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ABSTRACT

The general population is exposed to particulate air pollution from many different local and regional sources. Examples of local sources are traffic, biomass burning and resuspended dust, while regional sources are dominated by combustion processes from heating, traffic and industries. The overall aim of this thesis was to characterise the personal exposure to trace elements in fine particles, mainly $PM_{2.5}$ and investigate how the exposure is related to indoor and outdoor levels. Particulate matter was collected on filters and analysed for elemental content by X-ray fluorescence (XRF) spectroscopy.

In the general population in Göteborg, personal exposures to Cl, Ca, Ti and Fe were significantly higher compared with indoor, residential outdoor and urban background levels. Significant correlations were also found between urban background PM mass and personal exposure to elements related to both combustion (S, V and Pb) and resuspended dust (Ti, Fe and Zn), indicating that both sources could be relevant for health effects from urban background PM. In a community where wood burning for domestic heating is common, significantly (66–80%) higher personal exposures and indoor levels were found for K, Ca and Zn compared with a reference group living in the same area, indicating that these elements could be good markers for wood smoke. In a study in Stockholm concerning children's environments (home, school and preschool), higher indoor than outdoor levels of Ti were found, while long-range-transported (LRT) elements (S, Ni, Br and Pb) were higher outdoors. A community located 25 km from the city centre had significantly lower outdoor levels of crustal and traffic-related elements compared with both the city centre and a suburban area. The levels of Fe and Cu were four times higher in the central communities. Outdoors, Cu levels were found to correlate well with the traffic marker NO_2, making it a possible elemental marker for traffic-related aerosols in health studies. Roadside measurements of fine and ultrafine (<100 nm) particles were performed along a major approach road to Göteborg and the levels of ultrafine particles were influenced not only by traffic intensity, but also, by wind speed and direction, as well as boundary layer height. No correlation was found between $PM_{2.5}$ and ultrafine particles or traffic, but there was a correlation between $PM_{2.5}$ and particles sized 100–368 nm. In all environments studied, the origin of LRT air masses had a strong effect on exposure and levels of PM elements.

In conclusion, this thesis demonstrates that elemental analysis is a useful method for better characterising human exposure to fine particles. For several elements, the personal exposure is often higher than corresponding indoor levels. The origin of LRT elements affected not only outdoor levels, but also, the personal exposure and indoor levels, and should be taken into account in time series studies of air pollution and health.

Key words: particulate matter, $PM_{2.5}$, PM_1, ultrafine particles, trace elements, personal exposure, indoor levels, X-ray fluorescence (XRF), air mass back trajectories, long-range transport, domestic wood burning

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LIST OF PAPERS

This thesis is based on the following papers, which are referred to in the text by the Roman numerals I–IV:

I. Molnár, P., Janhäll, S., and Hallquist, M., **2002**. Roadside measurements of fine and ultrafine particles at a major road north of Gothenburg. *Atmospheric Environment 36(25) 4115–4123.*

II. Molnár, P., Gustafson, P., Johannesson, S., Boman, J., Barregard, L., and Sällsten, G., **2005**. Domestic wood burning and $PM_{2.5}$ trace elements: personal exposures, indoor and outdoor levels. *Atmospheric Environment 39(14) 2643–2653.*

III. Molnár, P., Johannesson, S., Boman, J., Barregård, L., and Sällsten, G., **2006**. Personal exposures and indoor, residential outdoor, and urban background levels of fine particle trace elements in the general population. *Journal of Environmental Monitoring 8(5) 543–551.*

IV. Molnár, P., Bellander, T., Sällsten, G., and Boman, J. Indoor and outdoor concentrations of $PM_{2.5}$ trace elements at homes, preschools and schools in Stockholm, Sweden. *Journal of Environmental Monitoring. Accepted.*

Contents

1. Introduction and background

Together with water and food, air is one of the fundamental bases of life for humans, animals and plants. Deprived of air, humans die within minutes, and the quality of the air we breathe is essential to our health.

The following definition of air quality (Willeke and Baron, 1993) is a broad but useful starting point when discussing air quality:

> *In air of good quality the levels of air pollutants must be below levels that can cause damage to humans, animals, plants or materials.*

The definition does not mention the form, or the chemical species or sources that may cause adverse effects. It is virtually impossible to make a list of all pollutants affecting air quality but the two major classes are *gaseous pollutants* and *particulate pollutants*. Both gases and particles can have different sources. The broadest source classification differentiates between natural and anthropogenic (human-made) sources. Natural sources include forests and forest fires, sea spray, volcano eruptions and wind-blown dust. Examples of anthropogenic sources are emissions from industries, burning of fossil fuel, combustion processes and traffic emissions. The abovementioned sources can emit both gaseous and particulate pollutants. It is not always easy to distinguish between natural and anthropogenic sources. For example, biomass burning and soil dust emissions can be of either type.

1.1. Air pollution from a historical perspective

The fact that air pollution can produce negative health effects has been known since ancient times. For instance, smoke from open fires causes irritation to the eyes and lungs. One of the first descriptions of the link between air quality and health can be found in *The Hippocratic Corpus* (c. 400 B.C.). Later, in ancient Rome, civil suits over smoke pollution were brought before Roman courts (Brimblecombe, 1999). In 1272 King Edward I banned the burning of sea coal (also known as peat) in London because of complaints about smoky air (Brimblecombe, 1999). Even in the literature, historical accounts of air pollution can be found. In Shakespeare's *Macbeth* (c. 1606), for instance, the witches chant, "Fair is foul, and foul is fair: Hover through the fog and filthy air."

Some 18th-century records describing negative effects of air pollutants other than smoke can be found. Most notable is the hazard described by the Italian doctor Bernardino Ramazzini in his book titled, *De Morbis Artificium* (Ramazzini, 1713). Among the occupations with risks related to air pollution were mining (and other work with metals and minerals), limestone quarrying, stone masonry, baking and milling. Ramazzini's knowledge of the physical and chemical properties of different pollutants was almost non-existent but he was able to describe the problems in a surprisingly accurate fashion. Regarding the diseases of bakers and millers, Ramazzini wrote in *De Morbis Artificium*,

> *They cannot avoid inhaling flour powder regardless of their efforts to protect their faces. The dust swells to a kind of dough in contact with saliva and blocks the throat, stomach and lungs, which leads to coughing, shortness of breath, hoarseness and finally asthma. The respiratory system gets a coating that*

> *prevents the air circulation … . Their habit to cover their mouth with a linen cloth is good but it does not prevent the inhalation of all the dust.*

In a study nearly 300 years after Ramazzini published his book, Brisman et al. (2000) confirmed that the risk of asthma among Swedish bakers was increased at higher inhalable dust concentrations.

The Swedish botanist, physician and zoologist Carl von Linné on his journey through the county of Dalarna, Sweden, noted the poor state of the men in one village who worked in the grindstone mines and rarely reached the age of 40 (von Linné, 1734). He concluded that the stone dust they inhaled during work caused their early deaths since the women and children in the village were not affected. He met only two elderly men in the village, a tailor and a shoemaker, and they had never worked in the mine.

What started the modern concern about air pollution is mostly attributed to the famous London smog event in December 1952, which caused about 4,000 excess deaths (Ministry of Health, 1954). The levels of SO_2 and smoke (i.e. particles) rose rapidly and persisted for 4 days (see Figure 1.1).

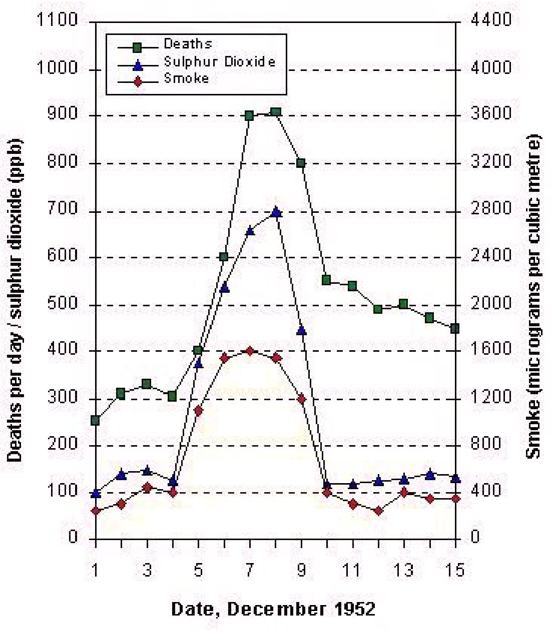


Figure 1.1. *The London fog event in 1952. The Figure shows smoke and sulphur levels and deaths per day.*

1.2. Properties of aerosols

Aerosols have been defined as “solid or liquid particles suspended in a gas (usually air)” (Hinds, 1999). Since the most common carrier gas is air, the interest is generally focused on the particles suspended in it. The size range of aerosol particles is limited downwards by cluster of molecules and upwards by the fact that the particle must be suspended in a gaseous medium long enough to be observed and measured. This gives a size range of approximately 0.001–100 μm (Willeke and Baron, 1993). The shape of particles can be anything from a long thread (e.g. an asbestos fibre) or a flake (e.g. fly ash) to a sphere (e.g. a liquid droplet). Since the actual shape and density of the particle is usually unknown, a shape-independent way to describe it must be used. The most commonly used description is aerodynamic diameter. The aerodynamic diameter is the diameter of a unit-density sphere having the same gravitational settling velocity as the particle in question. The equation below (Hinds, 1999) can be used to calculate the aerodynamic diameter, d_a, where η is the viscosity of air, v_{TS} is the gravitational settling velocity, ρ_0 is the density of water and g is the acceleration of gravity.

$$d_a = \sqrt{\frac{18\eta v_{TS}}{\rho_0 g}}$$

The settling velocity is a measure of how fast a particle of a certain size will fall. In the equation above, v_{TS} is proportional to the square of the aerodynamic diameter. Consequently larger particles introduced into the atmosphere will not reside in the atmosphere for as long as smaller particles and will therefore not be able to travel long distances.

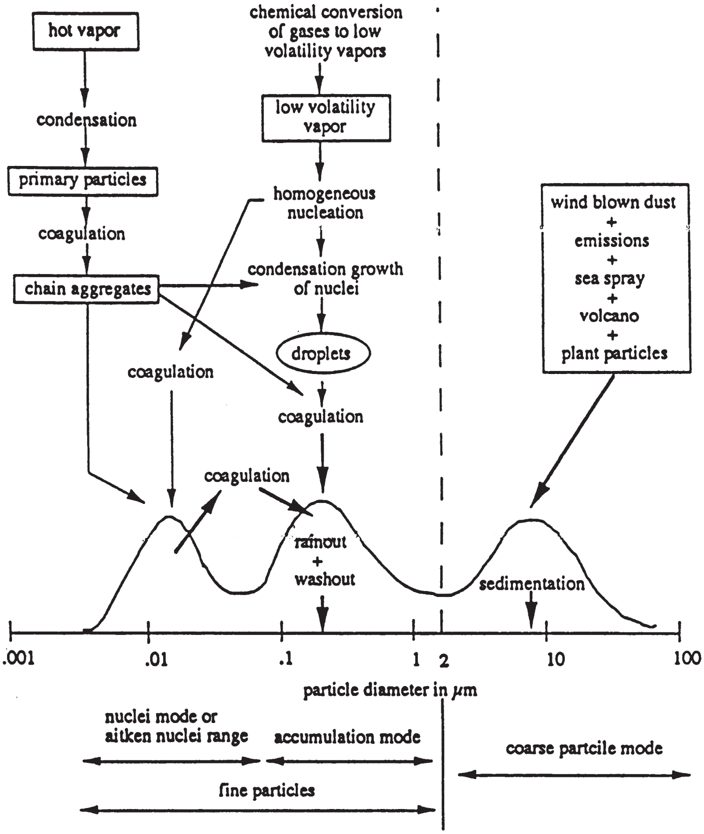


Figure 1.2. *Schematic representation of the tri-modal distribution of atmospheric particles together with the major formation mechanisms. (Adopted from Whitby (1978).)*

It is fairly common to group particles into different size categories based on their source, behaviour and/or effect. Figure 1.2 is a schematic representation of particle size distribution. The three groups shown are the nucleation mode (also known as ‘nuclei mode’ or the ‘Aitken nuclei mode’), accumulation mode and coarse mode, with size ranges of about <0.1 µm, 0.1–2 µm and >2 µm, respectively (Colbeck, 1995). Particles in the nucleation mode are usually called “ultrafine particles” and are primarily produced through gas-to-particle conversion or combustion processes. The two smaller modes are often combined as the fine particle mode. The upper cut-off size of coarse particle samplers is usually 10 µm since particles larger than 10 µm are believed to have little health significance (Harrison et al., 1999; Hinds, 1999). The two most common measures for collection of particulate matter (PM) are PM_{10} and $PM_{2.5}$. They are defined as the mass of PM passing a selective inlet (e.g. an inlet cyclone) with a 50% cut-off diameter of 10 and 2.5 µm, respectively.

1.3. Sources and transport of aerosols

Particles of different sizes often have a different origin and also a different composition (Seinfeld and Pandis, 1998). A summary of the formation and sources of particles, as well as chemical information, residence time and transport distance for fine and coarse particles is presented in Table 1.1.

Table 1.1. *Comparison of ambient fine and coarse particles. (From Seinfeld and Pandis (1998), with some modifications.)*

	Fine particles	**Coarse particles**
Formation pathways	Chemical reactions Nucleation Condensation Coagulation Cloud/fog processes	Mechanical disruption Suspension of dust
Sources	Combustion (coal, oil, petrol, diesel, wood) Gas-to-particle conversion of NO_x, SO_2 and VOC Smelters, mills, etc	Resuspension of industrial dust and soil Suspension of soil (farming, mining, unpaved roads) Biological sources Sea spray
Composition	Sulphate Nitrate Ammonium Elemental carbon (EC) Organic compounds Water Metals (Pb, Cd, V, Ni, Cu, Zn, Fe, etc)	Resuspended dust Coal and oil fly dust Crustal element (Si, Al, Ti, Fe, Mn, etc) oxides $CaCO_3$, NaCl Pollen, mould, spores Plant and animal debris Tire wear debris
Solubility	Largely soluble Hygroscopic	Largely insoluble Non-hygroscopic
Atmospheric lifetime	Days to weeks	Minutes to days
Transport distance	100s to 1,000s of km	Up to 10s of km

Coarse particles are generally not transported far but exceptions do occur. A volcano eruption is an example of such exceptions. During an eruption, the volcano emits an enormous number of particles, both fine and coarse, vertically at very high velocity. The plume is transported high up into the atmosphere, even up to the stratosphere, and therefore can be transported over very long distances. The volcanic cloud from the Mount Pinatubo eruption in 1991 encircled the earth within 22 days (Timmreck et al., 1999). Also, sometimes special meteorological conditions can favour long-range transport of coarse particles. For example, this occurred in October 2001 when Saharan dust was transported all the way north to southern Scandinavia and deposited in the area around Göteborg (Ullgren, 2001).

Fine particles as an entity are more intricate to describe in general terms since they often undergo transformations in the form of both chemical reactions and particle growth (Finlayson-Pitts and Pitts, 2000; Seinfeld and Pandis, 1998). In Figure 1.2 above, the primary produced nucleation mode particles grow quickly into the accumulation mode range, where their growth rate slows down. An effect of this is that nucleation mode particles do not travel very far before they are transformed into accumulation mode particles. This means that nucleation mode particles, measured by counting or collection, are generally locally produced in contrast to the larger size fraction of the fine particles.

Urban sources of ultrafine particles which contribute significantly to the number concentrations, are combustion processes from industry, traffic-related emissions and biomass burning. As traffic density is rapidly increasing in most parts of the world, emissions of traffic-related pollution will continue to be a concern, even if technical development can substantially reduce the emissions from each vehicle. Likewise, biomass burning for residential heating is growing rapidly, both globally because of the increased world population and in the developed countries as one of the steps to reduce the use of fossil fuels. The Clean Air for Europe (CAFE) programme (Amann et al., 2005) estimates that during 2000, 25% of the primary $PM_{2.5}$ emissions in the EU countries came from domestic wood burning. Based on this figure, in 2020, 38% will come from domestic wood burning.

1.4. Health effects of aerosols

The evidence of the association between airborne PM and public health outcomes is consistent in showing adverse health effects at exposures experienced by urban populations in cities throughout the world, in both developed and developing countries (WHO, 2005). The range of effects is broad, including effects on the respiratory and cardiovascular systems extending to children and adults within the general population (Pope and Dockery, 2006; Schlesinger et al., 2006; WHO, 2005), but also including lung cancer (Pope and Dockery, 2006; Schlesinger et al., 2006). The risk for various outcomes has been shown to increase with exposure and there is little evidence for a threshold below which no adverse health effects would be anticipated (WHO, 2005). In one WHO report (WHO, 2004) it is stated that the public health significance of long-term health effects of exposure to PM outweighs that of short-term effects. Short-term exposure effects have been documented in numerous time series studies, and guidelines for both the short (24 hours) and the long term (annual average) are recommended (WHO, 2004). The recommendation is that both $PM_{2.5}$ and PM_{10} be assessed and controlled since fine and coarse particles have different sources and may have different effects. Regarding ultrafine particles, information is insufficient to permit a quantitative evaluation of the risks of health effects of exposures (WHO, 2006). The recently adopted guidelines for annual means of PM are 10 $\mu g\ m^{-3}$ and 20 $\mu g\ m^{-3}$ for $PM_{2.5}$ and PM_{10}, respectively, while for 24-hour means, they are 25 $\mu g\ m^{-3}$ and 50 $\mu g\ m^{-3}$ (WHO, 2006).

Concerning the question about which types (i.e. composition and size) of particles cause adverse health effects, and the types of effects caused, much is still unknown. Two recent review articles (Pope and Dockery, 2006; Schlesinger et al., 2006) discuss the current knowledge about PM and particle size, and health effects. Both reviews (Pope and Dockery, 2006; Schlesinger et al., 2006) conclude that there tends to be a stronger relation between fine particles, $PM_{2.5}$, and most health effects than between PM_{10} and effects on health. Ultrafine particles contribute little to the PM mass concentration; however, they do influence the surface area by their large number and are of interest in toxicological studies (Schlesinger et al., 2006). Furthermore, since primary ultrafine particles are a source of fine particles and since poorly soluble ultrafine particles may be more likely than larger particles to translocate from the lung to the blood and other parts of the body they are of importance in future studies (Pope and Dockery, 2006).

Which particles are most hazardous to human health is not yet known but some groups of compounds have been suggested. Particulate organic compounds and chiefly polycyclic aromatic hydrocarbons (PAHs) are produced by incomplete combustion processes and some of those are known carcinogenic species, while others are suspected of being carcinogenic (Bostrom et al., 2002). Another group that has gained interest in recent years is metals. Schlesinger et al. (2006) have summarised current knowledge regarding trace metals and their health impact. The toxicological studies strongly suggest that transition metals such as V, Cr, Mn, Fe, Ni, Cu and Zn are components in PM with toxic capability based on their potential for oxidative activity and the production of reactive oxygen species (Schlesinger et al., 2006). Soil dust consists of crustal elements (e.g. Si, Ca, Al and Mg) and is present in ambient $PM_{2.5}$ but larger fractions are present in the coarse mode. Wind-blown soil dust, at least in rural areas, is not thought to be a significant health hazard but naturally occurring crustal material can be contaminated with road dust produced by moving vehicles. The contaminants can contain a variety of substances, including PAH and various metals (e.g. Zn and Pb) that may modify the toxicology of the crustal particles.

An example of possible metal toxicity is given in the review by Pope and Dockery (2006). A steel mill in Utah Valley, UT, USA, was closed for 13 months during 1986–1987. The average PM_{10} concentration decreased by 15 $\mu g\ m^3$ and mortality among the population in Utah Valley decreased by 3.2% during the closure period. The average decrease in metal concentration (in ng metal/mg extract) between pre- and post-closure was 96%. Extracts from PM filters have been shown to cause inflammation in both humans and animals (Ghio, 2004).

In recent years particles from burning of biomass for domestic heating have increased and become one of the major sources of $PM_{2.5}$ in Europe and other parts of the world (Amann et al., 2005). Incomplete combustion of biomass produces a multitude of different organic species as well as trace metals, but there have been too few studies to assess the relative toxicity of wood-smoke particles with respect to cardiovascular or cancer outcomes compared with other sources (Naeher et al., 2007). In a review of some epidemiological studies conducted in areas where wood smoke is common, Boman et al. (2003) came to the conclusion that PM from wood smoke seems to be at least as harmful as PM derived from other sources.

1.5. Sampling and analysis

Within the field of air pollution research a vast number of different types of instruments and range of different analytical techniques are available. For gaseous pollutants, online gas detectors are often based on fluorescence or chemiluminescence, and integrating sampling involves either passive sampling using diffusion samplers or active sampling using pumps.

For sampling of particles, two main tools exist, collectors and counters. Collectors are integrating samplers that collect particles on a substrate (e.g. a filter, quartz plate or metal foil) that enables subsequent analysis of mass concentration by gravimetrical methods as well as chemical analysis. Counters are typically online instruments that detect particles, usually by light scattering techniques. More advanced counters both count and determine the size of the particles. In recent years new instruments that combine different techniques have been developed. These instruments can count, determine size and provide chemical information. Examples are the Aerosol Time-of-Flight Mass Spectrometer and the Aerosol Mass Spectrometer.

Innumerable analytical techniques are available today. Some of the common techniques for analysing particles are atomic absorption spectroscopy, high-performance liquid chromatography, ion chromatography, inductively coupled plasma mass spectroscopy, particle-induced X-ray emission, and X-ray fluorescence (XRF). The two last techniques have the advantage of no, or only limited, sample preparation prior to analysis. The choice of instruments used is based on the objectives of the study. Important factors are time resolution needed, particle size range of interest, and need of subsequent chemical analysis, as well as the number of instruments needed, the total number of samples and of course availability of instruments. Below is a presentation of the instrument types and analytical techniques used in the studies on which this thesis is based.

1.5.1. Particle samplers

As mentioned previously, collecting particles on some type of substrate enables us to determine the mass concentration by gravimetrical methods, as well as to perform subsequent chemical analysis. The simplest way of collecting airborne particles is to draw air through a filter by using a filter cup connected to a pump and thus collect all suspended particles. Most widely used for limiting a size interval are different types of impactors that use the inertia of the particles following a bending airflow for collection of the particles. The principle of operation for the two most common types, the impactor and the cyclone, is shown in Figure 1.3. Impactors use the concept of particle inertia to size-select and/or collect particles of the studied size range. Particles are drawn into the instrument by a pump, and follow the air flow. Inside the impactor the geometry creates bending air flows. Large particles cannot follow the bending airflow through the bend and impact on the plate, while smaller particles continue (Figure 1.3a).

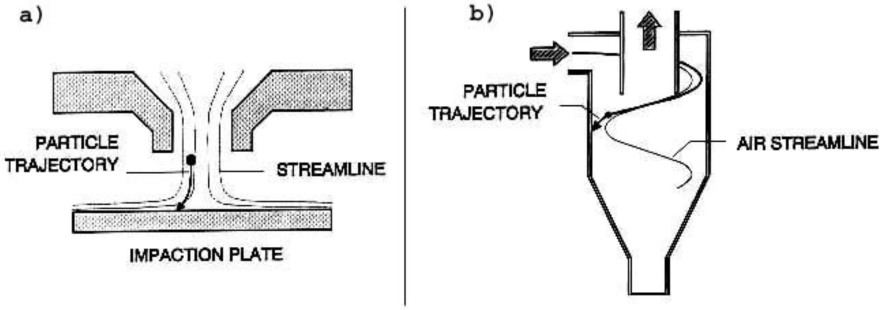


Figure 1.3. *Schematic drawings showing the principle of operation of an impactor **(a)** and a cyclone **(b)**.*

A cyclone uses the same basic principle as an impactor, viz. that of particles moving along a bending air flow. Again, since larger particles cannot follow the bending air flow they impact on the cyclone wall while smaller particles follow the flow upwards (see Figure 1.3b) and are collected on the filter. The main difference between impactors and cyclones is that impactors are designed to collect particles larger than the cut-off diameter while cyclones sort out and discard particles larger than the cut-off diameter. Furthermore, impactors can be designed to have a sharper cut-off function (Figure 1.4) than cyclones. As mentioned in section 1.2, the most common way to measure the concentration of airborne particles is through PM_{10} or $PM_{2.5}$ sampling, and it is for these PM sizes that guideline values exist. Lately PM_1 sampling (PM <1 μm) has also become more frequently used.

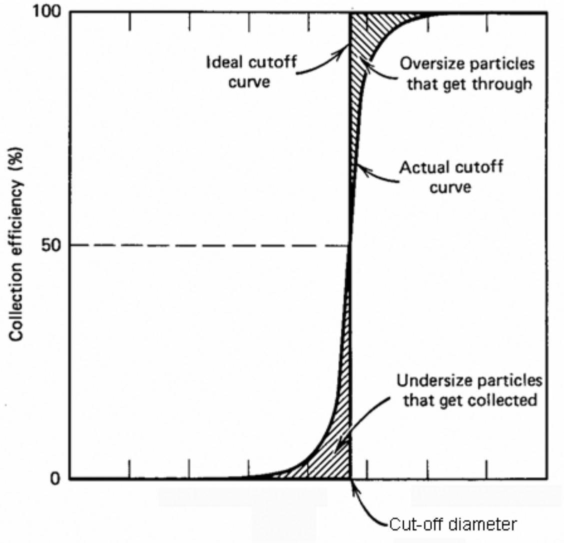


Figure 1.4. *The collection efficiency of an impactor. (Adopted from Hinds (1999).)*

1.5.2. Particle counters

Instead of collecting particles on a substrate it is possible to count the particles. A number of different counters exist based on different methods of detecting, counting and determining the size of the particles (McMurry, 2000). For particles in the size range 0.5–20 µm, optical methods are most widely used, but for smaller particles, the detection efficiency decreases dramatically and other methods must be used. For sub-micrometre particles, condensation particle counters (CPCs) are most commonly used (Figure 1.5). The principle of operation is based on drawing particles through a zone that is saturated with a suitable vapour (n-butanol, isopropyl alcohol or water), which is subsequently cooled to cause condensation of the vapour on the particles (Stolzenburg and McMurry, 1991). This causes the particles to grow to the order of 10 µm particle diameters, at which size they are very effective light scatterers. The lower cut-off size depends on the design and level of supersaturation achieved, but typical sizes are from 3 nm in ultrafine counters to 10 nm in regular ones. The upper size limit is dependent on the inlet and is usually around 1 µm.

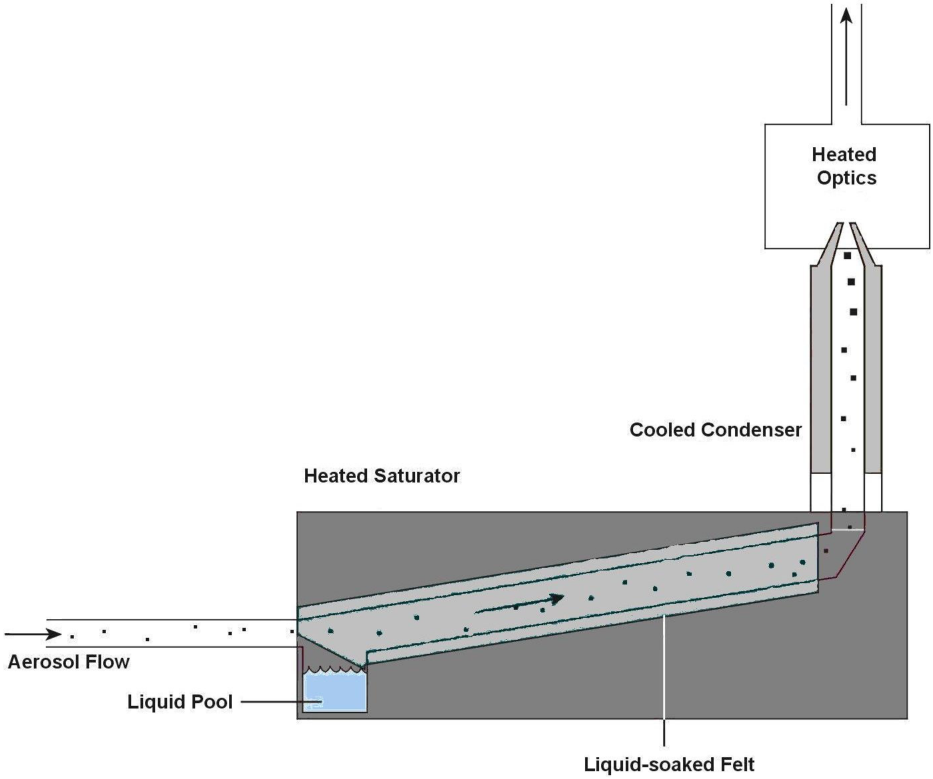


Figure 1.5. *The principle of operation of the condensation particle counter. Graphics © TSI Incorporated, St. Paul, MN, USA.*

The CPC itself is not able to give any information on the size distribution, giving only the total number concentration over the whole size interval. In order to obtain the size distribution a combination of an electrostatic classifier and a CPC is used. The function of the electrostatic classifier is to separate particles on the basis of their electrical mobility, which is a function of particle diameter (Zhang et al., 2005). This gives an accurate and effective method for size determination of sub-micrometre particles. The electrostatic classifier, also known as a "differential mobility analyser (DMA)" (Figure 1.6), is tuned through a combination of flows and voltages to transmit only particles with one selected diameter. The number density of the selected size is subsequently measured with the CPC. By changing the voltage in the DMA, different particle sizes may be transmitted sequentially and a complete size distribution is built up over a scan of a few minutes. Instruments using a DMA in conjunction with a CPC are named either "differential mobility particle sizer (DMPS)", if the voltage is changed stepwise, or "scanning mobility particle sizer (SMPS)", if the voltage is changed by a ramp function.

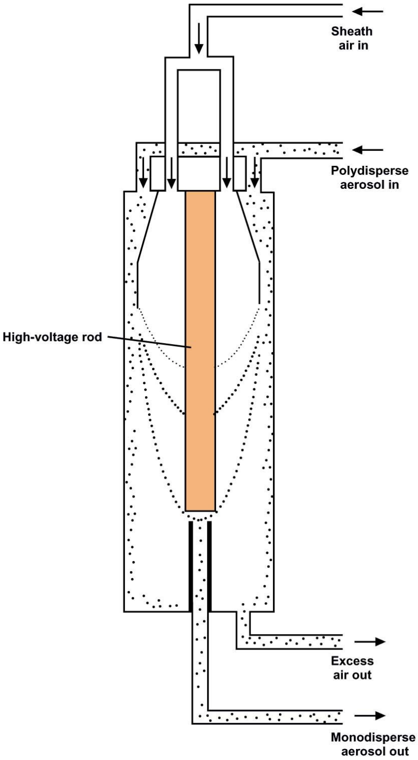


Figure 1.6. *The principle of operation of the differential mobility analyser (DMA). Graphics © TSI Incorporated, St. Paul, MN, USA.*

1.5.3. X-ray fluorescence

X-ray fluorescence (XRF) is an analytical technique based on the principle of having radiation from an X-ray source hit the sample (Jenkins et al., 1981). The radiation will excite the atoms by ejecting an inner shell electron, and thus create an inner shell vacancy. An outer shell electron will occupy this core hole and the energy difference between the inner and outer shell will be emitted as an X-ray photon. The energy of the X-ray photon is characteristic for the element in which the transition takes place (see Figure 1.7).

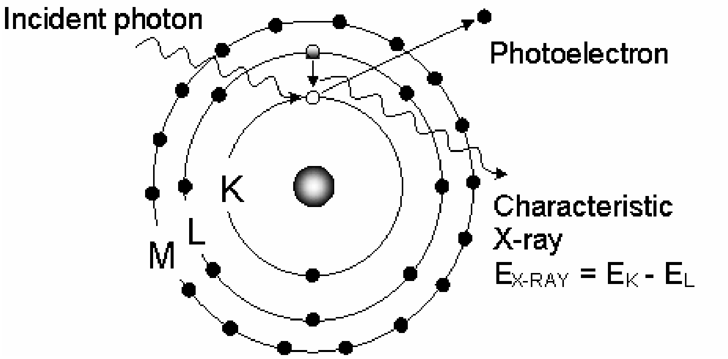


Figure 1.7. The fluorescence process used in X-ray spectroscopy.

The Energy-Dispersive XRF (EDXRF) spectrometer is a multi-element, non-destructive analytical instrument well suited for aerosol filter analysis. It enables quantification of elements with an atomic number of 14 (silicon) and higher. An example of a spectrum from the spectrometer can be seen in Figure 1.8 where the elements are given by their chemical symbol.

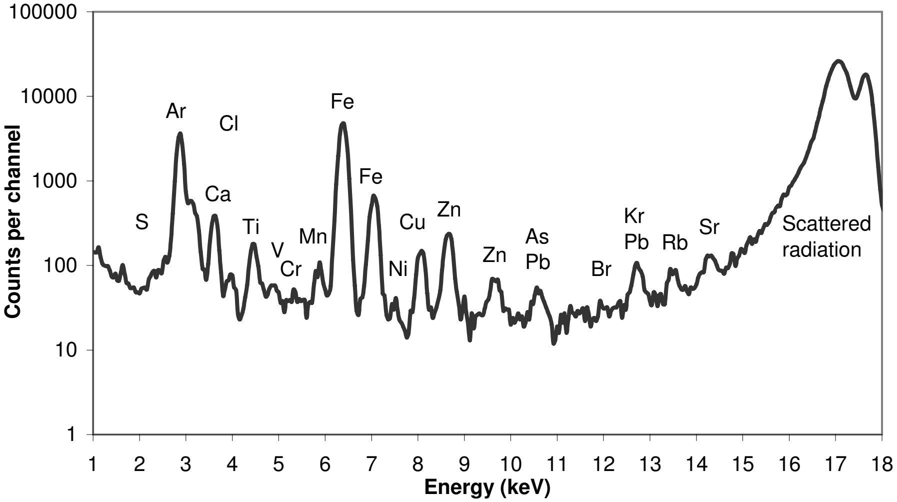


Figure 1.8. *An X-ray fluorescence (XRF) spectrum from a filter excited by molybdenum (Mo) K_α radiation. The peaks from some of the elements in the sample are marked with their chemical symbols. Note that argon (Ar) and krypton (Kr) do not originate from the sample but come from the excitation of the surrounding air during the analysis.*

1.5.4. Analysis of black smoke

Carbonaceous particles in the atmosphere consist of either elemental carbon (EC, also referred to as "graphitic", or "black" or "free" carbon) or organic carbon. Elemental carbon can be produced only in combustion processes and therefore consists of primary particles and the most abundant light-absorbing aerosol species in the atmosphere (Seinfeld and Pandis, 1998). The darkness of the particulate sample is consequently an indication of the amount of EC on the filter and is often referred to as “black smoke (BS)”. Analytical methods commonly used to detect EC (e.g. thermal optical analysis) are expensive and destructive to the sample material. Because EC is the dominant light-absorbing substance in the atmosphere (Hoek et al., 1997; Horvath et al., 1996; Seinfeld and Pandis, 1998), an alternative way to estimate EC concentrations in the atmosphere as BS is to measure light absorption or reflectance of PM, collected on filter media. Several studies have reported that BS, derived from absorbance coefficients, is well correlated with the concentration of EC or soot and can be recommended as a valid and cheap indicator in studies on combustion-related air pollution and health (Cyrys et al., 2003; Götschi et al., 2002; Janssen et al., 2001; Kinney et al., 2000).

The principle of a reflectometer is to irradiate the sample and detect the back-scattered light. The amount of reflected light is transformed into an absorption coefficient, *a*, according to the international standard (ISO9835, 1993) using the following equation:

$$a = \frac{A}{2V} \times \ln\left(\frac{R_0}{R_S}\right),$$

where A is the filter area (m^2), V is the sampled volume (m^3), R_0 is the average reflectance of field blanks, and R_S is the reflectance of the sampled filter. The absorption coefficient is expressed in the unit $10^{-5}\ m^{-1}$.

1.5.5. Meteorology

Meteorological information is essential if the aim is to understand and describe the measured air pollution situation. Several articles and textbooks discuss different aspects of the relations between meteorology and air pollution (see, e.g., Finlayson-Pitts and Pitts, 2000; Seinfeld and Pandis, 1998; Stull, 1995; Zhang et al., 2005). Common parameters such as temperature, wind speed and direction, solar radiation, air pressure, relative humidity and rain, but also, boundary level height and temperature inversions can have an effect on the composition of air. For instance, the direction from which the wind originates determines the influence of upwind sources. Higher wind speeds will increase the ground turbulence and resuspend particles, and a low boundary level height and especially a temperature inversion will trap the pollutants and increase the concentrations.

1.5.6. Air mass back trajectories

When an air parcel travels over time it picks up pollutants from emission sources it passes while other pollutants are removed through dry or wet deposition. Simultaneously, pollutants in the air parcel can change their chemical characteristics. Information about air mass origin or sources of the measured pollutants is often sought after, regardless of whether the aim is to do source apportionment or to describe reasons for differences between samples, over time or between locations. A number of techniques are available and in the current work, calculations of air mass back trajectories have been used.

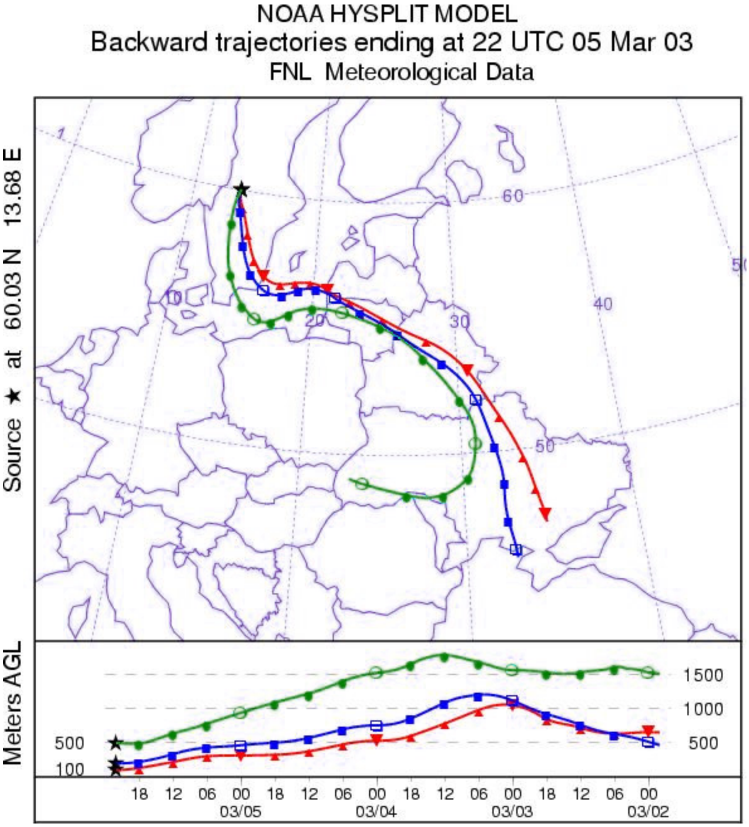


Figure 1.9. *An example of the output of a trajectory calculation in Paper II.*

An air mass trajectory is the curvilinear path an air parcel travels (in three dimensions) as a result of the wind field (wind speed and direction). Data sets of three-dimensional time-resolved wind field data exist and are used in weather predictions. These data sets can be used to calculate the path of an air parcel. The National Oceanic and Atmospheric Administration (NOAA) HYbrid Single-Particle Lagrangian Integrated Trajectory (HYSPLIT) model has been used throughout this work. The model, which is available at the website http://www.arl.noaa.gov/ready/hysplit4.html, can calculate backwards the path an air parcel has travelled before it reached the target area. An example of a trajectory calculation output is presented in Figure 1.9. By examining the path the air parcel has travelled before reaching the sampling location it is possible to identify emission areas of known types of pollutants (e.g. sulphur-containing particles from Eastern Europe).

2. Aims of the thesis

The aims of this thesis work were to –

- characterise the personal exposure to trace elements in fine particles (Papers II and III) and describe the relations between outdoor concentrations, personal exposure (Papers II and III) and indoor concentrations (Papers II–IV);
- investigate the impact of domestic wood burning on personal exposure to and indoor levels of fine particle trace elements (Paper II);
- evaluate and quantify the contribution of ultrafine particles from traffic to ambient air with respect to the size distribution and major meteorological parameters (Paper I);
- investigate differences between indoor and outdoor fine particle trace elements in children's environments and spatial variations within a city (Paper IV); and
- investigate the impact of long-range-transported (LRT) pollutants in urban environments (Papers I–IV).

3. Materials and methods

The instruments used in the different papers are summarised in Table 3.1 below. In addition to the instruments presented in the Table, meteorological data (wind speed, wind direction and temperature) were obtained from various meteorological stations near the investigated areas.

The instruments used for particulate sampling and counting included a TSI model 3932 (TSI Inc., St. Paul, MN, USA) DMPS used for particle counting and size determination. The following impactors were used: a PQ100 EPA-WINS Basel $PM_{2.5}$ sampler (BGI Inc., Waltham, MA, USA) using a flow rate of 16.7 L min^{-1}; a Sierra Andersen series 240 virtual dichotomous impactor (Andersen Instruments Inc. Dichotomous Sampler, Smyrna, GA, USA) with a flow rate of 16.7 L min^{-1}; Harvard impactors (Air Diagnostics and Engineering Inc., Harrison, ME, USA) with a flow rate of 10 L min^{-1}, and a PIXE I-1L cascade impactor (PIXE International Corp., Tallahassee, FL, USA) with a flow rate of 1 L min^{-1}. Two different models of cyclones were used, GK2.05 (KTL) (flow rate 4 L min^{-1}) and Triplex SCC1.062 cyclones (flow rate 3.5 L min^{-1}) (both from BGI Inc., Waltham, MA, USA). In addition, data from a tapered element oscillating microbalance (TEOM) instrument, R&P 1400 TEOM (Rupprecht & Patashnick Co., Inc., Albany, NY, USA), managed by the Göteborg Environmental Administration were used in one study.

Table 3.1. *Instruments used in the different studies.*

Instrument	Sampled variable	Paper No. I	II	III	IV
Differential mobility particle sizer TSI model 3932	Number concentration (10–368 nm)	X			
Sierra Andersen virtual dichotomous impactor	$PM_{2.5}$	X	X		
R&P 1400 TEOM[a]	$PM_{2.5}$	X			
PIXE I-1L cascade impactor	$PM_{0.25}$	X			
PQ100 EPA-WINS Basel $PM_{2.5}$ sampler	$PM_{2.5}$		X	X	
GK2.05 (KTL) cyclone[b]	$PM_{2.5}$		X	X	
Triplex SCC1.062 cyclone[b]	PM_1			X	
Harvard impactor	$PM_{2.5}$				X
Diffusive sampler[c]	NO_2				X
Tracer gas emitter + sampling tube[d]	Air exchange rate				X

TEOM = tapered element oscillating microbalance.

[a] Managed by the Göteborg Environmental Administration.

[b] Conected to BGI 400S personal sampling pumps.

[c] Results were analysed by the Swedish Environmental Research Institute (IVL), Göteborg, Sweden.

[d] Managed, and results analysed, by Pentiaq AB, Gävle, Sweden.

3.1. Particle instruments and measurement strategy

Paper I: Size distribution between 10 and 368 nm was measured continuously using a DMPS system. The number concentration data were recalculated to hourly averages to match the time resolution of the meteorological data, and were successfully collected for 430 out of a total of 500 hours. Roadside $PM_{2.5}$ was sampled daily (24 hours) using a Sierra Andersen virtual dichotomous impactor and the time resolution of the TEOM instrument (managed by the Göteborg Environmental Administration) was 1 hour. The choice of measuring site was crucial to the aims since we wanted to isolate the traffic as a known and dominating source. The highway known as Riksväg 45 (RV45) outside Surte was considered ideal since the road has a known and persistent traffic pattern dominated by commuter traffic with pronounced morning and afternoon rush-hour traffic. No other major sources of particulate air pollution exist nearby. At the measuring site, the RV45 is also a straight road, with a speed limit of 90 km h^{-1} and virtually all vehicle engines are warmed up before passing the sampling site.

Paper II: 24-hour sampling of $PM_{2.5}$ was performed at all measuring locations (personal, indoors and outdoors) simultaneously. BGI 400S personal sampling pumps connected to GK2.05 (KTL) cyclones were used for personal and indoor sampling while an EPA-WINS impactor (PQ100 EPA-WINS Basel $PM_{2.5}$ sampler) and a Sierra Andersen virtual dichotomous impactor were used for outdoor sampling. On all sampling days except one, at least one subject each from the wood-burning and the reference group was measured simultaneously. The outdoor measuring station was placed in the middle of the investigated area on the roof of a garage belonging to a subject in the reference group. Subjects kept time activity diaries in which they noted when they made fires, and how much and what type of wood they used. They also recorded their activities (at home and elsewhere) and where they had been during the day.

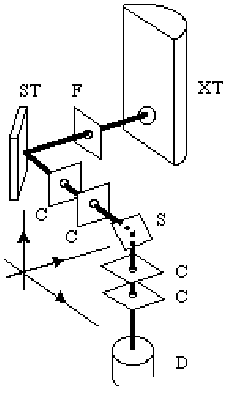
Paper III: Personal exposure and indoor and residential outdoor levels were sampled using BGI 400S personal sampling pumps and cyclones (GK2.05 (KTL) cyclones for $PM_{2.5}$ and Triplex SCC1.062 cyclones for PM_1). For the urban background sampling, an EPA-WINS impactor (PQ100 EPA-WINS Basel $PM_{2.5}$ sampler) was used. Subjects completed a questionnaire about age, occupation, type of home and heating system, as well as a daily activities diary. The diary included questions regarding smoking, exposure to environmental tobacco smoke, time spent at home, at work, indoors and outdoors, time spent in cars and buses, and occupational exposure.

The critical aspect of this project was the number of simultaneous samples (six or seven) and the total collected mass on the filters. From Paper II we knew that 24-hour sampling of $PM_{2.5}$ using the personal sampling pump (4 L min^{-1}) was sufficient to perform the XRF analysis and to exceed the limit of detection (LoD) of the elements of interest. For the PM_1 samples with a slightly lower flow rate (3.5 L min^{-1}) and a narrower size range, we needed to weigh the risk of non-detection against a longer sampling time. A longer sampling time (48 hours) would have removed the risk of non-detection but the additional annoyance to the subjects and the practical problems regarding instrument handling were more important.

Paper IV: Harvard-type impactors (with a flow rate of 10 L min^{-1}) were used for sampling indoor and outdoor fine particles. One of the objectives of this study was to investigate seasonal effects and by integrating the concentration over a long sampling period (about 2 weeks) a more representative measure for the season could be obtained. Using timers to switch the sampling pumps on and off according to a predetermined schedule prevented overloading of the filters. In schools and preschools, sampling was performed only during daytime on weekdays, since this was the time the children were present. Therefore, by programming the timers differently at each microenvironment we ensured that similar amounts of air were drawn through all filters. The sampling schedule was as follows: in subjects' homes the pump was turned on for 15 minutes every 2 hours both day and night for the whole 14-day period, while in schools it was turned on for 45 minutes every hour between 08:00 and 16:00 and in preschools it ran for 30 minutes every hour between 08:00 and 18:00. Measurements were not performed on Saturdays and Sundays at schools and preschools. The sampling schedule gave a mean sample volume of 26, 39 and 33 m^3 at homes, schools and preschools, respectively.

3.2. X-ray fluorescence

The instrument used in this work was an EDXRF spectrometer at the Department of Chemistry, Göteborg University. It uses a three-axial geometry (see Figure 3.1) to achieve optimum sensitivity (Öblad et al., 1982). The primary radiation from the X-ray tube hits the secondary target (in this case a molybdenum (Mo) target). The K_α radiation from the Mo hits the sample and the emitted radiation from the sample is detected by a Si(Li) detector.



XT: X-ray tube
ST: Secondary target
S: Sample
F: Filter
C: Collimator
D: Detector

Figure 3.1. *Schematic drawing of the X-ray spectrometer showing the three-axial geometry and the major components used.*

The spectrometer works in air, which affects the sensitivity of the lighter elements. The LoDs of elements investigated in the thesis expressed as airborne concentrations are presented in Table 3.2. The differences in LoD between personal exposure samples from Papers II and III and indoor concentrations in Paper IV for some of the elements arise partly from differences in the total volume of air drawn through the filters (i.e. the total sampled mass). The volumes were about 5.7 m^3 for personal and indoor samples in Papers II and III compared with 26 m^3 for the indoor and outdoor samples in Paper IV. The LoD can also be affected by the sample matrix, i.e. differences in concentrations between elements with characteristic energies close to each other (see the Mn and Ni peaks close to the Fe peaks in Figure 1.8).

Table 3.2. *Median limits of detection (LoDs), expressed as airborne concentrations (in ng m^{-3}), measured for personal exposure in Hagfors (Paper II) and Göteborg (Paper III) and at the homes of participating children in Stockholm (Paper IV).*

Element	Personal exposure, Hagfors (volume 5.7 m^3)	Personal exposure, Göteborg (volume 5.7 m^3)	Indoor concentration, Stockholm (volume 26 m^3)
S	150	120	60
Cl	66	45	[a]
K	12	12	5.7
Ca	6.7	7.1	3.5
Ti	3.4	3.5	1.9
V	[a]	2.7	1.5
Cr	1.5	1.7	1.1
Mn	1.2	1.5	0.83
Fe	1.2	1.1	0.65
Ni	0.80	0.88	0.65
Cu	0.69	0.65	0.58
Zn	0.65	0.63	0.50
Br	0.37	0.35	0.34
Pb	1.1	0.89	0.43

[a] Not analysed because of low detection frequency.

3.3. Smoke stain reflectometer

A smoke stain reflectometer was used in Paper II. After the elemental analysis the filters were examined for BS using an EEL 43 smoke stain reflectometer (Diffusion Systems Ltd., London, UK). Each filter was measured five times (in the centre and in each of the four main quadrants) and the average value was used in the calculations, as described in the ULTRA study manual and data book (Götschi et al., 2002; Pekkanen et al., 2000).

3.4. Subjects

In Papers II–IV subjects representing various populations, selected in the following ways: in Paper II a residential area in the town of Hagfors, Sweden, where domestic wood burning is common was selected. Based on the chimney sweeping register recording the type of heating system present, subjects were contacted and asked to participate, and were divided into a wood-burning and a reference group. Out of 18 households with wood-burning appliances used daily, 14 individuals (ten men and four women) agreed to participate. Twelve households from the same area using electrical heating or heat pumps were contacted and ten individuals (five men and five women) agreed to participate.

In Paper III, subjects were recruited from two groups. In the first group, 30 subjects were randomly selected from the adult population of Göteborg, and 24 agreed to participate. Four were excluded because of lack of possibilities of performing residential outdoor measurements. The second group consisted of ten volunteers among the staff of our department in Göteborg. In total, the study included 30 subjects, eight men and 22 women. The second group were recruited because we wanted to perform personal sampling of both $PM_{2.5}$ and PM_1 simultaneously; also, we wanted to sample two $PM_{2.5}$ samplers at the same time to investigate the precision of the personal exposure measurements. The need to carry a double setup, i.e. two cyclones and two pumps, was more complex, but these subjects were easier to instruct.

In Paper IV three areas in Stockholm, representing different local conditions, were selected. Schools and preschools in the chosen areas were contacted by telephone. Those that were interested in participating in the study were visited. To be selected the schools and preschools were required to have a safe outdoor location for placement of the pump during the measurements, and possibilities to connect tubes (and cord) from the pump outside to the impactor in the classroom. After the classrooms were selected, the school children's parents were asked to participate in the study and two families from every classroom were recruited. The children were 6–11 years old. The families had to be non-smoking, not use gas for cooking and have a balcony or some other safe place with electricity for the pump.

For Papers II and III, the subjects signed their informed consent. The studies were approved by the Ethics Committee at Göteborg University. In Paper IV informed consent was signed by the parents.

3.5. Measurement strategies and methods

The aims of a project or study establish the basis for designing the measurement strategies. In the present work, several of the projects had some matching aims but the measurement strategies for each project must be drawn up to achieve its main goals. There are usually two major types of concerns regarding the measurement strategies, viz. the technical and scientific concerns and a more practical or feasibility concern. Regarding the technical and scientific concerns one is often faced with balancing the sampling time and number of samples (or length of the data series) against the accuracy and the risk of not exceeding the LoD. The availability of instruments is often a limiting factor for one or more of the abovementioned factors. Another important factor is the amount of data information needed (i.e. sample size) to discard a hypothesis.

The other major concern is of a more practical nature. The number of sampling setups available, the analytical cost, the workload during sample collection and the project funding are all limiting variables that must be taken into account.

The traditional way to try to link air pollution to health effects has been to use a central outdoor monitoring station to represent the exposure in a population (within a city). Many studies have successfully used this concept, for instance the US six-city study (Dockery et al., 1993). However, we often do not know how well the central monitoring station represents the individuals' situation and uncertainties are usually large (Monn, 2001; Wallace, 2000). The need to measure closer to the individuals is apparent. Either many outdoor monitoring stations can be used and the closest one represents the individual's exposure or each subject should be measured individually. In today's society, people spend some 80–90% of their time indoors and indoor sources may play an important role in the total exposure. Still, a more accurate measure is the personal exposure. However, personal exposure measurements are time-consuming and expensive, plus the number of individuals who can be investigated is limited. The personal exposure measure is today the best estimate of what a person is actually exposed to in daily life. The recent development of a respiratory deposition instrument (Londahl et al., 2006) which measures the fraction of the inhaled aerosol that is deposited in the respiratory system has taken the estimate of the exposure one step further, but it is still limited to laboratory exposure studies.

One of the aims of this thesis work has been to establish the relationship between outdoor, indoor and personal exposure. In Papers II–IV we performed measurements in two or more of these environments and investigated the relations between them with regard to exposure to trace elements.

3.6. Air mass back trajectories

In Papers I–III 96-hour air mass back trajectories were computed using the NOAA HYSPLIT model (Draxler and Rolph, 2003) in order to obtain information on the history of the sampled particulate pollution. Each sampling day at startup and 6, 12, 18 and 24 hours later (end of sampling), trajectories were computed to obtain a good quality basis for the classification of the sampled air. The trajectories were then divided into classes, representing different source areas. The classification was done according to the criterion that all trajectories during a sampling period must have a major path belonging to the same class. Classes were defined separately for each study to optimise the interpretation. In Paper I two classes were used, a Nordic + marine class, with low levels of particulate pollution, and a continental European class, incorporating the British Isles, of more polluted air. For Hagfors during winter (Paper II), two very distinct classes dominated, a clean marine type and a polluted central European type (Figure 3, Paper II). In Paper III, four distinct classes were found, namely continental areas (central and Eastern Europe), marine areas, the Nordic countries Finland, Norway and Sweden, and the UK. Trajectories that shifted classes during the sampling day were classified as undetermined and were not used.

3.7. Statistical methods

In Paper I, Pearson correlations and varimax rotated principal component analysis were used. Complementary analysis in the thesis was performed using non-parametric tests (Spearman correlations and Wilcoxon's rank sum tests). In Papers II–IV statistical calculations were performed using the SAS System for Windows, version 9.1 (SAS, 2003). Correlations between concentrations in different microenvironments were assessed using the Spearman rank correlation coefficient (r_s) and differences between pairs of personal, indoor, outdoor, and ambient levels were calculated using the Wilcoxon signed-rank test. For unpaired observations, Kruskal-Wallis or Wilcoxon's rank sum test was used. Unless stated otherwise, statistical significance refers to $p<0.05$ in two-tailed tests. Non-parametric tests were used because in general the levels were not normally distributed. If the elemental concentration was below the LoD, the LoD divided by the square root of two was used in the calculations (Hornung and Reed, 1990).

4. Results

4.1. Paper I

In Paper I roadside measurement of traffic-emitted particles was conducted to estimate and describe the freshly emitted traffic particles. The number distribution of traffic-emitted particles peaked in the size range 15–50 nm (Figure 6 in Paper I). The mean number concentration of ultrafine particles (10–100 nm) was 2,000 cm^{-3} (range 330–11,000 cm^{-3}).

No correlation (Pearson) was seen between $PM_{2.5}$ and ultrafine particles by number or mass (Table 2 in Paper I). On the other hand, the lower accumulation mode (100–368 nm) was significantly correlated to $PM_{2.5}$, with regard to both number and mass. Spearman correlations between PM mass (at Surte and at the "Femman" urban background station in Göteborg) and the elemental concentrations measured in Surte are presented in Table 4.1 (not presented in Paper I). No significant correlations between $PM_{2.5}$ mass in Surte and elemental concentrations were found, but the elements S, K, V, Ni, Br and Sr (many of them commonly attributed to long-range transport) were all significantly correlated to both the mass of accumulation mode particles of 100–368 nm (referred to as dM 100–368) and $PM_{2.5}$ at Femman.

Table 4.1. *Spearman correlations between the mass concentrations ($PM_{2.5}$ at Femman, $PM_{2.5}$ at Surte and mass of accumulation mode particles (dM 100–368 nm) at Surte) and $PM_{2.5}$ elemental concentrations sampled at the roadside station in Surte (N=21). Significant correlations ($p<0.05$) are marked in bold.*

	Site	$PM_{2.5}$, Femman	$PM_{2.5}$, Surte	dM 100–368 nm, Surte
$PM_{2.5}$	Femman	1	**0.55**	**0.58**
$PM_{2.5}$	Surte	**0.55**	1	**0.50**
dM 100–368 nm	Surte	**0.58**	**0.50**	1
S	Surte	**0.59**	0.17	**0.56**
Cl	Surte	-0.33	-0.01	**-0.58**
K	Surte	**0.54**	0.19	**0.48**
Ca	Surte	**0.56**	0.10	0.36
Ti	Surte	0.28	-0.21	**0.42**
V	Surte	**0.50**	0.09	**0.47**
Mn	Surte	0.38	-0.11	**0.45**
Fe	Surte	0.31	-0.13	0.30
Ni	Surte	**0.53**	0.00	**0.52**
Cu	Surte	0.20	-0.19	0.27
Zn	Surte	0.25	-0.15	0.28
Br	Surte	**0.45**	0.01	**0.51**
Sr	Surte	**0.63**	0.29	**0.47**
Pb	Surte	0.38	0.06	**0.51**

Differences in mass and number concentration, which are due to differences in traffic patterns (workdays and weekends) and differences in regional pollution events (Nordic/Marine air masses v. continental/UK air masses), are presented in Table 4.2. For the mass measures of $PM_{2.5}$ at Femman and Surte, as well as for the mass of the accumulation mode particles, significant differences were found between different LRT air masses, but no differences were found with different degrees of traffic intensity. The effect of traffic intensity or air mass types on the roadside elemental concentrations was mostly non-existent. For the number concentration of the ultrafine particles, a significant difference was found between high and low traffic days, but not between different air masses.

Table 4.2. *Differences in mass and number concentrations (dN) between workdays and weekends, clean and polluted air, and clean and polluted air on workdays only, using Wilcoxon's rank sum test. Significant differences ($p<0.05$) are marked in bold.*

	Workdays (N=15) v. weekends (N=6)	Nordic/Marine (N=9) v. continental/UK (N=12)	Workdays Nordic/marine (N=7) v. workdays continental/UK (N=8)
$PM_{2.5}$ Femman	0.423	**0.020**	**0.032**
$PM_{2.5}$ Surte	0.340	**0.010**	**0.017**
dM 100–368 nm	0.903	0.063	0.077
dN 10–100 nm	**0.020**	1.000	0.955

There is diurnal variation in the number concentration of ultrafine particles. In Figure 4.1 we present mean hourly number concentrations of ultrafine particles under various conditions (adopted from Figures 3 and 4 in Paper I). Higher concentrations were found during workdays than on weekends and a morning rush-hour peak is visible (Figure 4.1a). During the afternoon rush hour (around 16:00−18:00) no peak was found. When comparing high and low wind speed situations (Figure 4.1b) a more pronounced difference was found at low wind speeds. A concentration peak was also seen in the afternoon rush hour, although it was weaker than the morning peak. The influence of the wind direction can be seen in Figure 4.1c. The data were split between winds coming from the road towards the sampling station, named "traffic sector (TS)" winds, and wind blowing away from the sampling station, named "non-traffic sector (NTS)" winds. As expected, winds from the road towards the sampling stations gave higher concentrations but the increase was not as pronounced at the rush-hour events as for the low wind speed events. The diurnal pattern of low wind speed occasions is presented in Figure 4.2. It is evident that low wind speeds were more frequent during the night and morning rush hour than during daytime and the afternoon rush hour.

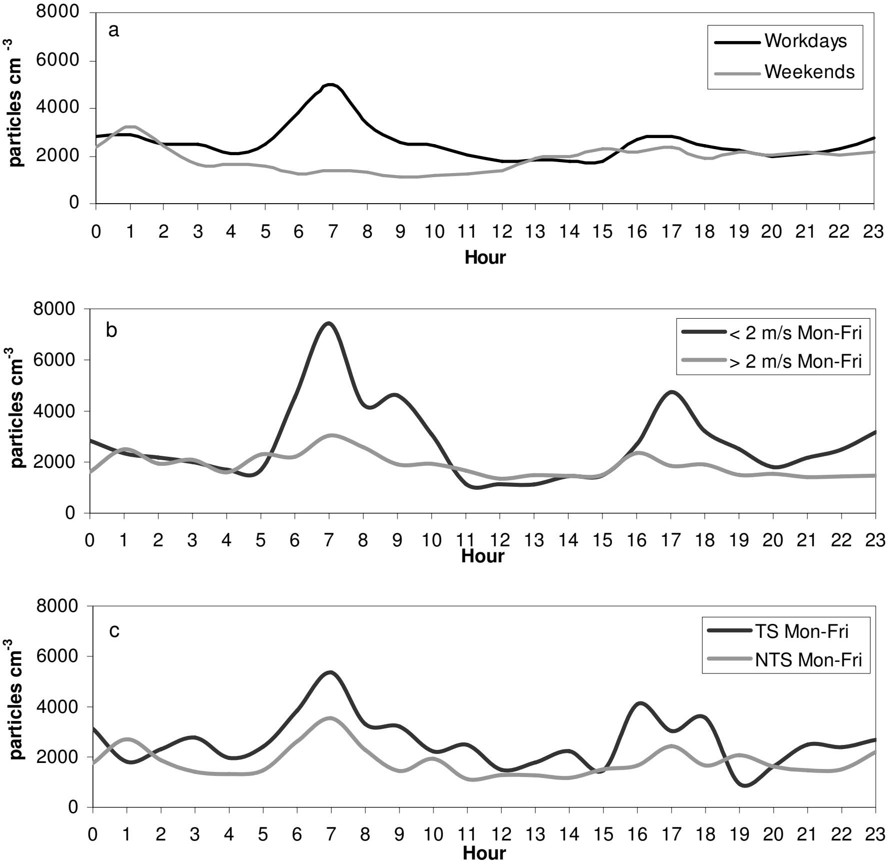


Figure 4.1. *Mean hourly number concentrations of ultrafine particles under various conditions.* ***a:*** *workdays and weekends;* ***b:*** *at low and high wind speed; and* ***c:*** *with the wind direction from the traffic sector (TS) or not (NTS).*

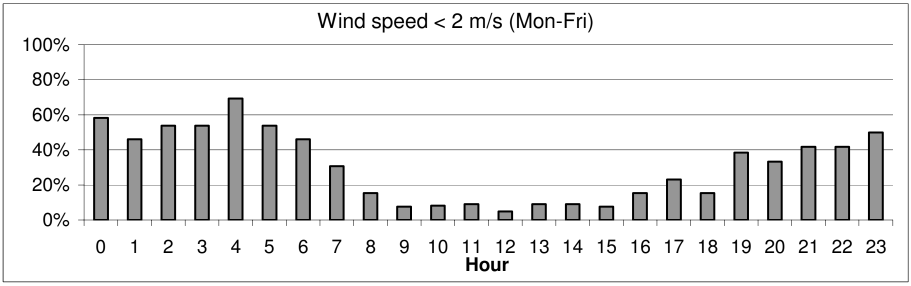
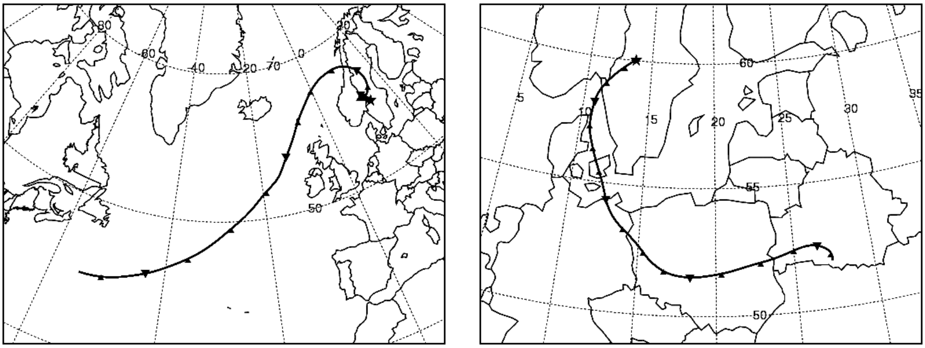


Figure ***4.2.*** *Hourly variation of low wind speeds during workdays.*

4.2. Paper II

Wood-smoke particles from domestic wood burning made statistically significant contributions of K, Ca and Zn to both personal exposure and indoor concentrations. The median levels of these elements were 66–80% higher for the wood-burning group compared with a reference group living in the same area. Some other elements, Cl, Mn, Cu, Rb, Pb and BS, were found to be possible wood-smoke markers, though not always to a statistically significant degree for personal exposure and indoor concentrations. The personal exposure was generally higher than the indoor levels and the correlations between personal exposure and corresponding indoor levels were good (r_s 0.48–0.94). High correlations (r_s>0.7) were seen for $PM_{2.5}$, BS, S, K, Zn, Br and Pb. The correlations between the outdoor and personal or indoor levels were, however, generally weak except for outdoor S and $PM_{2.5}$ levels which were highly correlated with both personal S exposure and indoor S levels (r_s>0.8). The infiltration of ambient particles indoors was calculated using the ratio between matched indoor and outdoor S concentrations and was found to be 0.5 (95% confidence interval (CI) 0.38–0.59).

Two types of air masses dominated during the study period (see Figure 4.3): air masses coming from the North Atlantic bringing in clean but Cl-rich air, and air masses coming from continental Europe and carrying elevated concentrations of elements attributed to industry and combustion processes (S, V, Ni, Br and Pb). In Figure 4.3 the mean concentrations of $PM_{2.5}$ and some elements are presented. The differences in ambient concentrations between the two types of air masses were large for these elements.



$PM_{2.5}$ = 6.5 µg m^{-3} S = 290 ng m^{-3}
Cl = 110 ng m^{-3} Pb = 4.8 ng m^{-3}
Number of days = 4

$PM_{2.5}$ = 22 µg m^{-3} S = 3700 ng m^{-3}
Cl = 43 ng m^{-3} Pb = 15 ng m^{-3}
Number of days = 4

Figure 4.3. *The two main trajectory types during the study period, with corresponding mean ambient concentrations of $PM_{2.5}$, S, Cl and Pb. The marine trajectory is shown to the left and the continental trajectory to the right.*

4.3. Paper III

Personal exposures to $PM_{2.5}$ comprising Cl, Ca, Ti and Fe were significantly higher compared with indoor, residential outdoor and urban background levels (Table 3, Paper III). Residential indoor levels were significantly higher than the corresponding outdoor levels for Ti and Cu, but lower for Br and Pb. Residential outdoor levels were higher than urban background levels for all elements and the differences were significant for most elements (Table 3, Paper III). Spearman correlations between personal $PM_{2.5}$ exposure and indoor, residential outdoor and urban background levels (Figure 1, Paper III) have been reprinted in colour and are presented in Figure 4.4. The associations varied between elements, from relatively high (r_s = 0.47—0.81) for Zn, Br (not shown in the Figure) and Pb, to no correlation at all for Ca and Cu (not shown in the Figure).

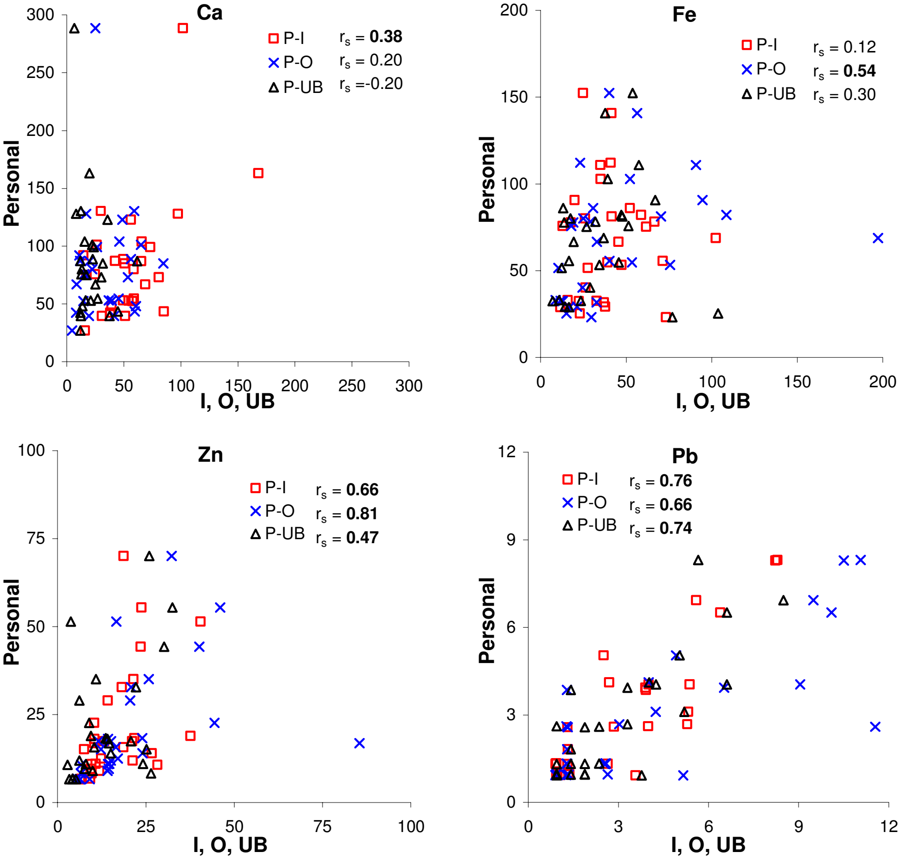


Figure 4.4. *Figure 1 in Paper III, reprinted in colour. Concentrations of Ca, Fe, Zn and Pb (in ng m^{-3}) in personal $PM_{2.5}$ exposure (P) v. indoor (I), residential outdoor (O) and urban background (UB) levels. Significant correlations are marked in bold. Note: For Ca, one high personal exposure (670 ng m^{-3}) and its corresponding indoor, outdoor and urban background values (450, 28, and 9 ng m^{-3}, respectively) are not shown in the graph.*

In Figure 4.5 the correlations between pairs of PM_1 and $PM_{2.5}$ samples for personal exposure and indoor and residential outdoor levels have been reprinted in colour from Figure 2 in Paper III. High correlations ($r_s \geq 0.75$) at all locations were found for Pb and moderate correlations were found for K ($r_s = 0.58–0.71$) (not shown in the Figure). For Br ($r_s = 0.86$) (not shown in the Figure) and Zn, correlations were high only outdoors. Weak correlations were found for Ca and moderate correlations were seen for Fe indoors and outdoors. The median $PM_1/PM_{2.5}$ ratios for mass and some selected elements are presented in Figure 4.6. For the pairs of parallel $PM_{2.5}$ and PM_1 personal, indoor, and outdoor measurements, only Ca and Fe levels were significantly higher for $PM_{2.5}$ than for PM_1 at all locations (Table 4, Paper III).

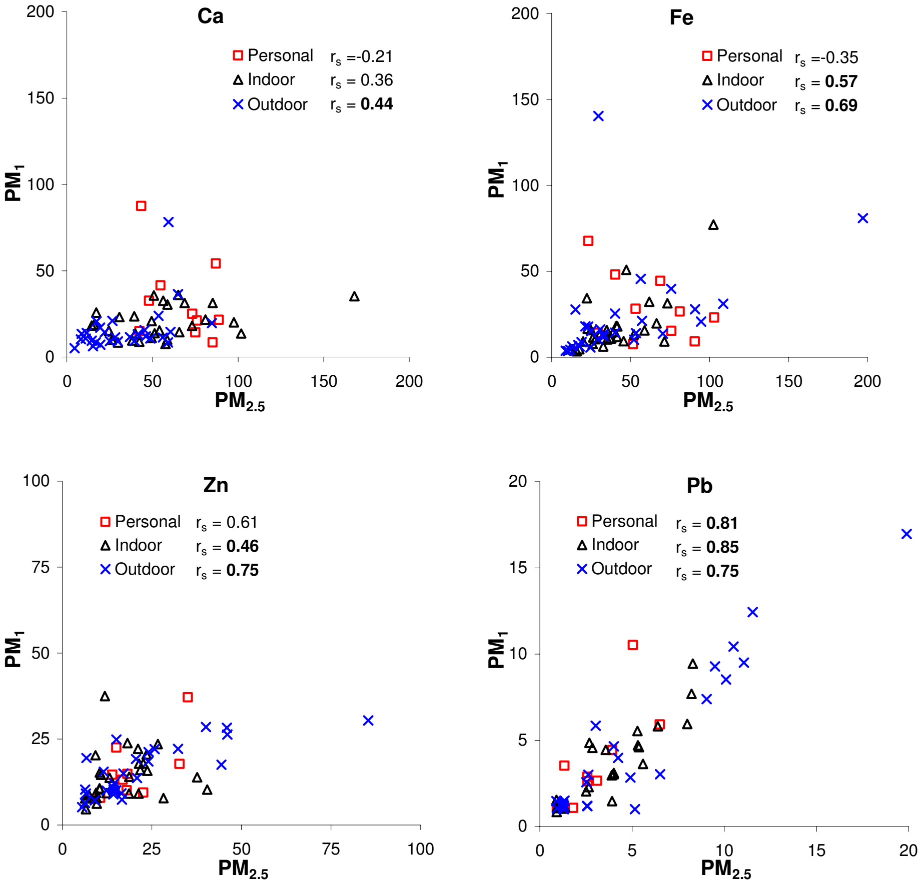


Figure 4.5. *Figure 2 in Paper III, reprinted in colour. The Figure shows concentrations of Ca, Fe, Zn and Pb in PM_1 v. $PM_{2.5}$ (in ng m^{-3}) at different locations. Significant correlations are marked in bold.*

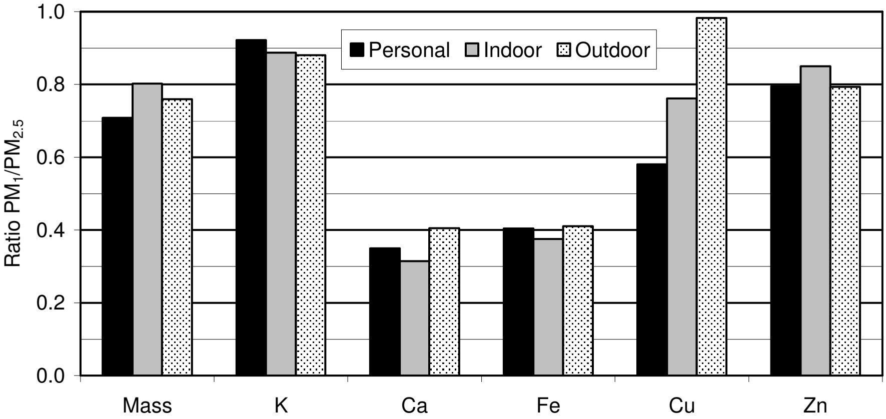


Figure 4.6. *Median ratios between pairs of $PM_1/PM_{2.5}$ samples for the personal exposure (N=10), indoor (N=30) and residential outdoor levels (N=29).*

The correlations between the urban background $PM_{2.5}$ mass, which measure is commonly used to monitor exposure, and the personal exposure to selected elements were statistically significant for S, Ti, V, Fe, Zn, Br and Pb (Table 4.3).

Table 4.3. *Spearman correlation between $PM_{2.5}$ urban background mass and $PM_{2.5}$ personal elemental exposure. Significant correlations are marked in bold.*

	S	Cl	K	Ca	Ti	V	Fe	Ni	Cu	Zn	Br	Pb
Urban background mass	**0.70**	0.07	0.16	0.31	**0.40**	**0.70**	**0.51**	0.09	-0.37	**0.54**	**0.59**	**0.40**

Air mass back trajectories were computed using the NOAA ARL HYSPLIT model to investigate the effect of long-range transported pollution (see Figure 3, Paper III). The origin of the sampled air strongly affected the measured urban background concentrations of many elements. Some differences between air masses were even large enough to be statistically significant also in the personal exposure and/or indoor levels (Table 4.4). Mean increases between low and high concentration air masses were in the range of 1.7–3.6 times for these elements for both indoor and personal exposures.

Table 4.4. *Statistically significant differences between trajectories for the trace elements at the urban background station (U), indoors (I) and for the personal exposure (P) are marked by the abbreviations U, I and P.*

Trajectories	S	Cl	V	Ni	Br	Pb
Nordic v. continental	U I		U P	U	U	U I P
Nordic v. marine		U	U	U		
Nordic v. UK	U		U I P	U I		
Continental v. marine	U	U I			U	U P
Continental v. UK		P	U			
Marine v. UK	U P	U				

4.4. Paper IV

The median outdoor levels of most elements were similar for homes and schools, while preschools tended to have lower levels. This general pattern was reproduced indoors, although some elements tended to deviate from the pattern (see Table 2, Paper IV). Significantly lower indoor than outdoor concentrations of S, Ni, Br and Pb were found at all locations, while only Ti was higher indoors at all locations (Table 3, Paper IV).

Three different communities representing the city centre, a suburban city area and a background area within the Stockholm metropolitan area were investigated. There were no differences between the city centre and the suburban city area but sampled sites in the city centre and in the suburban city area showed higher outdoor levels for all elements compared with sites in the background area, with similar differences for homes, schools and preschools (Table 4, Paper IV). Homes in the two more central areas showed significantly higher outdoor levels of Ca, Mn, Fe, Ni, Cu and Zn and preschools showed significantly higher outdoor levels of elements of crustal origin (Ca, Ti and Fe) compared with preschools in the background area.

Table 4.5. *Correlations between outdoor $PM_{2.5}$ levels and elemental concentrations. Significant correlations are marked in bold.*

	Homes (N=35)			Schools (N=20)			Preschools (N=20)		
	Total	Winter (N=13)	Spring (N=22)	Total	Winter (N=8)	Spring (N=12)	Total	Winter (N=10)	Spring (N=10)
S	**0.85**	**0.74**	**0.89**	**0.74**	0.40	**0.79**	**0.56**	**0.73**	-0.41
K	**0.90**	**0.86**	**0.90**	**0.86**	**0.95**	**0.83**	**0.72**	**0.73**	0.50
Ca	**0.67**	0.40	**0.72**	**0.68**	0.52	**0.68**	**0.46**	0.41	0.56
Ti	**0.59**	**0.57**	**0.55**	**0.51**	0.62	0.49	**0.49**	0.60	**0.70**
V	**0.84**	**0.81**	**0.80**	**0.45**	0.40	0.52	**0.73**	**0.90**	0.48
Cr				0.36	0.26	0.34	0.09	-0.45	**0.89**
Mn	**0.78**	**0.71**	**0.76**	**0.74**	0.52	**0.71**	**0.66**	0.50	**0.78**
Fe	**0.68**	**0.57**	**0.69**	**0.74**	**0.74**	**0.64**	**0.70**	**0.66**	**0.64**
Ni	**0.85**	**0.90**	**0.81**	**0.61**	0.59	**0.62**	**0.60**	0.32	**0.71**
Cu	**0.51**	**0.71**	0.41	**0.45**	**0.74**	0.27	**0.56**	0.36	**0.77**
Zn	**0.83**	**0.84**	**0.86**	**0.46**	0.67	0.40	**0.75**	0.32	**0.93**
Br	**0.89**	**0.76**	**0.94**	**0.76**	0.55	**0.82**	**0.64**	**0.65**	0.22
Pb	**0.85**	**0.72**	**0.91**	**0.72**	0.33	**0.86**	**0.77**	0.62	0.37

Significant correlations were found between $PM_{2.5}$ mass and all elements except Cr in all microenvironments (Table 5, Paper IV). By contrast, NO_2 was significantly correlated only to Cu and Zn in all microenvironments. In Table 4.5 correlations for winter and spring separately is also presented, which was not done in Table 5 in Paper IV. For $PM_{2.5}$ at homes (Table 4.5), correlations for winter and spring were similar for most elements, while at schools and preschools differences between seasons were found for many elements. For NO_2, on the other hand, seasonal differences were found at preschools and homes, with significant correlations only in spring for many of the elements (data not shown). Indoors, similar associations as outdoors were found between the trace elements and $PM_{2.5}$ mass while generally no associations were found for NO_2 (data not shown).

The infiltration of outdoor particles indoors was calculated as the ratio between matched indoor and outdoor concentrations of both S and Pb, for homes, schools and preschools separately. The median infiltration ratios for S were 0.61, 0.53 and 0.69 for homes, schools and preschools, respectively (Table 6, Paper IV). Corresponding values for Pb were 0.70, 0.59 and 0.70.

The median air exchange rates for homes, schools and preschools were 0.6, 1.2 and 1.2, respectively. No significant associations were found between the air exchange rate and the infiltration indoors for S or Pb at any location or season except for S at homes during winter (Figure 2, Paper IV). The exchange rates at the homes (range 0.2–1.3) were evidently lower than for schools and preschools (0.4–3.5 and 0.3–5.8, respectively).

5. Discussion

Elemental concentrations of ambient fine particles in the studies presented in this thesis were generally lower than the mean concentrations for central European cities, but similar to the Nordic cities presented for central urban monitoring sites in 20 European cities (Götschi et al., 2005). Some exceptions to this general pattern exist and the most noteworthy is the very high concentration of S in Hagfors, similar to the high concentrations in the northern Italian cities of Pavia, Turin and Verona (Götschi et al., 2005). Probable reasons for this finding are that measurements in Hagfors were conducted during a winter month (compared with the yearly mean for the Italian cities) and that a high frequency of the air masses originated from central and Eastern Europe where S-rich fuel is common (Isakson, 1998).

5.1. Personal exposure and indoor and outdoor levels of trace elements

Personal exposure and indoor and outdoor levels of trace elements were measured in Hagfors (Paper II) and in Göteborg (Paper III), while only indoor and outdoor levels were measured in Stockholm (Paper IV). The personal exposures among the reference group in Hagfors (Table 2, Paper II) and the personal exposures in Göteborg were similar for many elements. Higher exposures were, however, found in Göteborg for Ca, Ti, Fe and Cu, elements often associated with resuspended dust and brake wear. Higher exposures were found among the reference group in Hagfors of combustion and long-range transport-related elements, S, K and Pb. Higher indoor levels of the same elements, Ca, Ti, Fe and Cu, were found in Göteborg and Stockholm compared with the indoor levels for the reference group in Hagfors. Only S and Ni were higher indoors in Hagfors. A comparison of personal exposure and indoor levels in the studies (Table 4, Paper II, and Table 3, Paper III) showed statistically significant differences in both studies for only Ca and Fe.

Indoor and outdoor levels in Hagfors (Paper II) are not readily comparable with those in Göteborg and Stockholm (Papers III–IV) since the measurements in Hagfors were dominated by large ambient differences due to long-range transport of pollutants and were performed during winter conditions with full snow cover. In addition, the indoor concentrations of many elements were affected by domestic wood burning. Consequently only S was found to have a significant indoor-outdoor correlation in Hagfors. In homes in Göteborg and Stockholm significantly higher indoor levels were found for Ca and Cu in both studies. In addition, significantly higher indoor concentrations of K and Ti were found in Stockholm while these elements were higher but not significantly in Göteborg. Most of these elements are abundant in soil (Jaenicke and Schütz, 1988) and are therefore enriched indoors by transport of soil on shoes and later resuspended by indoor activities. The significantly lower indoor levels found for Br and Pb in both cities were expected since these elements are largely of long-range origin and therefore indoor concentrations were of ambient origin. In the homes in Stockholm some additional elements were found to have significantly higher outdoor concentrations, namely S, V and Ni (from long-range and combustion processes) and Mn, Fe and Cu (from non-tailpipe, traffic-related emissions).

Indoor and outdoor concentrations in schools and preschools cannot be compared directly with the samples in homes since the sampling schedules were different (schools and preschools were sampled during daytime on weekdays only). None the less, some characteristics were similar to those seen in homes. Significantly lower indoor levels were found for S, Ni, Br and Pb in both schools and preschools while only Ti (and Ca in schools) was significantly higher indoors.

A few other studies have presented data on elemental concentrations for both personal exposure and indoor and outdoor levels of fine particles. These were performed in Amsterdam and Helsinki (Janssen et al., 2005), New York (Kinney et al., 2002), Oxford (Lai et al., 2004) and Seattle (Larson et al., 2004), while in a study performed in Basel (Oglesby et al., 2000) only personal exposure and outdoor levels were sampled. The mean personal exposure and indoor and outdoor levels in these studies together with the levels in Papers II–IV are presented in Tables 5.1–5.3. Comparing results between different studies can often be difficult and caution must be taken since results are from different seasons, different types of samplers and different analytical instruments. None the less, some differences between the other studies and the ones in Sweden are noteworthy. In New York (Kinney et al., 2002) very high personal exposures to Fe, Ni and Pb were presented but no indoor or outdoor levels explained these results. No similar features were seen in any of the other studies and the authors suggest that some personal activity or microenvironments outside the homes may have been responsible. In Basel (Oglesby et al., 2000) both personal exposure and outdoor levels were higher than levels of $PM_{2.5}$ and all elements presented in the other studies, most likely due to a strong, and constant, influence of industry and combustion processes. The personal exposures in Oxford (Lai et al., 2004) were high for S, Cl, K, Ca and Cu but corresponding indoor levels suggested indoor sources and, in the case of S, also an infiltration of ambient pollution. The other sites, Seattle, Amsterdam and Helsinki, had more similar levels to Papers II–IV and where differences existed they may be explained by local conditions or seasonal effects.

Table 5.1. *Summary of the mean personal exposures to $PM_{2.5}$ ($\mu g\ m^{-3}$) and selected elements ($ng\ m^{-3}$) from some recent studies.*

	New York		Basel	Oxford	Seattle	Amsterdam	Helsinki	Hagfors	Göteborg
	Kinney et al., 2000		Oglesby et al., 2000	Lai et al., 2004	Larson et al., 2004	Janssen et al., 2005[a]		Paper II, ref. group	Paper III
	Winter	Summer	Full year	Full year	Sept.–May	Nov.–June	Nov.–Apr.	Feb.–Mar.	Spring + autumn
$PM_{2.5}$	17	18.5	23.7	17.4	10.5	14.5	9.4	16	11
S	947	1,100	2,700	1,500	289	910	600	870	
Cl				660	248	41	9.8	170	270
K	80	59	400	360	57	87	103	160	140
Ca	129	70	296	320	72	73	68.5	54	110
Ti	4.75	4.14		7.3	4			4.7	11
V	6.56	3.81		1.9				2.7	4.7
Fe	633	519		96	63	57	42	58	68
Ni	49.6	17.3		16	0			1.6	4.2
Cu	10.5	8.5		130	3	5.4	4.3	4.9	10
Zn	80.3	76.6		24		13	12	27	21
Br			8.1	6.7	3			1.2	2.0
Pb	16.1	88.85	22.9	30	2			5.0	2.9

[a] Median concentrations.

Table 5.2. *Summary of the mean indoor concentrations of $PM_{2.5}$ ($\mu g\ m^{-3}$) and selected elements ($ng\ m^{-3}$) from some recent studies.*

	New York		Oxford	Seattle	Amsterdam	Helsinki	Hagfors	Göteborg	Stockholm
	Kinney et al., 2000		Lai et al., 2004	Larson et al., 2004	Janssen et al., 2005[a]		Paper II, ref. group	Paper III	Paper IV, homes
	Winter	Summer	Full year	Sept.–May	Nov.–June	Nov.–Apr.	Feb.–Mar.	Spring + autumn	Dec.–June
$PM_{2.5}$	20.9	19	17.3	10.3	14	9.8	14	9.7	10
S	983	1,230	1,500	289	1,100	810	770		400
Cl			570	173	59	32	170	220	
K	84	64	290	54	95	110	160	140	170
Ca	92	54	170	46	66	45	26	69	76
Ti	2.94	3.46	3.7	3			4.0	8.0	9.0
V	9.49	4.17	1.8	1	2.7	4.5	2.7	4.5	3.1
Fe	84	95	48	35	58.5	42.5	31	39	70
Ni	31.6	12.6	14	0	1.4	1.9	9.1	4.6	1.1
Cu	7	10.3	99	4	8.1	5.5	1.9	9.8	13
Zn	121	86.2	20		16	12	21	17	16
Br			4.9	2			1.0	1.8	2.0
Pb	22.4	5.83	22	2			4.8	3.2	3.4

[a] Median concentrations.

Table 5.3. *Summary of the mean outdoor concentrations of $PM_{2.5}$ ($\mu g\ m^{-3}$) and selected elements ($ng\ m^{-3}$) from some recent studies.*

	New York		Basel	Oxford	Seattle	Amsterdam	Helsinki	Hagfors	Göteborg	Stockholm
	Kinney et al., 2000		Oglesby et al., 2000	Lai et al., 2004	Larson et al., 2004	Janssen et al., 2005[a]		Paper II, ref. group	Paper III	Paper IV, homes
	Winter	Summer	Full year	Full year	Sept.–May	Nov.–June	Nov.–Apr.	Feb.–Mar.	Spring + autumn	Dec.–June
$PM_{2.5}$	11.9	13.6	19	9.1	12.7	16	11	14	7.8	9.5
S	840	1,760	3,200	1,600	468	1,300	1,400	1,900	640	610
Cl				590	75	73	44	74	200	
K	44		312	130	78	70	94	140	82	91
Ca	65	47	94	33	36	40	36	18	34	40
Ti	2.45	3.54		1.4	3			1.7	6.3	6.7
V	7.68	4.62		–	2		7.2	1.5	5.5	3.5
Fe	107	114		29	61	71	79	83	45	94
Ni	32.3	11.7			1	1.7	3.2	1.1		1.4
Cu	6	12.6		3.4	2	2.5	1.8	2.5	2.6	4.2
Zn	35.8	34.8		18		18	19	68	22	18
Br			7.6	3.4	3			2.7	2.0	2.7
Pb	6.96	6.61	23.5	14	5			9.4	4.6	4.5

[a] Median concentrations.

5.2. Personal exposure v. indoor and outdoor levels

Median personal exposures tend to be higher than corresponding indoor levels for most elements although the difference is not always statistically significant. The elements that were significantly higher in the personal exposure in Papers II and/or Paper III were mostly of crustal nature and could be attributed to transport of soil from outdoors. Similar results, with higher estimates for personal exposure of this group of elements compared with indoor and outdoor levels, have been found by others (Kinney et al., 2000; Lai et al., 2004; Larson et al., 2004). The reason for the higher personal exposure is most likely indoor activities, both movement and other activities such as cooking. It has been shown that the increases in the "personal cloud" due to indoor activities v. the indoor concentration are of the order of 50–100% for most elements (Ozkaynak et al., 1996). The correlations between personal exposure and indoor levels varied between different elements and also somewhat between the two studies (Papers II and III). The highest correlations in both studies were generally found for elements of outdoor origin (S and Pb), while for elements with indoor sources, lower or weak correlations were found.

The higher personal exposure compared with outdoor levels for most elements except those of outdoor origin (e.g. S, V and Pb) was in line with results reported by others (Janssen et al., 2005; Larson et al., 2004; Oglesby et al., 2000). With regard to personal exposure v. indoor levels, the highest and most persistent correlations between personal exposure and outdoor levels (residential or urban background) were found for S and Pb, which are mostly of LRT origin with no indoor sources (Janssen et al., 2005).

The elements that were found to have significantly higher indoor v. outdoor concentrations throughout this work were Ca and Ti. Both are known to have either primary indoor sources (IARC, 1989) or to be resuspended by indoor activities (Koutrakis et al., 1992). Copper was found to be significantly higher in homes in Göteborg and Stockholm, but not in schools and preschools nor in the homes of the wood-burning community (neither among users of wood burners nor among the reference group). Suggested indoor sources and activities related to Cu are cooking and frying (See and Balasubramanian, 2006) (using Cu-containing pots and frying pans) and use of electrical appliances (e.g. vacuum cleaners and hairdriers). These are not applicable to schools or preschools, since none of these activities occurred there during daytime when sampling was conducted. Higher outdoor levels were only found for elements attributed to long-range transport, S, Br and Pb. Other studies report similar findings (e.g. Janssen et al., 2005; Larson et al., 2004).

5.3. Impact of domestic wood burning

The elements that were found to be significantly higher among the wood-burning group than among the reference group, with regard to both personal exposure and indoor levels, K, Ca and Zn, had a relative increase of 66–80%. This corresponds to median concentration differences of 94, 34, and 16 ng m^{-3} for personal exposures, and 83, 34, and 10 ng m^{-3} for indoor levels for these elements. Some other elements, Cl, Mn, Cu, and Rb, showed significant differences between wood burning and non-wood burning in personal exposure or indoor levels. For Pb, the differences were nearly significant for personal exposure, while for BS, the differences were nearly significant in both cases. The relative increases for users of wood burners in both personal exposure and indoor levels of these elements averaged 61%. All these elements are mentioned in the literature as being present in particles originating from biomass burning (Harju et al., 1997; Hedberg et al., 2002; Khalil and Rasmussen, 2003; Moloi et al., 2002; Selin et al., 1993). In a controlled exposure study of human exposure to wood smoke Sallsten et al. (2006) found considerably increased levels of many of these elements during the wood smoke sessions. The elements K, Zn, and Cl dominated, with a 50-fold increase in Zn levels compared with clean air.

The ratio between K and Ca is sometimes used to indicate the influence of biomass burning. Hedberg et al. (2002) state that the K/Ca ratio could be used to separate biomass emissions from traffic emissions. They state that the ratio for wood burning is 64 (range 30–330), while in background air it is about 2, and for traffic, it is around 0.8. Sallsten et al. (2006) found a ratio of about 30 in their exposure study. In the study in Hagfors, the mean K/Ca ratios found were 3.3 for the personal exposure, 8.9 for indoor levels and 9.3 outdoors, the results being similar for the wood-burning and the reference group.
In Göteborg (Paper III) and Stockholm (Paper IV) the ratios were in the range of 1.3–2.5 for personal exposure, indoor and outdoor levels, i.e. similar to background air (Hedberg et al., 2002). Care must, however, be taken when comparing these ratios since resuspension of indoor dust can be a significant indoor source of Ca (Koutrakis et al., 1992) and Ca is enriched in the personal cloud (Ozkaynak et al., 1996). The outdoor ratio on the other hand is not greatly affected by other sources since during the sampling period there was full snow cover and therefore no risk of resuspension of dust. In a study performed during the same winter in Växjö, Sweden, where about two-thirds of the domestic heating is achieved by biomass incineration, an outdoor K/Ca ratio of 8 was found (Selin Lindgren et al., 2006), similar to the results in Paper II.

5.4. Infiltration

Both S and Pb are suitable elements for calculating the infiltration of fine outdoor particles indoors since generally neither element has any indoor sources. The calculated median ratios of the indoor infiltration of ambient particles in Papers II—IV are presented in Table 5.4. Other studies have presented indoor/outdoor ratios for S or sulphate ranging from 0.6 to 0.9 (Geller et al., 2002; Janssen et al., 2005; Jones et al., 2000; Koistinen et al., 2004; Leaderer et al., 1999; Long and Sarnat, 2004; Sarnat et al., 2002; Wallace and Williams, 2005), with somewhat lower values found during winter than during the other seasons.

Table 5.4. *Median ratios of the indoor infiltration of ambient particles, calculated separately for sulphur (S) and lead (Pb).*

	Season	S	Pb
Hagfors	Winter	0.50	0.55
Göteborg	Spring and autumn	0.72	0.69
Stockholm, homes	Total (Winter, spring)	0.61 (0.47, 0.63)	0.70 (0.62, 0.70)
Stockholm, schools	Total (Winter, spring)	0.53 (0.36, 0.55)	0.59 (0.43, 0.64)
Stockholm, preschools	Total (Winter, spring)	0.69 (0.63, 0.90)	0.72 (0.63, 0.75)

Sweden has longer seasons of colder weather than do most countries, and Swedish homes are better insulated, with filtered ventilation systems that reduce the penetration factor of ambient particles. In the winter season the infiltration was lower owing to the need for energy conservation in buildings in boreal regions. The infiltration in Hagfors was similar to the winter values found for homes in Stockholm while schools had a lower infiltration ratio. A possible explanation is the presence of filtered mechanical ventilation in schools compared with natural draught ventilation in most homes, supported by the higher air exchange rates in schools compared with homes.

5.5. Spatial differences

In Paper IV the areas studied were the same as those studied in the impact of Traffic-Related Air Pollution on Childhood Asthma (TRAPCA) study (Cyrys et al., 2003; Emenius et al., 2003). They were Norrmalm in Stockholm's city centre, the municipalities of Solna and Sundbyberg located about 10 km NW of the city centre, and the municipality of Järfälla which lies about 25 km NW of the city centre. These areas are affected differently by local sources such as traffic, as presented by Emenius et al. (2003) for the traffic marker NO_2 and by Cyrys et al. (2003) for EC, BS and $PM_{2.5}$.

The elemental concentrations of outdoor fine particles in the two central areas were similar for almost all elements, while in the less densely populated area lower concentrations were found for many elements. The effect was most evident for Fe and Cu (with fourfold increases in the central areas) and Ca, Ti and Mn (with two- to threefold increases). A lower population density and the reduced traffic intensity can in part explain the lower concentrations in the background area. In addition, less densely populated neighbourhoods also have more green areas (private gardens and plantations) acting as deposition surfaces (i.e. particle traps) at the same time as having fewer particle sources. Episodes of high PM levels during spring are a well-known phenomenon in the Nordic countries (Omstedt et al., 2005). The main reason is thought to be that studded tyres break the surface of roads, which is brittle after the winter. Such road dust largely contributes to the coarse particle fraction (aerodynamic diameter larger than 2.5 µm), but an increase is also seen in the fine fraction. Traffic seems to be a strong factor for the spatial difference found, since vehicles emit exhaust particles, produce particles through tire-road wear and increase the resuspension of settled particles. In the present work, elements that had the most pronounced differences were those linked to these processes. For homes and preschools, the elements with statistically higher concentrations in the two central areas were mainly of crustal and road wear origin, probably caused by emissions of resuspended road dust due to the higher traffic intensity. Only elements that are strongly influenced by long-range transport showed no, or only weak, differences between areas. Similar results were seen in Cincinnati, OH, USA (Martuzevicius et al., 2004), where concentrations of a number of trace elements (Mn, Ni, Zn and Pb) decreased from the city centre to a suburban and rural area.

5.6. Roadside traffic emissions

The mean number concentration of roadside ultrafine (10–100 nm) particles was low compared with that reported in many similar studies (Harrison et al., 1999; Hitchins et al., 2000; Hughes et al., 1998; Morawska et al., 1999; Ruellan and Cachier, 2001; Ruuskanen et al., 2001; Vakeva et al., 1999) (see Table 4, Paper I). Some possible explanations for this low value are that (1) there are no other nearby sources, e.g. other roads, industries and parking lots; (2) the speed limit at Surte is 90 km/h, with a narrow speed distribution and no accelerations. Such conditions are favourable in terms of yielding low emissions from most vehicles. (3) In Sweden the sulphur content in diesel fuel was low already at the time of the study, viz. <10 ppm, in comparison with 350 ppm (the European content at the time), and sulphur content has an important impact on emissions of particles from vehicles (Palmgren et al., 2003; Wahlin et al., 2001). The current European directive stipulates use of low sulphur fuel for both gasoline and diesel (<50 ppm) from 2005 onwards and, furthermore, that sulphur-free fuel (<10 ppm) must be used by the year 2009 (European Parliament, 2003). (4) Finally, the lower size limit of the particle counter and its counting efficiency for the smallest particles may explain the low value in the present study compared with other studies.

The correlations between the mass and elemental concentrations (Table 4.1) clearly indicate that the local $PM_{2.5}$ concentration was not correlated to any of the analysed elements. However, a number of elements were indeed correlated to both urban background mass and the mass of accumulation mode particles. These elements, S, K, V, Ni, Br and Sr, are usually attributed to pollutants from combustion processes and industry, and are often long-range-transported. This suggests that the variation of $PM_{2.5}$ mass at the roadside is affected not by traffic but instead, by differences between different air mass origins. By comparing mass and number concentrations between different traffic patterns (workdays and weekends) and different regional pollution events (Nordic/marine air masses v. continental/UK air masses) further information can be obtained. The results presented in Table 4.2 illustrate that an association existed between the mass measurements of $PM_{2.5}$ at Femman and Surte, as well as the mass of the accumulation mode particles, and the different types of LRT air masses. No association was found with traffic intensity. When the number concentration of the ultrafine particles was used instead, a significant difference was found between high and low traffic days, but not between different air masses. All these results point to the fact that the freshly emitted traffic particles are a separate entity and must be measured and analysed separately and not as a part of the mass of PM_{10} or $PM_{2.5}$.

The highest concentrations of ultrafine particles from traffic were seen during morning rush hour and low wind speed conditions. The afternoon rush hour also produced a concentration peak, although it was weaker than the morning peak (Figure 4.1b). Winds from the road towards the sampling stations gave higher concentrations as expected, but the increase was not as pronounced at rush hour as for the low wind speed events. Low wind speed occasions were more common during the morning hours (see Figure 4.2). Also, the boundary layer height, i.e. the mixing height, is generally lower during morning hours.

The motorway E6 lies parallel to, and runs about 600 m west, of the RV45, with open fields between them. The mean weekday traffic density on the E6 at the time of the study was about 45,700 vehicles per day (Gothenburg Traffic Office, 2006), but this did not influence the sampled concentrations. It has been shown that with increasing distance, ultrafine particles rapidly decrease in particle number concentration and change in particle size distribution (Hitchins et al., 2000; Zhu et al., 2002).

5.7. Long-range transport

In the Nordic countries as in many other parts of the world, LRT particles are a major (and even dominating) source of the total particle mass concentration. Forsberg et al. (2005) estimate the average local contribution to PM_{10} to be about 30%, with it being somewhat lower in southern Sweden and up to around 50% in northern Sweden. This means that around 70% of the PM_{10} is of non-local origin, i.e. it is LRT pollution. Knowledge about where the sampled air originated and the path it has taken to reach the sampling area, and knowledge about the emission sources in different regions and about what elements (or species) are attributed to certain sources will enable us to estimate the contribution from different areas or types of emitters.

The air mass back trajectories computed in Papers I–III were classified as described in section 3.6. The general characteristics of the different classes (or source areas) are that Nordic air is typically clean, containing low $PM_{2.5}$ mass concentrations and low trace element levels. Marine air has high levels of sea salt particles (represented by high Cl levels) and elevated concentrations of V and Ni (from ship emissions), but low levels of other elements. Air masses from continental Europe typically have higher $PM_{2.5}$ mass than the other classes, with high levels of S, V, Ni, Br and Pb, all of which can be attributed to industry and combustion processes. Air masses passing over the UK have a mixture of marine and continental characteristics, with higher levels of S, V, and Ni and somewhat elevated levels of Cl, Br and Pb.

The mean ambient $PM_{2.5}$ concentrations for clean and polluted air masses were 4.5–6.5 $\mu g\ m^{-3}$ and 11–22 $\mu g\ m^{-3}$, respectively, in Papers I–III, corresponding to a two- to threefold increase in ambient concentration due to LRT pollutions. This corresponds well with the estimate made by Forsberg et al. (2005), which was that around 70% of the ambient PM_{10} was of long-range origin. For several elements that have sources related to a certain trajectory class, similar or larger differences can be found. The largest difference was found for S between air masses from continental Europe and marine air masses during the winter measurements in Hagfors (Paper II) where a 13-fold difference was found. In the two campaigns conducted during the warmer seasons, early summer (Paper I) and spring and autumn (Paper III), three- to sevenfold differences were found for S between different air masses. The emissions of S compounds have an annual variation, with higher emissions during winter (mainly in eastern continental Europe) due to the increased need for heating (EMEP, 2000; Simpson, 2006). The sea salt marker Cl had two to seven times higher concentrations during days with marine air compared with non-marine air, with the highest ratios in Göteborg for marine v. continental or Nordic air. For the other elements of combustion and industrial origin (V, Ni, Br and Pb), two to fivefold differences were found between clean and polluted air masses.

In Paper III the personal exposure and indoor levels of the elements were also classified and analysed by trajectory class (Table 4.4, section 4.3). Some of the differences between different air masses were large enough to be statistically significant for the personal exposure and/or indoor levels. Significant variations between air masses were found for S, V, Ni and Pb, which elements are associated with combustion processes, and for Cl particles, from sea salt. As could be expected, there were no differences between different air masses for elements of crustal origin. No other studies presenting data on the impact of air mass origin on personal exposure were found. A better understanding of how regional transport processes (and seasonal patterns) can influence personal exposure could be important for the design and interpretation of time series analyses of PM levels and short-term effects on health. It is also important in the context of estimating the contribution of local sources since the risk of misclassifying an exposure as being from a local source when it is of non-local origin, or vice versa, will be reduced.

5.8. Validity

Many factors can affect the results of a study and its conclusions. Are the sampling time, sampling points and/or subjects investigated representative? Are the sampled concentrations representative? What are the sensitivity and precision of the analytical techniques? And finally, how should the statistical analyses be interpreted?

The EDXRF spectrometer used in this work can detect all elements from about Si up to U (atomic numbers 14–92). However, with the EDXRF only total elemental concentration, but no speciation, can be obtained. The sensitivity is lower for the lighter elements (see Table 3.2). These elements are also most affected by the sample matrix, i.e. both the total amount of the collected mass (the general background level) compared with the concentration of the element and the concentration of elements with characteristic energy close to the target element (e.g. the Mn and Ni peaks close to the Fe peaks in Figure 1.8). This means that the LoD can vary between samples. In one sample it may be possible to determine a low concentration while in another sample a higher concentration may be below the LoD. Nevertheless, the repeatability of the instrument is high. For the spectrometer, the median analytical coefficient of variation (CV) for the elements was 5%.

The selection of subjects to be part of a study can bias the outcome and care must be taken in this regard. In Paper II, 78% of the available subjects using wood burning and 83% of the non-wood-burning individuals approached, agreed to participate in the study. The study was small but included different types of heating systems, which is normally the case in small communities. The results will not be seriously biased by the small percentages of drop-outs and it can be assumed that the subjects who participated in the study represent the population in the area of interest. In Paper III, however, besides the 20 randomly chosen subjects from the adult population in Göteborg, ten subjects were selected from the staff at our department. It can be questioned whether they also represent the general population. In another paper from the same study (Johannesson et al., 2006) no differences for PM mass were seen between the 20 subjects and the combined group of 30 subjects.

When comparing two groups using statistical tests to establish whether differences exist between the groups, the risk for Type I errors (a statistical difference when there is no real difference, also called “false positive”) increases if multiple significance tests are performed. In statistical textbooks this is referred to as “mass significance” and several methods have been proposed to deal with this problem (Altman, 1991). The disadvantage of these methods is that they are often “conservative”, meaning that they “overadjust”, with the result that the power decreases (i.e. there is a risk of concluding that there is no difference when in fact there is one). In this work the correction for mass significance was not used; instead, p-values are used in a more exploratory fashion when the results are discussed, as advocated by Rothman (1990). Since many elements have known sources this method can be used in the interpretation and conclusion. For instance, the elements S, V, Ni, Br and Pb are known to be of combustion or industrial origin and to be present in LRT particles. Significant differences between different air masses for a number (but possibly not all) of these elements indicate therefore that the differences are due to LRT pollutants from areas of known high emissions of these elements.

5.9. Implications for health studies

Throughout the work in this thesis it has been demonstrated that by measuring closer to the subjects of interest (i.e. personal or indoor sampling) and by complementing PM mass sampling with elemental analysis more information on the true exposure and different source contributions can be obtained.

Based on the results in Paper I, $PM_{2.5}$ concentrations will not necessarily be associated with the levels of ultrafine particles. The non-correlation between $PM_{2.5}$ and ultrafine particles calls for new practice in environmental aerosol measurements and restrictions.

Air mass origin can strongly affect the measured concentrations of a number of elements, not only outdoors but also in indoor and personal exposure. Air mass origin should therefore be taken into account in the description and interpretation of time series studies of air pollution and health in order to improve the knowledge about the local v. long-range contribution.

The high and consistent correlations between NO_2 and Cu found outdoors for all microenvironments and over both seasons studied (Paper IV) suggest that outdoor Cu may be a suitable elemental marker for traffic-related aerosols in health studies in areas without other significant outdoor Cu sources. Lead has traditionally been used as a marker of vehicle exhaust, but it is of less value today when most petrol is unleaded. Other elements related to traffic are Zn from tire wear, and crustal elements from road wear. Very high PM_{10} levels of resuspended road dust were reported in Stockholm during spring days with dry streets (Norman and Johansson, 2006), and the present study showed the highest associations for Cu with NO_2 levels during spring. Presumably other Nordic cities share similar features. Toxicological studies have suggested that transition metals such as V, Cr, Mn, Fe, Ni, Cu and Zn are PM components with toxic potential (Schlesinger et al., 2006). A number of these elements are abundant during dry street conditions, but not when streets are wet. NO_2 levels, by comparison, are not dependent on the wetness of the streets. Therefore, studies of short-term health effects of trace elements should preferably be performed in spring when the contrast between days may be high for these elements.

6. Conclusions

This thesis has demonstrated that elemental analysis is a useful method for better characterising human exposure to fine particles.

- Personal exposures were generally higher than both indoor and outdoor levels (residential outdoor or urban background) for several elements.

- Wood-smoke particles made statistically significant contributions of K, Ca, and Zn to both personal exposure and indoor concentrations.

  These elements are concluded to be good markers for wood smoke.

- The number distribution of freshly emitted traffic particles peaks in the size range 15–50 nm. The highest concentrations were seen during morning rush hour and under low wind speed conditions. Number or mass concentration did not correlate with $PM_{2.5}$, nor with accumulation mode particles.

  Freshly emitted traffic particles should therefore also be measured as a separate entity (preferably using particle counters) and not only as a part of PM.

- In children's environments (homes, schools and preschools), higher indoor levels of Ti were found, while LRT elements (S, Ni, Br and Pb) were higher outdoors. Lower concentrations outdoors of fine particle elements, mainly of crustal and traffic origin, were found in a detached area compared with urban Stockholm. For Fe and Cu, a fourfold increase was found and Cu was correlated with the traffic marker NO_2.

  Copper may be a suitable marker for non-tailpipe traffic-related particles in health studies.

- Long-range-transported particles strongly affected locally measured concentrations of a number of elements both indoors (S, Cl, V, Ni and Pb) and in personal exposure (S, Cl, V and Pb), with factors of 2–3 between days of clean LRT and polluted LRT air masses.

  The origin of LRT particles should be taken into account in the description and interpretation of time series studies of air pollution and health.

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