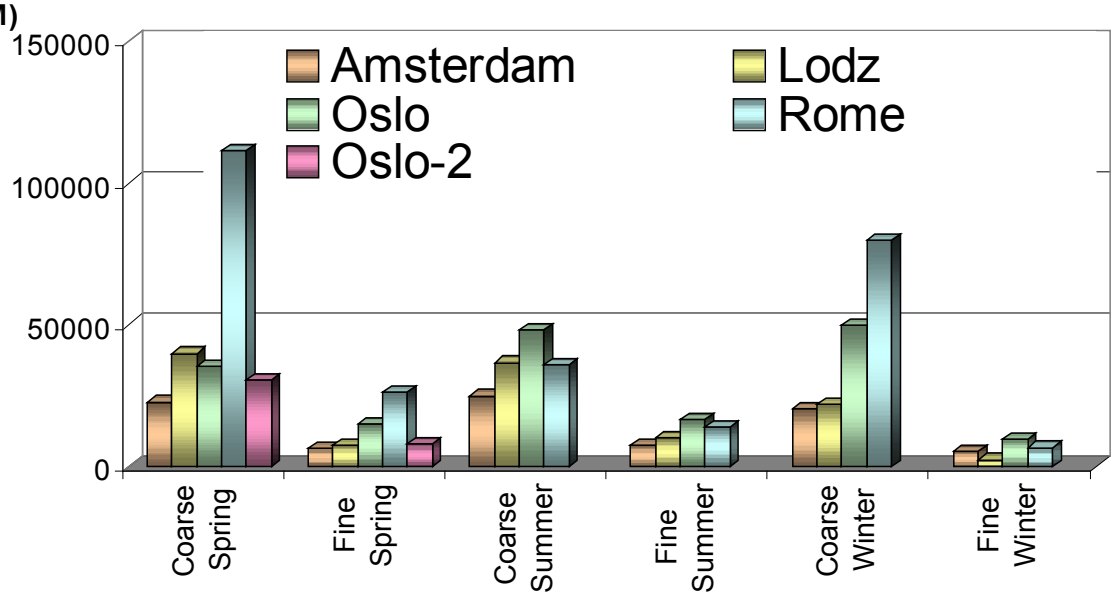
Site			Oslo				Oslo-2		Rome					
season	Spring	Spring	Summer	Summer	Winter	Winter	Spring 2	Spring 2	Spring	Spring	Summer	Summer	Winter	Winter
PMx	Coarse	Fine	Coarse	Fine	Coarse	Fine	Coarse	Fine	Coarse	Fine	Coarse	Fine	Coarse	Fine
17a(H)-22,29,30-Trisnorhopane	3.26	8.24	3.12	5.76	2.56	9.22	2.65	3.49	3.52	6.82	2.55	2.85	4.22	8.28
17a(H)-21b(H)-Hopane	6.37	17.58	5.93	10.43	7.33	12.89	7.84	9.58	6.90	18.59	6.04	9.54	10.07	17.09
	9.63	25.82	9.05	16.19	9.90	22.11	10.49	13.07	10.42	25.41	8.59	12.39	14.30	25.36
abb-20R-Cholestane	2.45	6.63	4.34	11.03	3.78	16.23	3.23	5.27	1.81	3.96	2.93	3.18	4.16	11.27
5a-Cholestane	0.84	2.40	1.84	5.05	1.58	6.66	0.94	2.15	0.86	2.10	0.88	1.70	2.17	6.11
abb-20R-24S-Methylcholestane	1.03	3.10	1.52	4.62	1.77	6.00	1.05	2.13	1.01	2.77	0.94	2.00	1.97	5.36
abb-20R-24R-Ethylcholestane	1.69	5.37	2.51	6.80	2.84	9.19	2.29	4.29	1.67	5.53	1.87	4.08	3.79	9.05

Code	Location	Season	Fraction	Assay for endotoxin		
				EPT suspensions ng/mg	LAL ultrasonificated ng/mg	LAL suspension ng/mg
11	A'dam	Spring	Coarse	4.37	6.67	3.33
14	A'dam	Spring	Fine	0.16	3.33	0.67
6	A'dam	Summer	Coarse	1.20	16.67	13.33
8	A'dam	Summer	Fine	2.55	0.67	3.33
22	A'dam	Winter	Coarse	1.38	0.17	6.67
16	A'dam	Winter	Fine	0.21	0.08	1.33
21	Lodz	Spring	Coarse	1.15	0.33	3.33
25	Lodz	Spring	Fine	1.01	0.67	1.67
17	Lodz	Summer	Coarse	1.03	13.33	13.33
5	Lodz	Summer	Fine	0.62	3.33	1.67
24	Lodz	Winter	Coarse	4.30	0.67	3.33
20	Lodz	Winter	Fine	0.08	0.04	0.00
2	Oslo	Spring	Coarse	2.00		
23	Oslo	Spring	Fine	0.70		
15	Oslo	Summer	Coarse	0.97	16.67	16.67
7	Oslo	Summer	Fine	1.04	6.67	6.67
18	Oslo	Winter	Coarse	2.44	0.33	3.33
10	Oslo	Winter	Fine	0.11	0.67	1.33
28	Oslo-2	Spring	Fine	0.45	0.33	1.67
27	Oslo-2	Spring	Coarse	3.40	33.33	33.33
1	Rome	Spring	Coarse	1.16	13.33	33.33
3	Rome	Spring	Fine	0.94	0.33	0.83
26	Rome	Summer	Coarse	2.37	16.67	13.33
19	Rome	Summer	Fine	2.23	0.08	0.67
13	Rome	Winter	Coarse	2.15	8.33	6.67
4	Rome	Winter	Fine	0.26	0.08	1.67
9	De Zilk	Autumn	Coarse	0.90	13.33	13.33
12	De Zilk	Autumn	Fine	0.51	0.33	1.67

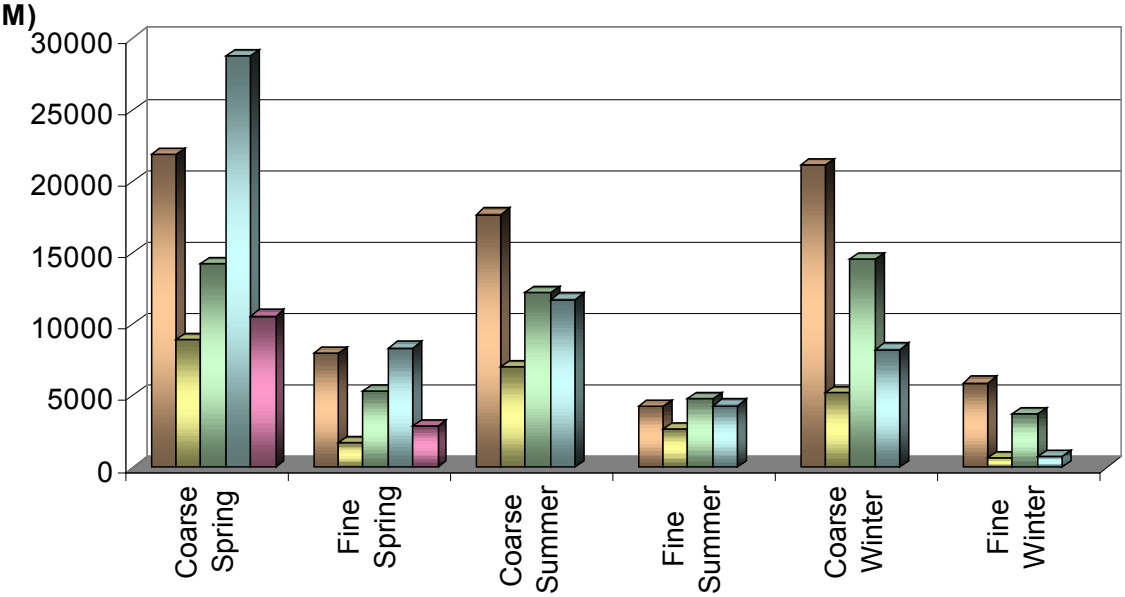
Concentration of endotoxins determined in PM per ml suspensions

Appendix 6: Figures

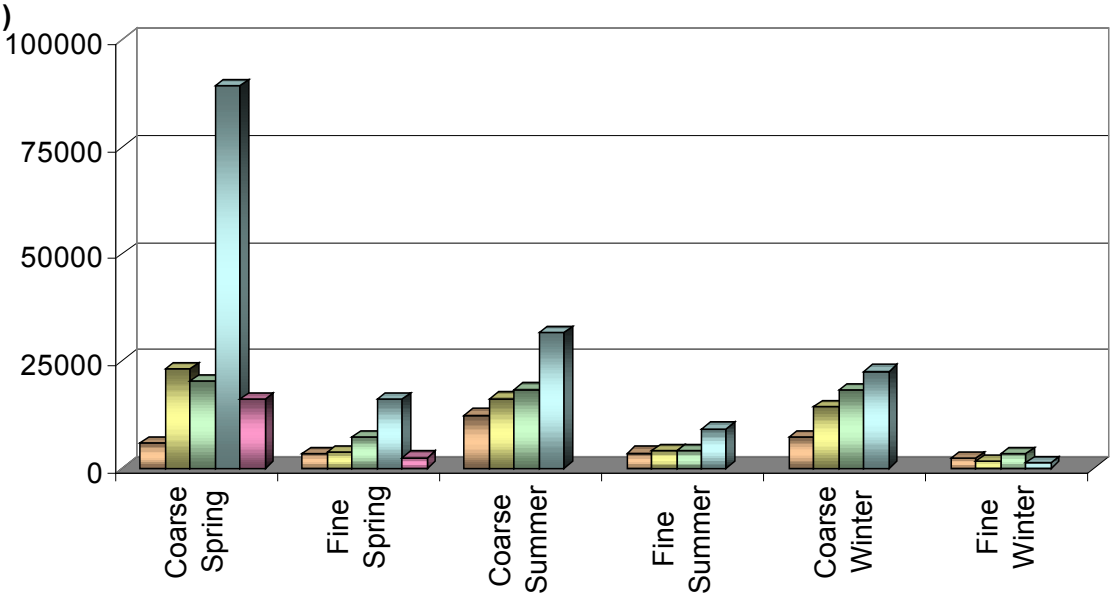
Fe (ng/mg PM)



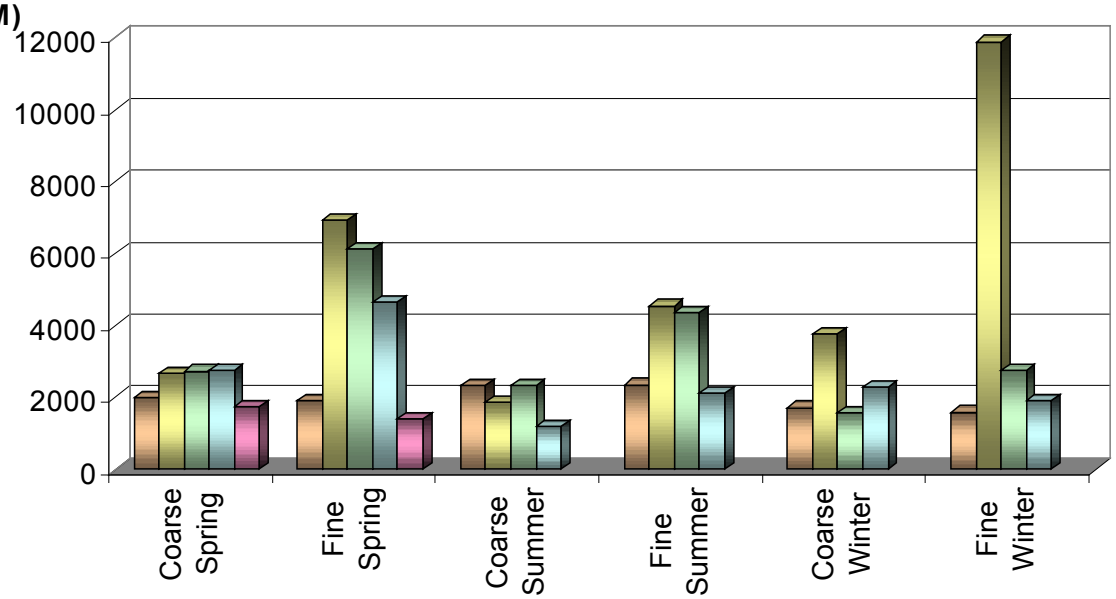
Mg (ng/mg PM)



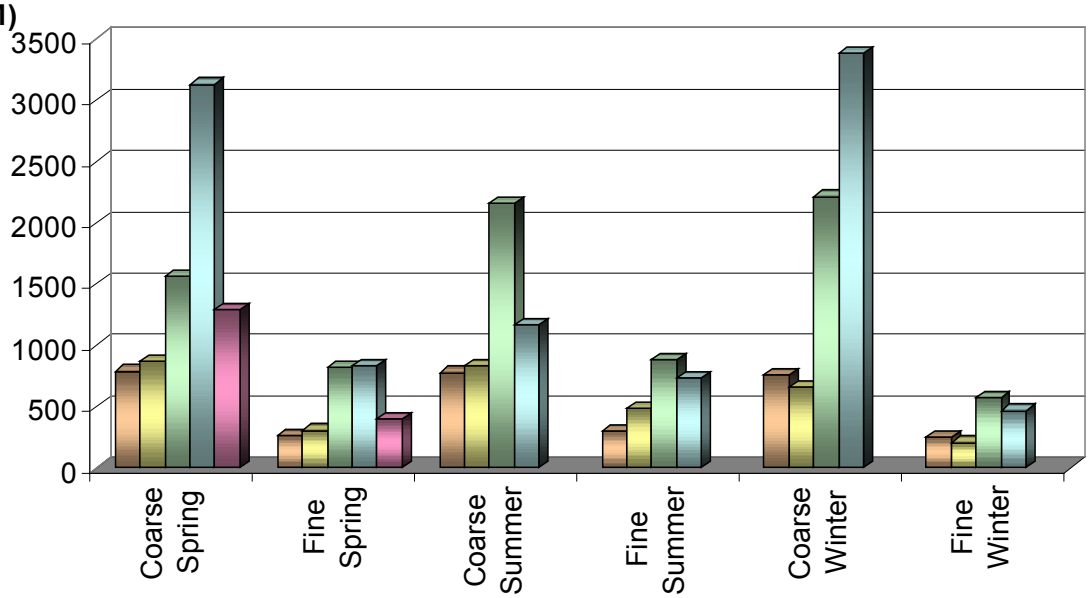
Al (ng/mg PM)



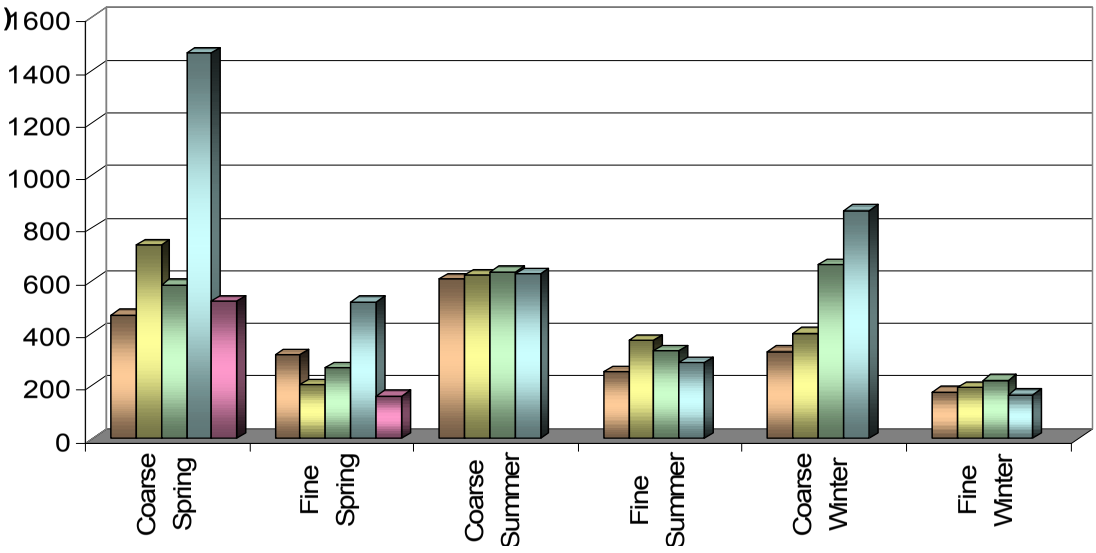
Zn (ng/mg PM)



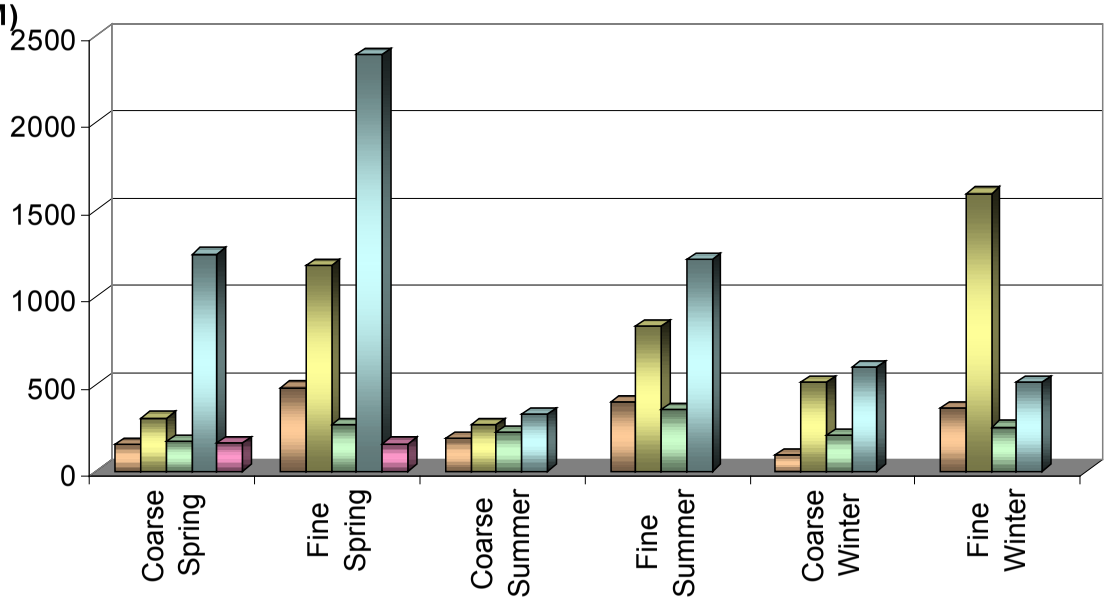
Cu (ng/mg PM)



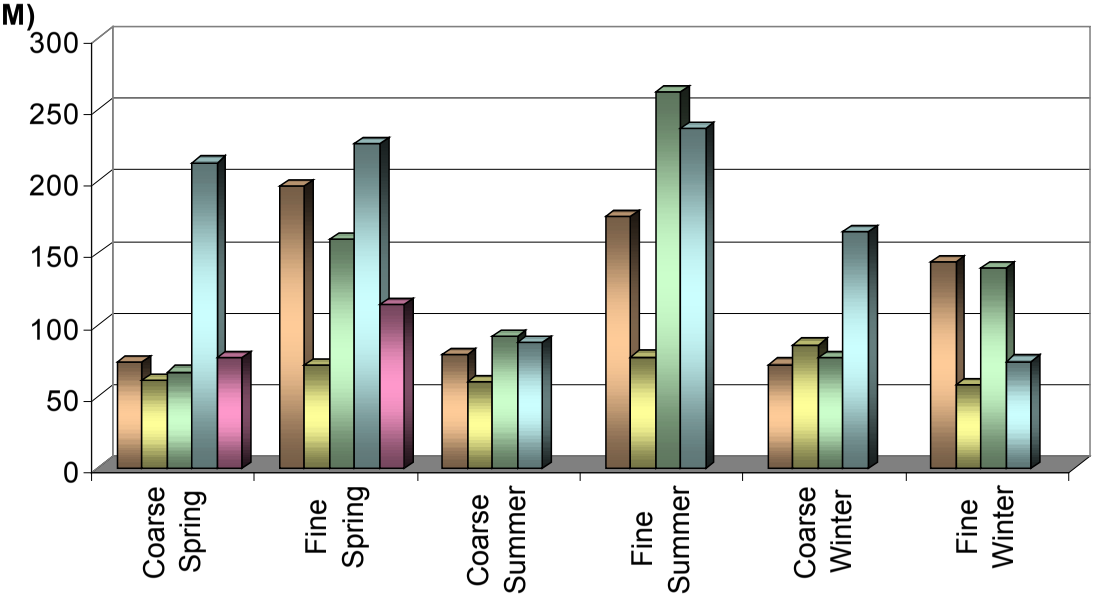
Mn (ng/mg PM)

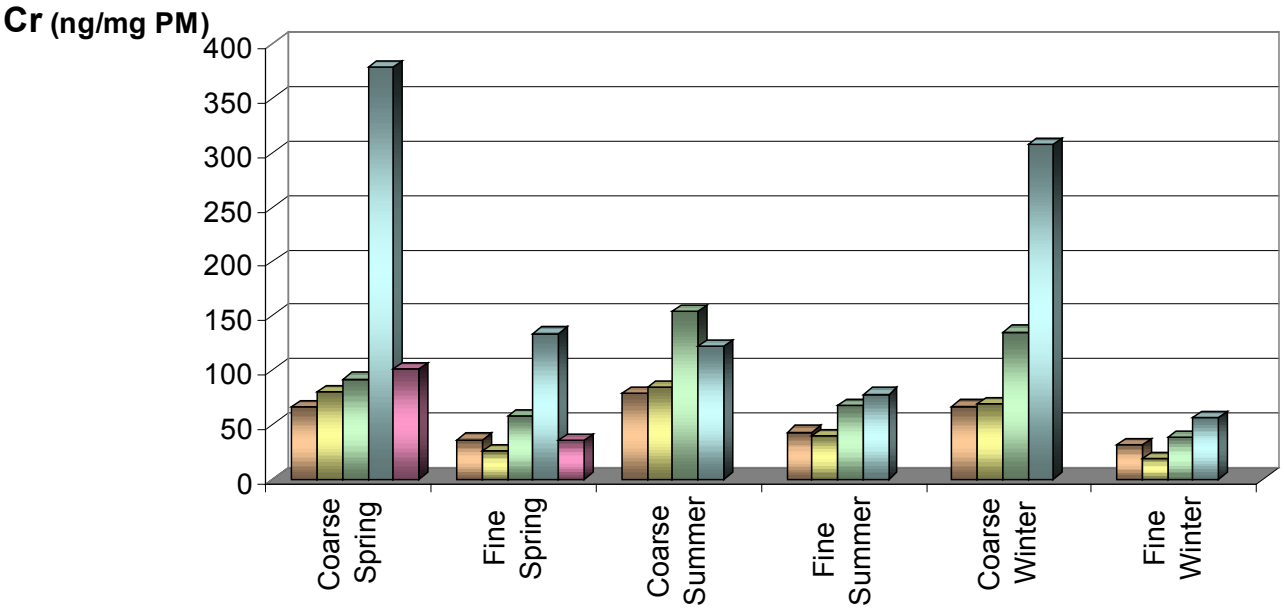


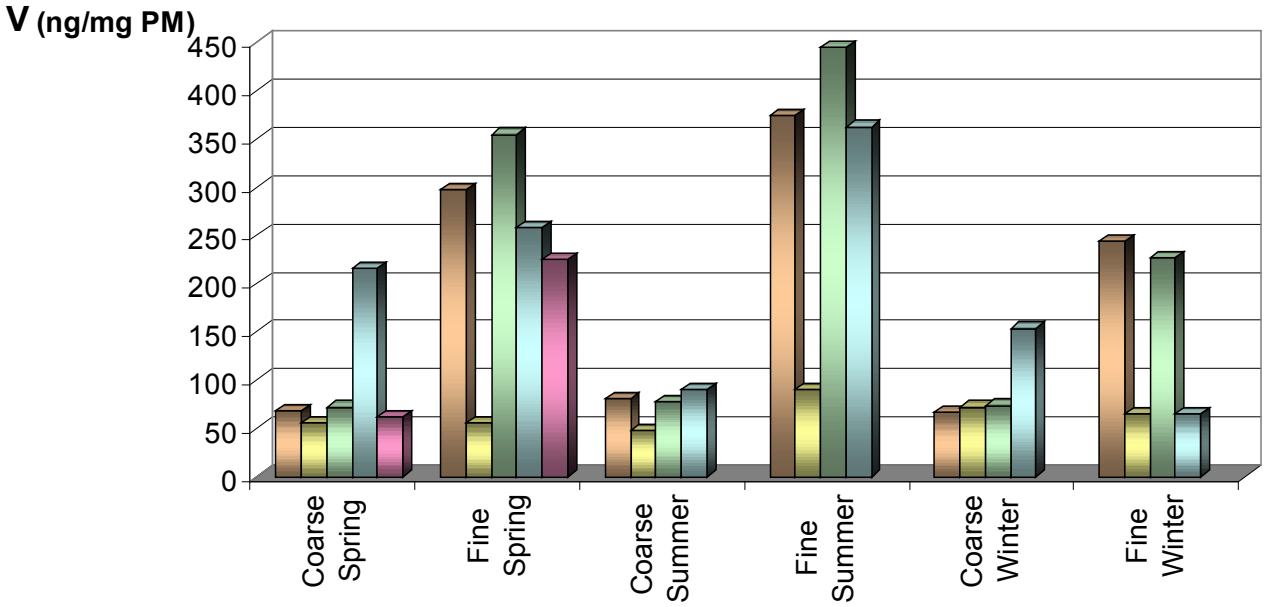
Pb (ng/mg PM)

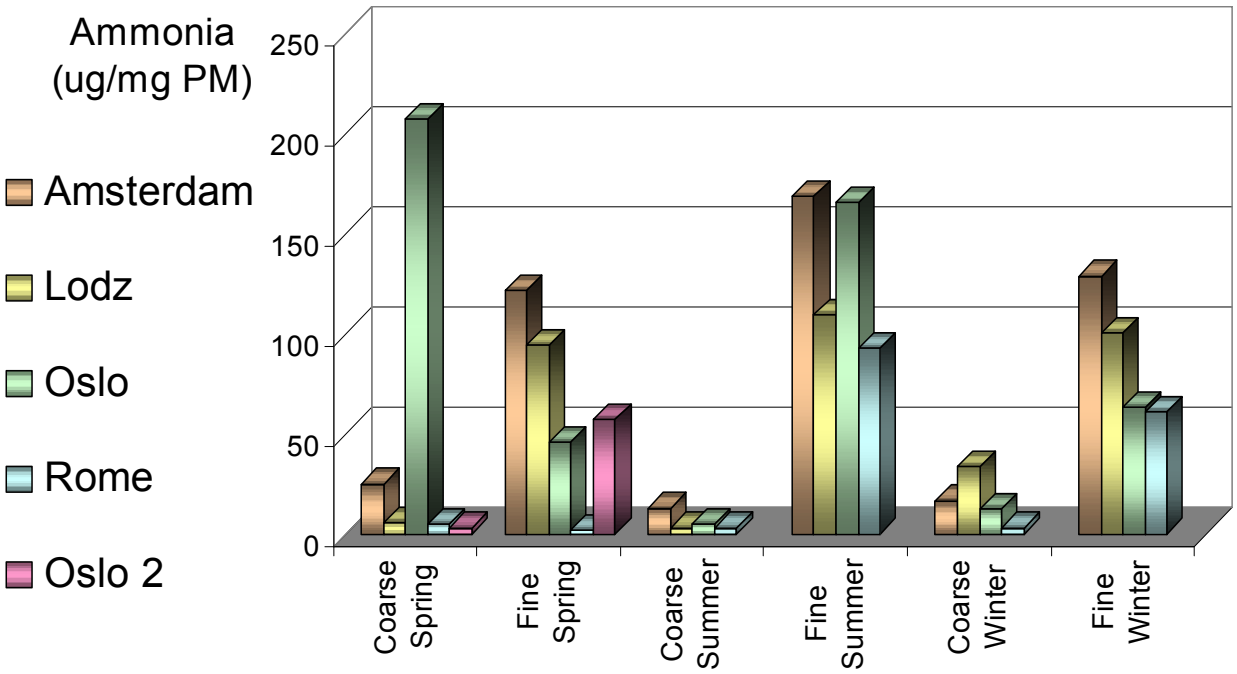


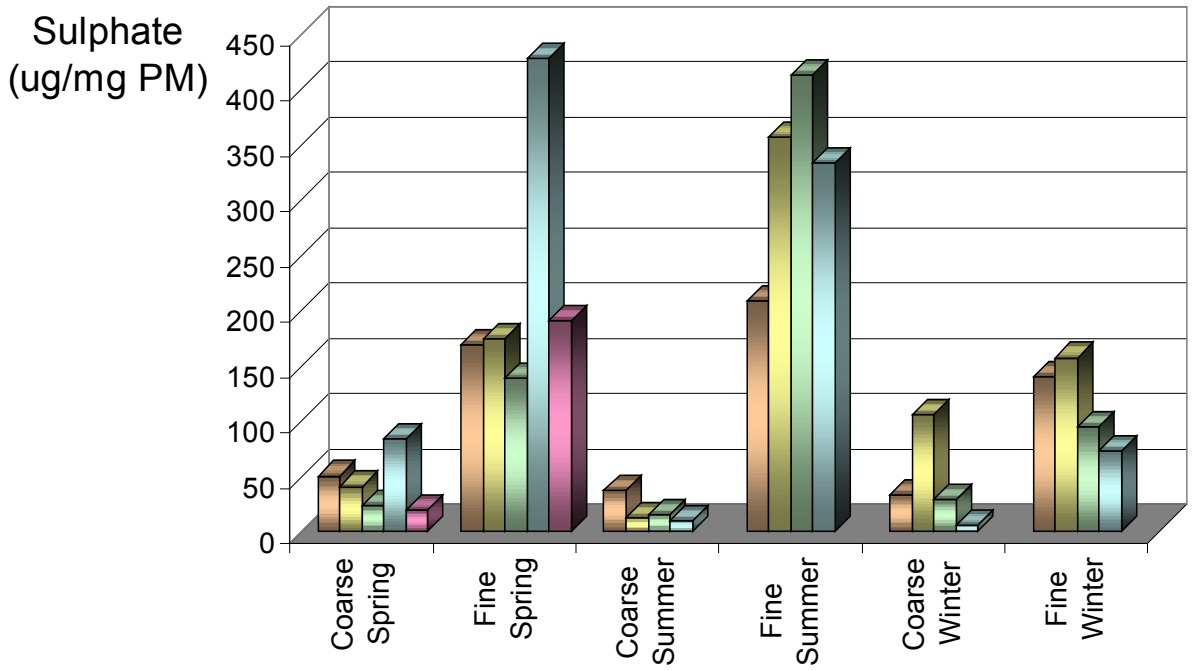
Ni (ng/mg PM)

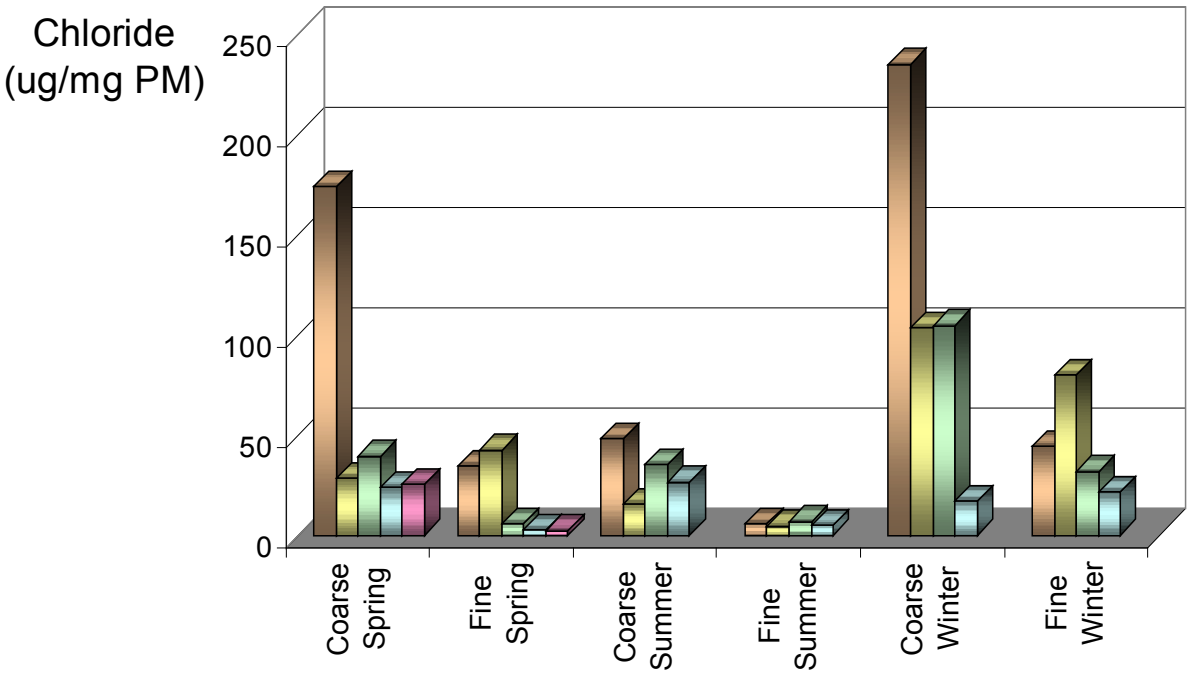


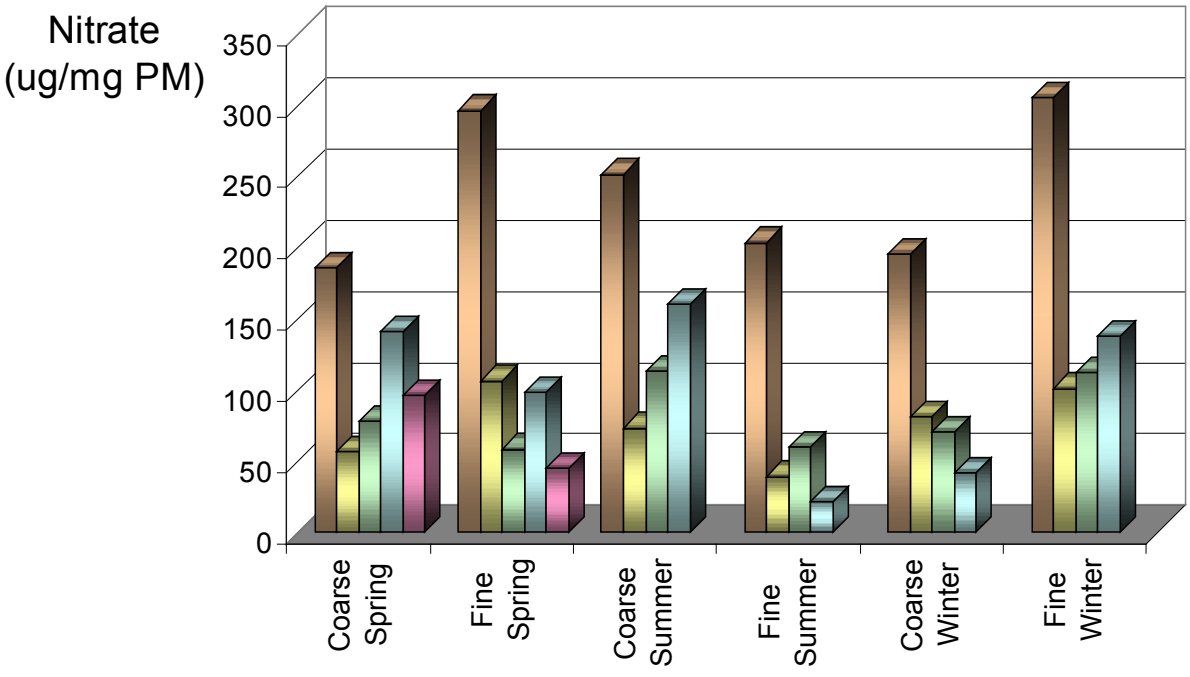

Cr (ng/mg PM)
400
350
300
250
200
150
100
50
0
Coarse Spring
Fine Spring
Coarse Summer
Fine Summer
Coarse Winter
Fine Winter


V (ng/mg PM)
450
400
350
300
250
200
150
100
50
0
Coarse Spring
Fine Spring
Coarse Summer
Fine Summer
Coarse Winter
Fine Winter

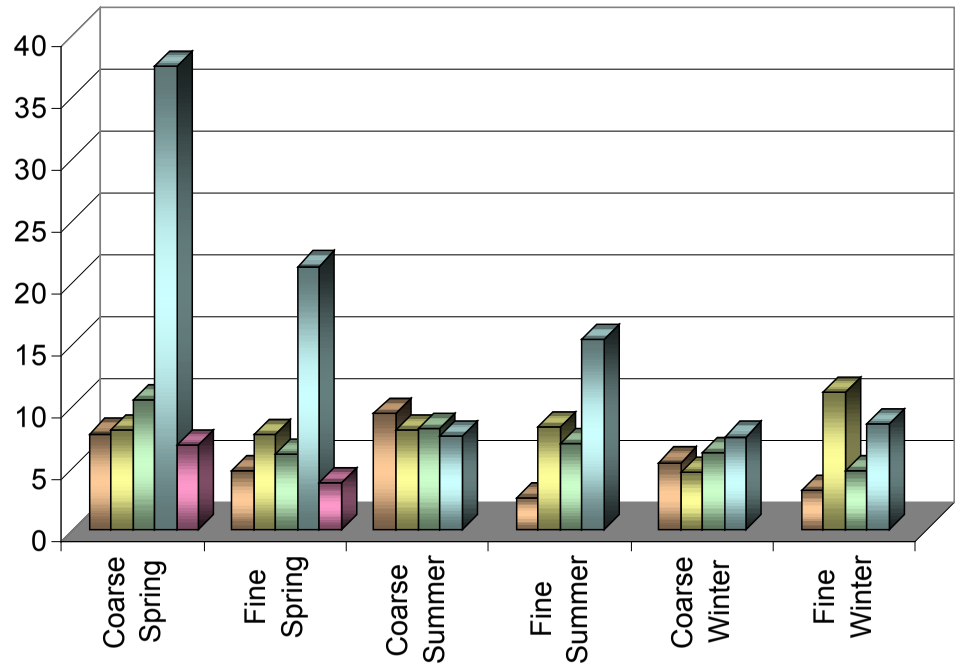

Ammonia
(ug/mg PM)
Amsterdam
Lodz
Oslo
Rome
Oslo 2
250
200
150
100
50
0
Coarse Spring
Fine Spring
Coarse Summer
Fine Summer
Coarse Winter
Fine Winter


Sulphate
(ug/mg PM)
450
400
350
300
250
200
150
100
50
0
Coarse Spring
Fine Spring
Coarse Summer
Fine Summer
Coarse Winter
Fine Winter

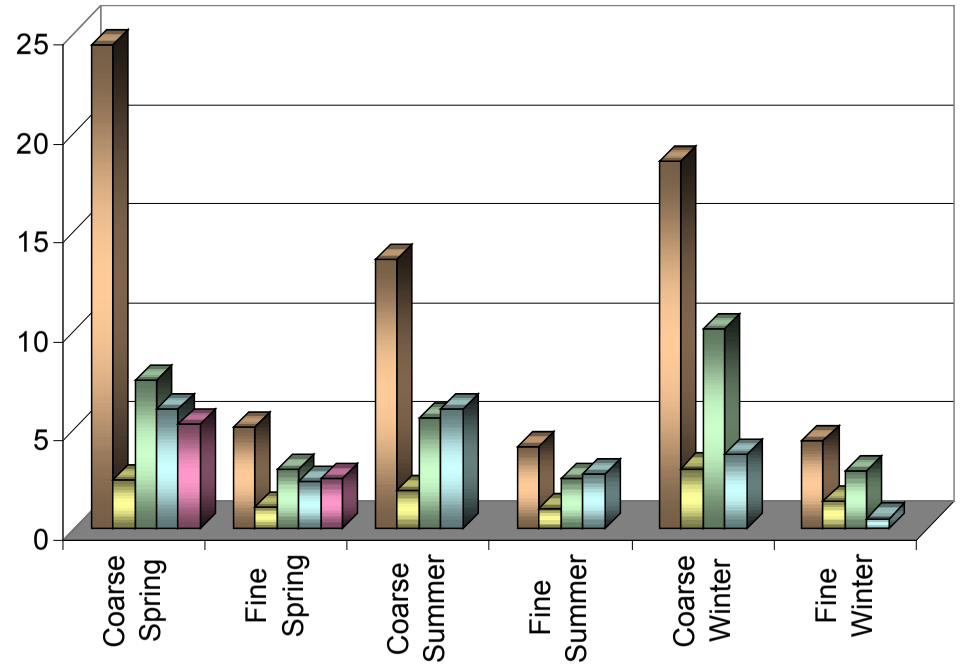

Chloride
(ug/mg PM)
250
200
150
100
50
0
Coarse Spring
Fine Spring
Coarse Summer
Fine Summer
Coarse Winter
Fine Winter

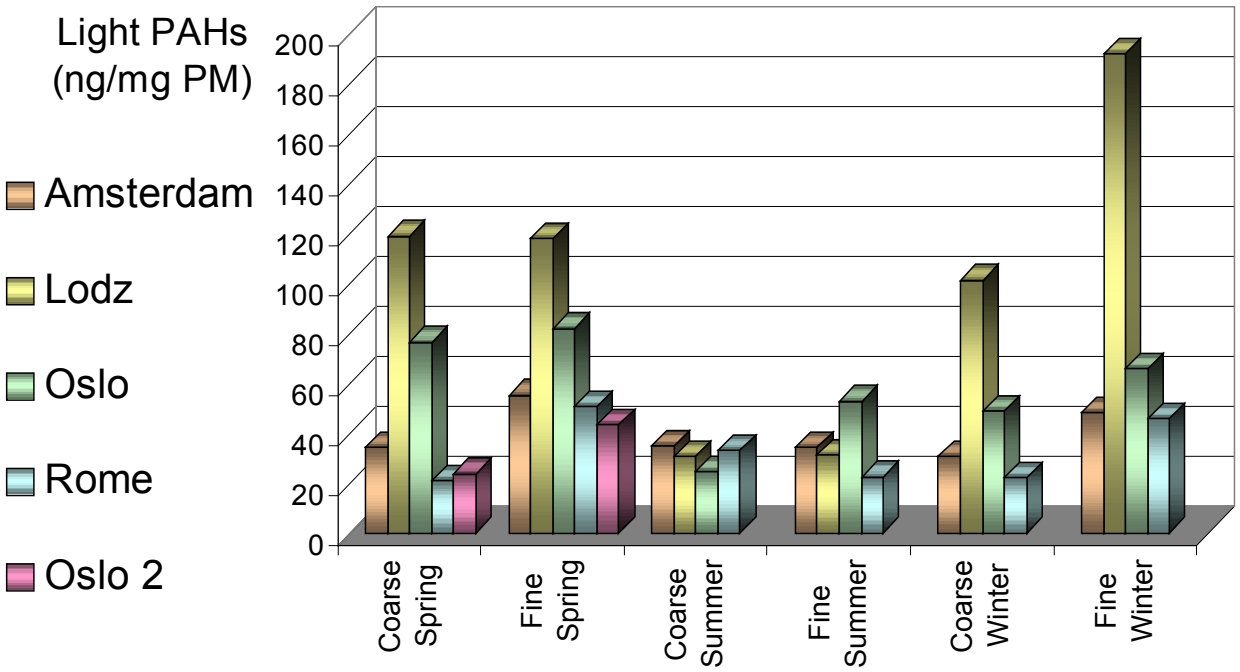

Nitrate
(ug/mg PM)
350
300
250
200
150
100
50
0
Coarse Spring
Fine Spring
Coarse Summer
Fine Summer
Coarse Winter
Fine Winter

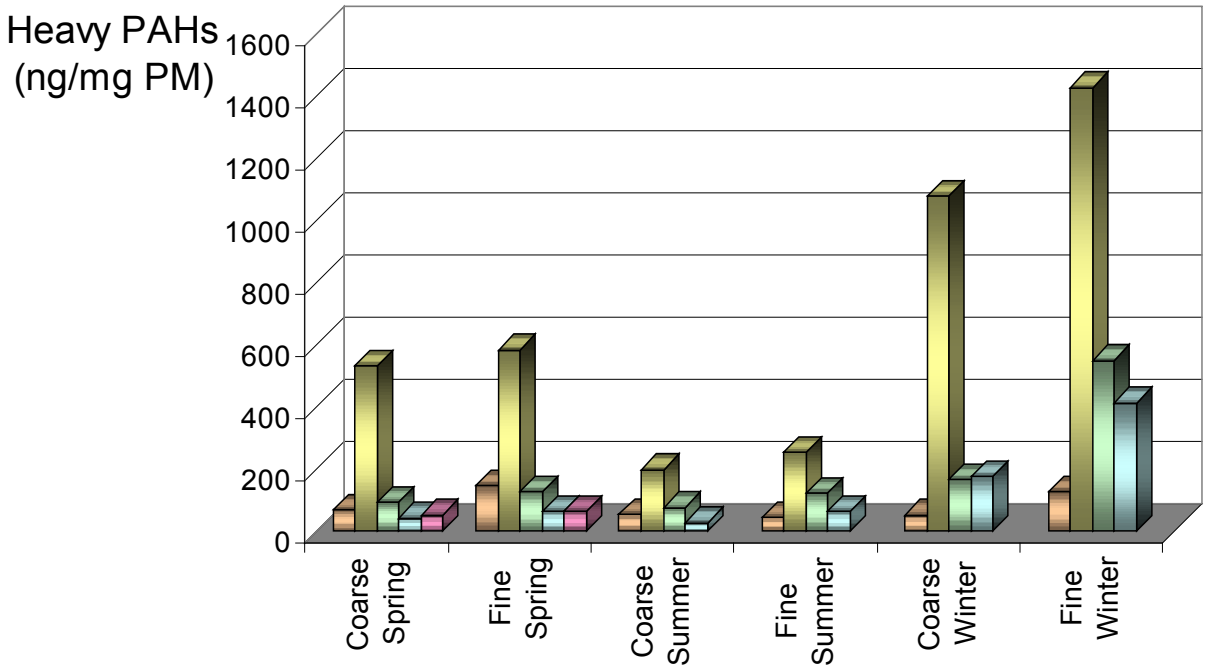
Potassium (ng/mg PM)

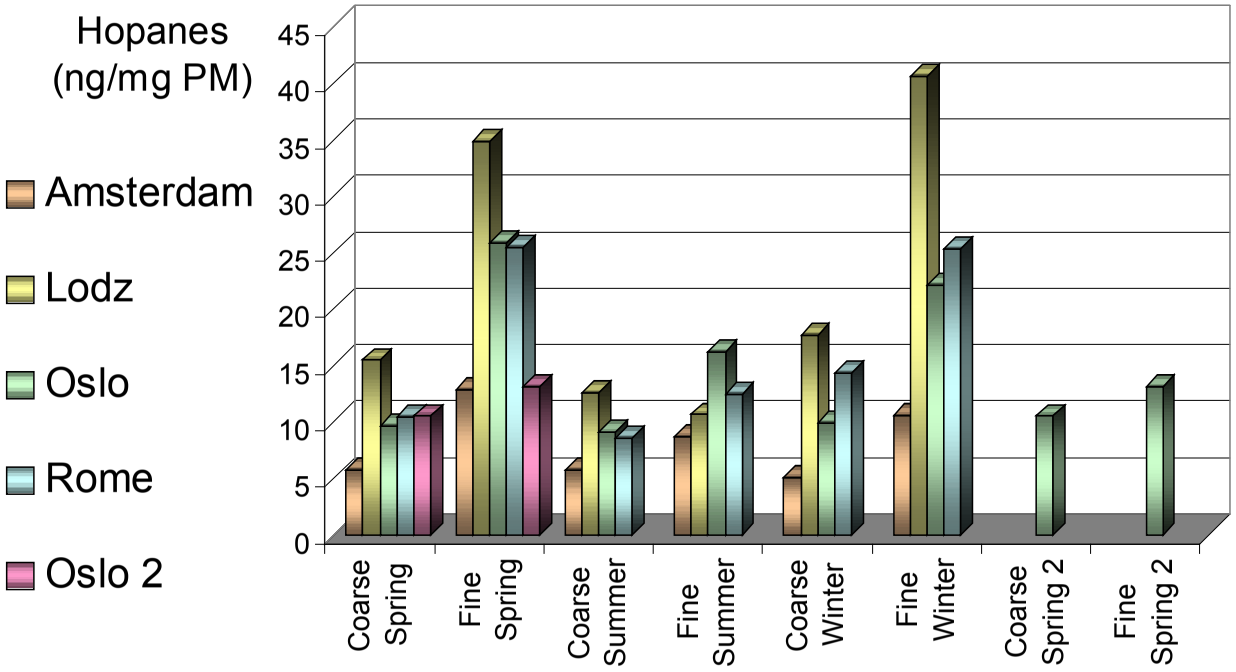


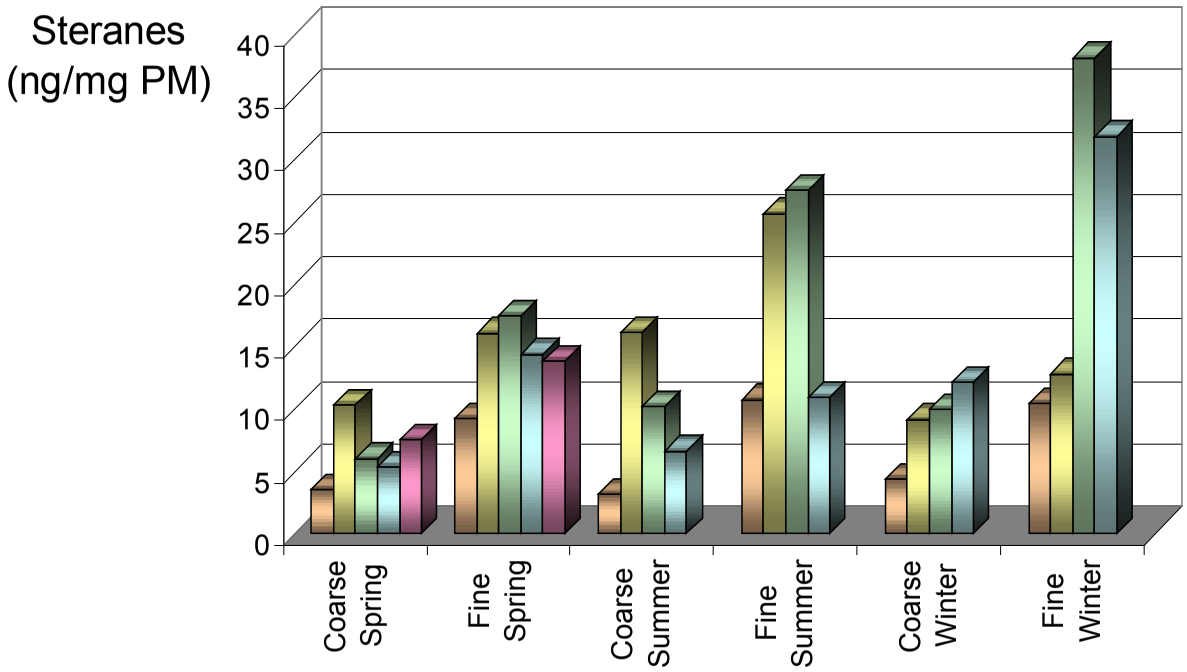
Sodium (ng/mg PM)




Light PAHs
(ng/mg PM)
Amsterdam
Lodz
Oslo
Rome
Oslo 2
200
180
160
140
120
100
80
60
40
20
0
Coarse Spring
Fine Spring
Coarse Summer
Fine Summer
Coarse Winter
Fine Winter


Heavy PAHs
(ng/mg PM)
1600
1400
1200
1000
800
600
400
200
0
Coarse Spring
Fine Spring
Coarse Summer
Fine Summer
Coarse Winter
Fine Winter


Hopanes
(ng/mg PM)
Amsterdam
Lodz
Oslo
Rome
Oslo 2
45
40
35
30
25
20
15
10
5
0
Coarse Spring
Fine Spring
Coarse Summer
Fine Summer
Coarse Winter
Fine Winter
Coarse Spring 2
Fine Spring 2


Steranes
(ng/mg PM)
40
35
30
25
20
15
10
5
0
Coarse Spring
Fine Spring
Coarse Summer
Fine Summer
Coarse Winter
Fine Winter