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Marko Vallius

CHARACTERISTICS AND SOURCES OF FINE PARTICULATE MATTER IN URBAN AIR

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Marko Vallius

National Public Health Institute
Department of Environmental Health
Unit of Environmental Epidemiology
P.O.Box 95, FI-70701 Kuopio, Finland

and

University of Kuopio
Department of Environmental Sciences
P.O.Box 1627, FI-70211 Kuopio, Finland

ACADEMIC DISSERTATION

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Publisher: National Public Health Institute
Mannerheimintie 166
FI-00300 Helsinki, Finland
Phone +358 9 47441
Telefax +358 9 4744408

Author's address: National Public Health Institute
Department of Environmental Health
P.O.Box 95, FI-70701 Kuopio, Finland
Phone +358 17 201211
Telefax +358 17 201265
E-mail marko.vallius@ktl.fi

Supervisors: Professor Juhani Ruuskanen, PhD
University of Kuopio
Kuopio, Finland

Professor Juha Pekkanen, MD
National Public Health Institute
Kuopio, Finland

Aadu Mirme, PhD
University of Tartu
Tartu, Estonia

Reviewers: Docent Tom Bellander, PhD
Stockholm County Council
Stockholm, Sweden

Docent Tuomo Pakkanen, PhD
Finnish Meteorological Institute
Helsinki, Finland

Opponent: Professor Jaakko Kukkonen, PhD
Finnish Meteorological Institute
Helsinki, Finland

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ABSTRACT

Particulate matter is an important component of the air pollution mixture that has been linked to various adverse health outcomes as well as having general environmental effects. It is not yet clear which causative agents and underlying mechanisms are responsible for these adverse health effects. However, it is likely that the source of the particles, a factor which influences their characteristics and composition, plays a role in determining the health effects of particles.

The focus of this thesis is first on characterizing urban ambient particulate matter with the emphasis on resuspended soil and street dust, and second, on the identification and comparison of major sources of urban particulate matter in Europe. The data for this work has been collected during three epidemiological studies conducted during 1995-1999 in Finland (Kuopio 1995, Number of measurement days=36; Helsinki 1996-97, N=185 and 1998-99, N=182), The Netherlands (Amsterdam 1998-99, N=237) and Germany (Erfurt 1998-99, N=177). Mass and number concentrations of several size fractions of particulate matter were monitored on a daily basis mainly during winter and spring months. Concentrations of gaseous air pollutants, elemental composition of PM samples and absorption coefficients of PM filters, a marker for carbonaceous particles from combustion sources, were also measured.

Average mass concentrations of particulate matter ($PM_{2.5}$ and PM_{10}) were notably lower in Helsinki compared to Amsterdam and Erfurt, but the difference was less clear for number concentrations of ultrafine particles (in this work, 10-100 nm) and absorption coefficient of $PM_{2.5}$, both of which are markers mainly for traffic-related fine particulate matter at the measurement sites used in this study. In Helsinki, the absorption coefficients of $PM_{2.5}$ and PM_{10} samples were rather similar and clearly higher than that of PM_1 samples, indicating that the fraction of particles between 1-2.5 μm in diameter contained substantial amounts of carbonaceous material. Absorption coefficients were better correlated with the number than with the mass of particles.

Sources of $PM_{2.5}$ were resolved from two measurement periods in Helsinki and one period in Amsterdam and Erfurt. Source categories with very similar elemental profiles were obtained for both periods in Helsinki and Amsterdam, with the exception that a component related to industrial activities was detected only in Amsterdam. In all cities, secondary and primary particles from long-range sources and local traffic were clearly the most important determinants of $PM_{2.5}$ concentrations. In Helsinki, the relative contribution of long-range transported air pollution to average $PM_{2.5}$ levels was clearly higher (50%) than in the two Central European cities (32-34%). On the other hand, traffic made more similar relative contributions to $PM_{2.5}$ in each city (23-36%). Owing to the higher $PM_{2.5}$ concentrations in Amsterdam and Erfurt, the $PM_{2.5}$ mass contributions from long-range transport were equal and contributions from traffic notably larger in these two cities compared to Helsinki. The other major components of $PM_{2.5}$ identified included soil, oil combustion particles, sea salt and particles from industrial sources.

A comparison of a statistical multivariate method (principal component analysis with multiple linear regression) and a deterministic method (chemical mass closure), indicated that the agreement of the two source apportionment methods was good for sources whose chemical composition is stable and well defined, such as crustal dust and sea salt. Source contribution estimates for the more complex sources of particulate matter, such as local combustion and long-range transported air pollution, differed substantially between the two methods.

Notable episodes of high resuspended dust concentrations took place at all monitoring sites. However, a seasonal influence of these episodes was seen only in Finland, shown by high concentrations of crustal dust during the spring months. These dust episodes affected the $PM_{2.5}/PM_{10}$ ratio more than the $PM_1/PM_{2.5}$ ratio. Also, the correlation of $PM_{2.5}$ with PM_{10} during winter was clearly higher than during spring, while the correlation of $PM_{2.5}$ with PM_1 did not change from season to season. The stability of the $PM_1/PM_{2.5}$ ratio suggests that in terms of variation of fine particle mass, monitoring of PM_1 did not significantly add to the information content already obtained from monitoring of $PM_{2.5}$. The major cause for elevated concentrations of resuspended dust in urban environments seems to be the turbulence and tyre stress related to traffic. Results from Kuopio also showed that resuspended particulate matter could contain considerable amounts of trace elements from anthropogenic sources.

In summary, the two most distinctive features in the Finnish cities (Helsinki and Kuopio) compared to Amsterdam and Erfurt were, in addition to the lower average mass concentrations of particles, the large relative contribution from secondary and long-range transported particulate matter and the seasonally dependent episodes of resuspended dust in urban environments.

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Marko Vallius

ABBREVIATIONS

$Abs_{2.5}$	Absorption coefficient of a $PM_{2.5}$ filter sample
CMB	Chemical mass balance
ED-XRF	Energy-dispersive X-ray fluorescence
ICP-MS	Inductively coupled plasma - mass spectrometry
MLR	Multiple linear regression
$NC_{0.01\text{-}0.1}$	Number concentration of particles ($1/cm^3$) in the size range 0.01-0.1 μm
$NC_{0.1\text{-}1.0}$	Number concentration of particles ($1/cm^3$) in the size range 0.1-1.0 μm
PCA	Principal component analysis
PM	Particulate matter
PM_X	Particulate matter in the air collected using an instrument with a 50% cut-off aerodynamic particle diameter of X μm
TSP	Total suspended particulate matter

LIST OF ORIGINAL PUBLICATIONS

This thesis is based on the following original publications, referred to in the text by the Roman numerals I-V. Some previously unpublished results are also presented.

I Vallius M, Ruuskanen J, Mirme A, Pekkanen J. Concentrations and estimated soot content of PM_1, $PM_{2.5}$ and PM_{10} in subarctic urban atmosphere. *Environmental Science & Technology* 2000; 34:1919-1925

II Hosiokangas J, Vallius M, Ruuskanen J, Mirme A, Pekkanen J. Resuspended dust episodes as an urban air-quality problem in subarctic regions. *Scandinavian Journal of Work, Environment & Health* 2004; 30 suppl 2: 28-35.

III Vallius M, Lanki T, Tiittanen P, Koistinen K, Ruuskanen J, Pekkanen J. Source apportionment of urban ambient $PM_{2.5}$ in two successive measurement campaigns in Helsinki, Finland. *Atmospheric Environment* 2003; 37: 615-623.

IV Vallius M, Janssen NAH, Heinrich J, Hoek G, Ruuskanen J, Cyrys J, Van Grieken R, Hartog JJ, Kreyling WG, Pekkanen J. Sources and elemental composition of simultaneously measured ambient $PM_{2.5}$ in three European cities. *The Science of the Total Environment* 2005; 337: 147-162.

V Vallius M, Ruuskanen J, Pekkanen J. Comparison of multivariate source apportionment of urban $PM_{2.5}$ with chemical mass closure. Submitted.

CONTENTS

1 INTRODUCTION

Increased awareness of health problems related to air pollution arising from urbanisation and industrialisation has, especially during the last two centuries, gradually created a demand for more efficient emission controls, especially in the developed world, and thus there has been a notable decrease in both the emissions and ambient concentrations of many air pollutants. Recently, problems caused by atmospheric particulate matter in urban air have received greater attention. Various health effects attributable to PM have been documented (WHO 1999, Brunekreef and Holgate 2002). The most conclusive evidence has been provided by cohort and time series studies that have linked elevated concentrations of PM to increased morbidity and mortality (Dockery et al. 1993, Pope et al. 1995, Katsouyanni et al. 1997, Samet et al. 2000). The majority of these studies have assessed the health effects of particles expressed as the risk per unit mass/m^3 of PM_{10} or $PM_{2.5}$. However, the cause-effect chain is thought to be very complex, including issues such as chemical composition and physical characteristics of the inhaled particles, and it is not yet clear which causative agents and underlying mechanisms are responsible for the adverse health effects. Therefore, identification of sources and characteristics of particulate matter that are responsible for the documented health burden to the public has become a crucial issue.

The majority of recent health studies suggest that fine particles ($PM_{2.5}$) arising mainly from man-made sources are more harmful than coarse particles (Schwartz et al. 1996, Laden et al. 2000, Mar et al. 2000, Hoek et al. 2002, Pope et al. 2002) and, therefore, the measurement of PM in health effect studies has currently focused on fine particulate matter ($PM_{2.5}$) rather than on coarse particles ($PM_{2.5-10}$). Several efforts have also been specifically aimed at studying concentrations and potential health effects of the so-called ultrafine particles in the size range below 0.1 μm (Peters et al. 1997, Ruuskanen et al. 2001, de Hartog et al. 2003). However, some studies have also detected adverse health effects related to coarse particles (Gordian et al. 1996, Tiittanen et al. 1999, Mar et al. 2000), highlighting the importance of controlling the concentration and studying the potential health effects of all PM size fractions. In addition, administrative guideline values in Europe are currently in place only for PM_{10} and TSP, although new $PM_{2.5}$ standards are now being considered.

The composition and size distribution of particles, and hence their harmful effects, depend strongly on particle formation processes, i.e., the sources of the particles, and this has been

explored in numerous studies with respect to PM_{10} and $PM_{2.5}$. The main sources of PM are traffic, energy production using fossil fuels and biomass, industrial sources, resuspension of soil, and sea salt spray, but the relative contribution of different sources varies greatly in time and location. Fugitive dust episodes cause some of the highest concentrations of ambient primary PM in many areas around the globe. These dust episodes often show seasonal concentration patterns that are much more pronounced than the concentration patterns of PM from most anthropogenic sources. Resuspension of accumulated crustal dust from the streets due to traffic and wind is a specific problem in subarctic urban areas where sanding of streets and studded tyres are used during the cold season. The inconsistent findings on health effects of resuspended particles (Gordian et al. 1996, Tiittanen et al. 1999, Mar et al. 2000, Englert 2004) require that their properties and potential effects be studied further. Also, resuspended dust episodes can cause exceeding of the limit values which are primarily aimed at regulating the concentrations of particulate matter from anthropogenic sources.

For risk management purposes, the crucial issue is the identification of the sources of particulate matter responsible for the health burden in the general public. A sound knowledge of the sources of particulate matter and possible differences in the health effects of particulate matter could allow the differentiation of sources regarding their importance for human health and thus permit a more efficient risk management. The sources affecting PM concentrations at a given location can be determined by applying source apportionment methods based on the chemical composition of PM, other air pollution measurement data and meteorological data. Source apportionment studies provide an estimate of the average source impacts on local air quality, as well as time series data (variability) on source-specific PM concentrations. The estimated daily concentration of PM from each source can then be related to the daily variation in the observed or measured health effects in epidemiological studies. Therefore, dividing particulate matter into sources and analysing their separate associations with health effects in the context of an epidemiological study could provide results that could be directly used in risk assessment, risk management, and in setting air quality guidelines and standards.

2 REVIEW OF THE LITERATURE

2.1 Particulate matter

Particulate matter refers to the solid and liquid particles that are dispersed into ambient air. These particles can be classified in several ways. Firstly, they can be classified into *primary* and *secondary* particles based on the mechanism of their formation. Primary particles are emitted directly as particles, whereas secondary particles are formed from precursor gases in the atmosphere via gas-to-particle conversion. Both types of particles are subject to growth and transformations since there can be formation of secondary material on the surface of existing particles.

Secondly, particles can be classified by their physical size; the size is from a few nanometers (nm) to tens of micrometers (μm) in diameter. Size is the single most important determinant of the properties of particles and it has implications on formation, physical and chemical properties, transformation, transport, and removal of particles from the atmosphere. Particle size is normally given as the aerodynamic diameter, which refers to the diameter of a unit density sphere of the same settling velocity as the particle in question. The notation PM_X refers to particulate matter comprising particles less than X μm in diameter (most often, X is 10, 2.5 or 1 μm). Particles greater than 2.5 μm in diameter are generally referred to as *coarse particles*, and particles less than 2.5 μm and 100 nm in diameter as *fine particles* and *ultrafine particles*, respectively. The term total suspended particles (TSP) refers to the mass concentration of particles less than 40 to 50 μm in diameter (Seinfeld and Pandis 1998).

Ambient particulate mass typically has a *modal* size distribution, meaning that the total mass of particulate matter tends to concentrate around one or more distinguishable points on the particle size scale. The modal character of the particle mass size distribution results from continuous processes leading to particle formation on one hand, and processes leading to removal of particles from the atmosphere on the other hand. Thus, the number of observable modes in particle size distribution varies depending on age of the aerosol and the vicinity of active sources of particles of different sizes. The definition of fine and coarse particles is an operational one based on a *bimodal* size distribution. Due to the overlap between fine- and coarse-mode particles in the intermodal region (1-3 μm), measurement of $PM_{2.5}$ is only an

approximation of fine-mode particles and measurement of $PM_{2.5-10}$ is only an approximation of coarse-mode particles (Wilson and Suh 1997).

The balance of the factors that lead to pollutant accumulation and the factors that lead to pollutant dispersion controls temporal and spatial variations in concentrations of pollutants (Fang et al. 2000). Firstly, the concentration and other characteristics of suspended particulate matter are determined by the presence and activity of sources. Once formed, particles change their size and composition by condensation or evaporation, by coagulating with other particles or by chemical reactions (Seinfeld and Pandis 1998). Meteorological factors such as wind speed and direction, temperature, amount of precipitation, and the height of the atmospheric boundary layer, are most important in governing the concentration variations of particulate matter (Pohjola et al. 2000). The highest PM concentrations are often reported during stable meteorological conditions such as inversion with low wind speeds (Pohjola et al. 2004). Also the physical and chemical processes affecting the particles are regulated to a great extent by meteorological factors.

PM from specific sources typically follow short-term and long-term (seasonal) trends (Yatin et al. 2000). For example, space heating generates more combustion-related PM emissions during the cold seasons while, at the same time, snow cover can inhibit PM emissions from the soil. Seasonal peak concentrations of $PM_{2.5}$ during the winter in polluted European areas have been reported (Van Dingenen et al. 2004). The authors hypothesised that this finding was mainly related to enhanced condensation of semi-volatile species during cold seasons leading to formation of large average sized fine particles. Generally, the total particulate mass has a lower temporal variability than any of the major components of the aerosol. This may be associated with opposite seasonal concentration variations in some of the major PM components, for example, the carbonaceous component and the secondary component (Kao and Friedlander 1995).

2.2 Characteristics of urban PM from different sources

The majority of total PM emissions to the atmosphere are attributable to natural sources, such as suspended terrestrial dust, oceans and seas, volcanoes, forest fires and natural gaseous emissions. However, these emissions are dispersed rather evenly into the atmosphere and, therefore, result in a relatively low tropospheric background PM concentration. The natural

sources that have the greatest impact on the urban PM concentrations in Europe include suspended terrestrial dust, sea salt spray (mainly at coastal sites) and biomass burning (forest fires) (Lazaridis et al. 2002). The major sources of anthropogenic, i.e., man-made, particles include transportation, stationary combustion, space heating, biomass burning, and industrial and traffic-related fugitive emissions (street dust). Urban PM from man-made sources is a complex mixture, since the majority of sources emit both primary particles and precursor gases for the formation of secondary particles. The majority of anthropogenic PM is emitted within relatively small urban and industrial areas, resulting in hot spots of high concentrations of particulate matter and other air pollutants. Man-made primary and secondary particles also affect regional background PM concentrations since a fraction of the emitted particles can remain in suspension for several days and travel up to thousands of kilometres in the atmosphere.

Air samples of particulate matter from urban areas from around the world typically show the same major components, although in considerably different proportions according to the sampling location (Harrison and Yin 2000). These major components are typically:

1) sulphate - derived predominantly from sulphur dioxide oxidation in the atmosphere; because SO_2 is oxidised only slowly, spatial gradients of sulphate on a scale of tens of kilometres are expected to be small, over hundreds of kilometres they can be significant, and over entire continents, very large;

2) nitrate - formed mainly from oxidation of nitrogen oxides (NO and NO_2) to nitrate; NO_2 oxidises much more rapidly than SO_2

3) ammonium - atmospheric ammonia forms ammonium salts in neutralisation reactions with sulphuric and nitric acids

4) chloride - main sources are sea spray and de-icing salt during winter; also from ammonia neutralisation of HCl gas from incineration and power stations

5) elemental carbon (EC) and organic carbon (OC) - combustion processes (in urban areas mainly traffic) emit primary carbonaceous particles and semi-volatile precursors

6) crustal materials - soil dusts and wind-blown crustal material; are quite diverse in composition reflecting local geology and surface conditions; their concentration is dependent on climate as the processes which suspend them into the atmosphere tend to be favoured by dry surfaces and high winds; these particles reside mainly in the coarse particle fraction (Harrison et al. 1997)

7) biological materials - bacteria, spores, pollens, debris and plant fragments; generally coarse in size, considered as part of the organic carbon component in most studies rather than as a separate biological component.

The distinction between anthropogenic and natural particle sources and the emitted particulate matter is sometimes difficult to make, for example, fugitive dust emissions and biomass burning (BéruBé et al. 1997). In addition, there are large differences in the relative importance of different sources from one geographical area to another. For example, the greater part of emissions of primary particulate matter in eastern parts of Europe originates from stationary combustion sources and processes, whereas in western parts of Europe, emissions are more evenly distributed among all economic sectors, although transport emissions play the most significant role at many locations (ApSimon et al. 2000). In the central and northern parts of Europe, anthropogenic sources dominate long-term average PM concentrations, while resuspended dust and forest fires are relatively more important in southern Europe (Lazaridis et al. 2002). In the following sections, the characteristics of particulate matter from some of the major source categories are discussed. Resuspended road dust has been discussed at more length due to its marked impact on urban ambient PM levels, and the inadequate scientific information on its composition and other characteristics.

2.2.1 Traffic

Vehicular particle emissions are the result of a great many processes, e.g. combustion products from fuel and oil, wear products from brake linings, tyres, bearings, car body and road material, and the resuspension of road and soil dust (Laschober et al. 2004). Traffic is an effective source of both fine and coarse mode primary particles, condensable organic gases, and a major source of nitrogen oxides that then form secondary nitrate aerosols. Particles of condensed carbonaceous material are emitted mainly by diesel vehicles and poorly maintained petrol vehicles (Vardoulakis et al. 2003). Diesel exhaust particles have been shown to display a multimodal size distribution (Kerminen et al. 1997) and are mainly carbonaceous agglomerates below 100 nm in diameter, whereas particles emitted by gasoline vehicles are also mainly carbonaceous agglomerates but considerably smaller, ranging from 10 to 80 nm (Morawska and Zhang 2002). Particulate matter originating from traffic can be present at elevated concentrations especially during high traffic density and poor dispersion conditions,

e.g. in street canyons, which can lead to high human exposures to traffic-related pollutants (Vardoulakis et al. 2003).

Identification of traffic related particulate matter in source apportionment studies has become difficult due to phasing out of Pb as an additive to gasoline. Elements that have often been associated with vehicular emissions include Cu, Zn, Pb, Br, Fe, Ca and Ba (Huang et al. 1994, Cadle et al. 1997, Kemp 2002, Morawska and Zhang 2002, Sternbeck et al. 2002). Emissions of many metallic elements from vehicular sources are mainly due to non-exhaust emissions, e.g., from the wearing of tyres, brakes and other parts of vehicles (Sternbeck et al. 2002, Adachi and Tainosho 2004, Laschober et al. 2004, Lough et al. 2005). In addition to road traffic, emissions from the main and auxiliary engines of ships can be a significant source of particulate matter and associated elements such as V and Ni (Lyyränen et al. 1999) at certain locations (Ohlström et al. 2000, Colvile et al. 2001, Isakson et al. 2001).

2.2.2 Stationary sources

The most significant stationary combustion sources include energy production facilities such as municipal power plants, waste incineration, and residential combustion. Several industrial processes, such as iron and steel production, also involve combustion of fossil fuels or biomass for generating power and heat needed for the process. Most of these sources are considered point sources, although smaller and more widespread sources such as residential combustion could also be considered as an area source. Physical and chemical characteristics of the particles emitted from these source categories depends on the combustion process itself, and the type of fuel burnt (solid, liquid, or gas). Combustion processes and properties of particulate matter emitted from these sources have been comprehensively reviewed by Morawska and Zhang (2002).

The major industrial processes include factories processing metals and chemicals, materials handling, construction and mining. Particulate matter from these sources are partly released as fugitive emissions, which are not collected and released in a controlled manner, but emitted from a variety of points and areas connected to a process (Seinfeld and Pandis 1998). Chemical and physical properties of fugitive emissions depend on the processes by which they are emitted. Since the bulk of most trace metals are nowadays emitted from industrial processes, their concentrations are spatially heterogeneous and subsequently, their

measurement is quite sensitive in terms of location; however, the reported concentrations of trace metals in major cities demonstrate rather similar levels of trace metals (Harrison and Yin 2000).

2.3 Resuspended dust

2.3.1 Sources

The term resuspension is commonly used to include both suspension of newly generated particles and re-entrainment of previously deposited particles into the atmosphere (Nicholson 1988). Resuspension is a complex process that can be initiated by mechanical disturbances such wind, traffic-induced turbulence and tyre stress, and construction activities. The wind-blown dust is often called 'natural dust' because of its origin from mostly non-urban areas that are subject to suspension by the wind (Chow et al. 1999). In non-arid urban environments, particulate matter can be made available for resuspension in a variety of ways, including application of traction sands or de-icing salts, track-out from construction sites and other unpaved areas, vehicle exhaust, tyre and brake wear, oil leaks and spills from vehicles, wearing and maintenance of streets, and atmospheric deposition of anthropogenic PM emissions (Claiborn et al. 1995).

Road dust is an agglomeration of contributions from several anthropogenic and biogenic sources of particulate matter (Rogge et al. 1993). In all road environments, the dust from various sources accumulates on road shoulders, near the curbs and along center dividers (Etyemezian et al. 2003). Resuspension, deposition, washout of materials on and off the road, and generation of new particles constitute a dynamic source and sink relationship in the traffic environment (Rogge et al. 1993, Kuhns et al. 2003). Paved and unpaved roads are among the largest emitters of particulate matter in many urban areas, and numerous studies have shown that traffic-induced resuspension is the predominant source of coarse particles and many elements at traffic-influenced sites (Pakkanen et al. 2001b, Ruellan and Cachier 2001, Manoli et al. 2002, Sternbeck et al. 2002).

Kupiainen et al. (2003 and 2005) have studied the effects of road sanding on the composition and concentrations of urban suspended road dust. They found that concentrations of suspended PM_{10} increased subsequent to application of traction sand. The observed increase

was larger when studded tyres were used and when the sand contained more small particle size fractions. One interesting finding was that the wear of the pavement was greatly increased by the grinding impact of sand under the tyres. This finding was corroborated by a subsequent field study showing that only about 10% of the number of all inorganic $PM_{1.5-10}$ particles and 17% of the number of all $PM_{1.5-10}$ mineral particles were directly associated with road sanding material (Kupiainen and Tervahattu 2004). Laschober et al. (2004) found that less than 5% of vehicular particulate matter emissions (no particle size segregation in sampling) were due to resuspension and road abrasion during a traffic tunnel study in Vienna, Austria. On the other hand, a Swedish traffic tunnel study revealed that as much as 50% of fine PM (0.6-2.5 μm) could be attributed to traffic-induced turbulence at vehicle speeds >75 km/h (Kristensson et al. 2004).

2.3.2 Impact of resuspension on concentrations of particulate matter

Resuspended dust is a major contributor to ambient particulate matter, especially in the coarse particle fraction. According to a European survey, the annual mineral dust load in PM_{10} varies from 13% to 37% in Europe, with an increasing trend moving from rural background sites to kerbside sites that are heavily influenced by traffic (Putaud et al. 2004, Van Dingenen et al. 2004). This proportion is significantly lower compared to proportions found in some arid areas, for example in Arizona and Nevada, U.S.A., where fugitive dust sources (paved and unpaved roads and construction activities) account for more than 80% of PM_{10} (Gertler et al. 1995, Chow et al. 1999). A comprehensive report on fugitive dust emissions and a bibliography of pertinent literature has been recently prepared by Watson and Chow (2000).

Wind-blown natural dust can contribute to high concentrations of coarse and fine particles measured at sites located hundreds or even thousands of kilometres from the source area. Contribution from major desert dust events to PM have been reported in numerous studies conducted in Europe (Pio et al. 1996, Querol et al. 1998, Rodriguez et al. 2001, Ryall et al. 2002, Đorđević et al. 2004, Koçak et al. 2004), North-America (Claiborn et al. 2000, Owega et al. 2004), Asia (Chun et al. 2001, Chen et al. 2004) and Australia (Chan et al. 1999). Southern Mediterranean countries experience several transient episodes (2-4 days) of transported Saharan dust each year, leading to levels exceeding 25 $\mu g/m^3$ and 10-15 $\mu g/m^3$ in daily PM_{10} and $PM_{2.5}$ concentrations, respectively (Rodriguez et al. 2002, Rodriguez et al. 2004).

The effect of seasonal phenomena on soil related fine and coarse particles has been reported from different regions around the world (Magliano et al. 1999, Chueinta et al. 2000, Yatin et al. 2000, Mugica et al. 2002, Kim et al. 2003). In Finland, resuspension of road dust is a major source of particulate matter especially during the spring, but also during late autumn (Kukkonen et al. 1999). In addition to several reports from Finland (Hosiokangas et al. 1999, Pakkanen et al. 2001b, Oravisjärvi et al. 2003, Ward and Ayres 2004), seasonal patterns in resuspension of road and soil dust have been reported from various locations around the northern hemisphere (Fukuzaki et al. 1986, Monn et al. 1995, Kantamaneni et al. 1996, Brook et al. 1997, Yatin et al. 2000, Kuhns et al. 2003).

2.3.3 Characteristics of resuspended dust

Prominent episodes of resuspended dust have been associated with clear changes in particle size distributions, chemical composition, and morphology (Haller et al. 1999, Manoli et al. 2002). Breed et al. (2002) found that in terms of particle numbers both non-episodic (<50 $\mu g/m^3$) and episodic (concentration >50 $\mu g/m^3$) PM_{10} samples were dominated by irregularly shaped particles, but the higher proportion of spherical particles and lower mean particle size in non-episodic PM_{10} samples were indicative of pronounced contribution of combustion and industrial sources.

Chemical composition of resuspended dust varies from location to location due to differences in the crustal composition. In addition to natural variation in composition of crustal dust in different regions, the composition of resuspended dust may also be altered by enrichment of pollution-derived elements in surface soil (Rogge et al. 1993, Yatin et al. 2000, Sternbeck et al. 2002, Begum et al. 2004, Conko et al. 2004). Hildemann et al. (1991) have reported that fine (<2 μm) paved road dust consists of 27% SiO_2, 17% organics, 11% Al_2O_3, 9% Fe_2O_3, and 4% Ca. In a Swedish study (Swietlicki et al. 1996), it was found that road dust was heavily enriched in Cu, Zn, Pb - elements that are all associated with vehicular emissions. Lough et al. (2005) have shown that the metallic fractions of PM_{10} (19% metals) and $PM_{2.5}$ (11.6% metals) in road tunnels were dominated by crustal elements (Si, Fe, Ca, Na, Mg, Al and K) but were also affected by tailpipe emissions and brake and tyre wear including (Cu, Zn, Sb, Ba, Pb and S). By using scanning electron microscopy, it has been shown that metals can become adherent to larger natural particles (Mugica et al. 2002). Together these results indicate that road dust can act as a repository for elements from anthropogenic sources, and

that resuspension could at certain locations contribute to the atmospheric concentration of these elements. The plausibility of this theory is supported by studies where it has been shown that larger particles are more easily resuspended by wind and traffic, and that deposited materials are more likely to become resuspended if they are associated with larger host particles (Nicholson and Branson 1990).

Although the majority of resuspended particles are in the coarse fraction, a notable portion is in the fine fraction. Mar et al. (2000) reconstructed a soil component in the fine aerosol fraction in Phoenix, U.S.A., and found that it contributed 18% to $PM_{2.5}$. Artaxo et al. (1999) obtained a 15% contribution for a geological component in $PM_{2.5}$ and 64% contribution for traffic source in Santiago, Chile. The road dust contribution of 28% to PM_3 and 57% to PM_{10} was found in Thessaloniki, Greece (Manoli et al. 2002). Several other studies have also reported a soil contribution to the fine fraction of PM (Van Borm et al. 1990, Alonso et al. 1997, Pakkanen et al. 2001b). The proportion of fine particles has two important implications on the health effects of resuspended dust episodes; firstly, fine particles can remain in suspension much longer than coarse particles and it can result in larger spatial impact by resuspended PM, and secondly, the fine fraction of resuspended particulate matter is more likely to comprise anthropogenic constituents that are potentially more toxic than the fine particles of pure crustal origin.

2.4 Relationship between different particle size fractions

Particles from different sources and emission processes are often distinguished by their physical size, as highlighted for total suspended particles (TSP) in Figure 1. Thus, the ratio between two fractions of PM is a simple, although crude, indicator of the amount of particulate matter from different types of sources.

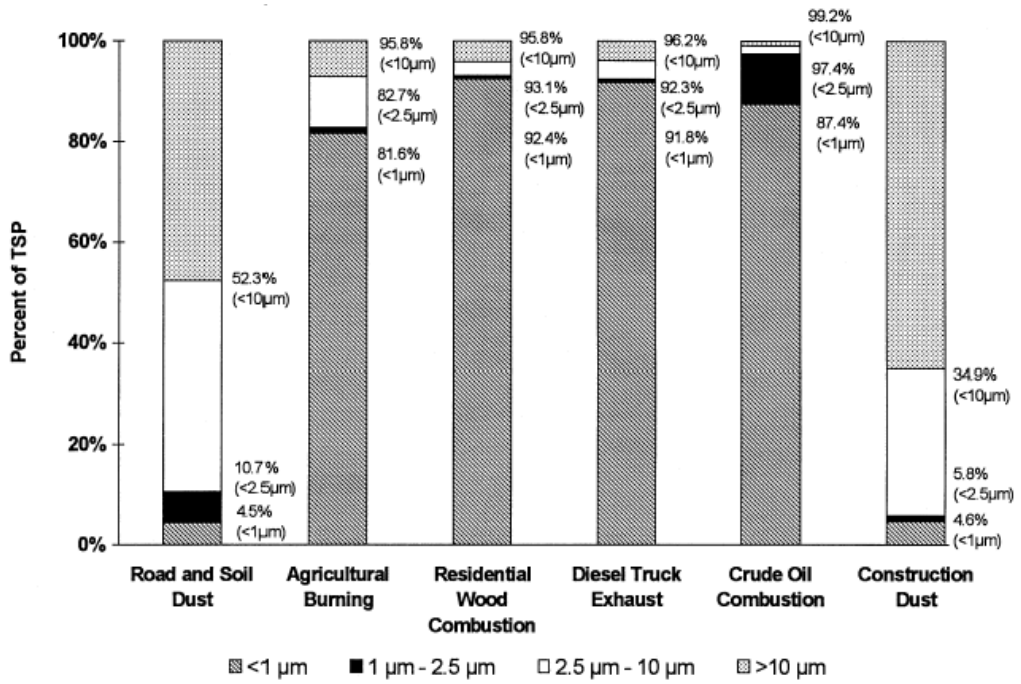

Figure 1. Size distributions of several TSP source emissions (Adapted from Watson and Chow (eds.), 2000).

Table 1 summarizes some of the recent studies that have measured two or more PM metrics simultaneously and reported their ratios; most commonly, the ratio between $PM_{2.5}$ and PM_{10} has been reported. It is important to bear in mind that the interpretation of the ratio between the two fractions depends on methods, location and time (season) of the measurements, which can affect the two fractions differently. Gomišček et al. (2004) have also compiled a summary of reported ratios.

Table 1. Reported ratios of PM fractions at different locations.

Reference	**Location**	**Season**	**$PM_{2.5}/PM_{10}$**
Van Dingenen et al. 2004	31 sites in Europe		0.73±0.15
Harrison et al. 1997	Birmingham, U.K.	summer winter	0.50 0.80
Marcazzan et al. 2003	Milan, Italy	all year	0.73±0.13 winter; 0.63±0.13 summer
Marcazzan et al. 2002	Milan, Italy Erba, Italy	winter winter	0.76±0.14 0.72±0.11
Ruellan and Cachier 2001	Paris, France	summer-autumn	0.66 ± 0.13
Van Der Zee et al. 1998	2 sites, The Netherlands	winter	0.55
Manoli et al. 2002	Thessaloniki, Greece	all year	0.76 ± 0.06 [(a]
Cyrys et al. 2003a	3 sites in Europe	all year	0.54-0.68
Laakso et al. 2003	3 sites in Finland	all year	0.51-0.54 urban 0.84 rural
Houthuijs et al. 2001	25 sites in Europe	all year	0.68 (0.55-0.78)
Gehrig and Buchmann 2003	7 sites in Switzerland	all year	0.75 - 0.76; 0.58 kerbside
Gomišček et al. 2004	4 sites in Austria	all year	0.70
Artiñano et al. (in press)	Madrid, Spain	all year	0.72
Claiborn et al. 2000	California, U.S.A.	-	0.33-0.75
Magliano et al. 1999	California, U.S.A.	winter	0.70-0.80
Schwartz et al. 1996	Six Cities Study, U.S.A.	all year	0.50-0.66
Mar et al. 2000	Phoenix, U.S.A.	-	0.30
Brook et al. 1997	19 sites, Canada	all year	0.38-0.59 urban; 0.60-0.65 rural
Lam et al. 1998	15 sites, Hong Kong	winter	0.70
Wei et al. 1999	8 sites, China	all year	0.52-0.75
Ho et al. 2003a	3 sites, Hong Kong	winter	0.53-0.73
Fang et al. 2002	Taiwan	-	0.60 pre-dust storm; 0.46-0.50 dust storm
Fang et al. 2000	3 sites, Taiwan	all year	0.56-0.72
Chan and Kwok 2001	Hong Kong	all year	0.74
Reference	**Location**	**Season**	**PM_{10}/TSP**
Röösli et al. 2001	Basel, Switzerland	spring-autumn winter	0.74 0.84
Monn et al. 1995	7 sites, Switzerland	all year	0.75 polluted urban; 0.57-0.62 rural, suburb
Reponen et al. 1996	4 sites, Kuopio, Finland	winter-spring	0.40-0.70
Mugica et al. 2002	5 sites, Mexico	all year	0.29-0.42
Fang et al. 2000	3 sites, Taiwan	all year	0.44-0.68
Chan and Kwok 2001	Hong Kong	all year	0.62
NOTE: a) PM_3/PM_{10} ratio			

An overall $PM_{2.5}/PM_{10}$ ratio of 0.73 has been reported based on measurements on 31 European sites (Van Dingenen et al. 2004). The authors concluded that although fairly constant ratios were observed at individual measurement sites, no universal ratio could be derived that would apply to all sites. Lower than average $PM_{2.5}/PM_{10}$ ratios were observed for kerbside sites compared to background sites due to the larger contribution of resuspended road dust in the coarse PM fraction at high density traffic sites. The authors furthermore reported an increasing general trend in $PM_{2.5}/PM_{10}$ ratio with increasing PM_{10} concentration, except at kerbside sites, indicative of predominance of $PM_{2.5}$ in total PM_{10} during episodes of high concentrations of anthropogenic air pollutants. $PM_{2.5}/PM_{10}$ ratios obtained from other studies in Europe agree rather well with the above 0.73 ratio, and maximum ratios are often reported to occur during local pollution episodes that are attributable to combustion sources (Marcazzan et al. 2002). North-American studies have reported slightly lower $PM_{2.5}/PM_{10}$ ratios compared to the European studies. A large dataset from 19 geographically diverse Canadian locations produced a highly variable and site-dependent $PM_{2.5}/PM_{10}$ ratio that ranged between 0.38-0.59 at urban sites and 0.60-0.65 at rural sites (Brook et al. 1997). $PM_{2.5}/PM_{10}$ ratios between 0.33-0.75 and an average ratio of 0.50 based on TEOM (tapered element oscillating microbalance) measurements were observed for two measurement periods in a semi-arid U.S. town, with a marked decrease in the $PM_{2.5}/PM_{10}$ ratio and indications of an increased $PM_{1\text{-}2.5}$ mass, but not PM_1 mass, during dust events (Claiborn et al. 2000).

2.5 Source apportionment of particulate matter

2.5.1 Methods

Source apportionment of particulate matter refers to the quantitative estimation of the contributions from different source categories to the concentrations of the measured PM in the atmosphere, based on chemical and physical characteristics of the particulate matter and temporal covariation of PM components. This procedure can be divided to *identification* of the sources and to *apportionment* of the measured PM to these sources. Source apportionment of urban ambient PM is complicated due to several reasons (APEG 1999); (1) there are numerous anthropogenic and natural source categories that contribute to urban primary and secondary PM; (2) not all PM emissions are adequately characterized; and (3) the geographic impact area(s) of different emissions are highly variable due to the different particle sizes, lifetimes of pollutants, varying weather conditions, and atmospheric chemistries.

Source apportionment models make use of the chemical composition of PM measured at a certain location ('receptor') to resolve the main sources of particulate matter at that site (Kao and Friedlander 1995). Particulate matter emissions from specific sources often have unique elemental profiles by which the contribution of these sources to the total PM at the receptor can be recognised. The most widely applied source apportionment methods have been chemical mass balance methods (CMB, mass reconstruction, mass closure) and several types of multivariate methods such as multiple linear regression (MLR), factor analysis (FA), principal component analysis (PCA), target transformation factor analysis (TTFA), positive matrix factorization (PMF), and combinations of the above. Principles, history and recent developments in the field of receptor modelling of particulate matter have been reviewed by Gordon (1988), Henry (1984, 1997), Seigneur et al. (1999), and Hopke (2003).

Chemical mass balance equations are based on the basic assumption that the measured amount of a chemical species in a sample is a simple sum of pollutant contributions affecting the sample (Christensen 2004). Other assumptions in CMBs are that all major sources affecting the airshed are identifiable, and that the chemical composition patterns of emissions from various sources ('source profiles') are known. The profiles should also be sufficiently different to facilitate identification of source contributions. Although CMBs have the advantage that they do not require many samples, they suffer from the need of quantitative and detailed information on the chemical profiles of emissions from all major sources that can contribute to PM at the receptor site (Magliano et al. 1999). The CMB method is not suitable for apportioning sources of secondary air pollution components, such as sulphate, because these components represent only up to a few percent of fine particle emissions though they often constitute a major portion of the mass of ambient PM samples due to gas-to-particle conversion (Pinto et al. 1998).

Mass closure (mass reconstruction) models are simpler mass balance models that can be used for apportionment of particulate matter between predefined sources. These models are based on the analysis of a number of chemical components (elements, ions, etc.), which can be used as tracers of major aerosol constituents (Andrews et al. 2000, Harrison et al. 2003). The estimation of source contributions by this method can be purely deterministic, that is, based on summing up the mass of measured and reconstructed chemical components, or it can involve some statistical procedures such as regression analysis.

Factor-analytic techniques, such as principal component analysis, are based on the idea that the time dependence of a chemical species at the receptor site will be similar to that of other species from the same source (Chueinta et al. 2000). Correlations of the measured chemical and other species are analysed and groups of underlying 'factors' that depict the common variability in the analysed dataset are extracted. Since the originally extracted factors are often difficult to interpret, the factors are usually transformed by a specific procedure called factor rotation. The most commonly used method is known as varimax rotation, which results in orthogonal factors that are virtually uncorrelated with each other and often easier to interpret than the original factors (Afifi and Clark 1984). The rotated factors are assumed to correspond to specific PM sources, or source categories. Since PCA as such does not yield quantitative source contributions, the apportionment of particulate matter between the identified source categories has to be done separately. This can be done by regressing the measured PM either directly on the source tracer elements (Hosiokangas et al. 1999, Oravisjärvi et al. 2003) or on factor scores obtained from PCA (Thurston and Spengler 1985, Van Borm et al. 1990, Pio et al. 1996, Ames et al. 2000, Marcazzan et al. 2003).

Seinfeld and Pandis (1998) have listed several assumptions on application of PCA to source apportionment purposes: 1) the composition of emission sources is constant, 2) chemical species used in PCA do not interact with each other and their concentrations are linearly additive, 3) measurements errors are random and uncorrelated, 4) the variability of the concentrations is dominated by changes in source contributions, 5) the effect of processes that affect all sources equally (e.g. atmospheric dispersion) is much smaller than the effect of processes that influence individual sources (e.g., wind direction), 6) there are many more samples than source types, and 7) the extracted factors and rotations are physically meaningful. Some of the limitations of factor-analysis methods include its inability to recognise more than (about) eight source categories, and that its ability to discriminate closely related sources is rather poor (Henry et al. 1984, Harrison et al. 1997).

2.5.2 European source apportionment studies

Comprehensive chemical speciation in combination with information on size distribution and morphology of PM, temporal variation of PM and gaseous pollutants, and meteorology allows for identification of PM sources. Numerous European studies have pointed to sources of urban particulate matter chiefly via a physico-chemical characterization of PM (Harrison et al.

1997, Pakkanen et al. 2001a, Pakkanen et al. 2001b, Visser et al. 2001, Koistinen et al. 2004). The number of European studies that have apportioned particulate matter (TSP, PM_{10} or $PM_{2.5}$) to the identified source categories by using statistical methods is still rather limited compared to the number of studies conducted in the U.S.

Table 2 lists a number of European studies that have used multivariate statistical methods to obtain information on sources of particulate matter. In most of these studies, four or five major source categories have been detected. These categories include natural sources, such as soil dust and sea salt spray, and anthropogenic sources, such as vehicular emissions, secondary PM, industry, refuse incineration, oil and coal combustion, and residential emissions related to heating and wood combustion. Traffic, secondary particulate matter, and soil or street dust were the predominant sources in most of the studies. Not surprisingly, the effect of crustal particles was more important in the PM_{10} fraction compared to $PM_{2.5}$, although the crustal source was also detected in most $PM_{2.5}$ studies. A straightforward comparison of the results from these studies is not feasible, however, due to differences in methods, measurements sites and interpretation of the identified source components.

Table 2. A summary of European receptor modelling studies.

Reference	**Study site**	**Method(s) ***	**Target PM fraction(s)**
Van Borm et al. 1990	Antwerp, Belgium	PCA, MLR	$PM_{2.5}$
Pio et al. 1996	Portugal	PCA, MLR	$PM_{0.95}$ & $PM_{0.95-10}$
Harrison et al. 1997	Birmingham, U.K.	PCA, MLR	$PM_{2.1}$ & $PM_{2.1-10}$
Pinto et al. 1998	Teplice, Czech Rep.	CMB	$PM_{2.5}$
Hosiokangas et al. 1999	Kuopio, Finland	FA, MLR	PM_{10}
Marcazzan et al. 2001	Milan, Italy	PCA, MLR	$PM_{2.5}$ & PM_{10}
Querol et al. 2001	Barcelona, Spain	PCA, MLR	$PM_{2.5}$ & PM_{10}
Manoli et al. 2002	Thessaloniki, Greece	PCA, MLR	PM_{3} & PM_{10}
Marcazzan et al. 2003	Milan, Italy	PCA	$PM_{2.5}$ & PM_{10}
Samara et al. 2003	Thessaloniki, Greece	CMB	PM_{10}
Oravisjärvi et al. 2003	Raahe, Finland	FA, MLR	$PM_{2.5}$
Yli-Tuomi et al. 2003	Kevo, Finland	ME	TSP
Salvador et al. 2004	Madrid, Spain	FA, MLR	PM_{10}
Querol et al. 2004	Spain	PCA, MLR	PM_{10}
* PCA principal component analysis; MLR multiple linear regression; CMB chemical mass balance; FA factor analysis; ME multilinear engine			

The results of the few previous efforts that have been made to elucidate sources of fine particulate matter in Helsinki are shown in Table 3. Based on correlation analysis, Pakkanen et al. (2001b) have identified a number of distinct groups (sources) of chemical constituents in

$PM_{2.3}$ (long-range transported, sea salt, oil combustion, organic anions); a crustal source was detected for the coarse particle fraction. The composition of $PM_{2.3}$ in their study agrees well with the reported $PM_{2.5}$ composition of residential outdoor samples (Koistinen et al. 2004). A 46% average local contribution to $PM_{2.3}$ in Vallila, Helsinki, has been reported based on particle size distribution comparisons between urban (Vallila) and rural sites (Pakkanen et al. 2001a). Ojanen et al. (1998) have estimated that approximately 60% of $PM_{2.3}$ in Vallila originates from long-range sources. The rest of $PM_{2.3}$ (40%) was reported to comprise mostly traffic-related particulate matter (elemental and organic carbon, nitrate) and resuspended crustal material.

Table 3. Results from previous studies on composition and sources of fine particulate matter in Helsinki, Finland.

Site and period (reference)	**PM fraction (average)**	**Component**	**mass ($\mu g/m^3$)**	**% (of PM)**
Urban background Vallila, Helsinki Apr 1996 - Jun 1997 (Pakkanen et al. 2001b)	$PM_{2.3}$ (11.8 $\mu g/m^3$)	SO_4 NO_3 NH_4 Sea salt Crustal Other (carbon. + H_2O)	2.5 1.4 1.1 0.4 1.4 5.1	21 12 9 3 12 43
Residential outdoor Helsinki Oct 1996 - Dec 1997 (Koistinen et al. 2004)	$PM_{2.5}$ (10.0 $\mu g/m^3$)	$SO_4 + NO_3 + NH_4$ Combustion particles Crustal particles Salt	4.6 3.5 1.6 0.3	46 35 16 3

3 AIMS OF THE STUDY

The overall objective of this study was to add to current knowledge on the characteristics and sources of urban ambient particulate matter.

The specific aims of the study were to

1. characterize determinants, elemental composition and concentrations of particulate matter in the urban atmosphere,

2. investigate the characteristics and determinants of resuspended road dust as a specific urban air quality problem in subarctic urban environments, and

3. determine and compare major sources of ambient fine particulate matter ($PM_{2.5}$) in different European urban sites.

4 MATERIALS AND METHODS

4.1 Study areas and measurement periods

This thesis is based on data collected during three epidemiological studies conducted in four European cities between 1995-1999. The field measurements were conducted in Kuopio and Helsinki (Finland), Amsterdam (The Netherlands) and Erfurt (Germany). In *Helsinki* (original publications I, III, IV and V), the measurement of $PM_{2.5}$ and particle counts took place at a monitoring site located in a small park about two kilometres northeast of the city centre (Pekkanen et al., 2000). Gaseous pollutants (NO, NO_2, CO, SO_2 and O_3) were monitored on a municipal network site located 40 m from the PM site. Distances of the municipal site and the PM site to a major north-south street running on eastern side of the site (about 14,000 vehicles/day on weekdays) were 10 m and 50 m, respectively. Since the vast majority of buildings were connected to the central heating network, local heating was not a major source of air pollution near the sampling site. Meteorological parameters were measured 50 m above ground level at a meteorological station located approximately 1.5 km from the air pollution monitoring site. Due to the maritime location and rather flat terrain of Helsinki, air pollutants generated in the city area are often diluted efficiently by winds blowing in from the sea and other less polluted areas surrounding the city. Data were collected from 29 October 1996 to 28 April 1997, and from 2 November 1998 to 30 April 1999.

Kuopio (II) is a town in eastern Finland with approximately 90,000 inhabitants. The air quality measurements were conducted in a small park close to the town centre, at a monitoring station belonging to the environmental office of the municipality. The measurement site was located next to a park area alongside a two-story office building, and about 40 meters from the nearest busy street on which the average daily traffic density was about 14,000 cars per 24 hours on weekdays, 11,000 cars on Saturdays and 9000 on Sundays. Meteorological data were obtained from a station located 1 km south of the air pollution monitoring site and at a height of 50 meters from the ground. The elevation difference between the meteorological station and the air quality monitoring station was approximately 25 m. Measurements were carried out for 36 days between March 19 and April 23, 1995.

In *Amsterdam* (IV), the measurements of particulate matter were conducted on the roof of a nursing home at the height of 7.7 m from the ground (1.7 m above the roof) in the southeast

part of the city, 10 km from the inner city of Amsterdam (727,000 inhabitants). No major sources of air pollution were located in the close vicinity of the PM measurement site. There was a gas-fired power plant 5.5 km north of the site and the nearest major street with a traffic count of 10,900 cars per day ran 250 m southwest of the site. Data on gaseous air pollution were available from an urban background site that was located in the northern part of the city 15 km away from the PM site. The Royal Dutch Meteorological Institute delivered hourly data on meteorological variables from the Schiphol international airport that is located 25 km west from the air pollution site(s). Altitude differences in Amsterdam are very small and play no role in determining local air pollution concentrations.

In *Erfurt* (IV), PM measurements were done in a small park next to parking facilities for approximately 20 cars. Sampling inlets for $PM_{2.5}$ and particle counters were installed outside a mobile laboratory at the height of 1.7 m and 4 m from ground level, respectively. The site was situated 2 km south of the inner city of Erfurt (210,000 inhabitants). Concentrations of gaseous pollutants were measured at this site, except for CO which was measured 2 km away by the local monitoring network. One major road from the downtown heading south ran 40 m east of the measurement site with 22,000 vehicles passing per day, including heavy-duty traffic. The only major stationary emission source was a power plant that was located 6 km south of the site. Meteorological data in Erfurt were obtained from two different sites. Wind speed and direction were measured at an official meteorological station (German Weather Service) located about 6 km west from the PM site, whereas temperature and relative humidity were measured at the PM measurement site. The city of Erfurt is located in a valley and is mostly surrounded by ridges rising up to 100-200 m except in the north, where several high buildings are likely to reduce air movements in the city area. Therefore, temperature inversions, which are frequent during winter, can cause elevated levels of locally generated air pollutants within the city.

4.2 Sampling equipment and methods

Table 4 summarizes the measurement methods used for sampling and analysing the elemental composition of particulate matter in the four different field studies.

Table 4. Summary of methods used for measurements of particulate matter.

Measurements of particulate matter	**Method**	**References**
PM_1 (I), $PM_{2.5}$, PM_{10} (I-V)	Harvard impactor	Marple et al. 1987
PM_{10} (Helsinki and Amsterdam 1998-99)	β-attenuation (ESM Eberline FH 62 I-R; FAG Eberline FH-62 I-N)	
Total Suspended Particles (II)	High volume sampler	EPA standard NAAQS 40 CFR 50
Black carbon (II)	Aethalometer (Magee AE-9 Aethalometer^{TM})	Hansen et al. 1984
Absorption coefficient (I, III-V)	Filter reflectance (EEL 43 smoke stain reflectometer)	ISO 1993
Particle number concentration (I-V)	Condensation particle counter (CPC)	
Particle size distribution, Finland (I-V)	Electrical aerosol spectrometer	Tuch et al. 2000, Mirme et al. 2002
Particle size distribution, Amsterdam (IV)	Differential mobility analyser + CPC + optical particle spectrometer	Khlystov et al. 2001
Particle size distribution, Erfurt (IV)	Differential electrical mobility particle analyser + CPC + optical particle spectrometer	Tuch et al. 2000, Khlystov et al. 2001
$PM_{2.5}$ elemental composition (II)	ICP-MS (Perkin-Elmer 8 SCIEX ELAN-500)	Jalkanen and Häsänen 1996
$PM_{2.5}$ elemental composition (IIIa)	ED-XRF (X-Lab 2000, SPECTRO Analytical Instruments, Germany)	Mathys et al. 2001
$PM_{2.5}$ elemental composition (IIIb-V)	ED-XRF (Tracor Spectrace 5000 system, Tracor X-ray, CA, USA)	Samek et al. 2002, Janssen et al. (submitted)

The $PM_{2.5}$ and PM_{10} Harvard impactors used in this study are similar to those described by Marple et al. (1987), except that they have only one impaction stage. The PM_1 impactor (I) was constructed from two stacked nozzles and had an airflow rate of 23 l/min compared to 10 l/min of the $PM_{2.5}$ and PM_{10} impactors. During 1998-99 in Helsinki and Amsterdam, PM_{10} was monitored continuously using β-attenuation particulate monitors (Thermo Electron Eberline). In the impactor sampling, 37 mm diameter polytetrafluoroethylene filters of 2 μm pore-size were used as the sampling medium. The filters were weighed before and after sampling in air-conditioned rooms using a microbalance with 1 μg accuracy. For all PM fractions, particles above the desired size range, determined in terms of aerodynamic diameter, were collected on porous impaction plates impregnated with silicon oil, which were cleaned and saturated with oil on a daily basis in order to prevent particle bounce. Airflow was controlled using glass critical orifices for the PM_{10} and $PM_{2.5}$ impactors and an adjustable valve for the PM_1 impactor. The sampling flow was measured at the beginning and end of every 24-hour sampling period with calibrated rotameters in Amsterdam (IV), Helsinki (I, III-V) and Kuopio (II), and continuously using a gas meter in Erfurt (IV).

After weighing of the PM filters, their reflectance was measured using an EEL model 43D smoke stain reflectometer (I, III-V). The ISO 9835 standard "Ambient air - Determination of a black smoke index" (ISO 1993) was applied to the calculation of the absorption coefficients of the PM filters. Roorda-Knape et al. (1998) have found a good correlation between the results of the traditional Black Smoke method ($\mu g/m^3$) and reflectometric analysis performed on PM_{10} sample filters collected at the same location at the same time (R^2=0.94; N=40). Reflectance measurements of filters from both Amsterdam and Erfurt were conducted in the Netherlands (IV). Black carbon (II) concentrations were measured with a computer-controlled aethalometer (Magee AE-9 Aethalometer^{TM}) (Hansen et al. 1984) based on a continuous measurement of optical attenuation resulting from the deposit accumulating on the filter.

In Helsinki (I, III-V) and Kuopio (II), size-segregated particle number concentrations were measured using an electrical aerosol spectrometer (EAS) which measures the particle size distribution in the size range 0.01-10 μm solely by an electrical method employing unipolar diffusion charging in the size range 0.01-0.5 μm in one analyser and a strong electrical field charge in the range 0.3-10 μm in the other (Mirme et al. 2002). In Amsterdam and Erfurt (IV), measurements were done using integrated spectrometer units consisting of a particle mobility analyser, a condensation particle counter and an optical particle spectrometer (Tuch et al. 2000, Khlystov et al. 2001).

Data on concentrations of gaseous air pollutants and meteorology were obtained from existing monitoring networks operated by the local authorities. More detailed information about the equipment can be found in the original publications and in Pekkanen et al. (2000).

4.3 **Analyses of elemental composition** (I-V)

Elemental composition of PM_{10} and $PM_{2.5}$ samples from Kuopio (II) were analysed at the Geological Survey of Finland using a Perkin-Elmer 8 SCIEX ELAN-500 ICP-MS instrument. The procedure of inductively coupled plasma mass spectrometry has been described elsewhere (Jalkanen and Häsänen 1996). Every second $PM_{2.5}$ sample from the Helsinki 1996-97 measurement period (IIIa) was analysed for elemental composition using energy-dispersive X-ray fluorescence spectrometry (ED-XRF). The analysis was performed using X-Lab 2000 (SPECTRO Analytical Instruments, Germany 1998) in the Institute for Mineralogy

and Petrography, University of Basel (Switzerland). A detailed description of the analysis method is presented elsewhere (Mathys et al. 2001). $PM_{2.5}$ samples from Amsterdam, Erfurt and Helsinki 1998-99 were also analysed using ED-XRF. Analyses of all filter samples were performed with an automated Tracor Spectrace 5000 system (Tracor X-ray, Sunnyvale, CA, USA) in the Micro and Trace Analysis Centre of the University of Antwerp, Belgium (http://www.uia.ac.be) (Samek et al. 2002).

4.4 **Source apportionment** (III-V)

Source identification and source apportionment were done for $PM_{2.5}$ from all sites except from Kuopio. Elemental composition and air pollution data were analysed using principal component analysis (PCA) in order to identify the main source categories of $PM_{2.5}$. The extracted principal components were interpreted as source categories contributing to PM concentrations at the sampling site. The identification of source categories was undertaken by examination of the profiles of the principal components, i.e., loadings of the elements and other variables on the varimax rotated (orthogonal) principal components.

Estimates of daily source-specific $PM_{2.5}$ concentrations at the measurement site were obtained by regressing the measured daily $PM_{2.5}$ on daily principal component scores. Selection of elements to PCA was done based on the percentage of detected samples. Other variables (NO_X, SO_2, CO, $Abs_{2.5}$, particle counts $NC_{0.01\text{-}0.1}$ and $NC_{0.1\text{-}1.0}$) were included one by one and in several different combinations to find optimal and the most plausible source apportionment models. Several criteria were used in selecting the optimal models: in terms of source identification (PCA), we required identification of major sources with physically reasonable principal components whose eigenvalues were larger than 1 after varimax rotation. In terms of source apportionment (multiple linear regression), we required positive regression coefficients for all sources, a positive and moderate model intercept, and a high model R^2. An introduction to the basics of the PCA methodology and calculations used in this work is given elsewhere (Thurston and Spengler 1985).

4.5 Quality considerations

4.5.1 Measurement sites

As listed above, the measurement equipment for all pollutants and other variables were not located at the same site in any of the four cities. This was due to limited resources available for the field studies, both in terms of measurement equipment and personnel. Therefore the data for meteorological variables and also for gaseous pollutants were mostly obtained from the nearest existing network stations that were sometimes not located in close proximity to the main air pollution monitoring site. The distance between measurement stations within a city may pose a problem regarding investigations of very localized phenomena, but for many of the pollutants considered in this study, the daily variations are rather similar across larger areas. Also, wind direction data obtained from a site that has been specifically designed for producing meaningful results that are more representative of larger areas, have actually proved better than data taken from the street level (I). In Amsterdam, a high correlation (0.86) between daily values of NO_X (measured at a site located 15 km from the PM site) and $Abs_{2.5}$ (PM site) suggests that their diurnal concentration variations were similar within a larger area and probably determined mainly by local meteorology.

There are also differences in the air pollution sites between the cities, since it was not possible to find exactly similar measurement sites from all cities regarding the distance to nearby streets or the sampling height. The distance of the site from a source will affect the measured concentrations of pollutants (but perhaps will not have as great an impact on variations) that exhibit strong concentrations gradients as a function of distance from the source. This may apply to some elements, ultrafine particle number, and nitrogen oxides.

4.5.2 Sampling of particulate matter

Each measurement contains a degree of uncertainty due to the limits of measurement equipment and the people using the equipment. The major sources of error concerning the sampling and analyses of particulate matter samples include 1) artifacts or contamination of samples, 2) loss of collected aerosol species during sampling or after sampling, 3) sample handling, transport and storage, 4) modification of samples during analyses, and 5) errors in data handling. In order to control and minimize the overall uncertainty caused by these

factors, the sampling of PM and weighing of filters were carried out according to a standard operation procedure to assure high quality of sample processing. Comparability of weighing and reflectance results between Amsterdam, Erfurt and Helsinki centres was ascertained by using a common study protocol (standard operating procedures available at http://www.ktl.fi/ultra) and by performing round-robin tests for reference samples collected in each centre.

The PM filters were weighed before and after sampling in air-conditioned rooms using a microbalance with 1 μg accuracy. In works I and IIIa, the blank and sample filters were weighed before and after sampling, always after a 24 h conditioning period at a constant temperature of 21 ± 0.4 ºC and a relative humidity of 38 ± 4%. Static charges within the analytical microbalance were removed by placing a radioactive ionizing unit (Am-241) in the weighing chamber and passing the filters over a similar ionizing unit prior to weighing. The estimated overall accuracy of measurements, for example, in the $PM_{2.5}$ results was ±0.6 $\mu g/m^3$. In works IIIb-V, the sample filters were stabilised at controlled relative humidity (range 30-40%) and temperature (range 19-24 ˚C) for at least 24 hours prior to weighing (Pekkanen et al. 2000). The effect of changes in atmospheric pressure between pre- and post-sampling weighing on the results was controlled for by using buoyancy correction (Koistinen et al. 1999). Since the humidity control in the weighing room was unreliable in work II, the effect of humidity on the filter weights was eliminated by means of a correction factor corresponding to the change in weight of a set of control filters, stored permanently in the weighing room and weighed every time alongside the sample filters. Their weight change was observed to be linearly dependent on the relative humidity of the weighing room.

In I and IIIa, the samples were accepted only if the end flow was over 8 lpm for the PM_{10} and $PM_{2.5}$ samplers and 21 lpm for the PM_1 sampler. The estimated relative errors in the rotameters used to measure sampling air flow in Helsinki were found to be about 2% when the calibration air flow was within the accepted limits specified for the field sampling. Field blank filters were taken during the measurement periods to determine the detection limit for the methods used. The detection limits for $PM_{2.5}$ during the 1998-99 study in Amsterdam, Erfurt and Helsinki were 2.1, 0.23 and 0.77 $\mu g/m^3$, respectively (de Hartog et al., in press). Estimated from duplicate samples, the precisions of $PM_{2.5}$ measurements expressed as median coefficient of variation (CV) were 1.9%, 2.5% and 7.8% in the three cities. In Kuopio, only two field blank filters and no duplicate filters were collected and, therefore, no meaningful

estimates on detection limits and precision can be made. The accuracy of the impactor PM measurement depends largely on the loss of material from the sample associated with the concentrations of volatile and semi-volatile compounds, which were not determined in this study. However, the overall uncertainty of the impactor method can be estimated to be of the order of 20%. A field comparison of the β-attenuation method with a gravimetric reference method (LVS-PM_{10} -FH 95 KF, ESM Andersen) has shown a very good agreement between the two methods, although the β-attenuation method gave slightly higher concentrations, especially during days of high relative humidity and low temperature (Salminen and Karlsson 2003).

During the measurements of PM filter absorbance ($Abs_{2.5}$), the reflectometer was calibrated using a pre-selected clean control filter taken from the same batch as the PM sample filters. This calibration was done at the beginning of each measurement session and repeated also during the measurement session to ensure comparable and reproducible results. The detection limits (precision as median coefficients of variation) for $Abs_{2.5}$ during the 1998-99 study were 1.5 $m^{-1} \cdot 10^6$ (2.9%) in Amsterdam and 0.80 $m^{-1} \cdot 10^6$ (4.7%) in Helsinki (de Hartog et al., in press). Quality control filters from Erfurt were not available for this analysis. Regardless of the excellent precision, the overall uncertainty of the reflectometric method as a measure of elemental carbon can be estimated to be around 25% (Sillanpää et al., submitted).

A side-by-side comparison of the electrical aerosol spectrometer used in Finland and the mobile aerosol spectrometer used in Germany was performed in the size range from 0.01 to 0.5 μm (Tuch et al. 2000). The results showed that the systematic differences between the instruments were within 10% and the correlation around 0.98 in the particle size range 0.01-0.5 μm. The results from a side-by-side comparison of all three spectrometers used in the different countries also showed excellent correlation (0.98) and geometric mean ratios ranging from 1.06 to 1.23 for ultrafine and accumulation mode particles in ambient air conditions (Mirme et al. 2002).

4.5.3 Elemental analyses

In the XRF analyses of 1996-97 $PM_{2.5}$ samples from Helsinki, the calibration was based on 35 standards applied for 36 elements on different media (Mathys et al. 2001). No field duplicate

samples were available from Helsinki 1996-97 to determine precision of the elemental analyses, but based on earlier analysis of similar samples, the precision varied from 2% to 30% depending on the element (Mathys et al. 2001). After the publication of III, the laboratory in Basel reported that they had found an error in their calculations and delivered new XRF data. The elements that were most affected were Na and Si whose average concentrations were increased by twofold compared to the original values. The effect on source apportionment in the Helsinki 1996-97 results was in the order of only a few percent, however. The same sources of $PM_{2.5}$ were identified with very similar average contributions, and the Spearman rank correlations of recalculated source components with the original components (III) were >0.93.

Calibration of the ED-XRF system used to analyse $PM_{2.5}$ samples from 1998-99 (Amsterdam, Erfurt and Helsinki) was based on thin film reference standards (Micromatter, Seattle, WA, USA) and evaluated by regularly analysing US EPA standard filter No's 1821 and 1829. The accuracy varied between 1% and 28% depending on the element and its concentration on the filter. Based on homogeneity tests run by the laboratory in Antwerp, the analytical precision of the method itself was about 4%, also depending on the element and concentration. The detection limits were defined for each element and sample individually, based on the uncertainty (standard deviation) obtained from three consecutive measurements of the sample. A number of field blanks were also analysed, and their median concentration was subtracted from the sample concentrations for each element. Based on the coefficient of variation in the field duplicate samples, the precision of $PM_{2.5}$ elemental analysis was markedly better in Amsterdam (2.9-50% depending on the element) compared to Helsinki (2.5-84.6%) (Janssen et al., submitted). The reason for the poorer precision in Helsinki cannot be confirmed, but it may be related to the fact that in Helsinki the duplicates were collected after the field campaign and during seven consecutive days when the ambient PM concentration was relatively low. Furthermore, precision of simultaneously collected indoor and personal duplicate samples was markedly better in Helsinki compared to outdoor samples. Quality control filters from Erfurt were not available to determine the precision for the Erfurt elemental samples. The overall uncertainty related to the elemental analysis of $PM_{2.5}$ samples was increased due to the poor precision, but can be estimated to be 30% or better for most elements.

The detector in the ED-XRF system became defective and was replaced before the analyses of outdoor $PM_{2.5}$ samples from Erfurt (1998-99). Therefore, 5 field blank filters, which had been collected during the 1998-99 in Helsinki using personal $PM_{2.5}$ monitors, were re-analysed in the same laboratory with the new detector. Comparison of the new and the original results indicate quite large differences in the reported values for most analysed elements (Janssen et al., submitted). This suggests that comparability of the results from Helsinki and Amsterdam with the results from Erfurt may suffer from the change of the XRF detector during the analyses series. The magnitude of the effect with respect to the outdoor samples containing higher concentrations of analytes is difficult to estimate, however.

4.5.4 Data management and statistical tools

Data acquisition and handling were carried out according to the study protocols. Raw data on manually operated measurement equipment were first entered on printed field forms and subsequently, typed into computer files which were checked for possible typing errors. Data from computer controlled measurement device were recorded into raw data files that were checked and combined to the final datasets, which were used in the statistical analyses. Outliers were not excluded systematically based only on any mathematical or statistical procedure, but were rather excluded on a case by case basis after plausibility checks. This procedure included both a statistical part (screening of outliers based on standard deviation and mean of a given variable) and a more subjective part (for example, retaining a peak elemental concentration for an element if it coincided with a high concentration for another element that probably originated from the same source). Data management procedures have been described in more detail in the original publications (I-V) and by Pekkanen et al. (2000) for III-V. For gaseous air pollutant data, daily average values were calculated from the raw data, which had first been cleaned of erroneous data points by the network operators according to their own data management guidelines. SAS/STAT® statistical software (SAS Institute Inc. 1999) Version 8.02 and statistical software package Statistica for Windows 5.0 (StatSoft Inc. 1996) were used for statistical procedures and calculations.

5 RESULTS

5.1 Concentrations of PM

Descriptive statistics of the measured parameters of particulate matter in the four study sites and three different measurement periods are summarised in Table 5. $PM_{2.5}$, PM_{10} and $PM_{2.5-10}$ concentrations in Helsinki were comparable during 1996-97 and 1998-99. In Kuopio, PM concentrations were higher than in Helsinki and very close to those measured in Amsterdam and Erfurt. Note that the measurements in Kuopio were made during the spring and for a significantly shorter period compared to the other studies. Amsterdam and Erfurt yielded similar statistics for $PM_{2.5}$ but differed in PM_{10} with high median concentration in Amsterdam. The concentration of coarse particles ($PM_{2.5-10}$, calculated as difference between PM_{10} and $PM_{2.5}$ concentrations) in Erfurt was very low compared to the other sites, which is also reflected in the high $PM_{2.5}/PM_{10}$ ratio compared to the other cities. $PM_{2.5}/PM_{10}$ ratios at other sites are more comparable. The average $PM_1/PM_{2.5}$ ratio in Helsinki during 1996-97 varied from 0.57 (spring) to 0.63 (winter). Resuspended dust episodes occurring in the spring in Helsinki had a clear effect on the $PM_{2.5}/PM_{10}$ ratio but not on the $PM_1/PM_{2.5}$ ratio.

The number concentrations of ultrafine particles ($NC_{0.01-0.1}$) were somewhat higher in Kuopio than in Helsinki. In Helsinki, there was no marked change in ultrafine particle concentration between 1996-97 and 1998-99. Erfurt had the highest concentration of ultrafine particles, especially regarding the maximum concentrations. The slightly higher concentration of particles in the accumulation size range ($NC_{0.1-1.0}$) during the latter study in Helsinki is consistent with the difference in $PM_{2.5}$ concentrations. The median concentration of accumulation mode particles ($NC_{0.1-1.0}$) was clearly lowest in Kuopio compared to all other sites. In contrast to ultrafine particles, accumulation particle numbers were higher in Amsterdam than in Erfurt.

In Helsinki, absorption coefficient of $PM_{2.5}$ filters ($Abs_{2.5}$) increased notably from 1996-97 to 1998-99. During 1996-97, absorption coefficients of $PM_{2.5}$ and PM_{10} samples were quite similar but the absorption coefficients of PM_1 samples were clearly lower. $Abs_{2.5}$ was lower in the Amsterdam study than in the other simultaneously conducted studies, but still higher than during the 1996-97 campaign in Helsinki. All statistics show that Erfurt had clearly the highest absorption coefficients of the three major cities.

Table 5. Descriptive statistics of the daily values of particulate matter (PM), particle number concentrations (NC) and $PM_{2.5}$ filter absorption coefficient ($Abs_{2.5}$).

$PM_{2.5}$ ($\mu g/m^3$)	N	Mean	Std	5th %	Median	95th %	Max
Kuopio 1995	36	17.7	12.9	4.35	14.3	44.4	54.6
Helsinki 1996-97	173	9.70	5.21	3.80	8.40	20.5	38.3
Helsinki 1998-99	164	12.8	6.74	5.17	10.6	25.7	39.8
Amsterdam 1998-99	224	19.9	13.2	6.07	16.8	47.0	82.3
Erfurt 1998-99	157	22.3	17.4	6.10	16.3	62.3	104

PM_{10} ($\mu g/m^3$)	N	Mean	Std	5th %	Median	95th %	Max
Kuopio 1995	36	32.5	29.2	5.66	25.3	93.7	122
Helsinki 1996-97	173	16.5	9.63	6.90	13.9	34.7	73.7
Helsinki 1998-99 (1	164	19.3	9.33	8.21	17.3	36.0	67.4
Amsterdam 1998-99 (1	194	36.4	16.7	17.8	32.1	70.0	112
Erfurt 1998-99	150	26.7	19.6	8.40	19.9	68.9	104

$PM_{2.5-10}$ ($\mu g/m^3$)	N	Mean	Std	5th %	Median	95th %	Max
Kuopio 1995	36	14.8	16.6	0.77	8.25	50.4	67.1
Helsinki 1996-97	168	6.97	6.84	1.40	4.70	22.4	49.3
Helsinki 1998-99 (1	164	6.55	5.73	0.83	4.77	19.0	37.0
Amsterdam 1998-99 (1	194	15.3	7.70	3.23	14.7	28.8	45.3
Erfurt 1998-99	150	3.93	5.71	-1.30	2.91	13.4	51.3

$PM_{2.5}$ / PM_{10}	N	Mean	Std	5th %	Median	95th %	Max
Kuopio 1995	36	0.63	0.16	0.43	0.60	0.90	0.92
Helsinki 1996-97	168	0.61	0.19	0.29	0.64	0.87	0.95
Helsinki 1998-99 (1	164	0.68	0.18	0.36	0.70	0.92	1.02
Amsterdam 1998-99 (1	194	0.56	0.19	0.25	0.56	0.88	0.98
Erfurt 1998-99	150	0.86	0.17	0.58	0.88	1.08	1.48

$NC_{0.01-0.1}$ ($1/cm^3$)	N	Mean	Std	5th %	Median	95th %	Max
Kuopio 1995	36	17600	8860	8410	15000	36200	40400
Helsinki 1996-97	165	15300	6610	7440	14500	28200	46500
Helsinki 1998-99	164	16800	9220	5940	14700	35800	50300
Amsterdam 1998-99	209	17300	6000	7370	17300	28100	37200
Erfurt 1998-99	157	20900	11800	7430	18700	40900	96700

$NC_{0.1-1.0}$ ($1/cm^3$)	N	Mean	Std	5th %	Median	95th %	Max
Kuopio 1995	36	451	203	172	414	777	907
Helsinki 1996-97	165	984	497	439	890	1920	2790
Helsinki 1998-99	164	1390	679	665	1190	2870	3780
Amsterdam 1998-99	195	2110	1100	797	1870	4240	6410
Erfurt 1998-99	157	1760	1170	591	1460	4730	6850

$Abs_{2.5}$ ($1/m * 10^6$) (2	N	Mean	Std	5th %	Median	95th %	Max
Helsinki 1996-97	172	13.3	6.02	6.21	11.6	26.1	40.4
Helsinki 1998-99	164	20.1	8.14	10.1	18.9	35.6	49.2
Amsterdam 1998-99	223	16.8	9.21	5.81	14.9	33.8	54.7
Erfurt 1998-99	156	24.6	14.1	8.12	20.3	51.1	78.0

1) PM_{10} monitored continuously; 2) not measured in Kuopio.

5.2 Elemental composition of PM

Descriptive statistics of the chemical components of $PM_{2.5}$ in Helsinki, Amsterdam and Erfurt are presented in Table 1 (III and IV). Note that the number of cases in Helsinki data was significantly lower for the 1996-97 campaign (N = 83), since only every second filter sample was analysed for elemental composition.

In Helsinki (III), median concentrations of several elements were clearly different during the two measurement periods. During the first campaign in 1996-97, concentrations of Ca, Fe and Ni were mostly below the detection limits, whereas during the second campaign in 1998-99 these elements were readily detected. As for the elements that were routinely detected, the concentration differences were most prominent for Al and Si which had 5-fold higher medians, and for Pb and V which exhibited 2-fold lower medians during 1996-97 compared to 1998-99.

We also found that median concentrations of all elements but Fe differed in Helsinki, Amsterdam and Erfurt (IV). Similarly to the Helsinki comparison (III), there were several elements (Al, Si, Ti, V, Mn, Ni, Br) that were readily detected in one or two cities but poorly detected in the others, reflecting clear differences in the concentrations of these elements between the cities. With regard to the better-detected elements, the concentration of Cu in Helsinki was low compared to Amsterdam and Erfurt. The Cl concentration was clearly higher in Amsterdam than in Erfurt or Helsinki. Erfurt had the lowest median concentration of S and highest median concentration of Ca and Zn.

Since the duration of the measurement campaigns was slightly different depending on the city, we compared concentrations of elements also for the period of five winter months (November 2 - March 31) when sampling was in progress in all three cities. The general pattern of differences in elemental concentrations remained similar during the truncated period; however, median concentrations of elements and PM's were generally higher compared to the complete periods. The percentage increase was >20% for Cl, Ni, Cu, Zn and $Abs_{2.5}$ in Amsterdam, >15% for Cl, Cu and Pb in Erfurt, and >10% for Mn in Helsinki. The median concentrations of a few elements decreased by more than 5% (S in Amsterdam, V in Erfurt, Al, Si and Fe in Helsinki).

5.3 Sources of urban ambient PM

5.3.1 Source identification

The results from the two sampling periods in Helsinki are presented in III and V, and the results from Amsterdam and Erfurt in IV. In Helsinki, five source categories were identified for both 1996-97 and 1998-99 study periods (see Figure 1 in III, and Table 1 in V). The identified $PM_{2.5}$ sources in Helsinki were 1) local traffic and miscellaneous combustion sources, 2) long-range transported and secondary particulate matter, 3) crustal source, 4) oil combustion and 5) salt. These five source components explained 76% and 82% of the total variance of the analysed data in 1996-97 and 1998-99, respectively.

In Amsterdam, six major sources of $PM_{2.5}$ could be identified, five of which were interpreted as being similar to those in Helsinki (IV, Figure 1). In addition, a component that was attributed to emissions from industrial activities was identified. The percentage of total variance in the analysed data that was explained by the extracted principal components varied from 90.6% to 91.6% depending on the PCA solutions.

Four source categories were identified in Erfurt. However, interpretation of the extracted principal components was not straightforward (IV, Figure 2). The first identified principal component was interpreted as combustion emissions mainly from local traffic, and the second component as secondary particulate matter. The major contributor to the third component was suspected to be resuspended soil and street dust around the measurement site. The fourth source was emissions from industrial combustion processes and incineration.

5.3.2 Source apportionment

Source apportionment by multiple linear regression showed that the contribution of long-range transported air pollution to $PM_{2.5}$ in Helsinki was rather stable with an average contribution of 51% during 1996-97 and 50% during 1998-99. The contribution of the other identified sources differed between the two campaigns (III, Figure 3), most prominently for oil combustion, crustal source, and sea salt.

Source apportionment results for Amsterdam and Erfurt (IV) were presented in a different scheme compared to that of the earlier study conducted in Helsinki only (III). Mass contributions of the identified source categories in Amsterdam and Erfurt were presented as averages of five plausible models that were selected from a larger group of tentative models. There are several distinct features that stand out from the comparative $PM_{2.5}$ source apportionment results from the three European cities (Figure 2; Table 2 in IV). First, traffic related combustion contributed more to $PM_{2.5}$ in Amsterdam and Erfurt compared to Helsinki. Second, the relative contribution of secondary particulate material, or long-range transported air pollution, was highest in Helsinki and on the other hand, very similar in Amsterdam and Erfurt. Third, the percentage of crustal material in $PM_{2.5}$ was significantly higher in Erfurt than in either Helsinki or Amsterdam. Fourth, the salt component in Helsinki was obviously affected by another interfering source component during 1998-99.

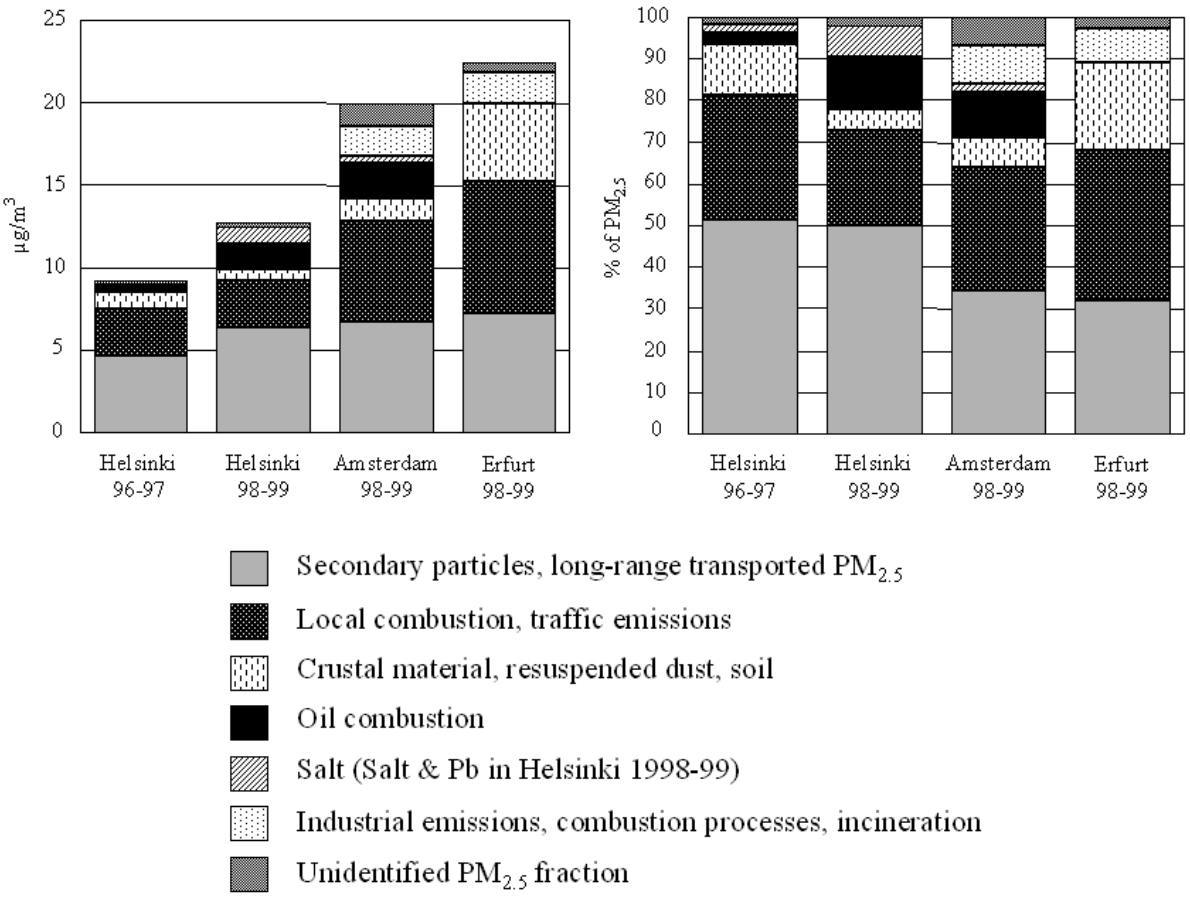

Figure 2. $PM_{2.5}$ source contributions in Helsinki, Amsterdam and Erfurt.

Secondary particles and local combustion (mostly traffic) made a 65% aggregate contribution to average total $PM_{2.5}$ in Amsterdam and Erfurt, and 73-81% contribution in Helsinki. The

relative impact of both of these source categories on average $PM_{2.5}$ was almost equal in Amsterdam and Erfurt, whereas in Helsinki, long-range transported and secondary particles were clearly the most important determinants of ambient $PM_{2.5}$ during both study periods. In terms of mass concentration, however, the contribution of secondary particles was very similar in all cities while average concentrations of traffic-related $PM_{2.5}$ were much higher in Erfurt and Amsterdam.

Correlations of the source-specific $PM_{2.5}$ with some of the measured parameters are tabulated in Appendix 1. The strong correlation of $PM_{2.5}$ with long-range transported and secondary PM shows the major role of this source component in the variations of $PM_{2.5}$ concentrations. The crustal source component had a moderate negative correlation with relative humidity in all cities, and a positive correlation with temperature in Amsterdam and Erfurt. As expected, coarse particles were positively correlated with the crustal source component. The diluting effect of local winds was also apparent from the correlation between local combustion and wind speed.

Based on examination of mean and standard deviation, short-term variability in the measured $PM_{2.5}$ was smaller than variability in any of the specific source categories at any measurement site. Time trend plots of source-specific $PM_{2.5}$ in the three cities (Appendix 2) indicate that seasonal phenomena do play a role in controlling the concentrations of $PM_{2.5}$ from some of the source categories. The estimation of seasonality is difficult, however, since the measurements did not span all of the seasons in any of these studies. Thus, not all seasons and meteorological conditions have been covered in this examination.

Concentrations of $PM_{2.5}$ associated with long-range transported air pollution and secondary particulate matter seemed to follow smooth and transient variations in concentration, which were seemingly not related to seasonal cycles. The traffic-dominated source component increased to some degree during the coldest months in Helsinki and Erfurt, but in Amsterdam this pattern was not apparent. The crustal, or soil, component followed a seasonal trend in Helsinki with lower values in the mid-winter and ascending values towards the spring. In Amsterdam and Erfurt, this pattern was not visible, although in Erfurt the concentrations were higher during March compared to the autumn values. $PM_{2.5}$ related to salt seemed to be elevated during winter in both Helsinki and Amsterdam. $PM_{2.5}$ from the rest of the identified

sources - oil combustion and industrial processes - appeared to be dominated by sporadic high concentrations rather than seasonal trends.

The results from multivariate source apportionment from Helsinki in 1998-99 were compared to results from mass closure (V), where major chemical components of PM are reconstructed from the measured trace elements. The modelled concentrations of particulate matter related to long-range transboundary air pollution from PCA-MLR and secondary ammonium sulphate from mass closure, were quite close to each other (V, Table 2) and the correlation coefficient between the modelled mass concentrations was quite high (r = 0.88). On the other hand, correlation coefficients of the combustion-related source categories (PCA-MLR: local combustion and traffic, oil combustion; Mass Closure: residual $PM_{2.5}$) estimated from the two methods were poor (r = 0.25-0.45), suggesting that these components represent different aspects of $PM_{2.5}$ at this measurement site. The medians of the contribution of the crustal source were similar for both methods and correlation was high (r = 0.90), although the two methods predicted the very high and very low concentrations of crustal particulate matter differently. The correlation of the contributions of the salt source was quite high (r = 0.83) between the different methods but the estimated mass concentrations differed.

6 DISCUSSION

6.1 Characteristics of particulate matter

6.1.1 Concentrations and determinants

The European Commission has set a strict PM_{10} limit value of 40 $\mu g/m^3$ (annual average) that has to be met by the year 2005 (European Communities Council Directive 1999/30/EC), and the lower annual $PM_{2.5}$ limit of 20 $\mu g/m^3$ has been recommended by the European Committee for Standardization (CEN). The mean values of PM_{10} in Amsterdam, and $PM_{2.5}$ in Erfurt and Amsterdam measured in this study are very close to these limit values. It is important to note, however, that our measurements did not cover a whole year. Average $PM_{2.5}$ concentrations measured in Kuopio and Helsinki were notably lower in comparison to values reported from most other European sites. The average concentrations in Helsinki were close to values found at Central European rural sites (Van Dingenen et al. 2004) and corresponded to 20-30% of the average concentrations found in Eastern European sites (Houthuijs et al. 2001).

Hoek et al. (1997) have reported a daily mean PM_{10} concentration of 18 $\mu g/m^3$ at an urban site in Kuopio during two winter months in 1993-94. This value is much lower than our results from Kuopio, but close to our results from Helsinki. The difference in mean values from Kuopio arises mostly from contribution of resuspended dust to our measurements since these were conducted intentionally during the most intense street dust events in the spring.

Average $PM_{2.5}/PM_{10}$ ratios in Kuopio, Helsinki and Amsterdam were comparable to the ratios reported earlier from other European studies (Van Dingenen et al. 2004). The high $PM_{2.5}/PM_{10}$ ratio and the low concentration of $PM_{2.5\text{-}10}$ particles indicate that in Erfurt, the majority of PM_{10} particles originate from traffic and other combustion sources, such as coal combustion, that emit primarily fine particles. As the measurement equipment was identical in all cities, the remaining other possible explanations for the higher ratio in Erfurt are a consistently too low sampling volume or a frequent overloading of the impactor plate resulting in particle bounce, both of which could increase the effective cut-point of the $PM_{2.5}$ impactor. Neither of these explanations are very plausible, however, since the $PM_{2.5}$ concentrations were not extremely high and the sampling flow was routinely checked with

calibrated equipment to detect possible leaks in the system. Maximum $PM_{2.5}/PM_{10}$ ratios are often associated with local pollution episodes that are associated to combustion sources (Marcazzan et al. 2002) and Erfurt is especially prone to experience local pollution episodes due to the special topography of the district. The low $PM_{2.5}/PM_{10}$ ratio in Amsterdam may be attributable to high concentrations of sea salt and sodium nitrate particles in the coarse fraction (Clarke et al. 1999). However, the composition of PM_{10} was not analysed in this study.

Changes in relative concentrations of PM_{10}, $PM_{2.5}$ and PM_1 (I) and source apportionment results (III) suggest that resuspended dust episodes affected the $PM_{2.5}$ fraction, as has been observed in previous studies (Claiborn et al. 2000). On the other hand, resuspended dust episodes occurring in the spring had a clear effect on the $PM_{2.5}/PM_{10}$ ratio but not on the $PM_1/PM_{2.5}$ ratio in this study, suggesting that in terms of the variation of particle mass, monitoring of PM_1 did not significantly add to the information content already obtained from monitoring of $PM_{2.5}$.

Ruuskanen et al. (2001) have reported concentrations and absorption coefficients of $PM_{2.5}$ and number concentrations of ultrafine (0.01-0.1 μm) and accumulation mode (0.1-0.5 μm) particles from Helsinki, Erfurt and Alkmaar (The Netherlands) during winter 1996-97. The data from Helsinki are the same that have been used in this thesis. $PM_{2.5}$ concentration and absorption coefficient in Erfurt were almost twice as high during winter 1996-97 compared to 1998-99 (Table 5). The simultaneous reduction in these parameters from 1996-97 to 1998-99 suggests that combustion sources have a major role in determining concentrations of $PM_{2.5}$ in Erfurt. The number concentration of accumulation mode particles in Erfurt was higher during 1996-97 compared to 1998-99, making the relative difference between Helsinki and Erfurt even larger during 1996-97 in comparison to the 1998-99 study. Apart from higher $PM_{2.5}$ concentrations, the reported values from Alkmaar during 1996-97 (Ruuskanen et al. 2001) were comparable with the results from Amsterdam in this study.

In the samples from Helsinki 1996-97, the absorption coefficients of $PM_{2.5}$ and PM_{10} were quite similar while those of PM_1 were clearly lower. It has been shown also in other data that the absorbance measurement of the $PM_{2.5}$ captures virtually all of the absorbance in total PM_{10} (Cyrys et al. 2003a). The clear difference between absorption coefficients of PM_1 and $PM_{2.5}$ samples, on the other hand, suggests that the PM fraction between 1-2.5 μm contains a

substantial amount of dark coloured carbonaceous material. An assessment on the relationship between elemental carbon and absorbance made by Cyrys et al. (2003a) highlighted the need for site-specific calibration of the absorbance method, since the agreement between these methods may depend on local characteristics. This suggests that in the present study, although comparable as such, the absorption coefficients may not give directly comparable results with respect to the concentrations of elemental carbon in the urban air.

6.1.2 Elemental composition

In Helsinki, the median concentrations of some elements, especially Al, Si, Pb and V, were notably different between 1996-97 and 1998-99, while $PM_{2.5}$ concentrations were approximately the same. Similarly, concentrations of many elements in Helsinki 1996-97 were notably different from those observed in Amsterdam and Erfurt during 1998-99. During 1996-97 in Helsinki, the concentrations of Ca, Fe and Ni were mostly below the detection limits, whereas during 1998-99 these elements were present in readily detectable concentrations. Notable changes in mass contributions from sources of these elements or source profiles between the two sampling periods could partly explain the differences. However, the average elemental composition of, for example, crustal $PM_{2.5}$ is not likely to change so extensively within two years at the same site. One possible explanation for the differences could be that the elemental analyses of the $PM_{2.5}$ samples from 1996-97 and 1998-99 were carried out in different laboratories.

The higher $PM_{2.5}$ values in Amsterdam and Erfurt compared to Helsinki were not systematically reflected in higher elemental concentrations in Amsterdam or Erfurt in the 1998-99 campaigns. Thus, the difference in total $PM_{2.5}$ must be associated with various organic and inorganic components of $PM_{2.5}$ that were not directly measured in our study. Concentrations of Cu, Zn and Br that are emitted mainly by anthropogenic sources were slightly lower in Helsinki than in Amsterdam and Erfurt. This is not surprising since Central-European cities are surrounded by greater population densities and more industrial sources and these will exert a more constant effect on the ambient PM concentration. On the other hand, the Al concentrations were much higher in Helsinki, this is possibly related to wintertime sanding of streets. The low concentration of Al and hence the low number of samples above the XRF detection limit, especially in Erfurt, in contrast to Si is peculiar since these elements are thought to originate mainly from soil dust (aluminosilicates). Also V and

Ni were rarely detected in Erfurt, which could be due to more irregular contribution of oil combustion to ambient $PM_{2.5}$ compared to Amsterdam and Helsinki, where closeby harbours and ship traffic constitute a constant source of oil combustion emissions.

Our results from elemental analyses of Amsterdam $PM_{2.5}$ samples are well comparable with the results based on ED-XRF analyses of filters from semi-continuous sampling performed by The National Institute for Public Health and the Environment (RIVM) in 1998-99 on two sites in Amsterdam (Visser et al. 2001). The ratios of the mean concentrations of elements at our site and the two RIVM sites ranged from 0.60 to 1.30. The elemental concentrations in Erfurt were systematically higher (ratio 1.3-2.8) in comparison to the results from a previous study conducted in Erfurt during 1997-98 (Cyrys et al. 2003b). These differences could be due to the different sampling period and instrumentation (2.5 μm cut-off Harvard impactor in this study vs. 2 μm cut-off cascade impactor in Cyrys et al. 2003b), different filter media (polytetrafluoroethylene vs. polypropylene) and different methods used for elemental analyses (ED-XRF vs. particle induced X-ray emission analysis).

In Helsinki, the results of our elemental analyses were rather similar to previous results from 1996-97 (Pakkanen et al. 2001b) with less than two-fold concentration differences (ratio 0.54-1.8) despite different sampling ($PM_{2.3}$; 2.3 μm cut-off virtual impactor with polytetrafluoroethylene filters and 10-stage Berner low-pressure impactor with greased polycarbonate films) and analytical methods (ICP-MS, instrumental neutron activation analysis, particle induced X-ray emission analysis) used in these two studies.

In this study, the average concentrations of most elements in fine particulate matter were either lower or at the same level compared to several other locations (Harrison and Yin 2000). However, such a straightforward comparison of the elemental concentrations will not be very informative without detailed information on each measurement location.

6.2 Sources of fine particulate matter

6.2.1 Identification of sources

Two aspects emerged from the comparison of the identified source categories in the three cities. First, oil combustion and sea salt components were extracted in Helsinki and

Amsterdam but not in Erfurt. Second, sources with same basic interpretation could be identified both in Helsinki and Amsterdam, with the exception of an additional industrial component in Amsterdam. The fact that a specific industrial source component was not identified in Helsinki may well reflect the lower number of significant industrial sources in the vicinity of this measurement site.

The key element useful in the identification of the long-range transboundary air pollution component was S, most of which probably was associated to secondary sulphate aerosols formed from sulphur dioxide emissions from coal combustion. Sulphate aerosol is also generated within the marine sulphur cycle, but the effect of the marine sulphate fraction on the total sulphate observed in this study is probably very small. In Helsinki, for example, practically all of the sulphate is attributable to long-range transported air pollution (Ojanen et al. 1998). In the present work, P, K, Zn, Pb, Br were also associated with this source component in the studied cities. The presence of P and S in the same source component in Erfurt (P was not analysed from other cities) supports the above conclusion, since phosphate is emitted during combustion of coal (Lee 2001). However, the low concentration of S and the absence of local large-scale coal combustion in Erfurt suggests that the majority of the secondary PM originated from mid- to long-range transported air pollution. Zn, Pb, Br have been linked to incineration and/or traffic in numerous studies (Chang et al. 1988, Olmez et al. 1988, Huang et al. 1994, Ramadan et al. 2000). Zn and Pb have also been linked to long-range transported particulate matter in a previous study in Helsinki (Pakkanen et al. 2001a).

The local traffic and combustion source category was identified chiefly based on high loadings of nitrogen oxides, ultrafine particles and the absorption coefficient. In addition, Cu, Zn, Fe, Mn, Br (in Erfurt) and accumulation mode particles were related to this component. The source profile of the traffic-related emissions component was very similar in Amsterdam and Helsinki. Cu in traffic environments may originate from diesel emissions (Swietlicki et al. 1996) or from wearing of vehicle brakes (Sternbeck et al. 2002, Laschober et al. 2004). Consistently, a wind direction analysis of Cu concentrations in Helsinki indicated a presence of a widespread source of Cu rather than any specific point source(s) near the measurement site. Zn can be traced to tyre wear particles (Hildemann et al. 1991, Swietlicki et al. 1996, Adachi and Tainosho 2004) and has been proposed a potential marker for traffic related emissions (Huang et al. 1994). Fe and Mn are crustal elements, which may have been present

in dust resuspended by traffic. Fe is also present in brake dust (Hildemann et al. 1991) and heavy-duty diesel emissions (Ramadan et al. 2000).

The soil source was straightforwardly identified based on common crustal elements such as Al, Si, Ca, Fe and Ti. The higher impact of the crustal component in Erfurt compared to Amsterdam and Helsinki was in agreement with the high concentration of Ca found in Erfurt. Calcium has been identified as a soil element in Erfurt based on its low enrichment factor (Cyrys et al. 2003b), but it has also been related to vehicular emissions in other studies (Cadle et al. 1997, Kleeman et al. 2000). The crustal $PM_{2.5}$ component correlated better with $PM_{2.5-10}$ than with $PM_{2.5}$ in all cities, emphasizing the true association of this source component with emissions of mechanically generated coarse particles. Apart from high loadings of Ca and other common crustal elements Si, Ti and Fe, there was a moderate loading of ultrafine particle counts ($NC_{0.01-0.1}$) and Cu to this component in Erfurt. These loadings suggest that this source component might be partly attributable to both direct and indirect emissions from traffic, i.e. exhaust and brake wear emissions and resuspension of street dust.

In Amsterdam, the interpretation on the crustal component was done based on the high loading of Ca. However, Ca is also emitted from cement production, iron and steel plants, and coal combustion in domestic and industrial boilers (Lee and Pacyna 1999). The PCA component including Ca was not associated with any specific wind direction, suggesting that Ca was not emitted by a single major point source in or near Amsterdam. Furthermore, there would have probably been a correlation of Ca with other tracers if this PCA component was to represent an other than a crustal source.

Oil combustion source was identified based on V and Ni, which are markers for heavy oil combustion (Olmez et al. 1988), and SO_2. The presence of gaseous phase SO_2 in this component suggests that V and Ni were emitted by mesoscale sources such as ships in harbours and along the coast, municipal district heating power plants and industrial power plants using heavy oil. It has been recognised that emissions from ships can be a significant source of gaseous pollutants and particulate matter at certain locations (Colvile et al. 2001, Isakson et al. 2001, Cooper 2003, Saxe and Larsen 2004).

Wind direction analyses showed that during both 1996-97 and 1998-99 in Helsinki, the bulk of the highest PM contributions from heavy oil combustion occurred when the wind was in a

southeasterly direction, i.e., blowing in from harbours and shipping channels in the vicinity of the measurement site. In Amsterdam, highest concentrations of $PM_{2.5}$ from oil combustion arrived at the site during winds from the southwest and west, sweeping over the Rotterdam area that has a number of large oil refineries close to the harbour and the coast of the North Sea. In the Netherlands, inland shipping via canals is a considerable source of particulate matter. Therefore, this form of transportation could also contribute to the oil combustion component. Although not extracted in this study, oil combustion has been identified as a potential source of fine particulate matter in Erfurt based on particle induced X-ray emission analyses of PM_2 samples collected during an earlier study in that city (Cyrys et al. 2003b).

Identification of the sea salt source in Helsinki and Amsterdam was based on loadings Cl and Na, although the high loading of Pb in Helsinki 1998-99 data complicated identification of this component (data on Na was not available for 1998-99). Evaporation of Cl from the sample can be significant (Pakkanen 1996, Yao et al. 2001) and affect both the concentration of Cl in the sample and its correlations with other elements. However, the high correlation of Na and Cl in Helsinki during 1996-97 suggests that Cl alone can also be used as a marker for sea salt particles.

In Amsterdam and Erfurt, the source category identified as industrial activities and/or incineration was associated mainly with Cl, Zn, K, Br, Mn and Pb, which have been linked to various metallurgical and industrial processes (Ramadan et al. 2000, Chow et al. 2004) as well as waste incineration (Olmez et al. 1988, Sweet et al. 1993). Separating various industrial pollution sources from each other is an extremely difficult task in source apportionment due to the diversity of the emissions. In the present work, the identification was attempted without prior information on the location and the composition of the process and fugitive emissions from these sources, which incorporates more uncertainty to the source analysis.

The set of variables available for source identification using principal component analysis were almost similar in all three cities. In addition to elemental tracers, we also included ultrafine and accumulation mode particle counts, $PM_{2.5}$ filter absorption coefficients and 24-hour average concentrations of gaseous pollutants (NO_X, SO_2, CO) in PCA in an attempt to facilitate the interpretation of the principal components. The tracers and source profiles in PCA that were used in the identification of source categories were generally similar in all studies and cities.

Ultrafine ($NC_{0.01-0.1}$) and accumulation mode ($NC_{0.1-1.0}$) particles were useful markers for particulate matter related to local traffic and long-range transboundary air pollution, respectively. In Amsterdam, however, the attempts to include particle number concentrations in source apportionment analyses failed due to a strong negative correlation between the secondary PM component and ultrafine particle concentrations. The absorption coefficient ($Abs_{2.5}$) was associated with both the local combustion (traffic) and long-range transported air pollution source components, which is expected since both are affected by various combustion sources emitting considerable amounts of elemental carbon (Morawska and Zhang 2002).

NO_X turned out to be a valuable marker for local traffic related emissions at our measurement sites. In fact, separation of the traffic related $PM_{2.5}$ fraction from other combustion-dominated sources without non-elemental markers proved very difficult, especially in Amsterdam and Erfurt. The correlation of SO_2 with V and Ni in Helsinki and Amsterdam suggests that most of SO_2 measured at these sites had been emitted by oil combustion source(s) with only a lesser contribution from other sources.

NO_X and SO_2 were the most critical and $Abs_{2.5}$ the least critical component for obtaining physically reasonable source apportionment results based on sensitivity analyses on data from Helsinki by using different combinations of alternative source markers (NO_X, SO_2, particle counts, $Abs_{2.5}$) in the analyses along with elemental concentrations. In all, inclusion of concentrations of gaseous pollutants, particle counts, and absorption coefficient in the analyses was valuable with regard to both source identification and source apportionment of $PM_{2.5}$. The usefulness of these alternative markers would be limited, however, at sites where more than one source can have a major effect on the variation of the marker concentrations.

6.2.2 Source apportionment

The estimated contribution of long-range transported air pollution to average $PM_{2.5}$ in Vallila, Helsinki, varied between 50% (III) and 58% (V). These estimates are very comparable with those of Ojanen et al. (1998), who have reported a 60% proportion of long-range transported $PM_{2.3}$ in Vallila. Based on ion-sum modelling, Karppinen et al. (2004) have arrived at a somewhat higher (64-76%) contribution of long-range transport to the measured outdoor $PM_{2.5}$ concentration in urban Helsinki. In previous studies, the local fraction of $PM_{2.3}$ (40-

46%) in Vallila has been associated with mostly traffic-related particulate matter (elemental and organic carbon, nitrate) and resuspended crustal material (Ojanen et al. 1998, Pakkanen et al. 2001a).

In the present work, the summed contribution of three source components of local nature (local combustion and traffic, oil combustion, crustal particles) varied from 41% to 45%. Koistinen et al. (2004) have reported a 51% aggregate fraction for combustion particles and crustal particles; however, their estimate for combustion particles was also influenced by non-local sources. The 12% contribution of crustal particles in Helsinki during 1996-97 found in this study is similar to the previously reported values of 12% (Pakkanen et al. 2001b) and 16% (Koistinen et al. 2004).

Ojanen et al. (1998) have estimated that during 1996-97, 39% of the total $PM_{2.3}$ mass in urban Helsinki consisted of long-range transported sulphate (SO_4), nitrate (NO_3) and ammonium (NH_4). In the current data from Helsinki (III), this percentage would result in 3.8 $\mu g/m^3$ (1996-97) and 5.0 $\mu g/m^3$ (1998-99) shares of the total $PM_{2.5}$ mass due to these three components. Furthermore, it has been estimated that annual mean concentration of long-range transported primary $PM_{2.5}$ over the southern parts of Finland is 2 $\mu g/m^3$ based on 1990 emission inventories for Europe (ApSimon et al. 2000). This 2 $\mu g/m^3$ fraction is equivalent to 40% (1996-97) and 31% (1998-99) of the estimated mass of long-range transported and secondary $PM_{2.5}$ in Helsinki in this study (III). When applied to the current study, the above estimates (Ojanen et al. 1998, ApSimon et al. 2000) produce 5.8 $\mu g/m^3$ (1996-97) and 7.0 $\mu g/m^3$ (1998-99) $PM_{2.5}$ contributions from the long-range transported and secondary source component. These estimates are only slightly higher than the 4.9 $\mu g/m^3$ or 51% (1996-97) and 6.4 $\mu g/m^3$ or 50% (1998-99) shares obtained in the current study.

The contribution of the crustal source component in Amsterdam was rather large, considering that only Ca, whose concentration in Amsterdam was not particularly high, was associated with this component and no other typical crustal elements such as Al and Si were routinely detected. This could be explained by a distinctive composition profile of the resuspended dust near the measurement site in Amsterdam. The different composition profile could be a consequence of more widespread use of road structures made of concrete in Amsterdam compared to the other cities. A higher $PM_{2.5}/PM_{10}$ ratio for fugitive dust from cement-related

dust (34%) than for unpaved road dust (20-26%) has been reported (Vega et al. 2001). This difference in size distribution of fugitive dust from different types of sources could partly explain the higher crustal $PM_{2.5}$ contribution in Amsterdam compared to the other centers, since the crustal component in Amsterdam was identified based solely on the high loading of Ca which is strongly associated with cement and paved road dust (Vega et al. 2001, Ho et al. 2003b).

The salt source accounted for 2% and 7% of the average $PM_{2.5}$ in Helsinki 1996-97 and 1998-99, respectively. The character of the salt component is somewhat different for 1996-97 and 1998-99, which probably resulted in different average mass contributions for this source component. Reanalyses of the 1998-99 data (V) resulted in a 2.4% salt percentage. The potential pre- and post-sampling evaporation of chloride from the sea salt fraction may have resulted in a somewhat lower salt concentration estimate than would have been found without any evaporation. However, our results are in accordance with those reported by Ojanen et al. (1998) who have reported a 3% average sea salt contribution to $PM_{2.5}$ in Helsinki. In Amsterdam, the salt component contributed only 2% to the $PM_{2.5}$. This percentage is both low and surprisingly close to that found in Helsinki, considering that the Atlantic has a much higher salinity compared to the Baltic Sea and that large parts of the Baltic are also covered with ice during winter months. In addition, the median Cl concentration in Amsterdam was three times higher than in Helsinki. Evaporation of chloride from the sea salt particles could have complicated the estimation of the true sea salt contributions to $PM_{2.5}$ if the correlation of Cl with other sea salt components were affected. Unfortunately, it was not possible to evaluate this effect since there were no other markers available for sea salt in addition to Cl.

The average $PM_{2.5}$ contribution from the industrial source category was very similar in Amsterdam and Erfurt. Industrial processes were not identified as a separate source category in Helsinki, probably due to low number of industrial sources in the vicinity of the measurement site and, subsequently, low ambient concentrations of fingerprint elements that could be used to identify and separate industrial emissions from the more dominant source categories in the principal component analysis.

The higher ratio of secondary $PM_{2.5}$ and traffic-related $PM_{2.5}$, and the lower average of total $PM_{2.5}$ in Helsinki compared to Amsterdam and Erfurt, reflect the lower population density and lower emission density of important precursor gases from traffic, energy production

facilities and industrial activities in Finland. This difference between the Scandinavian countries and Central European countries has been reported for concentrations of particulate matter (Hoek et al. 1997), NO_2 and SO_2 (Pacyna et al. 1991), and elemental carbon (Hamilton and Mansfield 1991). The negative correlation of traffic-related $PM_{2.5}$ with temperature and wind speed demonstrates the poor dilution of locally generated air pollutants during stagnant meteorological conditions.

6.2.3 Comparison of methods

There are few published comparative source apportionment studies using different methods on the same data. Chan et al. (1999) obtained a good agreement of source contributions by using target transformation factor analysis with multiple linear regression (TTFA-MLR) and chemical mass balance (CMB). The feasibility of two different multivariate methods for source identification has been compared by Morandi et al. (1991) and Huang et al. (1999). The dataset analysed in the first of these studies (Morandi et al. 1991) was rather similar with the datasets from the three cities in the present work, comprising 24-hour PM_{15} samples from 137 days. The authors reported the largest differences in the results between the compared methods for source types contributing less than 1 $\mu g/m^3$ to the measured PM concentration. The experiment by Huang et al. (1999) proved that different techniques could be modified to produce very similar results by 1) choosing the elements carefully, 2) trying various numbers of factors, and 3) using log-transformations of the data. The methods compared in the two studies (Morandi et al. 1991, Huang et al. 1999) were more closely related to each other than the ones compared in this work (V). Huang et al. (1999) also did not estimate possible differences between the two methods in terms of source contributions.

The problems that are associated with using fundamentally different source apportionment methods are illustrated in the comparative study (V), where two different methods were applied to the same dataset. The main conclusion from this comparison was that only the most distinct and easily interpretable source categories, such as crustal source and sea salt, were apportioned similar amounts of $PM_{2.5}$ by the two methods (PCA-MLR and mass closure), whereas apportionment results of the long-range transported and secondary particles, and the combustion-related component were rather difficult to compare. The current results suggest that source reconstruction possibly underestimates the total amount of $PM_{2.5}$ associated with the crustal source, since for example resuspended organic material is not taken into account in

the mass closure equations. On the other hand, if emissions from other source(s) correlated with emissions from the soil, particulate matter from this source could have been identified as being attributable to the crustal source component in the PCA-MLR process. The mass of ammonium sulphate estimated in the mass closure was very close to the mass of the total long-range transported particulate matter estimated by the multivariate method. However, these results highlighted an apparent discrepancy between the estimated amounts of long-range transported PM and secondary PM, since the long-range transported air pollution component as estimated based on S (sulphate aerosols) by PCA-MLR inherently consists of also other secondary inorganic compounds - mainly ammonium nitrate - and various primary and secondary carbonaceous compounds (Kim et al. 2003).

6.2.4 Plausibility of source analysis

The lack of unique and source-specific markers complicates the separation of collinear sources from each other, especially when their emissions have similar elemental profiles and some association with the same wind direction or other meteorological factors. The major cause of variability in ambient measurement data is often meteorology, not variations in sources (Henry et al. 1984). This results in correlated observations due to the common effect of meteorology on all source contributions at the receptor site, which impedes separation of sources (Ames et al. 2000). In addition, the varimax rotation results in unrealistic non-correlating source components due to forced orthogonality of the extracted components. Hence the source components can be biased due to the greater influence of local meteorology than actual source contributions. In this study, this problem was most prominent in Erfurt, where several elements had moderate to high loadings on more than one extracted principal component. These problems in PCA were probably associated partly with the topographical and meteorological characteristics in Erfurt leading to accumulation of pollutants in the area and subsequent covariation of pollution components from several sources. Very similar problems have recently been reported from a $PM_{2.5}$ source apportionment study in Milan, Italy, where the authors were able to extract only two principal components with eigenvalues >1 (Marcazzan et al. 2003).

Another problem was encountered in apportioning the $PM_{2.5}$ to source categories whose $PM_{2.5}$ contributions at the measurement sites were highly variable and clearly regulated by meteorological factors such as wind direction and atmospheric mixing. In Amsterdam and

Erfurt, the estimated contributions from industrial emissions varied substantially between the alternative source apportionment models, i.e., models with different groups of analysed variables. The observed large variability between contributions of sources that have a minor effect on the total PM mass corroborates the earlier finding by Morandi et al. (1991), who have reported large differences in results from comparative multivariate source apportionment analysis for source types which make only minor contributions to the total PM. Thus, the uncertainty associated with results on such PM sources can be significant, emphasizing the need for using more than one modeling method as a means for validating the source apportionment results, especially in complex urban airsheds.

Using positive matrix factorization, Hedberg et al. (2005) have found that when the numbers of included samples were decreased, the uncertainty of the modelled source contributions were increased most significantly for the industrial and combustion source types. In the present study, the correlation of the estimated daily source-specific PM concentrations obtained from the alternative models was high, irrespective of the variability in the modelled source contributions. This suggests that the results presented in this work are usable for epidemiological time series studies. However, the different elemental profiles of the source components makes it more difficult to compare the source categories, especially between Erfurt and the other two cities.

There is some evidence that particles from crustal sources exhibit a bimodal frequency distribution, possibly indicating contributions from several different sources that have similar chemical profiles (Kao and Friedlander 1995). Since we have no size-fractionated elemental data within the $PM_{2.5}$ component, we cannot validate this finding in our data. However, PCA results from Erfurt, in particular, suggest that the crustal source component was possibly mixed together with a local combustion component. Complications in separating the combustion and resuspension components related to traffic have been reported by several authors (Van Borm et al. 1990, Begum et al. 2004). The interrelation and mixing of particles can complicate separation of also other sources in source apportionment, especially when multivariate statistical methods are used (Morawska and Zhang 2002).

6.3 Resuspension

The main processes producing crustal PM in urban areas are the wear and damage to the road paving by vehicles and maintenance, and translocation of soil from unpaved areas to the streets. In addition, turbulent wakes by vehicles may suck some particulate matter lying off the road back onto parts of the road used by vehicles (Moosmuller et al. 1998). In countries like Finland where wintertime sanding of streets and studded tyres are used, resuspension potentials are further increased (Kupiainen et al. 2003, Kupiainen et al. 2005). In Japan, studded tyres have been banned largely because it was reported that their use was contributing to increased PM levels during winter and spring (Fukuzaki et al. 1986). In Finland, the majority of cars are equipped with studded tyres during winter, but in addition, road sanding is widely used especially in urban areas. It has been shown that sanding of a dry road results in a rapid though transient increase of road dust emission potentials for PM_{10} (Kuhns et al. 2003).

Natural dust events are dependent on high wind speeds, whereas resuspension due to traffic and other anthropogenic activities are thought to depend mostly on the humidity of surfaces, not so extensively on wind speed (Nicholson 1988). In this study, the crustal source component had a moderate negative correlation with relative humidity in all cities, and a positive correlation with temperature in Amsterdam and Erfurt, suggesting that resuspension of dust was inhibited during moist conditions and promoted by warm weather. This conclusion is supported by Kuhns et al. (2003) who have found that emissions from unpaved roads increased consistently with the number of days since the last precipitation. On the other hand, creation of spray droplets can evoke resuspension of particles also during humid conditions (Nicholson 1988).

A U-shaped function of coarse ($PM_{2.5-10}$) particles with wind speed has been reported in the U.K. (APEG 1999) consistent with our findings in Kuopio (II). This phenomenon can be interpreted as a twofold effect of wind speed with inefficient dilution of traffic-induced coarse particles during light winds and increasing wind-induced resuspension with high winds, resulting in a U-shaped dependence of PM concentration on wind speed. The same phenomenon was seen in Birmingham, UK, where PM_{10} was separated into two components in PCA: firstly to a traffic-related pollution component characterized by $PM_{2.5}$, NO_X, PM_{10} and negative loading of wind speed, and secondly, to a factor representing coarse-particle

episodes, characterized by high loadings of PM_{10} and wind speed (Harrison et al. 1997). Apart from the concentrations of coarse particles noted during the first study period in Helsinki, there was no clear indication for a similar twofold association of fine or coarse PM concentrations with wind speed in the 1998-99 periods. On the contrary, concentrations tended to decrease with increasing wind speed. These results suggest that resuspension caused by traffic is the main source of crustal particles in urban environments. Therefore, the present results (II) on the positive association of wind speed and coarse particle concentrations should be verified with larger data and in other urban locations.

In this study, it has been shown that the resuspended portion of PM can be associated with high concentrations of anthropogenic elements. Microscopic analysis of particles has revealed that metals and small spherical combustion-related particles with a high content of carbon can become adherent to larger natural particles (Mugica et al. 2002). It has also been reported that larger particles are more readily suspended compared to small particles, and that the depletion of resuspendable material from road surfaces occurs most rapidly for large particles (Nicholson 1988). Since a significant portion of deposited particulate material on a road can be resuspended by passage of only a few vehicles, it is likely that the amount of resuspended PM is controlled mainly by the rate of import of new material onto the road surface. Nicholson and Branson (1990) have suggested that moist conditions would induce this kind of particulate import and result in increased resuspension after the road surface has become dry. Thus, these findings support the hypothesis that large crustal particles may act as carriers for smaller anthropogenic particles and resuspended dust episodes may result in elevated concentrations of elements originating mainly from anthropogenic sources in urban ambient air.

Resuspension has been acknowledged to be a major source of ambient particulate matter, and emissions of road dust constitute a severe urban air quality problem also in many Finnish municipalities. It has been suggested that minimizing the deposition of material onto roadways and maximizing the removal of resuspendable material already on the roads by road cleaning equipment constitute the most efficient ways to control the amounts of road dust emissions (Kuhns et al. 2003). However, it has also been reported that street sweeping may not be an efficient way to reduce emissions (Chow et al. 1990), and that it may actually increase PM emissions immediately after sweeping, possibly due to redistribution of particles trapped in the holes and cracks of the road, spreading them across the road surface (Kuhns et

al. 2003). However, sweeping removes all visible sand from the roads, thereby reducing the total amount of sand depot by preventing the accumulation of the sand to the curbsides. In addition, it has been shown that sanding material enhances the wear and damage of the pavement (Kupiainen et al. 2003, Kupiainen et al. 2005). Thus, as a whole, sweeping will reduce the future resuspension potential of the road environment, especially if combined with subsequent washing of streets, and this will have a beneficial effect on air quality over the long term.

6.4 Suggestions for future research

Several issues related to sources and characteristics of particulate matter that will require further research were recognised during the course of this work. There is a need to set up a formal European enterprise that would (1) construct a comprehensive database on the work done so far on emissions, characterization and source apportionment of PM, (2) compile an accessible database on tracers and elemental profiles for various emission sources, (3) enhance the use of source apportionment techniques in European air pollution research. Taking these steps would result in accumulation of data that could be used in close collaboration between scientists from different disciplines to reduce the current uncertainties regarding the relative health relevance of particulate matter from this multitude of sources.

The present work has several more specific implications for future research linked to the points listed above. This work has revealed the need for further characterization of the fine and coarse particles during resuspended dust episodes, including the quantification of potentially detrimental components such as transition metals and biogenic material adhering to the resuspended particles. Also the health relevance of the peak PM concentrations during these episodes should be investigated further. A simple and affordable, yet specific, measurement technique to be used in long-term monitoring of traffic-related PM emissions should be developed and introduced to complement the currently used PM_{10} and $PM_{2.5}$ measurements. As an alternative, the continuation and even wider use of Black Smoke (or absorption coefficient) measurements as an indicator of mainly traffic-related particulate matter should be considered. Finally, the uncertainties in the current estimates of population and personal exposures to particulate matter from specific sources should be reduced through application of (more than one) source apportionment methods in future exposure and epidemiological studies on PM.

7 CONCLUSIONS

This thesis had three aims, and the main conclusions regarding the first stated aim of characterizing the determinants, elemental composition and concentrations of particulate matter in the urban atmosphere are:

- Between-city and within-city differences in the concentrations of many trace elements in $PM_{2.5}$ were observed in this study. These differences were considered to be related to specific local and regional sources affecting the measurement sites, though possibly also to differences in the laboratory analyses of elemental composition of particulate matter.

- Elemental concentrations in $PM_{2.5}$ in the three major cities were rather similar to the previously reported values from the same cities.

- Monitoring of PM_1 did not significantly add to the information content already obtained from monitoring of $PM_{2.5}$. In contrast, the clear seasonal variation in the $PM_{2.5}/PM_{10}$ ratio indicates that these indices represent quite different aspects of urban particulate matter.

The main conclusions regarding the second aim of investigating the characteristics and determinants of resuspended road dust as a specific urban air quality problem are:

- Apart from their obvious effect on the concentrations of typical crustal elements, the resuspended road dust episodes can temporarily increase the concentrations of elements from anthropogenic sources as well as concentrations not only of coarse but also of fine particulate matter, which may have implications for the health effects of the resuspended dust.

- The elevated PM concentrations caused by resuspension of road dust exhibited seasonal trends only in Finland, which is obviously due to the more pronounced seasonal differences in weather conditions in Finland compared to Central Europe.

- The prevailing mechanism of resuspension in urban settings seems to be traffic-induced turbulence rather than high wind speed.

The main conclusions regarding the third aim of determining and comparing major sources of ambient fine particulate matter ($PM_{2.5}$) in different European urban sites are:

- The major source categories of urban $PM_{2.5}$ in the three cities were secondary and long-range transport particles and traffic-related emissions, followed by the less influential crustal, oil combustion, sea salt and industrial source categories.

- The relative impact of both secondary particles and local combustion on average $PM_{2.5}$ was almost equal in two Central European cities. The mass concentration of the long-range transported PM fraction - containing both secondary and other particles - was very similar in all three cities, highlighting the great importance of this PM fraction as a determinant of ambient $PM_{2.5}$ concentrations in Helsinki. Knowledge on the relative importance of different sources on PM levels across different areas will help in targeting emission control measures against specific sources.

- Despite the differences in elemental concentrations, very similar source profiles were observed in Amsterdam and Helsinki for most major $PM_{2.5}$ source categories. In Erfurt, the source profiles were less well-defined and fewer sources of $PM_{2.5}$ could be identified with PCA compared to the other two cities. This problem in Erfurt was attributable to stronger intercorrelations of air pollution components caused by specific local topography and meteorology.

- Principal component analysis in combination with multivariate linear regression proved to be a useful tool for extracting sources $PM_{2.5}$ from complex urban PM mixtures, although the variability of the source apportionment estimates for some sources was rather large. The power of PCA to resolve sources was clearly improved when nitrogen oxides and other gases, particle number concentrations and absorption coefficients were included to the source analysis in addition to the elements. In all, the results obtained in this work were convincing enough to be used in epidemiological studies investigating the health effects of fine particulate matter from different sources.

- The results obtained from the comparison of two source apportionment methods were partially contradictory, especially regarding the most complex source types. The choice of variables also had a clear effect on the outcome of source apportionment analysis with principal component analysis. These results suggest that any source apportionment results should preferably be confirmed by using at least two different methods.

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APPENDIX 1. Spearman correlation coefficients of the identified source components with measured variables.

Helsinki 1996-97	$PM_{2.5}$	PM_{10}	$PM_{2.5-10}$	$Abs_{2.5}$	$NC_{0.01-0.1}$	$NC_{0.1-1.0}$	NO_X	SO_2	Temp	RH	WS
LoCo	0.29	0.11	-0.05	**0.72**	**0.86**	**0.64**	**0.88**	0.35	-0.32	0.19	**-0.52**
Oil	0.34	0.14	-0.04	0.10	-0.04	0.24	0.02	**0.60**	0.00	0.26	0.06
LRT	**0.65**	0.26	-0.15	0.28	-0.14	0.44	-0.17	0.26	0.04	0.39	0.11
Crustal	0.35	**0.67**	**0.58**	0.14	0.09	0.22	0.03	0.05	0.17	-0.27	-0.06
Salt	-0.05	0.11	0.23	-0.12	0.05	0.00	-0.01	-0.15	0.10	-0.17	0.22

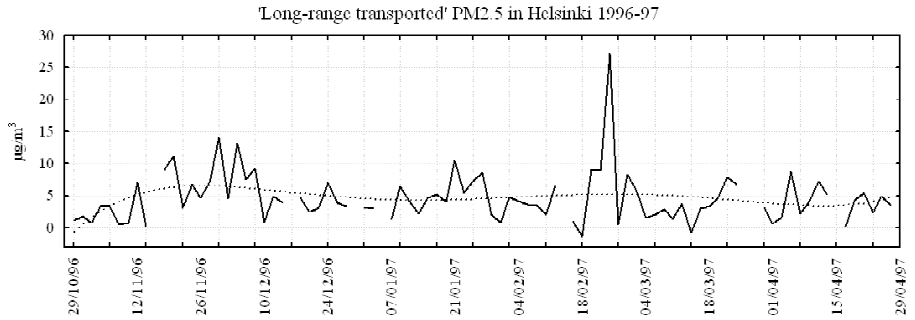
Helsinki 1998-99	$PM_{2.5}$	PM_{10}	$PM_{2.5-10}$	$Abs_{2.5}$	$NC_{0.01-0.1}$	$NC_{0.1-1.0}$	NO_X	SO_2	Temp	RH	WS
LoCo	0.26	0.12	-0.10	**0.74**	**0.79**	**0.60**	**0.86**	0.29	-0.40	-0.02	**-0.57**
Oil	0.35	0.29	0.06	0.24	0.20	0.32	0.15	**0.76**	-0.27	-0.20	-0.06
LRT	**0.82**	**0.57**	0.03	0.46	-0.19	**0.50**	-0.11	0.20	-0.02	0.11	0.01
Crustal	-0.01	0.30	**0.51**	0.14	0.22	0.14	0.15	0.05	0.04	**-0.58**	-0.01
Salt	0.18	0.11	-0.04	0.07	-0.04	0.15	0.01	0.03	0.17	0.14	0.18

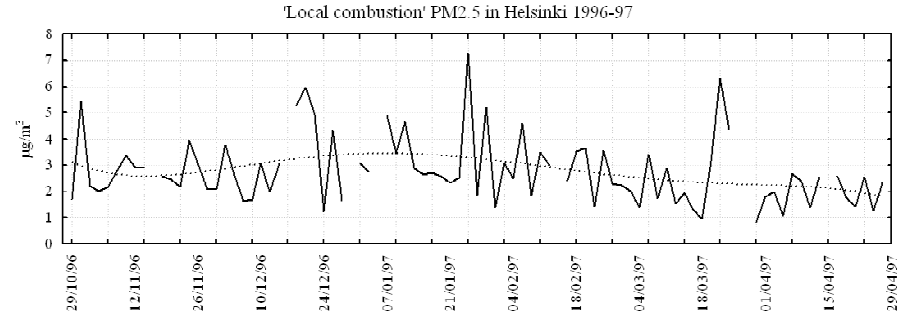
Amsterdam 1998-99	$PM_{2.5}$	PM_{10}	$PM_{2.5-10}$	$Abs_{2.5}$	$NC_{0.01-0.1}$	$NC_{0.1-1.0}$	NO_X	SO_2	Temp	RH	WS
LoCo	**0.50**	0.42	0.18	**0.87**	0.40	**0.62**	**0.89**	**0.52**	**-0.52**	0.34	**-0.55**
Industry	0.27	0.21	0.14	0.30	0.00	0.32	0.32	**0.51**	-0.06	0.21	0.18
Oil	0.18	0.19	0.08	0.13	0.44	0.34	0.22	**0.51**	0.14	0.37	0.16
LRT	**0.62**	0.48	-0.09	0.11	**-0.56**	0.28	-0.18	-0.12	0.22	-0.08	-0.17
Crustal	-0.15	0.16	0.45	-0.09	0.23	-0.07	-0.15	0.04	0.37	**-0.52**	0.21
Salt	0.04	0.12	0.12	0.01	0.09	-0.07	0.11	0.15	-0.42	0.21	0.19

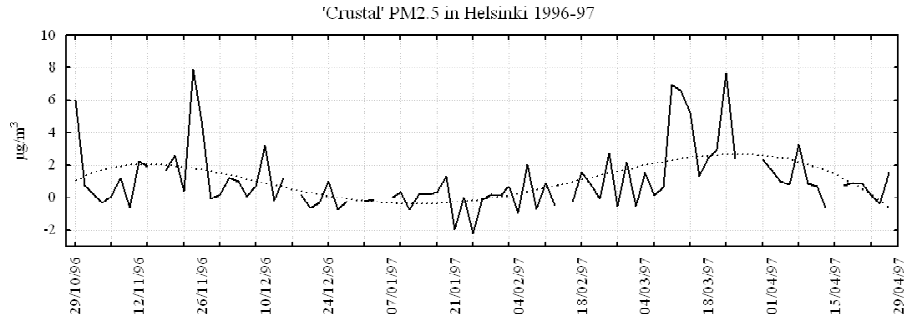
Erfurt 1998-99	$PM_{2.5}$	PM_{10}	$PM_{2.5-10}$	$Abs_{2.5}$	$NC_{0.01-0.1}$	$NC_{0.1-1.0}$	NO_X	SO_2	Temp	RH	WS
LoCo	0.32	0.32	0.15	**0.57**	**0.72**	0.48	**0.61**	0.48	-0.27	0.30	-0.41
Industry	0.41	0.44	0.11	0.29	0.08	0.41	0.32	0.18	-0.27	0.05	-0.29
LRT	**0.57**	0.47	-0.12	0.23	0.04	0.28	0.12	0.45	-0.29	0.06	-0.19
Crustal	0.19	0.28	0.49	0.22	0.26	0.19	0.21	-0.04	0.30	-0.36	-0.19

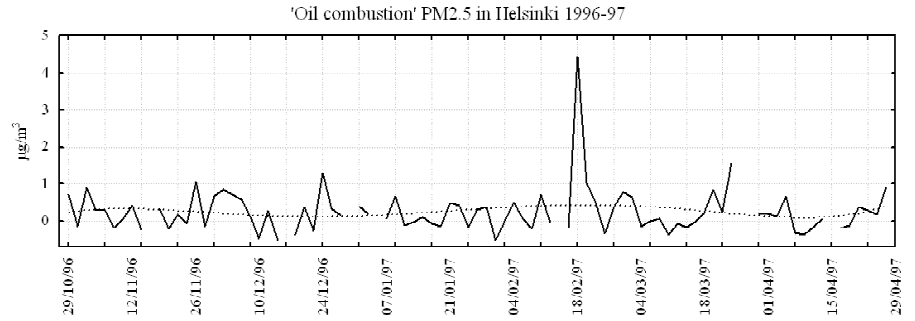
LoCo: Traffic and other local combustion; Industry: Industrial emissions, combustion processes, incineration; Oil: Oil combustion;
LRT: secondary particles, long-range transported $PM_{2.5}$; Crustal: resuspended dust, soil; Salt: sea salt;
$Abs_{2.5}$: filter absorbance; NC: particle number concentration; RH: relative humidity; WS: wind speed

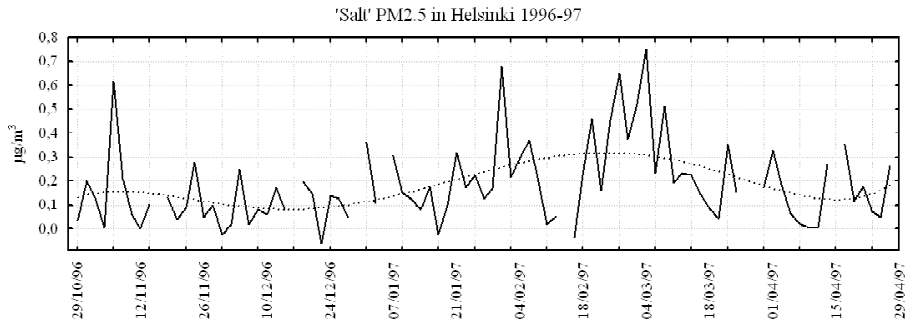
APPENDIX 2. Time trends of source-specific $PM_{2.5}$ in Helsinki 1996-97, Helsinki 1998-99, Amsterdam 1998-99 and Erfurt 1998-99.



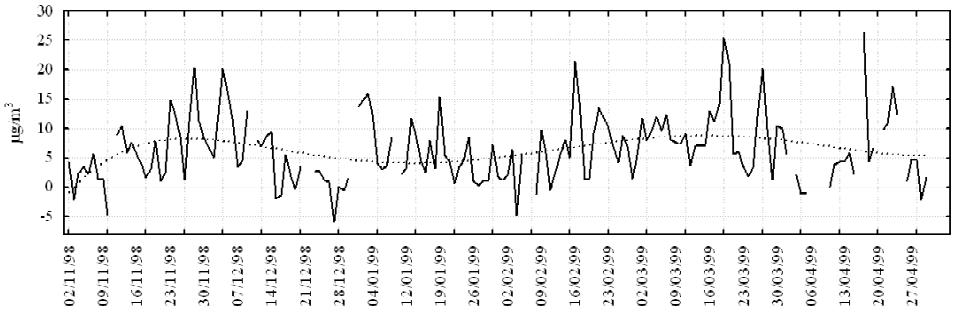




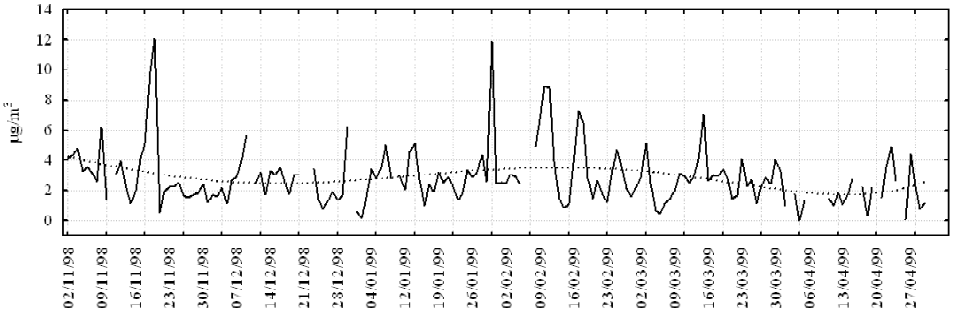




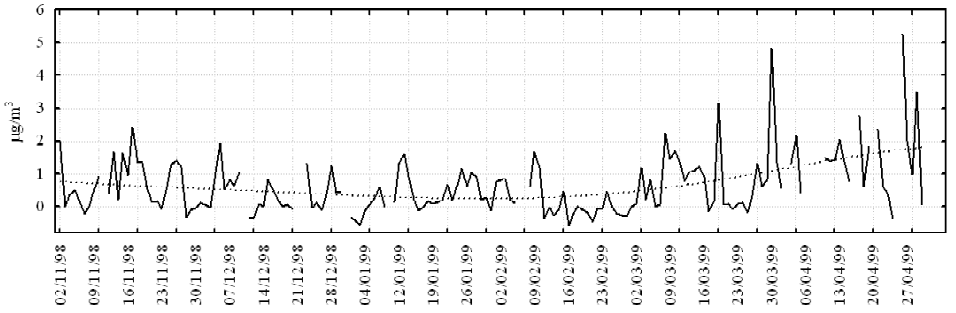
'Long-range transported' PM2.5 in HIelsinki 1998-99



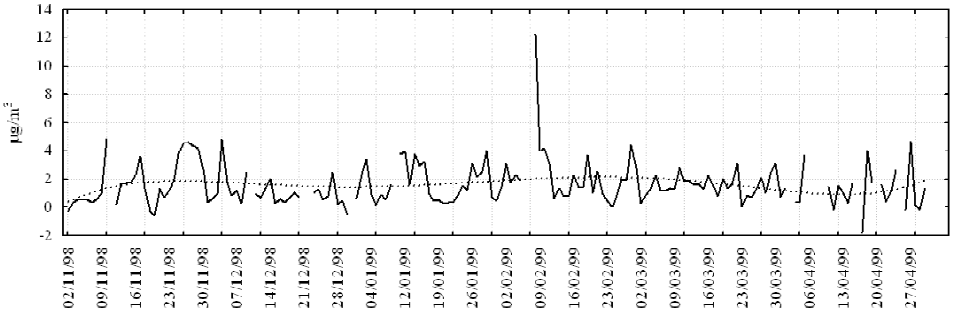
'Local combustion' PM2.5 in Helsinki 1998-99



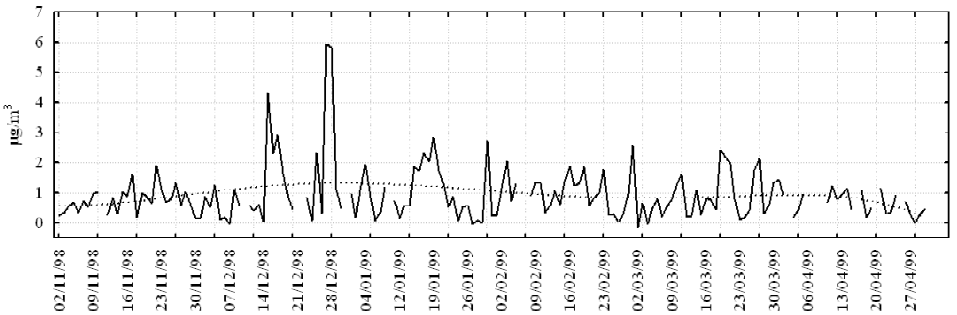
'Crustal' PM2.5 in Helsinki 1998-99

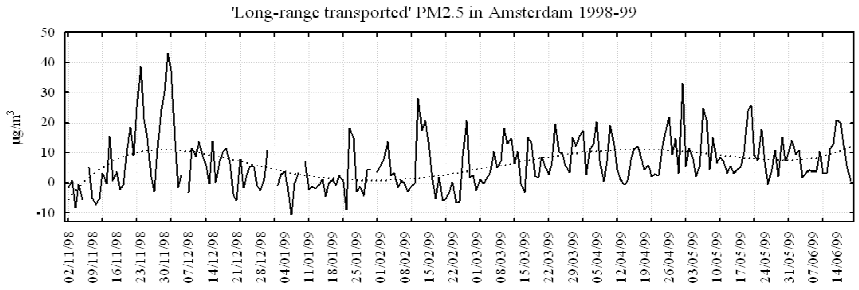


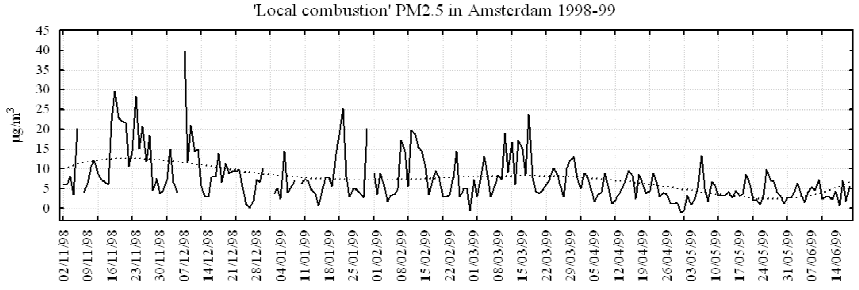
'Oil combustion' PM2.5 in Helsinki 1998-99



'Salt' PM2.5 in HIelsinki 1998-99




'Long-range transported' PM2.5 in Amsterdam 1998-99
µg/m3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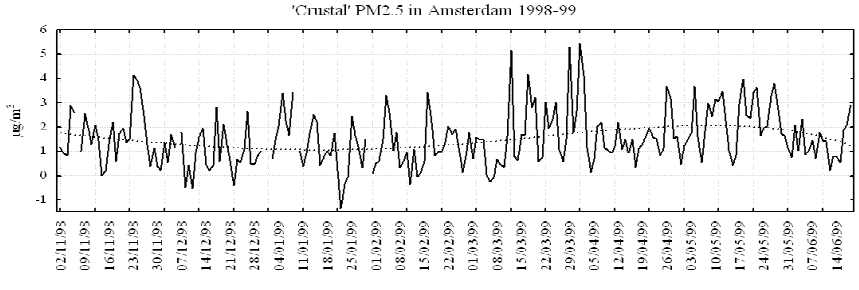
µg/m3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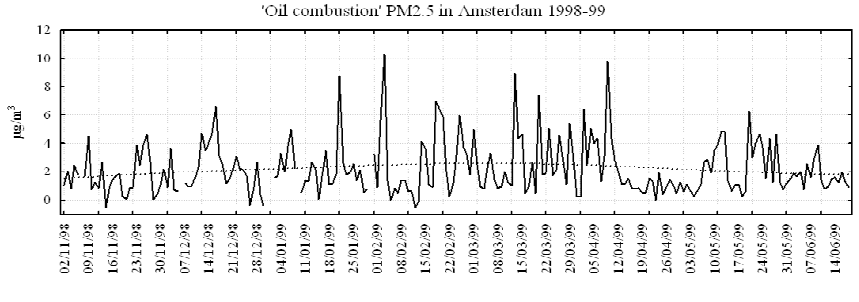
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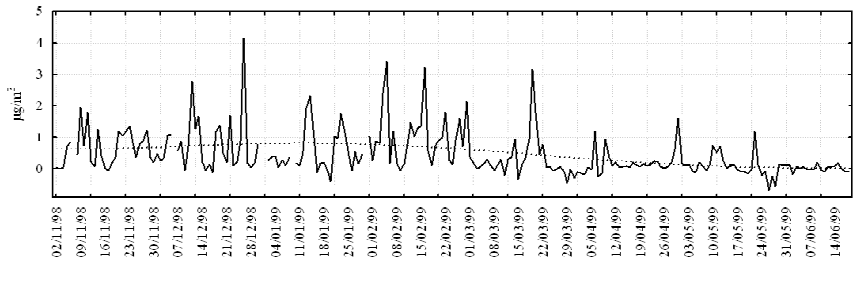
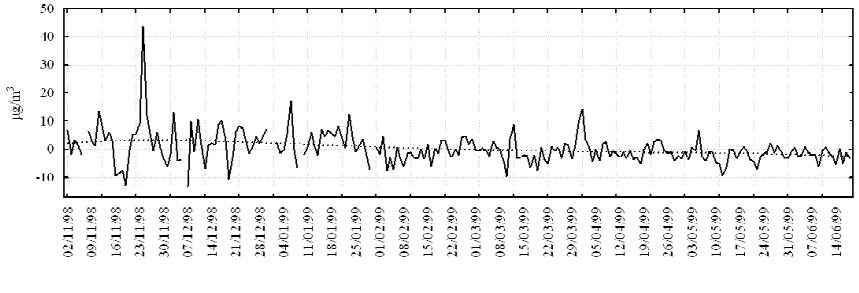
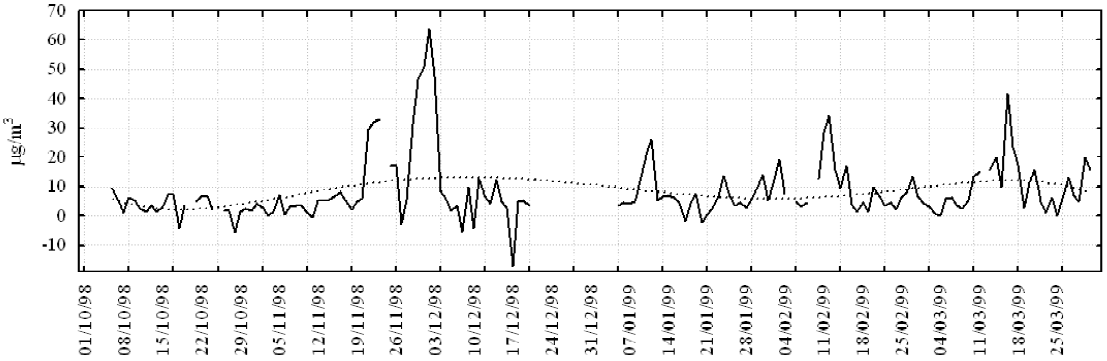
µg/m3

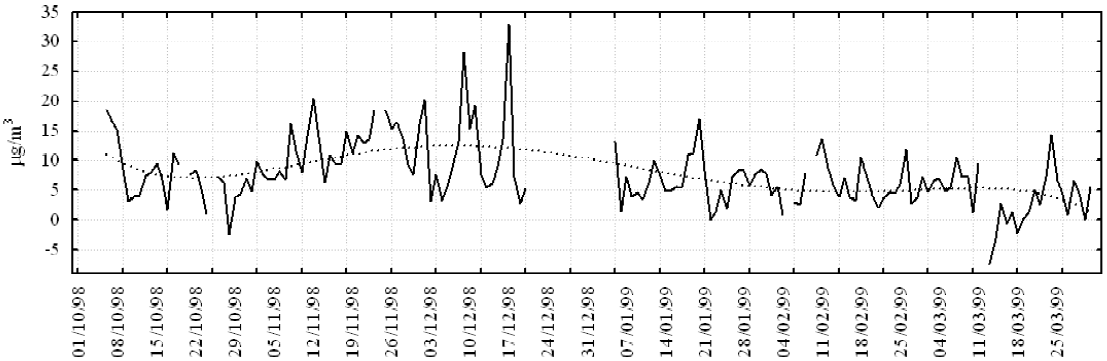

'Salt' PM2.5 in Amsterdam 1998-99
µg/m3


'Industrial' PM2.5 in Amsterdam 1998-99
µg/m3

'Long-range transported' PM2.5 in Erfurt 1998-99



'Local combustion' PM2.5 in Erfurt 1998-99



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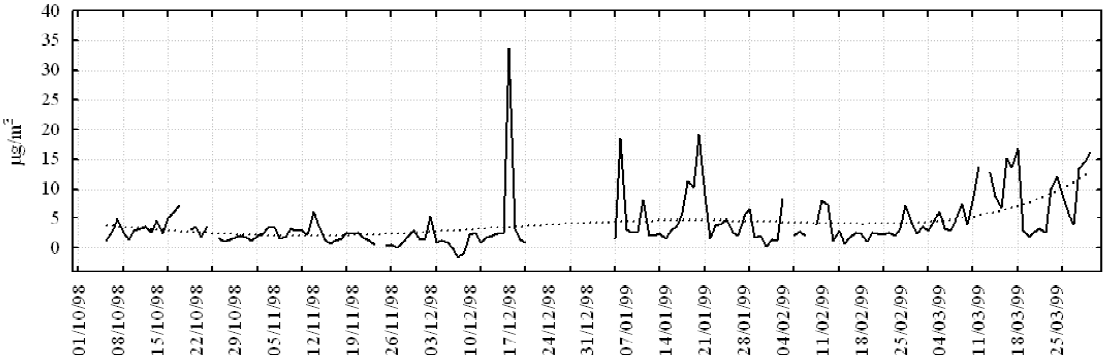

'Industrial' PM2.5 in Erfurt 1998-99