Mobile pollutant measurement laboratories - Spatial distribution and seasonal variation of aerosol parameters in the Zürich (Switzerland) and Minneapolis (USA) area

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MOBILE POLLUTANT MEASUREMENT LABORATORIES – SPATIAL DISTRIBUTION AND SEASONAL VARIATION OF AEROSOL PARAMETERS IN THE ZÜRICH (SWITZERLAND) AND MINNEAPOLIS (USA) AREA

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presented by

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This thesis presents mobile air pollution measurements as a novel way to measure and assess particulate air pollution in urban, suburban and rural areas. Increased particulate air pollution shows a significant potential for adverse health effects in the human airways. High levels of particulates are mainly found in urban and urban-influenced regions and are to a large extent attributable to increased traffic density in the last decades. Worldwide, federal agencies regulate particle emissions and ambient concentrations by means of aerosol mass concentration standards (aerosol: suspension of liquid or solid compounds in a gas, usually air). Commonly regulated parameters are PM10 and PM2.5 (particle mass concentration of particles with aerodynamic diameters smaller than 10 µm and 2.5 µm, respectively), which usually are monitored by a network of stationary measurements. Diesel engines contribute a major fraction to road traffic particulate emissions and typically produce major amounts of particles that are more than one order of magnitude smaller than 2.5 µm in diameter. On occasion of the project “Diesel Aerosol Sampling Methodology”, performed at the University of Minnesota (USA), real-world emissions from diesel engines were measured in mobile truck-chase experiments while driving on the road. The mobile emission laboratory (MEL) contained a variety of instruments for the physical characterization of aerosol particles in the 0.003 – 2.5 µm size range and was ideal for the measurement of highly dynamic vehicle exhaust plumes. Selected diesel trucks were followed and their exhaust was captured and analyzed a few seconds after its emission from the stack. Measured diesel particle number size distributions were typically characterized by a nanoparticle mode (d<50 nm, consisting of hydrocarbons and a small percentage of sulphuric acid and water, in most cases evaporating clearly below 300 °C), a diesel exhaust accumulation mode (80 nm <d<140 nm, “diesel soot”, i.e. agglomerates of elemental and organic carbon, coated with other condensable species like semi-volatile hydrocarbons, nitrates and sulfates) and a coarse mode (d>1 µm, particulate matter reentrained from the engine cylinders into the exhaust stream). The nanoparticle mode typically contained 1-20 % of the particle mass and more than 90 % of the particle number. The truck-chase experiments found that under ambient conditions large number concentrations of nanoparticles are formed, especially at cold ambient temperatures and at high average traffic speeds. They are rapidly formed by nucleation during the dilution and cooling of freshly emitted gaseous exhaust in the atmosphere. Hydrocarbons originating from engine lube oil and sulphuric acid from sulfur containing fuels are main gaseous precursors of primary ultrafine particles. Their lifetime is rather short (< 10 minutes in urban areas, corresponding to an area of influence of 100 m – 1 km). Both specific chase experiments and more general measurements in urban traffic showed that nanoparticles are not only produced by diesel vehicles, but also by mixed on-road traffic. Due to experimental conditions suppressing nanoparticle formation, the nanoparticle mode has hardly been observed in chassis dynamometer (test bench) measurements in the past. Therefore, chase experiments are an important complement to laboratory studies. Taking into account that they require highly time-resolved real-time instrumentation, combined condensation particle counter (CPC), photoelectric aerosol sensor (PAS) and diffusion charging sensor (DC) measurements have been shown to be a novel method for the determination of the relative fraction of nanoparticles in ambient air and the coating degree of combustion accumulation mode particles with condensable species. These three robust instruments have time resolutions lower than 10 seconds and are easy to use in field experiments.
At the Paul Scherrer Institute (PSI) another mobile pollutant measurement laboratory was constructed for highly time-resolved on-road ambient concentration measurements of a large set of gas phase, aerosol, geographical and meteorological parameters. During the project YOGAM (Year of Gas Phase and Aerosol Measurements) the spatial and temporal variation of fine (d<2.5 \mu m) and ultrafine (d< 100 nm) particles in urban, suburban and rural areas in the Zürich (Switzerland) area was assessed in 2001/2002 by means of on-road measurements along a specified route on 6-10 days per season. Particle background number concentrations (d>3 nm) were 35000 ± 30000 cm\(^{-3}\) (mean ± standard deviation) for urban regions and 15000 ± 12000 cm\(^{-3}\) for rural areas. Governed by meteorology (namely wind speed, wind direction, degree of vertical mixing and precipitation), the day-to-day variation was significantly larger than the spatial variation, but within one day a consistent regional pollution pattern was found. Freeway-influenced areas showed the highest background number concentrations (>80000 cm\(^{-3}\)), and peak concentrations from single vehicles easily reached 400000 cm\(^{-3}\). Agreeing with the results from the U.S. study, ambient particle number size distributions were mainly characterized by a combustion exhaust accumulation mode at d=80-140 nm with number concentrations depending on the distance to anthropogenic activity, and an ultrafine mode showing rather variable number concentrations. In urban areas, the ultrafine mode was dominated by combustion nanoparticles (d<50 nm) with an increased formation potential at low temperatures. These anthropogenic ultrafine particles are also defined as primary ultrafines. Contrastingly, levels of ultrafine particles were much lower in rural areas. Sporadic episodes with increased ultrafine particle levels during warm and sunny spring days suggested the presence of secondary ultrafine particles, i.e. products from gas-to-particle conversion after photochemical reactions in aged urban air plumes, or products from biogenic gaseous precursors. Concluding, the YOGAM mobile measurements have been shown to be suitable for long-term pollutant assessments, to obtain valuable information on spatial variability. Despite the fact that respective equipment currently lacks an official accreditation for legal use, both project described in this thesis support that future regulation of emissions and ambient aerosol concentrations will be required to not longer be solely based on mass measurements, but also on particle number or surface area concentration.
relativen Nanopartikelanteil eines Umgebungsaerosols und den Bedeckungsgrad von Dieselruss mit Kondensaten zu bestimmen. Alle drei Instrumente haben eine kleinere Zeitauflösung als 10 Sekunden und sind robust und handlich.

1 INTRODUCTION

1.1 THE ROLE OF PARTICULATE MATTER FOR ENVIRONMENT AND HEALTH

Anthropogenic air pollution is one of the major concerns in the sustainable development of our society. Starting from the worldwide industrialization in the mid-19th century, progresses in technology have resulted in an increased need for energy. The combustion of fossil resources in order to gain energy for manifold applications can be considered as major reason for the rapid increase of air pollution throughout the 20th century (for example automotive engineering and coal power plants). While there was evidence already in the 19th century that heavy indoor and outdoor air pollution is likely to lead to acute and chronic diseases (e.g. increased lung diseases among underground mine workers (US NIOSH, 1999)), the heavy smog episodes in London 1952, which caused approximately 4000 deaths for the first time revealed the tragic and dangerous potential of ambient anthropogenic air pollution and the importance of its regulation (Ministry of Health, 1954). Although the visible effects of particulate air pollution may seem more striking than for gaseous pollutants, environmental gas phase measurements and toxicological gas phase research was investigated in the 20th century with more emphasis than the corresponding research on particulate air pollution. Reasons for this may have been a better understanding of the toxicology of pollutant gases in the human body, but also the already relatively high-developed chemical detection methods that existed for gases, but not yet for particulates at this level.

Simultaneously to the increased efforts in air pollution research and regulation, the worldwide pollution levels increased for a large number of pollutant compounds, due to the broader use and accessibility of newly developed technology and the connected resource consumption. An important example is the rapid worldwide traffic development throughout the 20th century and the connected increase in pollutant emissions. Only in the last third of the century the knowledge gained by progresses in technology partly started to compensate for the environmental effects of the rapid global traffic development, when e.g. low-sulfur fuels were introduced and indeed helped to suppress a further increase in $\text{SO}_2$ ambient concentrations, or when the introduction of catalysts for gasoline cars triggered a reduction in $\text{NO}$ and $\text{NO}_x$ emissions. Also, the automotive industry started to equip diesel vehicles with particle traps in recent years, to reduce the emission of particulate matter (BUWAL, 2002a, b).

In the context of air pollution regulation, cost evaluations of anthropogenic air pollution have been performed by numerous national regulating agencies. It was soon recognized that particulate matter is a major contributor to adverse health effects caused by anthropogenic air pollution (see Chapter 1.4.1, Epidemiological studies). A study for Switzerland showed that 1996 totally 4.1 billion Euros of material and immaterial costs resulted from total particulate air pollution, whereof 2.2 billion Euros accounted for traffic-related air pollution (Seethaler, 1999; Künzli et al., 1999). In the United States, health costs for outdoor air pollution are estimated to be 40 – 50 billion USD per year (National Center for Health Statistics, 2001; Fuchs and Frank, 2002). A cost-benefit study found that between 1970 and 1990 totally 500 billion USD of compliance costs (including research and development) contrasted 22000 billion USD of estimated cost benefit by the Clean Air
Act program (U.S. Environmental Protection Agency, 1997). Of these 22000 Billions USD, approximately 16000 Billions are attributed to efforts in particulate matter (PM) research and regulation. Table 1.1 summarizes the current regulation standards for particulate matter in Switzerland, Europe and the United States. These standards are based on results from research on adverse health effects of particulate matter that has been performed in the last decades and also partly reflect different views on a suitable regulation of PM. While PM10 standards are set more conservatively in Europe, PM2.5 standards are currently only set in the US (see Table 1.1 for definitions).

Table 1.1: PM Regulation standards (U.S. Health Effects Institute, 2002).

<table>
<thead>
<tr>
<th>Time Period</th>
<th>PM10* ((\mu g \ m^{-3}))</th>
<th>PM2.5* ((\mu g \ m^{-3}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>Switzerland</td>
<td>Daily</td>
<td>50</td>
</tr>
<tr>
<td>Switzerland</td>
<td>Annual</td>
<td>20</td>
</tr>
<tr>
<td>EU</td>
<td>Daily</td>
<td>50</td>
</tr>
<tr>
<td>EU</td>
<td>Annual</td>
<td>20</td>
</tr>
<tr>
<td>USA (EPA)</td>
<td>Daily</td>
<td>150</td>
</tr>
<tr>
<td>USA (EPA)</td>
<td>Annual</td>
<td>50</td>
</tr>
</tbody>
</table>

*LRV98 (Luftreinhalteverordnung 1998)

b to be met in 2010

c under revision

*PM10/2.5: Particulate matter with an aerodynamic diameter smaller than 10 (2.5) micrometers

Despite the rapid advances in particulate matter research in the last decades, which have led to an advanced level of understanding in terms of the influence of aerosols on the environment, on climate and on human health, there still remain important open questions. While in the past decades the focus in ambient aerosol research and regulation was put on source-to-sink investigations of the particle mass, current research also involves extensive investigations on other parameters like particle number or particle surface (as it will be illustrated in this thesis) and size dependent chemical composition. For the future, a main challenge for aerosol research will be to contribute to new actions and technologies leading to a sustainable future, including the consideration of the needs of the modern society.

1.2 AEROSOLS. NOMENCLATURE OF PARTICLE SIZE RANGES

An aerosol is a suspension of liquid or solid compounds in a gas. The size of aerosol particles ranges from a few nanometers up to 100 micrometers. Some illustrative examples are pollens (10-100 \(\mu m\)), sea salt (1-10 \(\mu m\)), cigarette smoke (0.1-1 \(\mu m\)) or diesel soot (≈0.1 \(\mu m\)). To introduce the nomenclature that is currently used in atmospheric aerosol research for different particle size ranges being investigated in this thesis, Figure 1.1 shows an example size distribution for combustion aerosols, with its typical modes that are observed in the atmosphere.
There sometimes exists some inconsistency in the definitions shown in Figure 1.1. The limit between fine particles and coarse mode ranges from 1 to 2.5 micrometers, depending on the definition (Willeke and Baron, 1993; U.S. Environmental Protection Agency, 1996). The boundary of 50 nm for nanoparticles is widely in use, although different definitions may be found in literature. While in general ambient aerosol research the accumulation mode is often referred to as 100 – 1000 nm, it has become convenient in diesel exhaust research to describe size distributions in terms of their particle formation characteristics. Hence, diesel particle size distribution modes are often described (Kittelson et al., 2002) with the terms *nuclei mode* (particles with D = 5-50 nm or more recently 3-30 nm, formed by nucleation of new particles from the gas phase) and *accumulation mode* (D = 30-500 nm, i.e. diesel soot cores that are covered by condensed gaseous organics).

### 1.3 DIESEL PARTICULATE MATTER

Diesel technology has been patented by Rudolf Diesel in Germany in 1892. Similar to gasoline engines, diesel engines depend on internal combustion of a fuel to drive pistons that transfer energy to further mechanical power outlets. The main difference to gasoline engines is that the heat for diesel combustions is not a result from spark ignition, but from the compression of the fuel. Diesel fuel is less refined than gasoline and has got a higher energy content (Weinhold, 2002). The main reason why diesel vehicle emissions have been strongly connected to particulate air pollution concerns is the large emission of PM (commonly termed diesel soot) of vehicles that are not equipped with particle traps. PM
emissions from diesel vehicles without particle traps still are and still will be expected to be higher than for comparable gasoline vehicles in the near future. For an efficient reduction of diesel soot emissions, strong efforts have been made in the last years to reduce particle emissions, by developing effective diesel soot particle traps for heavy-duty and light-duty vehicles (BUWAL, 2000). Today, a variety of particle trap technologies are available and increasingly in use for passenger cars and machines in the off-road sector (BUWAL, 2002b). Despite these promising advances in soot reduction, the formation of particles ten times smaller (~10 nm) than diesel soot (~100 nm) during the dilution of both diesel exhaust and gasoline emissions emitted in the atmosphere has gained increasing attention in the last years. Particle traps cannot eliminate these particles, which show increased deposition efficiency in the human lung and therefore raise concerns about possible adverse health effects. Furthermore, PM is not the only pollutant species that has to be taken into account for comparing diesel with gasoline vehicles. Emissions of today’s diesel engines generally produce approximately three times more nitrogen oxides than gasoline engines (BUWAL, 2000). Comparing a diesel heavy-duty vehicle with a gasoline car equipped with a catalyst, the corresponding NOx emission ratio is larger than 10 (John et al., 1999). Efficient traps that eliminate both NOx and particles are under development but are not expected to be ready for serial use in the next few years. Finally, carbon dioxide emissions are generally slightly lower for diesel engines. The first part of this thesis will deal in more detail with the correct sampling and characterization of diesel exhaust in the atmosphere.

1.4 HEALTH EFFECTS OF PARTICULATE AIR POLLUTION

Next, special attention is given to adverse health effects of particulate matter, since these justify current efforts in ambient aerosol research. The fundamental question whether particulate matter in general and especially ultrafine particles show adverse health effects has been keeping the international research community busy in the last years and will equally be one main focus in upcoming years. It is a research effort that only can be achieved by interdisciplinary collaboration of epidemiologists, toxicologists and aerosol scientists. The complexity of this subject in general, and the relatively young age of this research field has so far given a lot of room for speculation and has non-surprisingly provoked manifold ways of interpretation of the experimental facts that have been collected so far. This section summarizes the most important and most recent research that has been performed to answer the lead question.

Epidemiological studies and laboratory studies with human volunteers and animals are two major approaches to study the effect of particulate air pollution on human health that have been used so far. They cover different aspects of the problem and hence complement each other. The disagreement in literature about the plausibility and causality of previously epidemiological work on adverse health effects of atmospheric particulate matter (Bates, 1992; Utell and Samet, 1993) triggered possibly a more intense toxicological and pathophysiological research on this topic (U.S. Health Effects Institute, 2001).
1.4.1 Epidemiological Studies

One of the probably most cited epidemiological studies is the Harvard Six Cities Study performed by (Dockery et al., 1993). They investigated the PM10 and PM2.5 values in six major U.S. cities, compared the measured values to excess mortality in the corresponding areas and concluded that PM2.5 showed a better correlation than PM10 and other atmospheric pollutants (including gaseous compounds). Briefly summarized, the researchers followed the same well-defined group of persons over several years in the selected areas (generally termed a closed-cohort study in epidemiology) and classified the reason of death of every person that died during the study period. All of the selected monitoring sites (Watertown MA, Kingston-Harriman, TN, St. Louis MO, Steubenville OH, Portage WI and Topeka, KS) were selected to represent central residential areas that are typical for the US. For the definition of excess mortality cases, non-natural deaths (accidents, crimes etc.) were excluded, and the rest of the death cases were classified into standard categories like total daily deaths, ischemic heart diseases, pneumonia and chronic obstructive pulmonary diseases (COPD). The quantitative result of the study states that a $10 \mu g/m^3$ increase in PM2.5 corresponded to a 1.5% increase in daily mortality in the selected areas. This study was not only an important key part showing this between PM2.5 and adverse health effects, but it is sometimes also used as argument to illustrate that ultrafine particles, which contribute very little mass to PM2.5, are not mainly responsible for adverse health effects of atmospheric aerosols (see Section 1.4.2, Laboratory studies). The mentioned health effect study has not established causal mechanisms nor has it focused on determining the physical and chemical characteristics of the aerosol to which people are exposed. A number of studies have been performed since then, trying to refine the original study approach by e.g. considering source specification. An association of PM2.5 from mobile and coal combustion sources with daily mortality is shown in (Laden et al., 2000). In this study, the original study interpretation was extended by looking at the elemental composition of the measured PM2.5 values, which was obtained by specific factor rotation analysis of 15 specified chemical elements. The source apportionment showed that a $10 \mu g/m^3$ increase in PM2.5 from mobile sources (i.e. traffic) corresponded to a 3.4% increase in daily mortality in the selected areas, whereas PM2.5 from coal combustion accounted for a 1.1% increase. Crustal PM2.5 showed no increase in daily mortality.

Another closed-cohort study on daily mortality caused by PM2.5 that is often mentioned in literature is the American Cancer Society (ACS) Study performed by (Pope et al., 1995). This study focused especially on the distinction between lung cancer and cardiopulmonary diseases as reason for mortality among a large selection of US adults. After corrections for numerous factors, of which cigarette smoking being the most important one, they found a robust association of PM2.5 and sulfate with mortality caused by the two above disease categories. A similar long-term study (AHSMOG Seventh Day Adventist Study) showing similar results was performed by (Abbey et al., 1999).

Since epidemiological studies generally are of a complex nature, they base on a number of assumptions and criteria that may influence the analysis and the results, e.g. the medical history or the cigarette smoking behavior of the test persons. It has been recognized that a critical review of current and previous studies is a crucial step towards a profound quantitative understanding of adverse health effects (Laden et al., 2001). For
example, the US Health Effects Institute (HEI) completely reanalyzed the data from the ACS and the Harvard Six Cities Study in manifold ways and confirmed the main results from both studies, but show that especially absolute numbers are strongly dependent on the exact choice of analysis, corrections etc. Additionally, they found that in both studies the association of mortality with air pollution was greatest among those persons with less than high school education (U.S. Health Effects Institute, 2000b, 1995). This example illustrates that social structures and all implications connected with them may also strongly influence air quality epidemiological studies.

In contrast to the above closed-cohort study types, another study type, i.e. a time-series study, has been selected in numerous (over 150) epidemiological studies investigating the link between air pollution and adverse health effects (Dockery and Pope, 1994; Schwartz and Dockery, 1992; Schwartz, 1994; Schwartz et al., 1996; Seaton et al., 1995; Le Tertre et al., 2002). A typical example for an easy conductible time-series study is the investigation of the relation between the rate of hospital admissions due to selected diseases and increased air pollution. This allows for the calculation of daily mortality rates, but in contrast to the ACS and the Harvard Six Cities Study, no information on long-term effects can be obtained in this way, since these studies deal with acute cases and an uncontrolled population coverage. However, this study type is important for the investigation of the influence of air pollution on acute diseases also with minor implications than mortality, e.g. an increased heart rate variability (HRV) during PM peak episodes (Magari et al., 2002). In the US, one of the largest recent studies in this category was the NMMAPS (National Morbidity, Mortality and Air Pollution Study, see Samet et al., 2000a,b), in which the researchers focused on the mortality increase rather by PM10 than by PM2.5. This study states that a 10 µg/m³ increase in PM10 corresponded to a 0.5% increase in all-cause daily mortality in the selected areas (20 major metropolitan areas with totally 50 millions inhabitants). Also here, the absolute numbers have been debated recently (Brunekreef and Holgate, 2002; Knight, 2002; Zeger et al., 2000).

In Europe, the correlation between particulate air pollution and adverse health effects was studied for 29 cities on occasion of the APHEA (Air Pollution and Health: a European Approach) time-series study (Katsouyanni et al., 1995, 1997, 2001; Atkinson et al., 2001). Similar to the NMMAPS study, a 0.6 % increase in all-cause daily mortality was found for a 10 µg/m³ increase in PM10. One result of the study that is especially worth being mentioned here is that cardiovascular disease increased by 0.5% per 10 µg/m³ PM10, but by 1.1 % per 10 µg/m³ black carbon, which establishes a link to the ongoing debate about adverse health effects of diesel exhaust (see Section 1.4.2, Laboratory studies).

Alternatives to cohort studies on mortality are cross-sectional long-term studies, which assume that the current air pollution exposure is representative of previous exposure, to establish a link with the current health status of the investigated individuals. With this method, morbidity endpoints can be estimated. This study approach has been used in Switzerland, on occasion of the SAPALDIA and the SCARPOL studies, which followed adults and children in different areas across Switzerland (Zemp et al., 1999; Wüthrich et al., 1999; Röösli et al., 2000; Oglesby et al., 2002; Schindler et al., 2001; Monn et al., 1999; Braun-Fahrlander et al., 1997, 2001). For non-smoking adults, a reduced lung function could be associated with increased PM10, TSP (total suspended particles), NO₂,
and environmental tobacco smoke, accompanied by chronic phlegm production, breathlessness during the day and/or at night and dyspnea on exertion, but not by asthma. A similar result was found for children. Asthma symptoms were only found in current smokers. In former and current smokers, no associations between PM10 and chronic phlegm production were found.

Using results from epidemiological studies as input, Künzli et al. (2000) estimated the impact of total and traffic-related particulate air pollution on public health in Switzerland, France and Austria. In this modeling study, PM10 population exposures were estimated, extracting the traffic-related (primary plus secondary particulates) fraction of PM10 from emission inventories. Disease and mortality cases attributable to air pollution were estimated from epidemiology-based exposure-response functions. The study states that in the selected countries air pollution accounted for 6% of total mortality, of which 50% are related to traffic. Traffic-related air pollution was also estimated to cause more than 25000 new cases of chronic bronchitis in adults, over 290000 episodes of bronchitis (children), more than half a million asthma attacks and more than 16 million person-days of restricted activities (all numbers per year).

Summarizing, there already exist a large number of epidemiological studies associated with PM10 and PM2.5. However, there is still a large lack of epidemiological evidence on possible adverse health effects of ultrafine particles. One of the major reasons for this is the relatively young age of the research on ambient ultrafine particles. A constant and area-covering monitoring of ultrafine particles is still scarce, which is the very base for any type of epidemiological study. A time-series study performed in Erfurt, Germany found that daily mortality was associated with the ambient level of both ultrafine particles and fine particles, with a time lag for the ultrafine particles and a more direct effect for the fine particle fraction (Wichmann and Peters, 2000; Peters and Wichmann, 2002). However, these findings are still debated in literature (U.S. Health Effects Institute, 2000a). Other epidemiological studies found that the levels of ambient ultrafine particles are also associated with a reduced peak expiratory flow in persons suffering from asthma and other non-mortal diseases (Peters et al., 1997a,b; Peters and Wichmann, 2001; Penttinen et al., 2001; Lippmann and Ito, 2000; Pekkanen et al., 1997; Tiittanen et al., 1999; von Klot et al., 2002).

1.4.2 Laboratory Studies

In contrast to epidemiological studies, laboratory studies try to elucidate the mechanisms and processes that particulate matter undergoes in the human body, and explain a possible toxicity. Since aerosols are not only possibly harmful agents, but also a common application form for medicaments, the research on the destiny of supermicron particles (> 1 micrometer) in the human airways has already got a long history and the findings and results are well established by now. However, while epidemiological studies are of a descriptive nature and directly deal with humans, a large number of laboratory studies on the toxicity of particulate matter involve in-vitro and in-vivo experiments that can only be performed with animals. These studies and experiments are of a more direct type and involve fewer assumptions on the one hand, but are confronted with differences between species on the other hand.
Figure 1.2 and Table 1.2 illustrate the anatomy and morphology of the human airways. The airways can be divided into 3 main compartments: The nasopharyngeal region (head airways), the tracheobronchial region and the pulmonary region. The process chain that aerosols undergo when they are entering the airways involves 3 main steps: a) Inhalation, b) deposition and c) clearance.

Table 1.2: Morphology and histology of the human airways (Weibel, 1973).

<table>
<thead>
<tr>
<th>Generation</th>
<th>Name</th>
<th>Diameter</th>
<th>Length</th>
<th>Number per generation</th>
<th>Histology</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>Trachea</td>
<td>1.8 cm</td>
<td>12 cm</td>
<td>1</td>
<td>Goblet cells</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Ciliated epithelial cells</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Sero-mucous glands</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Cartilage rings</td>
</tr>
<tr>
<td>1</td>
<td>Primary Bronchi</td>
<td>1.2 cm</td>
<td>4.8 cm</td>
<td>2</td>
<td>Goblet cells (fewer)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Ciliated epithelial cells (shorter)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Sero-mucous glands</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Cartilage Smooth muscle</td>
</tr>
<tr>
<td>2</td>
<td>Lobar Bronchi</td>
<td>0.8 cm</td>
<td>0.9 cm</td>
<td>5</td>
<td>Goblet cells (fewer)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Ciliated epithelial cells (shorter)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Sero-mucous glands</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Cartilage Smooth muscle</td>
</tr>
<tr>
<td>3</td>
<td>Segmental Bronchi</td>
<td>0.6 cm</td>
<td>0.8 cm</td>
<td>19</td>
<td>Goblet cells (fewer)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Ciliated epithelial cells (shorter)</td>
</tr>
<tr>
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<td></td>
<td></td>
<td>Sero-mucous glands</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Cartilage Smooth muscle</td>
</tr>
<tr>
<td>4</td>
<td>Subsegmental Bronchi</td>
<td>0.5 cm</td>
<td>1.3 cm</td>
<td>20</td>
<td>Goblet cells (fewer)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Ciliated epithelial cells (shorter)</td>
</tr>
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<td></td>
<td></td>
<td></td>
<td>Sero-mucous glands</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Cartilage Smooth muscle</td>
</tr>
<tr>
<td>5 → 10</td>
<td>Small Bronchi</td>
<td>0.1 – 0.4 cm</td>
<td>0.5 – 1.1 cm</td>
<td>40 – 1020</td>
<td>Goblet cells (fewer)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Ciliated epithelial cells</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>No cartilage</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Smooth muscle</td>
</tr>
<tr>
<td>11 → 13</td>
<td>Bronchioles Primary &amp; Secondary</td>
<td>0.1 cm</td>
<td>0.3 – 0.4 cm</td>
<td>2058 – 8190</td>
<td>Goblet cells (fewer)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Ciliated epithelial cells</td>
</tr>
<tr>
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<td></td>
<td></td>
<td></td>
<td>No cartilage</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Smooth muscle</td>
</tr>
<tr>
<td>14 → 15</td>
<td>Terminal Bronchioles</td>
<td>0.1 cm</td>
<td>0.2 cm</td>
<td>16380 – 32770</td>
<td>No goblet cells</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Ciliated epithelial cells</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Cuboidal cells</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Smooth muscle</td>
</tr>
<tr>
<td>16 → 18</td>
<td>Respiratory Bronchioles</td>
<td>0.1 cm</td>
<td>0.1 – 0.2 cm</td>
<td>65540 – 262140</td>
<td>Ciliated epithelial cells (disappearing)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>No smooth muscle</td>
</tr>
<tr>
<td>19 → 23</td>
<td>Alveolar Ducts</td>
<td>500 µm</td>
<td>0.5 – 1 mm</td>
<td>524290 – 8390000</td>
<td>No ciliated epithelial cells</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Cuboidal cells</td>
</tr>
<tr>
<td>24</td>
<td>Alveoli</td>
<td>244 µm</td>
<td>238 µm</td>
<td>3000000000</td>
<td>Type I and II cells (Pneumocytes)</td>
</tr>
</tbody>
</table>
a) Inhalation: In 1995, the American Industrial Hygiene Association (AIHA) defined three terms for inhalation into different airways compartments, which are often used in literature (Vincent, 1995):

- Inhalable: Aerosol fraction that enters the nose and/or mouth during breathing
- Thoracic: Subfraction of inhalable that penetrates below the larynx
- Respirable: Subfraction of inhalable that penetrates to the alveolar region

b) Deposition: Based on the output of numerous deposition studies, the International Commission on Radiological Protection (ICRP) published 1994 an estimated deposition efficiency curve for the human airways (Figure 1.3), covering all airway compartments and particle sizes from 1 nm to 100 micrometer (ICRP, 1994). The nose (or more generally the nasopharyngeal region) scavenges the particles larger than 10 micrometers and therefore can be considered as a natural PM10 impactor. The remaining particles enter the pharyngeal and the tracheobronchial region. In the latter, the inhaled air is warmed up and humidified, and the air velocity changes. Main mechanisms of particle deposition in these compartments are (depending on particle size) impaction, interception and diffusion. Finally, the air is transported to the pulmonary zone, where the gas exchange between the alveoli and the blood as well as immunological reaction take place. In this compartment, deposition takes mainly place by diffusion, but also by impaction, interception and sedimentation. Looking at the ICRP deposition efficiency curve, increased deposition efficiency is reported in the alveolar region for particles in the size range 7-100 nm (see also Bates et al., 1966; Raabe, 1982). This fact has evoked large research efforts in recent years, since it raises concerns about an enhanced risk for adverse health effects of ultrafine particles.
particles which are reported to be formed in large number concentrations e.g. by automotive exhaust (see below and Chapters 2 and 3).

![Image: Particle deposition efficiency in the human respiratory tract (from ICRP, 1994). ET: extrathoracic, ET\(_1\): anterior nose, ET\(_2\): posterior nasal passages, larynx, pharynx and mouth, BB: bronchial region, bb: bronchiolar region, Al: alveolar-interstitial region. AMTD: Activity median thermodynamic diameter (diffusion related), AMAD: Activity median aerodynamic diameter (settling related). Original legend text: Fractional deposition in each region of respiratory tract for reference worker (normal nose breather). Deposition is expressed as a fraction of activity present in volume of ambient air that is inspired, and activity is assumed to be log-normally distributed as function of particle size (for particles of density 3.00 g cm\(^{-3}\) and shape factor 1.5).]

**c) Clearance:** Clearance specifies the movement and transport of deposited particles from the place of deposition to their final destination in the human body or to the outside. Based on the inner lining of the airways, the human airways can be divided into two areas, the upper and the lower respiratory tract, which show different clearance properties.

The upper respiratory tract (or conducting zone) includes the nasopharyngeal and the tracheobronchial region. In this region mucus (produced by goblet cells) and ciliated epithelial tissue are mainly involved in the clearance mechanism (Alberts et al., 1995). Mucus specifies a gel (high viscosity) layer that floats on the cilia (hair-like cell compartments) of the epithelial cells. The cilia are thereby wetted by a sol (low viscosity) layer. The mucus layer itself is no area-covering layer, but forms islands or streams on top of the periciliar sol layer. It protects, lubricates and humidifies the airways surface and collects contaminants and debris deposited in this airway region. There is another liquid layer present, directly at the air/liquid interface on top of the mucus, which helps to dislocate deposited particles into the mucus layer due to its low surface tension. This surfactant (“surface active agent”) mainly consists of phospholipides. Once the deposited particles are transferred to the mucus, the cilia move the mucus upstream, either to the outside (coughing) or to the gastrointestinal tract by vibrating in a wave-like pattern with a frequency of approximately 10-30 Hz. This whole clearance mechanism is widely known as tracheobronchial or mucociliary clearance. However, there exists sometimes some inconsistency in literature on whether the differentiation between a gel and a sol layer is
really correct (Geiser et al., 1999). Additionally, there still are several open questions about details on the formation, structure and presence of the surfactant layer. Beside this major clearance mechanism for the upper respiratory tract, which is relatively fast (< 24h) and especially relevant for relatively large particles, there is evidence that smaller particles penetrate the mucus layer and are translocated to the cell tissue by macrophage phagocytosis or undergo other, so far not well characterized interactions with the epithelium tissue (McWilliam et al., 2000). After phagocytosis, the particles are transferred to the lymphatic system or stay in the cell interstitium (Gehr et al., 1991). Possible effects of these clearance pathways will be discussed below, in the context of specific toxicity of ultrafine particles.

In the lower respiratory tract, i.e. in the pulmonary zone, (or respiratory zone), where no mucus or cilia are present, particles are believed to be removed mainly by alveolar macrophage phagocytosis. In this region the surfactant layer is mainly responsible to prevent alveolar collapse and maintain the surface tension. The macrophages phagocytize deposited particles, cellular debris and old surfactant and are then either transported upstream to the mucociliary escalator or to the lymphatic or blood system. Clearance in this region is much slower (days to weeks).

Known classes of disease caused by deposited particles in the airway compartments are irritation with subsequent inflammation, oral or laryngeal cancer (nasopharyngeal region), “lung” cancer (e.g. from tobacco smoking) and allergic reactions (tracheobronchial region). In the pulmonary zone, disruption of immune reactions, fibrosis and emphysema are diseases possibly caused by deposited particulate toxins (e.g. asbestos, see Singh and Davis, 2002). Furthermore, there are indications that deposited particles in the lung region may under certain conditions cause severe cardiovascular effects (i.e. myocardial infarct, see Peters and Pope, 2002). The reasons for this are still being investigated (see further below), and there exist several hypotheses. The most common explanation is that the deposited particles result in pulmonary inflammation, accompanied by a release of cytokines, which is known to lead to cardiovascular problems. Other explanations of such cardiovascular effects involve an altered cardiac autonomic function, leading to changes in heart rate variability (see also the corresponding epidemiological studies), or a translocation of particles from the lungs into the circulation system, where they may influence cardiovascular endpoints more directly (Nemmar et al., 2002b).

The above processes have become rather well established in the last years. However, the picture becomes much less clear for the inhalation, deposition and clearance of ultrafine particles and their possible toxicity. Numerous new findings have been published just in the last few years, contributing new information on possibly increased toxicity of particles in this size range. Although there were earlier studies on this subject (Ferin et al., 1990, 1992; Oberdörster et al., 1990, 1995), one of the studies that are cited most frequently in the context of possible toxicity of ultrafine particles was performed by Donaldson et al., (1998). They investigated the potential of ultrafine transition metal compounds (e.g. TiO$_2$) for inflammation and oxidative stress in rat lung tissue and reviewed similar experiments reported in the literature. These materials per se show no intrinsic toxicity as for example quartz, which is considered to be cytotoxic due to its surface reactivity, or asbestos, which shows a high toxicity for long fibers. However, transition metal compounds show an enhanced surface chemistry forming potential for free radicals and oxidative agents. They
found that the large number concentrations of ultrafine particles and the consequently high surface area showed more harmful effects on lung tissue than the same mass deposition in form of larger respirable particles. The large number of ultrafine particles overloads the macrophage phagocytosis in the lung region and leaves a large number of ultrafine particles that get in direct contact with epithelial cells. Due to the large surface area of the phagocytized ultrafine particles there is an increased potential for surface chemistry (especially free radical formation) with subsequent formation of oxidants (Donaldson et al., 1996). This exerts oxidative stress on the macrophages, resulting in a secretion of cytokines and other mediators leading to an inflammation. Additionally, depending on the surface chemistry and other so far not fully elucidated reasons, the excess ultrafine particles may be taken up into the interstitium of the epithelial cells, since they are much smaller than epithelial cell structures. This causes additional oxidative stress and stimulates interstitial macrophages to release pro-inflammatory mediators. Ongoing inflammation and oxidative stress of this type in the lung region possibly leads to further development of diseases (e.g. fibrosis or tumors).

The finding that a relevant fraction of ultrafine particles deposited in the alveolar region escape the normal clearance pathway by macrophage phagocytosis resulted in the question about the further destiny of these ultrafine particles. This question has been addressed in several respiratory studies with human volunteers. For example, in a study in which 5 healthy volunteers inhaled Tc-99m-labelled carbon ultrafine particles, (Nemmar et al., 2002b) found that the translocation of ultrafine particles into the human blood circulation system in significantly enhanced for particles with diameters less than 100 nm. This translocation takes place rapidly (1-20 minutes). The transfer to the blood may happen due to the fact that ultrafine particles match the size of proteins and other macromolecules that pass the alveolar-capillary barrier via transport caveolae (Gumbleton, 2001). A rapid epithelial uptake of ultrafine particles compared to larger particles has also been reported in other studies (Brown et al., 2002). Comparing healthy individuals with persons suffering from COPD, it has been reported (Brown et al., 2002) that persons with obstructed lungs accumulate higher ultrafine particle doses than healthy persons, but that there is no significant difference in the clearance rate. However, despite the large number of spirometry studies using technetium-labeled ultrafine particles to follow inhaled particles in healthy humans and COPD patients, there is yet no consistent picture about the target region in the human body in which the ultrafine particles are preferably accumulated after dislocation from the lung. It is reported that intravenously injected ultrafine particles were found to cross the blood-brain barrier (Kreuter, 2001; De Lorenzo and Darin, 1970), to accumulate in the liver (Nemmar et al., 2002a,b) and other organs like bladder, stomach and thyroid or salivary glands (Brown et al., 2002). From animal studies, it is even reported that ultrafine particles may find their way out of the respiratory tract via neurons by transsynaptic transport, or that the central nerve system is another target organ for ultrafine particles (Calderon-Garciduenas et al., 2002).

Finally, the toxicity of diesel exhaust should be briefly mentioned. It is assumed that in urban areas 70% of the total cancer risk resulting from air pollution has to be attributed to diesel exhaust (CARB, 2001). From epidemiological studies an increased relative risk (RR) for lung cancer (RR=1.3, Bhatia et al., 1998) and also bladder cancer (RR=1.13 – 1.3, Boffetta and Silverman, 2001) has been found for long-term diesel exhaust exposure. Beside the lung as main target for diesel exhaust toxicity, an effect on the urinary bladder
has been stated to be plausible, since metabolites of PAHs (polycyclic aromatic hydrocarbons) and nitro-PAHs (both being compounds of diesel exhaust) are concentrated in the urine. However, it has been stated that the specific toxicity of PAHs accounts for only a small percentage of the carcinogenic potential in the lung region (BUWAL, 1994). The main pathways for diesel exhaust cancerogenesis in the lung are the same as described for PM in general in the previous paragraphs (irritation, inflammation and oxidative stress). Recent toxicological studies furthermore suggest that the bare soot component of diesel exhaust exhibits a different biological action in the lung airways than the semiorganic compound (i.e. aged soot mode but also nanoparticles), but that both fractions involve the induction of cellular oxidative stress (Seagrave et al., 2002; Ma and Ma, 2002). Beside lung cancer, the combined effects of both exhaust fractions are suspected to inhibit cell-mediated immunity toward infectious agents, stimulate respiratory allergy and cause DNA damage. Other studies suggest that the fractal structure of diesel soot particles may enhance the possibility of taking up additional toxic substances (e.g. PAHs), or that the fractal structure makes the particles less rigid, which makes them more transportable in the lung epithelium (BUWAL, 1994).

1.5 AMBIENT ULTRAFINE PARTICLES

One main message that medical research on ultrafine particles is promoting is that ultrafine particles due to their size and their typical ambient inhalation number concentrations show a clearly different clearance behavior in the airways compared to larger particles, which possibly may induce adverse health effects in organs other than the respiratory tract. Furthermore, the surface properties and especially the large surface area of large number concentrations of ultrafine particles are suspected to be important for the degree of toxicity directly in the lung. Thus, it has become crucial for the environmental aerosol scientists to study the formation, abundance, composition and the dynamics of ambient ultrafine particles in accurate detail. However, similar to the discussion about possible adverse health effects of ultrafine particles, the important question of when, where and why these particles are being formed is still lacking a satisfying answer.

Continuous monitoring of ultrafine particles technically started with the development of suitable techniques for particle sizing. Starting in the early 1990ies, the SMPS (Scanning mobility particle sizer) has become a standard instrument for measuring particle size distributions down to 3 nm (Wang and Flagan, 1990). As a consequence, numerous experiments were performed in which particle number size distributions were measured at a manifold variety of locations, ranging from marine air to high alpine measuring sites and highly polluted urban areas. Soon, a reasonably broad understanding was achieved for processes determining the usual shape of the upper size range (100 nm – 1 micrometer) of ambient particle size distributions. Since SMPS measurements only allow for the physical characterization of aerosols, they mostly are combined with other measurements, to gain also chemical information on the sampled ambient aerosols. Ultrafine particles have a very small mass, which makes it extremely difficult to perform common filter-weighing based experiments without losing too much time resolution. Convenient ways to chemically characterize ultrafine particles do not exist in large number yet, but promising techniques like aerosol mass spectrometry have been established in the last years (Brand et al., 1992; Noble and Prather, 2000). As it will be discussed in Chapters 2 and 3, mass spectrometry
has recently been used for chemical analysis of diesel exhaust nanoparticles (Tobias et al., 2001). Nevertheless, the variation of ultrafine particles as a function of other pollutant parameters, location and meteorology has so far been described in ambient air studies on a rather phenomenological base, since the size distributions in most cases have been the only characterization tool for ultrafine particles.

It has soon been recognized that the occurrence of ultrafine particles in ambient air has to be split into different categories. Already in 1994, a large ultrafine particle mode was found in road tunnel air measurements (Weingartner et al., 1997), pointing to an involvement of traffic activity in the formation of certain types of ultrafine particles. Similar observations also were made in measurements at traffic-rich locations (Whitby et al., 1975). On the other hand, episodes with bursts of ultrafine particles have been reported to occur in many different countries, a lot of them taking place at rural or remote sites. These particles obviously have no direct anthropogenic origin, but were attributed to gas-to-particle conversion from biogenic gaseous emissions. To establish uniform terms for these two different types of ultrafine particles, Baltensperger et al. (2002) recently introduced the following definitions:

- **Primary ultrafine particles** include particles that are formed as a direct consequence of traffic exhaust. Under certain meteorological conditions and depending on traffic type (fleet) and condition (speed) they are formed during the cooling and dilution process of emitted gaseous exhaust. The formation and initial growth to detectable sizes takes place within seconds, without significant changes due to chemical reactions.

- **Secondary ultrafine particles** more broadly denote ultrafine particles formed by gaseous precursors that can be of either anthropogenic or biogenic origin. In contrast to primary ultrafine particles, gaseous precursors are formed by atmospheric reactions on a longer time scale (hours to days). Such reactions may involve photochemistry and oxidation, to form non-volatile species from volatile precursors.

The investigation of primary ultrafine particles has already been covered by a number of studies in the past. Since their connection to traffic activity, numerous stationary roadside measurements of ultrafine particles have been made (Zhu et al., 2002; Molnar et al., 2002; Mäkelä et al., 2000; Pitz et al., 2001). The formation, characteristics and dynamics of primary ultrafine particles is also a main subject to investigation in later chapters of this thesis. Due to their dynamic nature, the measurement of primary ultrafine particles was one main challenge during the described on-road experiments. As it will be further shown in the corresponding chapters, the investigation of primary ultrafine particles is tightly connected to engine and fuel technology.

In contrast, the level of understanding of secondary ultrafine particle formation is lower. Figure 1.4 shows an example of a particle burst with subsequent growth over a boreal forest (taken from Boy and Kulmala, 2002b). Due to the appearance of such secondary ultrafine particle events in time-versus-diameter contour plots they are often referenced to “banana-type plots” in literature. After their initial publication in literature, they were reported in other studies to occur at a large variety of countries and locations, but always under similar conditions that will be specified in the following.
The occurrence of particle bursts over boreal forests in Finland has been subject of numerous studies performed by Kulmala and coworkers (Boy and Kulmala, 2002a,b; Väkevä et al., 2002; Kulmala et al., 2000). Their current theory suspects that almost everyday thermodynamically stable clusters (TSCs) are formed by nucleation in the investigated areas, depending on the air mass history. These TSCs, having diameters of about 1 nm, then grow to detectable sizes (>3 nm) under special conditions. The researchers showed in several studies that high solar UV-A radiation, a low H₂O content and a low particle background caused by corresponding mixing layer conditions favor this initial growth. The initial growth rate for growth up to 3 nm was described to be best fit for the ternary nucleation system H₂O-NH₃-H₂SO₄, taking into account the typical atmospheric concentrations of these species (for ammonia usually a few ppt). Further growth from 3 to 50-100 nm, characterized by a typically 6-8 hours growth time, is assigned to condensation of organic species. The same researchers recently stated that these boreal ultrafine particles possibly consist of primarily organic species such as pinonic or pinic acid (O’Dowd et al., 2002). Statistically the nucleation events more often occurred during spring, summer and autumn than during wintertime.

Other research groups found similar results, pointing to primary and secondary ultrafine particles. Birmili and Wiedensohler (2000) and Wiedensohler et al. (2002) observed an ultrafine mode of 10-20 nm in size during sunny summertime episodes with large photochemical activity in rural and urban background aerosols measured in Germany. The growth time of the nucleated particles are similar to those observed in Finland. In
wintertime, when usually less convection occurs, a large mode between 20-30 nm was observed in urban areas during rush hour periods. Similar to the boreal forest studies, Coe et al. (2000) observed episodes with increased levels of ultrafine particles at a rural site in the UK. These episodes usually started approximately one hour after sunrise on sunny days with low temperature and increased levels of NH$_3$ and also SO$_2$. This connection of ultrafine particle bursts with increased levels of SO$_2$ was also found in a study investigating urban aerosol in Atlanta (Woo et al., 2001; McMurry and Woo, 2002). The authors of that study specified three types of episodes: a) The formation of 3-10 nm particles during warm mid-day periods with low background NO$_x$, b) increased number concentrations in the 10-35 nm range on cold days with high primary NO$_x$ levels, and c) a large peak between 35 and 45 nm during warm periods with increased NO$_x$. The number concentrations in these modes were found to be significantly higher than for similar studies in Europe. These observations indicate that primary and secondary ultrafine particle events do not exclude each other and are observable at the same respective locations, as it is also explicitly shown by Baltensperger et al. (2002) for the Milan, Italy region.

An important key to the understanding of the above observations and processes is the lifetime of different types of ultrafine particles. Again, there exists a clearer picture for primary ultrafine particles. In a recent study Capaldo and Pandis (2001) investigated the lifetime of diesel aerosol under typical ambient conditions. They used a one-dimensional Lagrangian model to simulate the dispersion, mixing with ambient particles, coagulation and dry removal of emitted particles and used real-world data to verify their model (Kittelson et al., 2002). They estimate that a 90% reduction of the ultrafine particle number concentration from their initial value in the plume takes place within a few minutes under representative atmospheric conditions, connected with a characteristic transport distance of 100 – 1000 m. Corresponding values for a 99% reductions are 20-30 minutes and 0.5 – 10 km. The exact values are mainly dependent on the degree of atmospheric mixing (wind speed and vertical structure of the atmosphere) and the concentration of the preexisting aerosol background. Contrastingly, little information is available on the lifetime of secondary ultrafine particles besides the boreal forest studies mentioned above. The latter indicate a longer lifetime and larger spatial distribution of secondary ultrafine particles compared to primary ones, but the open questions about diversity, composition and formation do currently not allow general statements.

1.6 GOAL OF THIS THESIS - MOBILE MEASUREMENTS

The issues that have been discussed in the previous sections make it clear that a better area-covering long-term inventory not only for PM10 or PM2.5 is necessary, but also for other aerosol parameters, like number concentration of different size fractions or surface measurements. Such inventories are a necessary requirement for future epidemiological work on ultrafine particles and modeling studies. Furthermore, the investigation of processes leading to the formation of ultrafine particles in ambient air will need more support from experimental data to answer open questions about occurrence and lifetime. Due to the regulatory strategy that most environmental protection agencies follow, a widespread network of stationary PM measurements currently exists. Such networks are generally connected with relatively high costs, since one instrument per station has to be purchased. This does not give much room for testing new techniques and equipment.
Furthermore, cross-calibration of the instruments is necessary, and there is a higher risk for constant local artifacts at a specific station. In this thesis a new approach for monitoring spatial and temporal variation of ambient aerosol parameters is discussed, which involves mobile measurements. The basic idea has been to design a mobile laboratory that allows for on-road measurements, i.e. measuring pollutants while driving. There are major conceptual differences from monitoring networks. The instrument need is lower (only one set of instruments is needed), no extensive cross-calibration is necessary, and there is a wide field of applications for mobile laboratory measurements. Thus, a major scope of this thesis was to evaluate the applicability of mobile laboratories for different study types. Chapters 2 and 3 describe the construction and use of a mobile emission laboratory in the United States to perform chase experiments of diesel trucks and characterize primary ultrafine particles directly after emission from the exhaust pipe. Within the scope of this thesis a focus was put on elucidating the usefulness and relevance of real-time instrumentation that currently exists, since high time resolution is a major requirement to track highly dynamic transient pollutants during on-road measurements. In Chapter 4, the set-up of another mobile pollutant measurement laboratory built at the Paul Scherrer Institute is shown, which was used to assess the temporal and spatial variation of both aerosol and gas phase ambient concentrations in the Zürich (Switzerland) region (Chapter 5). In contrast to the U.S. study, this second study focused both on primary and secondary ultrafine particles and on the investigation of total particle concentration levels in the selected area. An area-covering mapping of fine and ultrafine particles was achieved for a one-year period, along with detailed studies of the processes and environmental conditions that influence the formation of fine and ultrafine particles.


John, C., Friedrich, R., Staehelin, J., Schläpfer, K. and Stahel, W.A., 1999. Comparison of emission factors for road traffic from a tunnel study (Gubrist tunnel, Switzerland) and from emission modeling. Atmospheric Environment 33, 3367-3376.


U.S. Environmental Protection Agency, 1996. Air quality criteria for particulate matter. EPA-600-P-95-001aF-cF, National Center for Environmental Assessment, Research Triangle Park, NC.


2 AN INTRODUCTION TO MOBILE POLLUTION MEASUREMENTS

DIESEL AEROSOL SAMPLING IN THE ATMOSPHERE


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Author remark: This chapter represents the standard of knowledge at the time of publication. Later chapters of this thesis will partially take up open questions and future goals that arise here.

ABSTRACT

The University of Minnesota Center for Diesel Research along with a research team including Caterpillar, Cummins, Carnegie Mellon University, West Virginia University (WVU), Paul Scherrer Institute in Switzerland, and Tampere University in Finland have performed measurements of diesel exhaust particle size distributions under real-world dilution conditions. A mobile aerosol emission laboratory (MEL) equipped to measure particle size distributions, number concentrations, surface area concentrations, particle bound PAHs, as well as CO$_2$ and NO$_x$ concentrations in real time was built and will be described. The MEL was used to follow two different Cummins powered tractors, one with an older engine (L10) and one with a state-of-the-art engine (ISM), on rural highways and measure particles in their exhaust plumes. This paper will describe the goals and objectives of the study and will describe representative particle size distributions observed in roadway experiments with the truck powered by the ISM engine.

2.1 INTRODUCTION

Recent studies have linked environmental exposure to fine particles less than 2.5 $\mu$m aerodynamic diameter to adverse health effects (Dockery et al., 1993; Donaldson et al., 1996; Ferin et al., 1992; McAughey, 1997; Pope et al., 1995; Seaton et al., 1995), although no causal mechanisms have been identified. The relationship between fine particles and health is a logical link because the efficiency of particle deposition in the respiratory tract is a function of particle size. Figure 2.1 illustrates relationships between idealized diesel particulate matter (DPM) number and mass weighted size distributions (Whitby and Cantrell, 1975) and the alveolar deposition curve (Morrow et al., 1964; Raabe, 1982). As DPM increases in size, the deposition efficiency decreases.
DPM follows a lognormal, trimodal size distribution with the concentration in any size range being proportional to the area under the corresponding curve in that range (Dolan et al., 1975, 1980; Baumgard and Kittelson, 1985; Abdul-Khalek and Kittelson, 1995; Abdul-Khalek et al., 1998b; Kittelson, 1998). Nuclei-mode particles range in diameter from 0.005 to 0.05 µm (5-50 nm). Based on physical arguments, they are believed to consist of metallic compounds, elemental carbon and semi-volatile organic and sulfur compounds that form particles during exhaust dilution and cooling (Abdul-Khalek and Kittelson, 1995; Abdul-Khalek et al., 1998b; Kittelson, 1998). The nuclei mode typically contains 1-20 % of the particle mass and more than 90 % of the particle number. The accumulation mode ranges in size from roughly 0.05 to 0.5 µm (50-500 nm). Most of the mass, composed primarily of carbonaceous agglomerates and adsorbed materials, is found here. The coarse mode consists of particles larger than 1 µm and contains 5-20 % of the DPM mass. These relatively large particles are formed by reentrainment of particulate matter, which has been deposited on cylinder, and exhaust system surfaces. Also shown in Figure 2.1 are size range definitions for atmospheric particles: PM10 (diameter < 10 µm), fine particles (diameter < 2.5 µm), nanoparticles (diameter < 0.05 µm or < 50 nm), and ultrafine particles (diameter < 0.10 µm or < 100 nm). The interest in nanoparticle emissions from internal combustion engines, particularly diesel, has been recently heightened by engine laboratory studies that showed an increase in nanoparticle emissions from low-mass emission engines, and engines equipped with emission control technologies such as oxidation catalysts and/or traps (Bagley et al., 1996; Bagan, 1999; Krüger et al., 1997; Mayer et al., 1995). In a study funded by the Health Effects Institute (HEI), Bagley et al. (Bagley et al., 1996) compared size distributions from a 1988 Cummins engine with those from a 1991 engine of the same family. Figure 2.2 includes
two plots of the number concentration distribution function, $dN/d\log(D_p)$, against particle diameter, $D_p$, that have been constructed from data given in that study. Compared to the 1988 engine, the 1991 engine showed a roughly 3 fold decrease in mass emissions (indicated by the decrease in $dN/d\log(D_p)$ in the accumulation mode size range) but a 10 to 30 fold increase in number concentration (indicated by the $dN/d\log(D_p)$ increase in the nuclei mode size range). This raised concerns that new, low mass emission engines might be producing a new problem in high emissions of nanoparticles. Although this concern about nanoparticle emissions is new, nanoparticle emissions are not. High concentrations of nanoparticles have been observed on and near roadways for many years (Whitby et al., 1975; Wilson et al., 1977; Kittelson et al., 1988; Harrison, 1996; Weingartner et al., 1997). Data from a 1979 roadway study (Kittelson et al., 1988) are also shown in Figure 2.2. These data were collected with a mobile laboratory driving on a rural freeway behind a tractor-trailer powered by Cummins engine from the same engine family as those used in the HEI study. The results are similar to those observed for the 1991 engine used in the HEI study.

The basic question is whether nanoparticle emissions from engines are changing as technology improves and emission standards are made more stringent. It is an objective of the project described here to answer this question. Often more than 90% of the nanoparticles emitted by engines are formed from volatile particle precursors during exhaust dilution (Abdul-Khalek et al., 1998a, 1999, 2000). These precursors are presumably the lower vapor pressure compounds usually associated with diesel particulate matter, like sulfuric acid and condensable hydrocarbons. Particle dynamics during sampling and dilution are highly nonlinear - large changes in particle number may result from small changes in dilution and sampling conditions. Sampling and dilution parameters like dilution ratio, temperature, humidity, and residence time strongly influence nanoparticle formation. Up to two orders of magnitude difference in nanoparticle emissions were observed for an engine running at the same steady-state condition, but
with different dilution schemes (Abdul-Khalek et al., 1999) as illustrated in Figure 2.3. Similar sensitivity was observed to primary dilution ratio and primary dilution temperature (Abdul-Khalek et al., 1999).

Nucleation and growth of particle precursors to form nanoparticles during dilution are strongly influenced by the presence of other particles (Abdul-Khalek et al., 2000). When carbon is removed from the exhaust, material that would adsorb onto carbonaceous agglomerates nucleates and grows to form nanoparticles. This process is very nonlinear and strongly dependent upon dilution conditions. Thus, the influence of dilution conditions may be even greater when most of the solid carbon is removed from the exhaust. Changes up to nearly four orders of magnitude in nanoparticle concentration with changing dilution conditions were observed when the same engine as used in (Abdul-Khalek et al., 1999) was fitted with a wall-flow exhaust particle filter (Abdul-Khalek et al., 1998a).

As engines become cleaner, it will become increasingly difficult to make representative measurements of exhaust size distributions. The Coordinating Research Council (CRC) E-43 program, described here, is intended to determine how to make such measurements. This paper is a progress report on the E-43 program, which is currently only about 25% complete. We expect that future information derived from this research program will recommend which combination of primary dilution ratio, residence time, primary dilution temperature, and other factors will best represent real world dilution conditions.
2.2 OBJECTIVES OF THE CRC E-43 PROGRAM

There are four primary objectives of the CRC E-43 Program:

1. Measure on-road particle size distributions (number, volume, surface area) in the exhaust plume of heavy-duty diesel vehicles.
2. Attempt to reproduce these results under laboratory conditions (chassis dynamometer, wind tunnel, engine dynamometer).
4. Determine size fractionated chemical composition of diesel particulate matter collected in the laboratory and in a wind tunnel.

These objectives are described in more detail in:
http://www.me.umn.edu/divisions/mel/reports/crcsum1.pdf

A very important fundamental goal of the project is to understand the nature of the tailpipe to nose process as it takes place on and near roadways. This is where the highest exposures to nanoparticles are likely to occur.

The project may be divided into 7 phases:

1. On-road chase experiments with an old technology and a new technology Cummins powered tractors,
2. Wind tunnel tests with the new technology Cummins powered tractor,
3. Chassis dynamometer experiments with the two Cummins powered tractors,
4. Engine dynamometer tests with the engine from the new technology Cummins powered tractor,
5. On-road chase experiments with an old technology and a new technology Caterpillar powered tractors,
6. Chassis dynamometer experiments with the two Caterpillar powered tractors,
7. Engine dynamometer tests with several new technology Caterpillar engines.

The experimental portions of phases 1 and 2 have been completed. A very large body of data has been collected and partially analyzed. This paper will describe some of the initial results from phase 1 of the project.

2.3 EXPERIMENTAL PROCEDURE AND RESULTS

The heart of the project is the mobile emission laboratory (MEL). It has been designed and built to allow comparison of diesel exhaust aerosol characteristics measured in chase experiments under real world highway conditions with simulations of those conditions in a wind tunnel, on chassis dynamometers, and on engine dynamometers. The MEL was installed in a cargo container that was mounted on a Volvo container truck. During the
chase experiments, illustrated in Figure 2.4, exhaust plumes are collected with a 3.6 m long aluminum boom mounted over the cab of the truck. The boom brings the sample stream to a distribution manifold in the interior of the MEL. A flow-regulating vane pump provides a large bypass flow for the instruments maintains constant suction at the inlet of the boom. The primary particle-sizing instrument used in these experiments is a TSI scanning mobility particle sizer (SMPS). It was used to obtain particle size distributions in the 9 to 300 nm diameter range. This instrument requires at least 30 s to complete an entire size scan and is not suitable for making measurements in the rapidly varying plume encountered in chase experiments. Therefore it was necessary to use a bag sampler with the SMPS. A portion of the aerosol entering the sampling boom is used to fill a large plastic bag in about 5 s to obtain a snapshot of the plume for analysis by the SMPS. One or more size distribution scans are run on each bag sample, each taking about 90 s. Repeated scans have shown that the bag sample procedure does not significantly change the size distribution of the collected aerosol. Furthermore, comparisons between direct samples (bypassing the bag) and bag samples obtained with steady aerosols show no significant differences. On the other hand, all size distributions reported here are for fresh roadway aerosols with little atmospheric aging. The role of aging is being addressed in modeling effort that is a part of the E-43 program, but has not yet been completed.

![Fig. 2.4: University of Minnesota, E-43, mobile aerosol laboratory during a roadway chase experiment.](image)

The other aerosol and gas instruments in the MEL sampled continuously from the distribution manifold. The instruments used in the Cummins chase experiments included the following:

1. An electrostatic low pressure impactor (ELPI) to determine particle size distributions based on the aerodynamic aerosol diameter in the 29 to 2500 nm range.
2. A condensation particle counter (CPC) to measure total aerosol number concentrations for particles larger than about 3 nm.
3. An epiphanometer to determine the Fuchs surface area of the aerosol (Gäggeler et al., 1989). This well characterized measuring method is the standard for the other surface measuring instruments, despite its relatively slow (5 minute) time resolution.

4. A photoelectric aerosol sensor (PAS) to measure photoemitting substances on the surface of aerosol particles. Diesel soot has been found to show a large response.

5. A diffusion charger (DC), consisting of a diffusion charging section combined with a current sensor, to measure the surface area concentration of the aerosol. Its fast response time (0.5 s) made the instrument useful as a fast plume indicator. The combination DC/PAS has been described as a powerful tool for the identification of diesel soot (Matter et al., 1999).

6. High sensitivity CO$_2$ and NO$_x$ analyzers to track the plume and in conjunction with a stack sampler mounted in the chased truck used to determine dilution ratios.

The MEL was used during on-highway, truck chase experiments. The following test conditions were used in the Cummins chase experiments: idle; 55 mph cruise, light and heavy load; and 40 – 55 mph acceleration, light and heavy load. We also attempted to do chase experiments during decelerations but the plumes were too weak to detect. Two different tractors were used, a 1999 model powered by a 1999 specification ISM engine and a 1988 model powered by a 1988 L10 engine. Two fuels were used with the ISM engine: a standard federal fuel and a reformulated California fuel. Only the federal fuel was run in the L10 tests. The diesel exhaust plume of the truck being chased was captured and analyzed 1-3 s after it was emitted from the exhaust stack. Following distances ranged from about 15 to 50 m. The plume was tracked by monitoring the DC and/or NO signal in real time. When a strong steady signal was observed, a bag sample was taken.

2.3.1 SMPS Size Distribution Measurements

Results are reported here for the 1999 ISM engine running on the California fuel under light load cruise and acceleration conditions. Figures 2.5 and 2.6 show results of SMPS scans on bag samples obtained in replicate chase experiments for cruise and acceleration conditions. Plume and background samples are shown. These are uncorrected measurements so that the absolute concentrations are expected to vary with the extent of dilution of the plume at the time the sample is obtained. The size distribution shape similarities of Figures 2.5 and 2.6 indicate that roadway experiments were replicated well even though a roadway test is more difficult to control than a laboratory test. Each data curve in these two figures represents slightly different dilution because roadway conditions are not exactly the same. Although the absolute concentrations go up and down with dilution, the shapes are quite consistent for a given operating and sampling condition. The plume concentrations may be converted to stack equivalent concentrations using the following relationship (2.1):

$$\frac{dN}{d \log(D_p)}_{\text{stack}} = \left( \frac{dN}{d \log(D_p)}_{\text{plume}} - \frac{dN}{d \log(D_p)}_{\text{background}} \right) \times \text{Dilution Ratio}$$

(2.1)
Dilution ratios are being determined from stack, plume, and background NO concentrations. However, validations of these values are still underway. Regardless of whether or not the dilution ratio is known, the shape of the size distribution is determined from the plume minus background difference distributions. These difference distributions may be conveniently compared by normalizing them to a unit volume concentration of $1 \mu m^3/cm^3$.

![Figure 2.5: Typical chase experiment size distributions. California Fuel, light load, 55 mph cruise with ISM engine powered truck.](image)

When a size distribution is normalized in this manner it has the convenient property of giving the number emitted per unit mass emitted because it is reasonable to assume that the volume and mass concentrations are proportional to one another (Kittelson, 1998). Figure 2.7 shows such normalized distributions for data obtained on two consecutive days. The shapes of these size distributions are quite similar except that the data for the cooler day suggest relatively more nuclei mode particles are formed during dilution under cooler ambient conditions. This is not surprising because the vapor pressures of condensable species like sulfuric acid and high molecular weight hydrocarbons are lower at lower temperatures so that the driving force for nucleation and growth of nanoparticles will be stronger. This is consistent with the common observation of steam plumes behind vehicles in cold winter weather.
Fig. 2.6: Typical chase experiment size distributions. California Fuel, light load, 40-55 mph acceleration with ISM engine powered truck.

Fig. 2.7: Normalized average difference size distributions for 2 consecutive days, 6 and 7 October 1999 with different ambient temperatures. The results are normalized to a unit volume concentration of 1 µm³/cm³. California Fuel, ISM truck, light load.
We have also observed an increase in nanoparticle formation during dilution under laboratory conditions intended to simulate atmospheric dilution. Figure 2.8 shows this effect using a single stage dilution tunnel developed to simulate atmospheric dilution temperatures and rates by Wei (1999). These experiments were done with a 1995 medium-duty diesel engine designed to meet 1994 heavy-duty standards running at medium speed and load. Note the effect of dilution temperature on nanoparticle formation. The concentration of particles in the nuclei mode increases by nearly a factor of 10 as the temperature is reduced from 25 to 15 °C. This suggests that there could be differences in the tendency to form volatile nanoparticles between, for example, Minnesota and Arizona, not because of changes in engine emissions but because of changes in what happens in the atmosphere.

In addition to the temperature effect observed here is the important consideration of how long these nanoparticles will survive in what atmospheres, under what dilution conditions, and if, after reaching a decision of how to most appropriately dilute, how important this temperature effect will be at that dilution condition. At present, the time dimension (i.e., the lifetime) of these nanoparticles has not been determined, and is planned as future research.
2.3.2 Measurements Made with Real Time Particle Instruments

The Cummins chase experiments have yielded more than 400,000 individual records and we have only started to analyze this vast data set. However to give a sense for the type of data collected some representative DC and CPC data are shown below. It is necessary to correct for differences in lag and response times when comparing continuous instruments. Their response lag times were determined by repeatedly switching between a sample stream and a filtered stream. It was found that the combined internal and transfer line lag time of the CPC was 6 s longer than that of the DC. Therefore in the data shown below the CPC response is shifted 6 s relative to the DC response. Figure 2.9 shows the instantaneous variations of the DC and CPC response during a short time window of the chase experiments for the ISM truck, 55-mph cruise, light load, California fuel. Note that the instruments track very well. Figure 2.10 is a plot of the DC response against the CPC response for a more extended time period, but the same operating conditions. A linear regression line through the data is also shown and has an $r^2$ value of 0.75. Assuming that the background and stack conditions are steady, the slope of such a plot is the ratio of the particle surface to the particle number added by the plume, or the S/N ratio. This ratio may be related to the diameter of average surface, $D_{av}$, through:

$$D_{av} = \left( \frac{S}{\pi N} \right)^{0.5} \quad (2.2)$$

For the data shown in Figure 2.9, $D_{av}$ is 25 nm.
Comparison of CPC and Diffusion Charger Response
7 October 15:28-16:09

![Graph showing comparison between CPC and Diffusion Charger response.](image)

The slope of this line is related to particle size. The diameter of average surface is given by:

\[ D_{av} = \left( \frac{S}{\pi N} \right)^{0.5} \]

Fig. 2.10: Comparison between condensation particle counter and diffusion charger response for a time window during roadway chase experiments on 7 October 1999. ISM powered truck, CA Fuel, 55 mph cruise, light load.

## 2.4 CONCLUSIONS AND ONGOING WORK

The experimental work for the first 2 phases of the CRC E-43 Project, Cummins chase experiments and wind tunnel experiments have been completed, but analysis of the collected data continues. Some preliminary results of the chase experiments have been reported here. The mobile emission laboratory built for this project has performed very well in the Cummins chase experiments. These experiments have shown that it is feasible to characterize the particle emissions of diesel powered vehicles under real world conditions. For the engine and test conditions that we have encountered the sensitivity of nanoparticle formation to dilution temperature suggests that these nanoparticles are volatile and form by nucleation during dilution. Nucleation is highly nonlinear and very sensitive to conditions. Consequently the first step in understanding this process, and in accessing the nature of real world exposures, must be taken under real world conditions. We have found that for the engines and conditions examined so far, the SMPS size distributions are quite similar in shape to those found in some laboratory studies. The submicron size distributions are bimodal (the supermicron coarse particle mode is not considered here) with a nuclei mode in the 10 to 20 nm range containing 60 to 95 % of the number and an accumulation mode in the 40 to 60 nm range containing 90 to 99 % of the volume (or mass). The main chase experiment sampling parameter observed to influence the size distribution is ambient temperature, with larger relative concentrations of nanoparticles formed during dilution at lower ambient temperatures. Ongoing work includes instrument and sampling system calibration and validation as part of a quality assurance program. We expect to do chassis and engine dynamometer tests at Cummins in April and May 2000; chase, chassis and engine dynamometer experiments with Caterpillar engines during the late spring and summer of 2000.
In addition to these general test descriptions and locations are the more complex aerosol physics concepts that need to be resolved. More on-road particle size distributions will be obtained to verify data collected thus far. The Cummins and Caterpillar tests will compare laboratory dilution tunnel size distributions and concentrations with on-highway data to determine the proper laboratory method of dilution rate, ratio and aerosol residence time. Atmospheric aging and dispersion of freshly emitted diesel aerosols will be modeled for comparison with data obtained in these experiments. Finally, although the low mass of nanoparticles makes chemical analysis challenging, a limited number of chemical analyses are planned.

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REFERENCES


McAughey, J.J., 1997. Regional lung deposition and dose of ambient particulate in humans by particle mass and number. AEA Technology, Aerosol Science Centre, Oxfordshire, UK.


3 MOBILE POLLUTANT MEASUREMENTS IN MINNEAPOLIS (USA)

REAL-TIME CHARACTERIZATION OF ULTRAFINE AND ACCUMULATION MODE PARTICLES IN AMBIENT COMBUSTION AEROSOLS

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ABSTRACT

The Diffusion Charging Sensor (DC), Photoelectric Aerosol Sensor (PAS) and Condensation Particle Counter (CPC) are real-time particle instruments that have time resolutions < 10 s and are suitable for field use. This paper shows how the relative fraction of nuclei mode particles (D ≤ 50 nm) in ambient combustion aerosols can be determined, along with the coverage degree of the respective accumulation mode particles with a modal diameter of ~100 nm. Main tools for interpretation are the diameter of average surface Dₘᵋ₈ (obtained from CPC and DC measurements) as well as PAS/DC versus Dₘᵋ₈ scatter plots. Compared to the scanning mobility particle sizer (SMPS), which is a standard instrument for aerosol particle size distribution measurements, the presented method has a limited accuracy, but is substantially faster. Additionally, it is experimentally less demanding than SMPS measurements, especially for field applications.

3.1 INTRODUCTION

In the past, numerous studies were conducted to characterize airborne particles near or on highways (Whitby et al., 1975; Kittelson et al., 1988; Harrison, 1996; Weingartner et al., 1997). On-road submicron particle number size distributions typically contain an accumulation mode with an estimated number mean diameter of 100 nm, consisting of carbonaceous agglomerates (elemental carbon and organic carbon that includes polycyclic aromatic hydrocarbons, PAHs). As the aerosol ages the particles become coated by other condensable species (mainly semi-volatile hydrocarbons, nitrates and sulfates). Accumulation mode particles are primarily produced by automotive traffic, and heavy-duty diesel trucks are one source under investigation due to visible smoke emissions under certain operating conditions (Lawson and Smith, 1998). An aerosol from a spark ignition engine is typically composed of a higher proportion of organic carbon (OC) and less elemental carbon (EC) than diesel aerosol (Burtscher et al., 2001). Diesel and spark ignition vehicles also contribute to the occurrence of a nuclei mode that is between 5-50 nm in diameter. The nuclei mode is of scientific interest because of its composition and potential health effects, since the particle number concentration of this mode – once it is formed – is usually higher than the accumulation mode particle number.
concentration. For a diesel aerosol the nuclei mode typically contains less than 10% of the particle mass and up to 90% and more of the particle number. Nuclei mode particles are widely referred to as ultrafine particles or nanoparticles (see for example Kittelson et al., 2000). The experimental fact that a substantial fraction of nuclei mode particles evaporate at temperatures far below 300 °C (Abdul-Khalek and Kittelson, 1995; Matter et al., 1999) indicates that these particles do not consist primarily of elemental carbon. Baltensperger et al. (2002) found that 20 nm diameter particles at an urban site (Milan, Italy) during morning rush hour were characterized by a high volatility and a non-hygroscopic behavior, suggesting that these particles consisted mainly of hydrophobic organic material. These observations are consistent with recent laboratory investigations that suggest that nuclei mode particles from diesel engines are formed by condensation after combustion and consist mainly of hydrocarbons similar to the higher molecular weight fraction of lubricating oil along with a small percentage of sulphuric acid and water (Tobias et al., 2001).

Formation of the nuclei mode is extremely dependent on the dilution conditions (especially the dilution ratio) of the engine exhaust (Abdul-Khalek et al., 1999; Wei et al., 2001a,b). In combined dynamometer/dilution tunnel experiments they showed that a long residence time in the dilution volume and a low dilution air temperature favored nuclei mode particle formation. These parameters determine the temperature and concentration of condensable species and thus their supersaturation in the diluted exhaust and the time available for growth. Higher sulphur diesel fuels lead to more nuclei mode particle formation, since more sulphuric acid nuclei are formed after the combustion process (Wei et al., 2001a; Johnson and Baumgard, 1996), but Abdul-Khalek et al. (2000) suggest that there is not enough sulphuric acid present to explain observed growth rates during dilution and hydrocarbons are likely to be an important constituent. Other aerosols present in the diluting atmospheric air are also believed to effect the nucleation and growth processes of exhaust particles (Kittelson, 1998; Abdul-Khalek et al., 2000). The less surface there is available for condensation of supersaturated gaseous species the more new particle formation by nucleation is favored. Nanoparticles may form by primary processes (direct condensation of hot exhaust gas without atmospheric chemical reactions), or by secondary processes (condensation of products from atmospheric reactions, Mäkelä et al., 1997). Size distribution measurements at urban sites give evidence for both types of these condensation particles (Baltensperger et al., 2002).

The great variability in ambient aerosol characteristics results in a demand for fast response instrumentation that provides information on particle number and surface area concentration in near real-time. The Scanning Mobility Particle Sizer (SMPS) has been a standard instrument for measuring highly size resolved, mass-independent particle number distributions (Wang and Flagan, 1990) in the laboratory, but its relatively slow response time and need for an aerosol with steady physical characteristics make it difficult to use in on-road experiments where the ambient aerosol is changing constantly. The Diffusion Charging Sensor (DC) and the Photoelectric Aerosol Sensor (PAS) have been presented as additional monitors for diesel and ambient aerosols (for example Matter et al., 1999). Both instruments have a time resolution of < 10 seconds, making them quite suitable for on-road measurements. The aim of this study is to examine the possibilities and limits of these instruments, combined with Condensation Particle Counter (CPC) measurements, for real-time ambient monitoring. The main question will be whether combined PAS, DC and
CPC measurements, without simultaneous SMPS measurements, can deliver useful information on the characteristics of urban aerosols. For this purpose, PAS, DC and CPC data from different experiments, along with corresponding SMPS results, were used to check the consistency of the results of both approaches.

3.2 METHODS AND EXPERIMENTS

3.2.1 The University of Minnesota Mobile Emission Laboratory

The experiments described in this paper were performed with the University of Minnesota (UMN) Mobile Emission Laboratory (MEL), which was constructed as part of the US Coordinating Research Council (CRC) E-43 project titled “Diesel Aerosol Sampling Methodology” (1998-2002). The principal project goal was to develop sampling and measurement methods that allow the simulation of on-road aerosol submicron size distributions in laboratory dynamometer tests. In this project, on-road diesel truck chase experiments were performed, in which diesel exhaust plumes of followed trucks were captured by the MEL sampling inlet and transferred to a variety of instruments, where the exhaust plume was analyzed several seconds after emission from the exhaust stack. Additionally, several chassis dynamometer (vehicle test bench) experiments took place during the project period. A detailed description of the MEL and the project in general can be found in Kittelson et al. (2000). One of the main innovations of the mobile emission laboratory was the ability to measure a large variety of aerosol parameters while driving on the road under real traffic conditions.

The following MEL instruments were involved in the experiments discussed in this paper: A Diffusion Charging Sensor (LQ1-DC, Matter Engineering, Wohlen, Switzerland), a Photoelectric Aerosol Sensor (PAS2000, ECO Chem, USA), a Condensation Particle Counter (CPC 3025, TSI Inc., St. Paul, MN, USA) and a Scanning Mobility Particle Sizer (SMPS, TSI Inc., St. Paul, MN, USA). An external dilution system was built by UMN for the CPC. The DC, PAS and CPC were continuously connected to the same sample distribution manifold in the MEL. The SMPS requires a steady aerosol, but on-road exhaust plumes are not steady. Therefore, a different sampling system was used for the SMPS. This system employed a bag sampler to capture the on-road aerosol so that the SMPS could complete the size distribution measurement. Urban ambient data for this paper were collected in October 1999 in the Minneapolis city region, while chassis/engine dynamometer data and additional ambient data were collected in April/May 2000 in Columbus IN (USA). DC ($\mu m^2/cm^3$), PAS (fA) and CPC ($cm^{-3}$) data were logged in 1-s intervals and were corrected for sampling time lags and individual instrument response times during data analysis. No correction for particle losses in the sampling lines was applied. SMPS raw data were treated with TSI SMPS software version 2.4, including charge correction. Further details on the sampling conditions will be given in the context of each experiment. The following Sections will give a brief overview about important aspects on PAS and DC measurements, which served as a base for the interpretation of the results gained during this study.
3.2.2 The Photoelectric Aerosol Sensor (PAS)

The PAS responds to photoemitting substances on the surface of aerosol particles. Ultraviolet irradiation of the sampled aerosol leads to the emission of photoelectrons from surface material that readily undergoes photoemission (Burtscher, 1992). The remaining positively charged aerosol particles are separated from the electrons and collected on a filter connected to an electrometer. The measured current is a function of the UV irradiation wavelength and intensity, the total available surface area and the photoemission properties of the surface materials. Commercially available instruments usually have a wavelength of 222 nm. Diesel accumulation mode particles strongly respond to the PAS (Matter et al., 1999). Although the PAS originally was promoted as a monitor for surface-bound PAHs, recent investigations more generally stated that PAHs show a high photoelectric (PE) yield, causing a high PAS signal, while EC (elemental carbon), which has a significantly lower PE yield, leads to a only moderate PAS response (see Baltensperger et al., 2001; Siegmann and Siegmann, 2000). However, for diesel accumulation mode particles the contribution from PAHs to the PAS signal may be much lower than the EC contribution. In such cases the PAS signal for diesel aerosol measurements is predominantly correlated with the EC surface concentration of the diesel accumulation mode particles, despite the lower PE yield of the EC surface. In mixed urban aerosols on the other hand, where the PAH surface concentration (for example from spark ignition engines) may be much higher, the high PE yield of the PAHs dominates the PAS response. Therefore, PAS signals can only be quantitatively interpreted in a certain context. Nevertheless, PAS signal observations are useful for monitoring of relative changes using the measured electrometer response (usually fA units). These values are corrected for lamp fluctuations etc., which enables good instrument-to-instrument comparability in commercially available instruments.

3.2.3 The Diffusion Charging Sensor (DC)

The Diffusion Charging Sensor (DC), consisting of a diffusion charging section combined with a current sensor, measures the active surface area of the aerosol particles (Baltensperger et al., 2001). The measured surface does not correspond to the surface area obtained by BET measurements, but represents the portion of the total aerosol surface area that is actively involved in the diffusion charging process or more generally the part of the surface which is accessible by direct diffusion. To prevent electrostatic repulsion by ions already attached to the particle surface, the charging level is kept on a low level by default, so that the ion attachment is still comparable to the attachment of neutral atoms. While this surface portion previously has been described as Fuchs Surface for the attachment of neutral atoms (Fuchs, 1964; Gaggeler et al., 1989), Siegmann and Siegmann (2000) recently introduced the measured quantity as “active” surface for atom or ion attachment. The active surface $S_a$ is calculated using equation (3.1):

$$ S_a = \frac{1}{3kT} \cdot \frac{dn}{dt} = \text{const} \cdot \frac{dn}{dt} \quad (3.1) $$
where \( n \) is the concentration of atoms or ions with the mass \( m \), \( k \) the Boltzmann constant, \( T \) the temperature, \( dn/dt \) the measured ion attachment rate and \( \text{const} \) the calibration constant which is determined during instrument calibration. A detailed calibration procedure for the DC is described in (Siegmann and Siegmann, 2000). According to theory the active surface corresponds to the geometric surface for particles smaller than the particle mean free path (Fuchs, 1964; Allen and Raabe, 1982). The DC signal is controlled by Brownian diffusion and is therefore material independent. However, for particles smaller than 10 nm the image potential becomes important, leading to a material dependent ion attachment rate, which is (on a relative level) higher than for the same total active surface formed by larger particles (Baltensperger et al., 2001).

3.2.4 PAS/DC Ratio

The PAS/DC ratio has been described as a characteristic property for individual types of combustion aerosols (Matter et al., 1999). A plot of PAS response versus DC surface has been found to yield a linear relationship for any individual type of combustion aerosol (for example diesel particulate matter, cigarette smoke, candle smoke, wood fire). Since both instrument responses are a function of the aerosol surface area concentration, the slope of PAS versus DC plots can be considered as the capability of the surface to undergo photoelectric charging, which depends on the surface material.

3.2.5 The Diameter of Average Surface, \( D_{\text{Ave,S}} \)

If both the surface concentration \( S \) and the total number concentration \( N \) of a specified sample volume are known, one can define the diameter of average surface, \( D_{\text{Ave,S}} \), as

\[
D_{\text{Ave,S}} = \left( \frac{S}{\pi \cdot N} \right)^{0.5}
\]  

(3.2)

(see Kittelson et al., 2000). Thus, \( D_{\text{Ave,S}} \) represents the diameter of a hypothetical monodisperse aerosol that has the same surface area concentration as the measured polydisperse aerosol. In this paper, the diameter of average surface calculated with the DC signal \( (S_a) \) and the CPC total number concentration will be termed \( D_{\text{Ave,S(A)}} \). In an equal way, \( D_{\text{Ave,S}} \) can be obtained using the total surface area concentration calculated from SMPS number size distributions, assuming spherical particles with their respective mobility diameter. \( D_{\text{Ave,S}} \) values calculated with this method will be termed \( D_{\text{Ave,S(SMPS)}} \). Since the size and shape of the accumulation modes of diesel particle number size distributions, in most cases, do not vary greatly with engine type or operating conditions (see Harris and Maricq, 2001), \( D_{\text{Ave,S}} \) can be interpreted as an indicator for the presence of a nuclei mode during time series experiments. A higher concentration of nuclei mode particles will result in a decreasing \( D_{\text{Ave,S}} \). In contrast, a change in the total particle number concentration will not affect \( D_{\text{Ave,S}} \) as long as the shape of the size distribution remains fairly constant.
To give a graphic impression on the value of $D_{\text{Ave},S}$ in a given number size distribution, Figure 3.1 shows four examples of number size distributions where the diameter of average surface (in this case $D_{\text{Ave},S(\text{SMPS})}$) is indicated for fresh/aged diesel aerosol with/without nuclei mode particles. The $D_{\text{Ave},S(\text{SMPS})}$ values range between 30 and 100 nm. There are two main factors, which influence the diameter of average surface and have opposite effects. First, a large increase of nuclei mode particles with a constant accumulation mode causes a decrease in $D_{\text{Ave},S(\text{SMPS})}$. On the other hand, a shift of the accumulation mode towards larger diameters due to coagulation and condensation processes results in an increase in $D_{\text{Ave},S(\text{SMPS})}$. As it will be shown later (Fig. 3.11), $D_{\text{Ave},S(\text{SMPS})}$ is in good agreement with $D_{\text{Ave},S(A)}$ for the particle size range considered in this paper. It will also be shown (Fig. 3.8) that changes in $D_{\text{Ave},S(A)}$ are clearly recognizable in $D_{\text{Ave},S(A)}$ time series plots.

Fig. 3.1: Examples of particle size distributions for diluted fresh diesel exhaust (top graph) with and without a nucleation mode (dilution ratio ~ 800:1), and for urban ambient aerosol with and without nucleation mode (bottom graph). For each distribution $D_{\text{Ave},S(\text{SMPS})}$ is indicated. The depicted distributions are examples from the University of Minnesota CRC E-43 project “Diesel Aerosol Sampling Methodology”.

![Graph showing particle size distributions](image-url)
3.3 METHOD COMPARISONS

3.3.1 Characterization of Diluted Diesel Exhaust During Chassis Dynamometer Tests

As described by Abdul-Khalek et al. (1999) and Wei et al. (2001a,b), the dilution process of raw diesel exhaust is strongly dependent on the predominating conditions (dilution tunnel design, temperature, humidity of the dilution air, as well as the dilution ratio and the residence time). In the experiments done on the chassis dynamometer (vehicle test bench), the raw exhaust was diluted using a two-stage dilution tunnel and then sampled by the MEL. The tunnel was operated with a primary dilution ratio of roughly 20 and a residence time of about 0.3 s. The secondary dilution ratio was about 40 giving an overall dilution ratio of 800:1. Figures 3.2 - 3.4 show the effect of a 16 °C to 24 °C temperature change of the dilution air during a chassis dynamometer experiment in which a diesel engine truck was running at conditions that simulate a 55 mph on-road no load cruise. It is clearly seen that the particle characteristics change with time, which can mainly be assigned to the changing dilution air temperature (Figs. 3.2, 3.3a-e). The clear change in particle characteristics around 8:20 can, however, not be assigned to a temperature change, but is due to other changes in the conditions mentioned above. The NOx level in the dilution tunnel system remained fairly constant at 775 ± 40 ppb (after background level subtraction) throughout the experiment.

![Graph of SMPS number size distributions](image)

**Fig. 3.2:** SMPS number size distributions (S1-S5) during a diesel engine chassis dynamometer experiment. The shown data illustrates the effect of a change in dilution air temperature (16 °C to 24 °C at a dilution ratio of 800:1) and other factors (see text) on the diesel exhaust characteristics. The exact measurement times of the shown distributions are given in Figure 3.3e.
Fig. 3.3: Temporal course of the measured aerosol parameters during the chassis dynamometer experiment described in the text (raw exhaust dilution ratio ≈ 800:1). Arrows S1-S5 mark the starting points of the SMPS size distribution measurements shown in Figure 3.2. Due to the high range of the CPC signal a logarithmic scale is shown in plot a).
At the beginning, a large nuclei mode is present in the SMPS number size distributions (Fig. 3.2) with the mode at approx. 10 nm that changes its concentration with time and finally disappears. At the end, only the accumulation mode, showing a constant concentration throughout the experiment, is left. The same behavior is also reflected in the $D_{Ave,S/A}$ evolution, calculated with the DC and CPC data (Figs. 3.3a,b,d), also demonstrating the shift towards larger particle diameters. Furthermore, as long as a nuclei mode is present, PAS and DC signals (Figs. 3.3b,c) show opposite behavior. However, as soon as the nuclei mode has disappeared, there is a continuous increase of both the PAS (strong increase) and the DC (slight increase) signal. Plotting the PAS signal vs. DC surface area concentration (Fig. 3.4) reveals two branches of data for the above situations, each of them indicating a different relationship between the two instrument responses. In the absence of a nuclei mode, a highly positive slope results, indicating a high positive charge collected on the PAS current filter. On the other hand, the presence of a large nuclei mode concentration prevents a large positive PAS signal (see Matter et al., 1999), and a negative slope is obtained for this situation. During further data analysis, a physical explanation of this phenomenon was searched, which will be given in Section 3.4.

![Fig. 3.4: PAS/DC plot for the chassis dynamometer experiment described in the text (raw exhaust dilution ratio 800:1). The existence of two evident branches is subject of discussion in this publication.](image)

### 3.3.2 Ambient Monitoring

The same plot types were created with ambient air data collected by the MEL on different occasions. Again, SMPS size distributions are compared to DC, PAS and CPC data. Figure 3.5 shows PAS vs. DC plots for two time periods in which the MEL monitored the air near a loading dock with ongoing diesel truck parking traffic. The sampling air was sucked directly from outdoors to the MEL. As a further example, Figures 3.6a,b show PAS and DC
data for a half-day freeway ride (October 4, 1999) in the Minneapolis city region with continuously changing ambient conditions. For comparison, SMPS size distributions for all the above ambient conditions (plus the chassis dynamometer experiment) are summarized in Figure 3.7.

In Figure 3.5 the same type of relationship between the PAS and DC signals can be observed as during the chassis dynamometer experiment. Again, two distinct branches are present for surface area concentrations higher than 500 $\mu$m$^2$/cm$^3$. The two branches in Figure 3.5 with a high slope show different zero offsets with respect to the PAS response, an observation that will have to be considered in the final interpretation of the results (see next section). The corresponding SMPS size distributions in Figure 3.7 (loading dock 4/28/00 and 5/1/00) reveal only a low concentration of nuclei mode particles for this situation.

![Fig. 3.5: PAS/DC plot for ambient air containing high concentrations of diesel exhaust. The data were collected on two different days near the same loading dock (see text).](image)
Fig. 3.6: Upper graph (a): PAS/DC plot of data collected during an autumn ½-day freeway ride with the University of Minnesota Mobile Emission Laboratory (see description in the text). There is evidence of two branches, as described in Figures 3.4 and 3.5. Lower graph (b): Frequency distribution of the PAS/DC ratio values shown in (a). Gaussian fitting yields a major and a minor but distinct Gaussian component.

Fig. 3.7: SMPS number size distributions for the situations discussed in the text. Each size distribution represents the average of all size distributions measured during the corresponding situation.
Plotting PAS vs. DC for the half-day freeway ride (Figure 3.6a) results in a similar two-branch graph as for the previous situations, but with considerably more data scattering. For proper analysis and interpretation a frequency distribution of the PAS/DC ratios has been added (Figure 3.6b), which confirms that there is a small but distinct second ratio mode. It is important to note that a flat branch in a PAS/DC plot is not only caused by the presence of a nuclei mode, but also by situations in which the concentration of surface PAH and EC is low (see Section 3.2). However, these two situations can be distinguished by considering $D_{Ave,S(A)}$.

Finally, Figure 3.8 shows $D_{Ave,S(A)}$ for the half-day freeway ride, along with corresponding SMPS size distributions, confirming that independent measuring methods are consistent; i.e., the combination of DC and CPC generate average surface diameter values that correspond with SMPS size distribution results.

![Graph](image)

Fig. 3.8: $D_{Ave,S(A)}$ for the half-day freeway ride described in the text with four SMPS number size distributions measured at indicated times. The presence of a nuclei mode is clearly reflected in $D_{Ave,S(A)}$, which is low when a strong nuclei mode is present in the SMPS number size distributions.

### 3.4 DISCUSSION AND MODEL DEVELOPMENT

In order to combine the empirical findings discussed in the previous section with the existing knowledge about the PAS and DC instrument responses and the chemical composition of both the nuclei mode particles and the accumulation mode particles (see Introduction), a suitable way to present the overall data is needed. In simple PAS/DC plots there is no possibility to consider particle size, since a large DC signal can both be caused both by a large accumulation mode concentration and a large nuclei mode concentration. However, as stated by Matter et al. (1999), nuclei mode particles consist of material...
inhibiting the PAS response, while the accumulation mode particles are known to cause high PAS signals. If the PAS/DC ratio is plotted against the diameter of average surface, one obtains a triangle-like distribution of all data points (Fig. 3.9). In Figure 3.9 all data previously discussed in this study are used, plus one additional loading dock data set in which a large nuclei mode was present. This kind of data presentation eliminates all secondary dilution effects (for example by meteorological processes), since it is based entirely on intensive parameters.

![Fig. 3.9: PAS/DC vs. D_{\text{ave,SMPS}} plots for all sampling situations presented in this publication. A triangle-like arrangement of the data points is evident, which is discussed in the text. The corresponding SMPS number size distributions are shown in Figure 3.7.](image)

For further discussion, we focus on the vertices of the triangle in Figure 3.9. As a summary, Figure 3.10 illustrates general interpretation aspects of PAS/DC vs. $D_{\text{ave,SMPS}}$ plots. The top of the triangle represents data points with a large PAS/DC ratio. As shown above, this is the case for plume samples in which no or only a small nuclei mode was found (see Figs. 3.4, 3.5). Since accumulation mode particles become covered by non-photoemitting material with time after emission (nitrate, sulfate, water, hydrocarbons, see Section 3.1) it can be assumed that these “triangle-top” plumes only contain fresh diesel accumulation mode particles. This is also indicated by $D_{\text{ave,SMPS}}$ values around 40-50 nm (Fig. 3.9). This range agrees well with the corresponding values for fresh accumulation mode particles without coexisting nuclei mode particles in Figure 3.1.
At the right vertex of the triangle larger $D_{\text{Ave,S}(A)}$ values can be found (70-90 nm). Data points in this region are attributed to low PAS values and fairly low CPC values. There are two possible explanations for this behavior. It may result from aged accumulation mode particles, which typically are larger than freshly emitted diesel aerosol particles and coated with at least one monolayer of non-photoemitting material. This coating is due to condensation of condensable material on the fresh particulate matter core and may occur on relatively short time scales (minutes to hours). Alternatively it may result from an engine condition that gives relatively high emissions of large accumulation mode particles that act as a sink for volatile species that suppress photoemission. Either case could be associated with higher $D_{\text{Ave,S}(A)}$ values (see for example Figure 3.1).

Finally, the left vertex shows situations in which a large nuclei mode was present in the sampling volume (see size distributions in Fig. 3.7), while the corresponding $D_{\text{Ave,S}(A)}$ values range between 20 and 30 nm. As stated above, these ultrafine particles, which far exceed the accumulation mode particles in concentration during such situations, are composed of non-photoemitting material (hydrocarbons, sulphuric acid, water). This agrees with the low PAS values for this situation. The high concentration of nuclei mode particles indicates that the coexisting accumulation mode particles are most probably also coated by condensing material. This is also shown in Figure 3.4, where the PAS signal is basically suppressed as long as nuclei mode particles are present. Only for moderate nuclei mode concentrations the PAS response is not suppressed (see Figures 3.5 and 3.7, loading dock situation 4/28/00). These findings are in accordance with a study by Steiner and Burtscher (1993), where they showed that desorption of volatile material from diesel combustion particles leads to higher PAS signals.
The discussed triangle vertices represent extreme situations. As seen in Figure 3.9, samples from highway samples yield data points in the middle of the triangle, since a mix of all three corner-situations is present. Nevertheless, the distinct dynamic distribution of these points (see $D_{\text{Ave},S(A)}$ in Figure 3.8) reflects the changing nature of the sample plumes.

It also has to be mentioned that PAS/DC vs. $D_{\text{Ave},S(A)}$ plot axes are not independent, since the DC signal is included in both axes. In order to check the degree of this bias, $D_{\text{Ave},S(SMPS)}$ was calculated with the corresponding SMPS data sets. Figure 3.11 shows the comparison of $D_{\text{Ave},S(A)}$ with $D_{\text{Ave},S(SMPS)}$ for all data used in Figure 3.9. Comparing the resulting data with the 1:1 relationship, it is evident that for large particles $D_{\text{Ave},S(A)}$ is considerably smaller than $D_{\text{Ave},S(SMPS)}$. As stated earlier in this paper, the active surface does not correspond exactly to the geometric surface area obtained by mobility measurements, but corresponds closely to SMPS results over most of the size range of interest for combustion aerosols.

For interpretation of new data sets according to this triangle model, defined high and low concentration levels for the DC, PAS and CPC are first required (see Figure 3.10). This is preferably done by combustion aerosol measurements including PAS, DC, CPC and SMPS under controlled conditions, prior to the planned ambient air experiments.

### 3.5 CONCLUSIONS AND SUMMARY

Chassis dynamometer experiments as well as the ambient monitoring confirmed that the response of the PAS is strongly influenced by semi-volatile species, which partially condense on the accumulation mode particles and are responsible for the formation of nuclei mode particles. In PAS/DC plots there are hardly any data points between the two branches, which often are found in plots from urban ambient aerosol measurements.
The diameter of average surface calculated with DC and CPC data \( D_{\text{Ave,S(A)}} \) delivers information on the relative concentration of nuclei mode particles throughout an experiment, assuming a fairly constant size and concentration of the diesel accumulation mode particles. Since the physical principles to determine the DC active surface and the CPC particle number concentration are basically independent from each other, \( D_{\text{Ave,S(A)}} \) can be considered as a reliable relative parameter. It has also been shown that the relationship between \( D_{\text{Ave,S(A)}} \) and \( D_{\text{Ave,S(SMPS)}} \) is in good agreement with the Fuchs theory.

For a series of measurements, a triangle-like arrangement of the data has been obtained in PAS/DC vs. \( D_{\text{Ave,S(A)}} \) plots. The corner regions of these plots can be assigned to three different situations regarding the composition of the sampled aerosol in the particle size range \( D < 200 \text{ nm} \). The plot helps to distinguish between the presence/absence of nuclei mode particles and the presence/absence of an adsorbed layer on accumulation mode particles. The high time resolution of the involved instruments allows for stand-alone and real-time monitoring of exhaust particles and enables qualitative, but reliable statements about the quality of the measured air, which can give valuable input to the ongoing discussion about the influence of particle surface and number concentrations on health and environment. These statements can be obtained without making simultaneous SMPS measurements. Quantitative statements are not possible so far, since no simple physical or chemical parameters can be assigned to the PAS measurements according to current knowledge. Further limitations are the relatively large signal variability and a certain threshold aerosol concentration (higher than approx. 1000 particles per \( \text{cm}^3 \)) that is needed for a reasonable interpretation of the results. However, for most urban or motor traffic measurements concentrations are sufficiently high.

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REFERENCES


A MOBILE POLLUTANT MEASUREMENT LABORATORY – MEASURING GAS PHASE AND AEROSOL AMBIENT CONCENTRATIONS WITH HIGH SPATIAL AND TEMPORAL RESOLUTION

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Author remark: This chapter represents the standard of knowledge at the time of publication. Later chapters of this thesis will partially take up open questions and future goals that arise here.

ABSTRACT

A mobile pollutant measurement laboratory was designed and built at the Paul Scherrer Institute (Switzerland) for the measurement of on-road ambient concentrations of a large set of trace gases and aerosol parameters with high time resolution (< 15 s for most instruments), along with geographical and meteorological information. This approach allowed for pollutant level measurements both near traffic (e.g. in urban areas or on freeways/main roads) and at rural locations far away from traffic, within short periods of time and at different times of day and year. Such measurements were performed on a regular base during the project YOGAM (year of gas phase and aerosol measurements). This paper presents data measured in the Zürich (Switzerland) area on a late autumn day (6 November) in 2001. The local urban particle background easily reached 50000 cm$^{-3}$, with additional peak particle number concentrations of up to 400000 cm$^{-3}$. The regional background of the total particle number concentration was not found to significantly correlate with the distance to traffic and anthropogenic emissions of carbon monoxide and nitrogen oxides. On the other hand, this correlation was significant for the number concentration of particles in the size range 50 – 150 nm, indicating that the particle number concentration in this size range is a better traffic indicator than the total number concentration. Particle number size distribution measurements showed that daytime urban ambient air is dominated by high number concentrations of ultrafine particles (nanoparticles) with diameters < 50 nm, which are immediately formed by traffic exhaust and thus belong to the primary emissions. However, significant variation of the nanoparticle mode was also observed in number size distributions measured in rural areas both at daytime and nighttime, suggesting that nanoparticles are not exclusively formed by primary traffic emissions. While urban daytime total number concentrations were increased by a factor of 10 compared to the nighttime background, corresponding factors for total surface area and total volume concentrations were 2 and 1.5, respectively.

4.1 INTRODUCTION

In the last decades it has been recognized that airborne particles in the range 0.001 – 10 μm play an important role in atmospheric processes. It has become clear that especially emissions from road traffic and industry have a large impact on the air quality of the lower
troposphere. The characterization of regional, local and micro-scale mechanisms for formation and transformation of different aerosol types (source-to-sink investigations) has become a hot research topic in recent years. In the worldwide attempt to regulate particulate emissions, PM10 (mass concentration of particles with an aerodynamic diameter D < 10 $\mu$m) has become a common parameter to characterize and legally control particulate emissions and ambient concentrations, since this is the particle mass concentration that is actually inhaled by the human nose. Several studies indeed showed that high PM10 concentrations are likely to cause adverse health effects (Dockery et al., 1993; Künzli et al., 2000). In recent years, a new focus has been put on a new class of non-soot particles, which have been observed near roadways and have particle diameters D < 50 nm and are thus smaller than soot particles (Whitby et al., 1975; Weingartner et al., 1997). These particles are widely termed ultrafine particles or nanoparticles. In contrast to the large number concentration in which they occur, their mass contribution to PM10 is negligible. In current medical research the potential of nanoparticles for adverse health effects is an important issue, since particles of this size (D < 50 nm) have been shown to possibly have a much higher impact relative to their mass than larger particles (Donaldson et al., 1996). For the development of future legal standards for emissions and ambient concentrations it will have to be discussed whether other parameters beside mass concentrations will have to be considered, such as number concentration or surface area concentration.

The lifetime of ultrafine particles is relatively short. Assuming (a) a coagulation coefficient $K$ of $8 \times 10^{-9}$ cm$^3$s$^{-1}$ for coagulation of D = 20 nm particles with D = 100 nm particles, (b) $K = 1.2 \times 10^{-9}$ cm$^3$s$^{-1}$ for monodisperse coagulation of particles with D = 20 nm (Seinfeld and Pandis, 1998) and (c) a typical urban concentration of ~5000 cm$^{-3}$ for particles with D = 100 nm, the half-life of D = 20 nm particles at typical urban peak concentrations of ~100000 cm$^{-3}$ is less than 1.5 h for monodisperse coagulation and simultaneous coagulation with D = 100 nm particles. A highly spatially and temporally resolved mapping of gaseous and aerosol parameters is a necessary base for a detailed discussion of local and regional pollutant distribution, for an investigation of relevant atmospheric processes, as well as for the verification of models simulating atmospheric processes. This is already reality for some trace gases such as ozone in many regions, since measuring sites of the authorities are required to monitor gaseous pollution levels to comply with environmental law. However, for aerosols an area-covering inventory of aerosol parameters other than PM10 is still scarce.

In current gas phase chemistry research, the investigation of processes leading to high levels of lower tropospheric ozone during summer smog situations is a major focus. It has been recognized in the last decades that ground-near ozone shows harmful effects in living organisms. Ozone is produced in the lower troposphere as a result of different chain processes, and its formation is mainly governed by the availability of either NO$_x$ (sum of nitric oxide and nitrogen dioxide) or VOCs (volatile organic compounds). So far, NO$_x$ sensitive ozone production has been observed during summer in rural areas of the Swiss Plateau (Dommen et al., 1995), while VOC sensitive production may occur down-wind of urban and industrial areas. This dependency of the ozone formation on NO$_x$ or VOCs has been studied in many Eulerian photochemical models (e.g. Kleinman, 1991; Sillman, 1995). However, there are only few experimental studies so far elucidating the transition of NO$_x$ sensitivity in summer to VOC sensitivity in winter (Jacob et al., 1995).
4.2 THE PROJECT YOGAM (YEAR OF GAS PHASE AND AEROSOL MEASUREMENTS)

A suitable way to obtain information on the spatial and temporal distribution of atmospheric trace gases and aerosol parameters, without the need of a dense network of stationary measuring sites, is the use of a mobile laboratory. Mobile laboratories have been reported in literature to be in use for example for vehicle chase experiments and other applications (e.g. Kittelson et al., 2000; Seakins et al., 2002). At the Paul Scherrer Institute (PSI, Villigen, Switzerland), a mobile pollutant measurement laboratory with a large set of gas phase and aerosol instruments was constructed on occasion of the project YOGAM (Year of Gasphase and Aerosol Measurements, February 2001 - May 2002). The PSI mobile laboratory followed a selected route (Figure 4.1) in the Zürich (Switzerland) area on a regular base, to monitor the seasonal and spatial variation of relevant ambient aerosol parameters and trace gases. The route included downtown Zürich (400 meters above sea level, m a.s.l.), suburban areas (small towns, airport and industry, 400 – 500 m a.s.l.) and rural regions (500 – 900 m a.s.l.). In addition to seasonal variations, short time variations, for example between daytime and nighttime or between weekday and Sunday were investigated. Within short time intervals, ambient air under heavy traffic conditions could be compared to ambient air far away from traffic. In contrast to a network of stationary measuring sites, no intercalibration experiments had to be performed with the mobile laboratory, since a specific parameter was always measured by the same instrument. Main goals and innovations of YOGAM were the spatially and temporally resolved mapping of aerosol parameters for the selected area in detail, and the investigation of the indicators for \( \text{NO}_x \) or VOC sensitivity of the ground-near ozone formation in the same area. This paper describes the design and construction of the PSI mobile laboratory, focusing on the various aspects that have to be taken into account for sampling ambient air while driving. In addition, first results from YOGAM will be presented, showing both a regional distribution of aerosols in the Zürich region and the various possibilities for data analysis of spatially and temporally resolved aerosol and trace gas measurements. Within the scope of this paper, mainly aerosol measurements are discussed.

![Fig. 4.1: Route of the YOGAM project (solid black line). Dark gray filled areas represent lakes, and the contours show the altitude profile (z, meters above sea level). The two main cities in the selected area, Zürich and Winterthur, are also indicated. Swiss X and Y designate the coordinates in the official Swiss kilometer grid.](image-url)
4.3 THE MOBILE LABORATORY

4.3.1 Vehicle Design and Power Supply

An IVECO Turbo Daily Transporter (length 5.1 m; width 2 m; height 2.6 m; max. gross weight 3.5 tons) was selected as rolling platform for the measuring equipment, which is a van size suitable for driving also on small roads, but with a maximal utilization of van room and engine power. Thus, a multi-purpose use of the measuring van is possible for different scientific problems. A diesel vehicle was chosen for instrument power consumption reasons. Controlling self-contamination during the measurements was an important issue, and its achievement will be described in this paper. To continuously operate the complete set of measurement equipment with a total weight of approximately 1000 kg and a total power consumption of 1.6 ± 0.2 kW while driving, a second alternator was built into the van engine system. With this setup, the running van motor delivered 2.8 kW power, which was stored in two 12V/110Ah batteries. These batteries served as buffer in case of short-time power interruptions (up to ½ h). During stationary measurements, the batteries were externally fed and recharged with 380 V from the Swiss electricity network via a voltage transformer. The batteries were connected to two sinus inverters (90% efficiency), yielding 2 x 720 W with 220 V and 2 x 100 W with 12 V available to operate the measuring equipment.

Gas phase and aerosol instruments were separately mounted in two 19-inch racks. To prevent instrument damage from vibration shocks while driving, shock absorbers were installed between the rack shelves and the individual instruments. Special precaution had to be taken for some instruments like the Condensation Particle Counter (CPC, see next section), which is particularly sensitive to shocks. Therefore, additional rubber foam layers were used to support shock dampening. Additionally, the interior of the van was air conditioned to remove the heated air caused by the power consumption of the instruments.

4.3.2 Inlet System

A schematic picture of the mobile laboratory is given in Figure 4.2. To catch the ambient air while driving before it is affected by the own van exhaust, and to minimize turbulence caused by the van front, the main inlet was located above the van front end, at a height of 2.35 m. This inlet height was also adapted to the YOGAM project goal, where the focus was put on ambient concentrations, which should not be affected by road-near dust perturbation. Due to the different sampling system demands for gas phase and aerosol compounds, two separate inlet systems were constructed. To better correlate data from the different inlet positions (e.g. in truck chase experiments, when a small exhaust plume only hit one inlet), two individual CO₂ monitors were connected to the two different inlets. In this way, the gas phase measurements could be linked to the aerosol measurements.
The inlet system material for the gaseous compounds was Teflon (PFA), to minimize chemical reactions with the inlet walls, while the aerosol inlet was constructed of steel, and was based on isokinetic sampling calculations and aerosol fluid dynamic properties. The aerosol inlet and flow system dimensions were designed such that laminar flow was prevailing. The conical inlet (1 cm diameter at the entrance, see Figure 4.2, position A) enabled isokinetic sampling at 50 km h\(^{-1}\) (14 m s\(^{-1}\)) driving speed, reducing the air velocity in the sampling system to 0.5 ± 0.1 m s\(^{-1}\), which is close to the highest flow velocity possible for laminar flow under these conditions (Flow Reynolds number Re ~ 1800). This constant flow was provided by a heavy-duty blower at the end of the entire inlet system (position E). A transfer section then transported the sampled air to the interior of the van. The SMPS (Scanning Mobility Particle Sizer) system, located on the van roof, was branching off its sampling air from the main air stream already before the transfer line entered the van (position B). A similar sampling air branch-off was constructed for the OPC (Optical Particle Counter) at the van entrance, to keep the sampling line for coarse mode particles (1-20 µm) short and to prevent particle losses by gravitational settling (position C). With the selected setup, losses for particles with D = 2.5 µm were calculated to be < 2 %, < 10% for D = 6 µm and < 20 % for particles with D = 10 µm. Inside the van, the main sampling air stream was slowed down in a cylinder (position D) to a constant laminar flow velocity of 0.06 ± 0.02 m s\(^{-1}\). For further distribution of the sampling air to the individual instruments, different inlet tips were mounted inside the distribution cylinder. These tips were adapted to each individual instrument flow rate, enabling isokinetic sampling. The time delay of the sampling air between the main inlet tip and the distribution cylinder was 10 ± 3 seconds.
4.3.3 Instrumentation and Quality Assurance

Table 4.1 gives an overview of all measured parameters, including geographical and meteorological parameters. Gas phase parameters are listed in the table, but are not subject to this paper with exception of carbon monoxide (CO), ozone (O₃) and nitrogen dioxide (NO₂). The measuring method of the CO monitor used in this study is based on the fluorescence of CO in the vacuum ultraviolet (VUV) at a wavelength of 150 nm (Gerbig et al., 1999). The instrument was automatically zeroed and calibrated every 2 h by a certified 2 ppm calibration standard. Calibrations usually varied less than 5% during one cruise. The ozone (O₃) instrument is based on the conventionally used UV absorption technique. The instrument was intercompared before and after each cruise with a laboratory reference instrument. Nitrogen dioxide (NO₂) is measured by a miniaturized luminol-based chemiluminescence technique (Wendel et al., 1983; Dommen et al., 2002). The obtained signals are non-linear and the instrument is therefore calibrated before and after each cruise with at least 10 different calibration gas concentrations (diluted from certified 1 and 10 ppm NO₂ calibration standards) from the sub-ppb range up to 400 ppb. During each calibration, the interference of ozone is quantified and afterward taken into account in the data treatment. Real-time determination of position, altitude and driving speed of the mobile laboratory was achieved using a Global Positioning System (GPS Type). All pollutant parameters shown in Table 4.1 were logged in real-time (<10 s) intervals, except for the SMPS (3 min time resolution), aethalometer (1 min), betameter (1/2 h), as well as for the peroxide (H₂O₂) and formaldehyde (HCHO) data (3 min).

As mentioned above, the SMPS (Wang and Flagan, 1990) was located on the roof of the van. With this outdoor setup, the measured aerosol is kept at ambient temperature and humidity during the entire scanning mobility process, preventing volatilization of water and other highly volatile aerosol compounds during the measurement (Nessler et al., 2003). Additionally, the sheath and excess air flows (10 lpm) were handled in a closed-loop arrangement, in which the flow was kept constant with a mass flow controller. This setup has the advantage of a large flow stability and an identical composition of the sheath and sampling air. Since the upper particle size limit was 310 nm, isokinetic sampling was not a critical issue for this instrument. Size calibration of the SMPS was performed using monodisperse Latex spheres with D = 79 nm. Sheath air and aerosol flows were monitored daily. The Ultrafine Condensation Particle Counter (CPC) Model 3025 has been found to be the most suitable CPC model for stand-alone use in mobile applications (Kittelson et al., 2000). Since peak number concentrations for urban on-road measurements often exceed 200 000 cm⁻³, and the upper detection range of this instrument is 100 000 particles per cm³, a clean-air dilution system was designed for the CPC, yielding a 1:4 to 1:8 dilution of the CPC sampling air (see (Weingartner et al., 1997). A recalibration of the clean-air dilution flow and the resulting dilution ratio was performed in regular intervals. To check long-term stability of the SMPS, CPC and also the Diffusion Charging Sensor (DC), constant laboratory indoor background aerosol was measured prior to every measuring ride, typically described by a log-normal particle number size distribution with N_{tot} = 4000 – 7000 cm⁻³, a mode between 80 and 100 nm and a geometric standard deviation of 2.0 ± 0.2. Total particle number concentrations measured by the CPC and calculated from fitted SMPS number size distributions agreed within 10% for these measurements. Additionally, the active surface area concentration S_{active} was calculated from SMPS size distributions according to equation (4.1):
\[ S_{active} = \int \frac{\phi \lambda}{1.5 \eta b(D)} dD \approx \sum_i \frac{dN}{d \log D}(D_i) \cdot \frac{\Delta \log D \cdot D_i}{C_c(D_i)} \]  

(4.1)

where \( \phi \) is a scattering parameter \((\phi = 1.695)\), \( \lambda \) the mean free path of gas molecules (air \( \approx 66 \text{ nm} \)), \( b \) the mobility, \( \eta \) the viscosity of gas (air \( \approx 1.81 \cdot 10^{-5} \text{ N s m}^{-2} \)), \( C_c \) the Cunningham Slip Correction, \( N \) the particle number concentration and \( D \) the particle diameter (see Siegmann and Siegmann, 2000). The active surface area concentration was compared to the corresponding DC values (see also Bukowiecki et al., 2002). Both for laboratory background aerosol and outdoor diurnal averages, the ratio between the DC signal and the active surface area concentration calculated from SMPS was constant within 15% throughout the project. The Optical Particle Counter (OPC) was calibrated with latex spheres by the manufacturer twice during YOGAM. To maintain data quality for the OPC (and also for the aethalometer and the betameter), instrument-specific internal calibration procedures were performed according the manufacturer’s recommendations, along with monitoring the long-term signal stability.
Table 4.1: Instrumentation of the PSI mobile pollutant measurement laboratory. The indicated time resolutions represent instrument time resolutions. The system time resolution for the aerosol and gas phase instruments is $10\pm 3$ s.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Instrument Method / Type</th>
<th>Time Resolution</th>
<th>Detection Limit</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Aerosols</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Size Distribution D = 7-310 nm</td>
<td>SMPS (Scanning Mobility Particle Sizer) / TSI DMA 3071, CPC 3010</td>
<td>3 min</td>
<td>not defined</td>
</tr>
<tr>
<td>Number Concentration D &gt; 3 nm</td>
<td>CPC (Condensation Particle Counter) / TSI UCPC 3025</td>
<td>1 s</td>
<td>0.5 cm$^{-3}$(1s)</td>
</tr>
<tr>
<td>Size Distribution D = 0.3-20 µm</td>
<td>OPC (Optical Particle Counter) / Grimm Dustmonitor 1.108</td>
<td>6 s</td>
<td>1 particle/l (6s)</td>
</tr>
<tr>
<td>Active Surface Area</td>
<td>DC (Diffusion Charging Sensor) / Matter Engineering LQ1-DC</td>
<td>1 s</td>
<td>10 µm$^2$ cm$^{-3}$</td>
</tr>
<tr>
<td>Black Carbon Mass Concentration</td>
<td>Aethalometer (Visible Light Absorption) / Magee AE-10</td>
<td>1 min</td>
<td>40 ng m$^{-3}$ (5 lpm, 5 min)</td>
</tr>
<tr>
<td>PM2.5</td>
<td>Betameter (Beta radiation absorption) / Eberline FH 62 I-R</td>
<td>½ h</td>
<td>3 µg m$^{-3}$ (½ h)</td>
</tr>
<tr>
<td>O$_3$</td>
<td>Ozone-Monitor (UV absorption) / constructed by PSI</td>
<td>2 s</td>
<td>1 ppb</td>
</tr>
<tr>
<td>CO</td>
<td>CO – Monitor (Vacuum UV resonance fluorescence) / Aerolaser AL-5002</td>
<td>1 s</td>
<td>2 ppb</td>
</tr>
<tr>
<td>CO$_2$</td>
<td>CO$_2$ – Monitor (IR absorption) / LI-COR</td>
<td>1 s</td>
<td>0.1 ppm</td>
</tr>
<tr>
<td>NO$_x$, NO$_y$, HNO$_3$, PAN</td>
<td>NO$_x$To$_x$ (Chemiluminescence) / constructed by MetAir / PSI / Juelich</td>
<td>1 s</td>
<td>200 ppt</td>
</tr>
<tr>
<td>H$_2$O$_2$, total peroxide</td>
<td>Peroxide Monitor (Fluorescence) / Aerolaser AL-2002</td>
<td>120-180 s</td>
<td>200 ppt</td>
</tr>
<tr>
<td>HCHO</td>
<td>Formaldehyde Monitor (Fluorescence) IFU Garmisch</td>
<td>120-180 s</td>
<td>200 ppt</td>
</tr>
<tr>
<td><strong>Gas Phase</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Geographical information</td>
<td>GPS/Garmin 11plus</td>
<td>2 s</td>
<td>common standard</td>
</tr>
<tr>
<td>Temperature</td>
<td>Thermilinear Thermistor Network/YSI 44203</td>
<td>&lt; 1 min</td>
<td>common standard</td>
</tr>
<tr>
<td>Pressure</td>
<td>constructed by PSI</td>
<td>&lt; 1 min</td>
<td>common standard</td>
</tr>
<tr>
<td>Relative humidity</td>
<td>HUMICAP sensor/Vaisala HMP 31UT</td>
<td>&lt; 1 min</td>
<td>common standard</td>
</tr>
<tr>
<td>Wind direction</td>
<td>constructed by PSI</td>
<td>1 s</td>
<td>common standard</td>
</tr>
<tr>
<td>Global radiation</td>
<td>Pyranometer/Kipp&amp;Zonen “Solarimeter” CM10</td>
<td>&lt; 1 min</td>
<td>common standard</td>
</tr>
</tbody>
</table>
Although the OPC measures particle diameters up to 25 µm, particle diameters > 10 µm are not analyzed in this study due to the uncertainties resulting from the mobile application. To avoid self-contamination, the relative wind direction (front or back wind) as well as the vehicle driving speed (from GPS measurements) was logged for every measured data point. All sampling situations in which both the vehicle driving speed was close to zero and the relative wind was from the back (where the van exhaust pipe was located) were identified during raw data processing, and the corresponding data were marked as possibly influenced by self-contamination. Typically, 15% of the on-road data was assigned to driving speeds slower than 5 km/h, whereof < 30% showed backwind situations, yielding a net percentage of < 5% for possibly self-contaminated on-road data. A video camera installed in the driver cab of the van recorded the traffic situation in front of the mobile laboratory. These videotapes were important during the data analysis process, since they helped much for the interpretation of the measured signal curves.

4.4 HIGH TIME RESOLUTION MEASUREMENTS

Measurements and data analysis of particle number concentrations, carbon monoxide, ozone and nitrogen dioxide will be shown and discussed both for a part of and along the entire YOGAM route (Figure 4.1). Figure 4.3 shows signals measured along a short stretch (11 km) with both heavily traffic-influenced and rural sectors. The measured particle number concentration is highly dynamic during on-road ambient concentration measurements. With the help of the video records, peak concentrations of > >100000 particles per cm³ could be clearly assigned to exhaust plumes from single vehicles driving in front of the mobile laboratory. However, the measured concentrations cannot be assumed to represent the immediate vehicle emission, since the regional particle background concentration is expected to be equally higher for traffic-rich regions.

To separate peak concentrations from the background, the background signal has first to be estimated. As a background, one could for example determine the minima over one minute. However, these minima can be influenced by instrumental signal noise, yielding too low background concentrations. The alternatives are low percentiles that are not influenced strongly by the signal noise but still represent the background concentration. The determined background does not depend very strongly on the exact percentile value and the arbitrarily chosen 5% percentile proved to be a good choice for our purposes. Compared to the 5% percentile values, the corresponding 3% percentile values differed less than 0.5%, while the 10% percentile values were 8% higher. It is known from truck chase experiments (Kittelson et al., 2000) that the duration in which the exhaust plume of a preceding vehicle is constantly captured, does in most cases not exceed 10 –15 s. Furthermore, the average time behind a specific vehicle in normal urban main road traffic is estimated to be 15 – 45 s. Based on these values, the use of a minimum of 1-min 5%-percentiles seems reasonable to obtain an estimation for the local particle background at the position where the mobile laboratory was driving (assuming an average driving speed of 50 km h⁻¹, the spatial window for 1 min was ~800 m).
As an illustration, Figure 4.3a shows the original particle number concentration and the baseline (derived from the 5% percentiles) for a 16-min period. For the selected example, the rural particle background ranged between 5000 and 15000 particles per cm$^3$, while the local background on busy main roads easily reached 30000 - 50000 cm$^3$. Once the particle background is determined, one can estimate the peak particle number concentration resulting from a vehicle in front. As seen in Figure 4.3b and based on video observations, concentrations can increase up to 400000 particles per cm$^3$ for mixed traffic (diesel and gasoline) with a low percentage of heavy duty vehicles. The average distance to the vehicles in front was approximately 50 m. In contrast, Figure 4.3a shows that the use of averages does not allow distinguishing between background and individual plumes.
In addition to the particle number concentrations, ozone and nitrogen dioxide concentrations are shown in Figure 4.3c. Two channels of the chemiluminescence instrument were used to measure NO$_2$ and they can hardly be distinguished, thus providing confidence in the data. In the traffic-rich regions, NO$_2$ concentrations are high due to the reaction of the emitted nitric oxide (NO) with ozone and to a lower extent by direct emissions of NO$_2$. Accordingly, the ozone concentrations are very low when high concentrations of NO$_2$ are found.

To examine background variations on a larger temporal and regional scale, Figure 4.4 shows the moving 5-min 5% - percentile of the total particle number concentration and the carbon monoxide (CO) mixing ratio along the entire YOGAM route for a selected day (November 6, 2001). The spatial range for 5 min at an assumed driving speed of 50 km h$^{-1}$ is $\sim$4 km, which is essentially larger than the spatial range of most point emission sources (farm activity etc.). The evolution of the 5% - percentile curve for CO, a direct indicator for traffic emissions, shows a clear background trend throughout the selected day with higher concentrations in the city and busy suburban areas and lower concentrations in the rural part. On top of the baseline there are peaks from immediate CO emission sources (mostly traffic) sticking out, reaching concentrations that are up to one order of magnitude higher than the baseline level.

In contrast, the background level of the total particle number concentration (see 5% - percentile curve) shows a significantly less pronounced variation between the different regions. Furthermore, the peak pattern is much denser than for CO, and single peaks can even not be separated on this 9-h time scale (in contrast to Figure 4.3). Thus, background level differences of the total particle number concentration are either non-linearly related to traffic density, or due to other particle sources (e.g. secondary aerosol formation). However, it is known from other studies that ambient concentrations of particles with 50 nm < D < 150 nm are well correlated with traffic activity (Bukowiecki et al., 2002). The lowermost graph in Figure 4.4, showing the integrated SMPS number concentration in the particle size range 50 – 150 nm, indeed shows a correlation to the CO background and hence to traffic activity ($R^2 = 0.4$ for 5-min averages and 0.63 for 30-min averages, respectively). The corresponding $R^2$ values for the comparison of the integrated SMPS number concentration of ultrafine particles (7 nm < D < 50 nm) with the CO background are significantly lower, i.e. < 0.3 for both the 5-min and 30-min average values. Obviously, neither the total particle number concentration nor the ultrafine particle level in ambient air can be considered as exclusive indicators for traffic. Finally, it is interesting to note that the correlation of CO with particles with 50 nm < D < 150 is significantly weaker for the CO 5-min and 30-min average values ($R^2 = 0.2$ and 0.38, respectively) than for the corresponding CO background values (see above).
Fig. 4.4: Moving 5-min 5 %-percentile curves for the total particle number concentration and the CO mixing ratio (solid black lines, graphs a and b) and the corresponding one-second interval raw data (thin gray lines, graphs a and b). The curves represent data collected along the YOGAM route (Figure 4.1) on November 6, 2001. On the top, sampling area types are shown (U: Urban, S: Suburban, R: Rural). The lowermost graph (c) depicts the integrated SMPS number concentration in the particle diameter range 50 – 150 nm.

4.5 REGIONALLY AND SPATIALLY RESOLVED PARTICLE NUMBER SIZE DISTRIBUTIONS

Figure 4.5 compares particle number size distributions measured during a clear weather period in November 2001, in which the mobile laboratory followed the regular YOGAM route during a selected night (5-6 November, 2001) and the subsequent day. SMPS and OPC particle number size distributions were averaged over periods during which the van measured rural (Zürcher Oberland, Switzerland) and urban (Zürich downtown area) ambient air along the route shown in Figure 4.1. The averaging was performed for both daytime (urban 10:30 – 11:30; rural 15:00 – 16:00) and the corresponding nighttime
Looking at Figure 4.5 it is obvious for the considered situations that the largest difference and statistical variation in dN/d(logD), i.e., in the particle number concentration of a specific size range, occurs in the nanoparticle region (D < 50 nm). The formation and transformation of particles in this size region is known to be complex and highly dynamic in ambient air, since such processes depend on a number of highly variable parameters: Supersaturation of freshly emitted traffic gas emissions and subsequent nucleation of particles has been shown to be a process which instantly (1-3 s) yields high number concentrations of particles with D < 50 nm in diameter (Kittelson et al., 2000). These particles have been termed as primary nanoparticles (Baltensperger et al., 2002). Recent research states that primary nanoparticles are mainly composed of hydrophobic organic material and only a small percentage of sulphuric acid (dependent on the diesel fuel sulphur content) and water (Tobias et al., 2001; Baltensperger et al., 2002). Furthermore,
especially the triggering of the nucleation process is known to be strongly dependent on small changes in parameters like ambient temperature and relative humidity (Abdul-Khalek et al., 1999; Bukowiecki et al., 2002). This is all reflected in Figure 4.5 (left graph), which yields high concentrations of ultrafine particles (> 50000 cm\(^{-3}\)), along with a large concentration variation (see 25%- and 75%-percentiles), for the urban daytime 1-h average. The comparison to the corresponding nighttime situation, in which motor traffic was minimal, clearly illustrates the large effect of motor traffic activity on ultrafine particle formation in urban areas. In contrast to these traffic related primary ultrafine particles, secondary ultrafine particles represent products from gas-to-particle conversion e.g. after photochemical reactions in air plumes from urban areas, but also from biogenic gaseous precursors (Mäkelä et al., 1997). The right graph in Figure 4.5 shows corresponding daytime and nighttime particle number size distributions for the rural area. The ultrafine particle level is generally lower than in the urban area graph (left) and shows less variation during daytime. However, for this rural area episode there was a large variation of the ultrafine particle size range during nighttime, indicating that non-photochemical processes apparently governed the (low) secondary ultrafine particle concentration. It is clear however, that a separation of primary and secondary ultrafine particles is not possible by simply considering particle number size distributions. Baltensperger et al. (2002) showed that there is evidence for both types of ultrafine particle formation in daytime urban aerosols. Finally, the presence and characteristics of both particle types influence total particle number concentrations in rural and urban regions and lead to total number concentration background levels as observed in Figure 4.4.

In contrast, the particles larger than 50 nm show less spatial and temporal variation. In urban areas, this part of the size distribution is primarily characterized by soot particles (50 – 150 nm) emitted from motor traffic (especially diesel vehicles). This is evident in Figure 4.5 (left), which shows a particle number concentration in the range 50 – 150 nm that is approximately half an order of magnitude higher during daytime than the corresponding nighttime concentration. There is a rather constant concentration level of this mode in all non-traffic situations. As a result of the low statistical variation of this concentration, a diameter shift towards higher particle diameters is observed in the rural nighttime particle number size distribution (Figure 4.5, right). Considering the measured relative humidity (70 % during daytime and 85 % during the night) it can be estimated that particle size due to a higher relative humidity was 10 % larger during nighttime than during daytime, assuming a hygroscopic growth factor of 1.3 at 85 % relative humidity (Baltensperger et al., 2002). Thus, hygroscopic growth accounts only partially for the observed diameter shift, while the rest of this particle growth for the rural nighttime situation is likely to be caused by coagulation and condensation.

It is also seen in Figure 4.5 that no relevant number size distribution changes occur in the range 500 – 1000 nm, regardless of time of day and location. This has been observed in other studies (Imhof et al., 2002) and implies that concentration variations in this particle size range are hardly affected by direct human activities on a local to regional scale. For larger particles, a clear difference in daytime/nighttime and urban/rural variation is again observed. In contrast to the ultrafine size region, main concentration changes in this size range are not so much caused by tailpipe emissions, but by other factors like resuspension, industry emissions or primary biogenic emissions (the latter being more active during other seasons). Accordingly, there is a distinct concentration increase indicated in Figure 4.5 for
both the urban and the rural areas during daytime. Finally, total number, surface and volume concentrations are summarized in Table 4.2 for all size distributions shown in Figure 4.5. Urban daytime particle concentrations were increased by factors of 10, 2 and 1.5 in number, surface area and volume, respectively, compared to the corresponding nighttime situations. There was no significant change in surface area and volume concentrations for all other situations (nighttime urban, daytime and nighttime rural).

Table 4.2: Total number \(N_{\text{tot}}\), surface \(S_{\text{tot}}\) (geom./active) and volume concentrations \(V_{\text{tot}}\) for the size distributions shown in Figure 4.5. All calculations were performed based on the measured SMPS number size distributions.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Unit</th>
<th>Urban Daytime</th>
<th>Urban Nighttime</th>
<th>Rural Daytime</th>
<th>Rural Nighttime</th>
</tr>
</thead>
<tbody>
<tr>
<td>(N_{\text{tot}})</td>
<td>(\text{cm}^{-3})</td>
<td>7.8 (10^4)</td>
<td>7.8 (10^3)</td>
<td>1.5 (10^4)</td>
<td>5.7 (10^3)</td>
</tr>
<tr>
<td>(S_{\text{tot}}) (geom.)</td>
<td>(\mu m^2\text{cm}^{-3})</td>
<td>865</td>
<td>450</td>
<td>387</td>
<td>481</td>
</tr>
<tr>
<td>(S_{\text{tot}}) (active)</td>
<td>(\mu m^2\text{cm}^{-3})</td>
<td>552</td>
<td>256</td>
<td>225</td>
<td>257</td>
</tr>
<tr>
<td>(V_{\text{tot}})</td>
<td>(\mu m^3\text{cm}^{-3})</td>
<td>33</td>
<td>20</td>
<td>18</td>
<td>23</td>
</tr>
</tbody>
</table>

### 4.6 CONCLUSIONS AND OUTLOOK

Mobile measurements have proven to be useful for the assessment of spatial and temporal variations of air pollutants and allow investigations that cannot be performed with data from a single monitoring site. This case study confirms that there is a large diurnal and regional variation of ultrafine particles for both urban and rural areas, showing the different origins and the dynamic nature of the formation and transformation of these particles. Diurnal variations showed that neither the ultrafine particle fraction nor the total particle number concentration is an exclusive indicator of primary traffic emissions. Since nanoparticles are subject to investigation in current medical research with respect to possible adverse health effects, detailed knowledge on their origin, dynamics and composition is important for highly populated regions. Many of these questions will be addressed in the further analysis of the YOGAM data, where the discussion of the findings of this case study will also be extended to seasonal variations.

### ACKNOWLEDGEMENTS

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REFERENCES


Fine and Ultrafine Particles in the Zürich (Switzerland) Area Measured with a Mobile Laboratory: An Assessment of the Seasonal and Regional Variation Throughout a Year

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ABSTRACT

On occasion of the project YOGAM (year of gas phase and aerosol measurements), the spatial and temporal variation of selected aerosol and gas phase parameters was assessed for the Zürich (Switzerland) area with a new mobile pollutant measurement laboratory. This assessment based on on-road measurements along a specified route on selected days during different seasons in 2001/2002, covering urban, suburban and rural regions. Special focus was put on the investigation and characterization of particles in the fine (particle diameter D<2.5 µm) and ultrafine (D<100 nm) size ranges. Analysis of Variance (ANOVA) showed that the variance of all considered fine and ultrafine aerosol parameters (i.e. particle background and total number concentration for particles larger than 3 nm, number concentrations in the size ranges 7–30 nm and 80–140 nm, as well as the active surface area concentration) was significantly larger for day-to-day than for spatial variation. However, Principal Component Analysis (PCA) found a similar regional pollution pattern within every single measuring day. Lowest particle background levels (D>3 nm) were found in rural areas at higher elevation (15000 cm⁻³), while corresponding mean background values for urban and freeway-influenced areas were typically 35000 cm⁻³ and >80000 cm⁻³, respectively. Meteorology, i.e. prevailing weather conditions not only governed the day-to-day concentration variations in the selected area, but also influenced the formation of primary (directly traffic-related) and in few cases secondary (biogenic or anthropogenic) ultrafine particles. Overall, low temperatures regularly enhanced primary ultrafine particle formation in urban areas. There was a possible indication for relatively low number concentrations of secondary ultrafine particles during a few warm and sunny spring days. Mobile measurements as they were performed in this study have been shown to be suitable for pollutant assessments to obtain good information on spatial and day-to-day variability. For experimental studies concerning spatial resolution on a relatively short time scale (<1 day), a mobile measurement design may even be more appropriate than a network of stationary measuring sites.

5.1 INTRODUCTION

In recent years the potential of particulate matter to cause adverse health effects has been investigated in numerous epidemiological and laboratory studies. For PM10 (mass concentration of particles with an aerodynamic diameter Dₐ<10 µm) and PM2.5 (fine particles, Dₐ<2.5 µm), a significant correlation with adverse health effects could be shown (Dockery et al., 1993; Katsouyanni et al., 1997; Laden et al., 2001; Pope et al., 1995;
For ultrafine particles (particle diameter D<100 nm) extensive epidemiological studies have not been performed yet, but the few available investigations point to an increased health effect potential of particles in this size range due to their special interaction pattern in the human airways (Donaldson et al., 1998; Oberdörster and Utell, 2002; U.S. Health Effects Institute, 2002; Wichmann and Peters, 2000). In ambient aerosol research, strong efforts have been made in the last years to obtain a clearer picture not only on the spatial and temporal distribution of PM10 and PM2.5, but also on other aerosol parameters like particle number size distributions, surface or volume.

Ambient ultrafine particles have gained special attention in the last years and typically show complex formation and occurrence patterns. So far, it has been recognized that ambient ultrafines can be split into primary and secondary ultrafine particles (Baltensperger et al., 2002). Primary ultrafines and nanoparticles (D<50 nm) are mostly traffic-related and are rapidly formed by nucleation during the dilution and cooling of freshly emitted gaseous combustion exhaust in the atmosphere, depending on the meteorological conditions. It has been shown that their formation is favored at low ambient temperatures and is lower for low-sulfur fuel vehicles (Abdul-Khalek et al., 1999, 2000; Kittelson et al., 2002). When formed, they show large number concentrations in the area of emission, but have a limited lifetime (<10 min in urban areas) and therefore a typical area of influence of 100 m – 1 km (Capaldo and Pandis, 2001). They are composed of hydrocarbons and a minor fraction of sulphuric acid and water, and are believed to partially originate from lube oil substances in vehicle engines (Tobias et al., 2001). On the other hand, secondary ultrafines describe ambient ultrafine particles that are not directly formed immediately after emission, but are rather formed from chemically transformed gaseous precursors, i.e. by condensation of products from atmospheric reactions (e.g. photochemical reactions, see Mäkelä et al., 2000). Nucleation bursts of secondary ultrafines have been reported to occur worldwide in remote, rural and even urban areas and are strongly influenced by meteorological parameters like solar radiation or temperature, but also by background concentrations of other pollutants, i.e. the local particle background concentration (Baltensperger et al., 2002; Birmili and Wiedensohler, 2000; Boy and Kulmala, 2002a,b; McMurry and Woo, 2002). Their lifetime and composition is so far less elucidated, though there is evidence that they mainly consist of organics and that they persist longer (in the range of hours) in the atmosphere than primary ultrafines, mainly due to slower coagulation with typically lower concentration levels of background aerosol (O'Dowd et al., 2002).

However, for numerous regions no area-covering inventory of combined aerosol and other parameters exists for a longer period of time. Such monitoring is often restricted to PM10 or PM2.5 due to national regulation standards. In an earlier publication (Bukowiecki et al., 2002) we showed a case study involving mobile pollutant measurements in the Zürich (Switzerland) area, in which we investigated spatial and temporal differences in pollutant levels for an autumn two-day period. While we focused on short-time signal variations and day/night differences in that case study, this paper will present an analysis of particulate pollution variation on a larger time scale. It is the goal of this study to obtain statistical information on both spatial dependence and seasonality of particulate air pollution in the Zürich area with the help of mobile pollutant measurements, and also to have a closer look at the processes leading to the formation of fine and ultrafine particles. A focus will be put on particle number size distributions, total particle number concentration, active
5.2 METHODS

5.2.1 Experimental

On occasion of the research project YOGAM (Year of Gas Phase and Aerosol Measurements, 2001/2002), a mobile laboratory was constructed at the Paul Scherrer Institute (Villigen, Switzerland), allowing for on-road measurements of a variety of aerosol parameters and gas phase parameters, along with geographical information (GPS, Garmin IIPlus) and meteorological data (temperature, pressure, humidity, global radiation and relative wind direction). The setup of the mobile laboratory is discussed in detail in Bukowiecki et al. (2002). Data included in this paper were measured by a scanning mobility particle sizer (SMPS, DMA TSI 3071 and CPC TSI 3010), a condensation particle counter (CPC, TSI UCPC 3025), an optical particle counter (OPC, Grimm 1.108), a diffusion charging sensor (DC, Matter Engineering LQ1-DC) and a carbon monoxide (CO) monitor (Aerolaser AL-5002). Since measurements could be performed while driving, highly time-resolved (1 s – 3 min time resolution for most parameters) and spatially resolved information (continuously) on the ground pollutant level in the testing area was obtained. During YOGAM, a selected route in the Zürich area (Fig. 5.1) was driven on a regular base throughout the course of a year, including downtown Zürich (400m a.s.l.), suburban areas (400–500m a.s.l.) as well as rural sites (500–900m a.s.l.). For the time frame chosen, additional data from official monitoring stations were available for comparison.

5.2.2 Data Analysis Strategy

The large number of parameters measured during YOGAM required a careful development of a suitable data analysis strategy. In contrast to stationary measurements, mobile measurements have a simultaneous signal variation in time and space. To find a way to categorize such data it is necessary to know the signal dynamics along both the time and location axis. As shown earlier (Bukowiecki et al., 2002), regional signal variations (< 5 min) of the measured parameters occurred more rapidly than temporal variation (< 4 h). Thus, a temporal classification of the data in morning and afternoon loops on the YOGAM route was appropriate. As shown in the next section, spatial classification of the data was achieved by binning the raw data into different location bins along our measuring route. This binning per location and measuring day allowed for analysis of variance (ANOVA), which turned out to be especially suitable for looking at the whole-year data set with respect to signal variations at different locations and different days. However, this 3-dimensional measuring approach (signal vs. time and two-dimensional space) and the large number of parameters measured push the use of low-dimensional statistics to a limit. Hidden connections can essentially influence and jeopardize the pure investigation of single dependencies. Multivariate statistical tools are often used in ambient aerosol research. Principal Component Analysis (PCA) and Factor
Analysis (FA) are useful statistical methods to explore and explain relevant variations in large data sets. In source apportionment studies these techniques are often used for quantitative analysis and underlie a large number of critical boundary conditions. For the YOGAM data set, a PCA was selected as an adequately simple multivariate tool to find unobvious patterns in the data and reveal hidden correlations between different parameters. The findings of PCA were then used as input for further process studies.

5.2.3 Data Preparation

This section describes how raw data collected during YOGAM were processed to finally get appropriate input data for ANOVA and PCA. With the help of GPS, every raw data point (1 s intervals) of the total aerosol number and surface area concentration as well as of the CO concentration measurements was assigned to a geographical position. In a first step, we defined a set of location bins along the YOGAM route, based on geography and population density considerations. Thus, all raw data points were attributed to corresponding location bins. In this way, 75 location bins were obtained (see Table 5.1 and Fig. 5.1), each containing approximately 180–360 raw data points, which corresponded to 3–6 min driving along the route with the mobile laboratory (except the Zürich city bins, which also included midday stationary measurements during 30–60 min). Since local changes in location type occurred very quickly while driving along the YOGAM route (often within a few minutes, which is faster than the average day-to-day deviation from the route schedule (±1.5 h)), the concept of forming location bins was found to be more reliable than a time-averaging approach. All parameters were corrected for instrument and sampling time delays (see Bukowiecki et al., 2002), and all data were checked for plausibility and validity. Next, the data in each location bin were statistically treated according to Table 5.2. For the CPC, both average concentrations and 5% percentile values were formed. The latter statistical parameter has been shown to be suitable to eliminate plumes originating from single vehicles and thus to estimate the local (i.e. the road-near) particle background (which is influenced both by fresh traffic plumes and aged/dispersed plumes of anthropogenic and biogenic origin, see Bukowiecki et al., 2002). For all meteorological parameters and carbon monoxide, average values per location bin were calculated, except for the global radiation. Since numerous low values resulting from bridges, buildings, trees or tunnels biased the measured global radiation throughout a measuring day, the use of 95% percentiles was shown to be appropriate to get the regional daily variation of this parameter. Average values were also calculated for the active surface area, since the measured DC signal included too much noise for reasonable percentile calculations. For all parameters, standard deviations were calculated for every location bin. Furthermore, SMPS and OPC particle size distributions were linked, to obtain an average size distribution from 7 nm to 10 micrometer for every location bin.
Fig. 5.1: Main (solid black line) and access (thin black line) route of the YOGAM project. Dark gray filled areas represent lakes, and the contours show the altitude profile (z, meters above sea level). The two main cities in the selected area, Zürich and Winterthur, are also indicated. Swiss X and Y designate the coordinates in the official Swiss kilometer grid. Additionally, location bin classifications according to Table 5.1 (R: rural, S: suburban, U: urban, HT: heavy-traffic areas) and official meteorological monitoring stations (M1-M7) are shown.

Table 5.1: Classification of individual stretches of the YOGAM route into 75 location bins regarding altitude and vicinity to anthropogenic activity. R: Rural, S: Suburban, U: Urban (downtown Zürich), HT: Heavy traffic area. Altitudes are indicated in meters above sea level. The bins are sorted chronologically, in the order how they were passed while driving on the route. A normal measuring day included the access route from Paul Scherrer Institute to the loop starting point (1-9), followed by two subsequent runs along bins 10-75.

<table>
<thead>
<tr>
<th>Bin No.</th>
<th>1</th>
<th>2</th>
<th>3</th>
<th>4</th>
<th>5</th>
<th>6</th>
<th>7</th>
<th>8</th>
<th>9</th>
<th>10</th>
<th>11</th>
<th>12</th>
<th>13</th>
<th>14</th>
<th>15</th>
</tr>
</thead>
<tbody>
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<td>Altitude</td>
<td>356</td>
<td>364</td>
<td>398</td>
<td>432</td>
<td>446</td>
<td>497</td>
<td>576</td>
<td>577</td>
<td>564</td>
<td>515</td>
<td>527</td>
<td>428</td>
<td>424</td>
<td>433</td>
<td>482</td>
</tr>
<tr>
<td>Type</td>
<td>R</td>
<td>S</td>
<td>S</td>
<td>HT</td>
<td>HT</td>
<td>S</td>
<td>S</td>
<td>S</td>
<td>S</td>
<td>S</td>
<td>U</td>
<td>U</td>
<td>U</td>
<td>U</td>
<td>U</td>
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<td>485</td>
<td>503</td>
<td>534</td>
<td>529</td>
<td>542</td>
<td>540</td>
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<td>S</td>
<td>S</td>
<td>R</td>
<td>R</td>
<td>R</td>
<td>R</td>
<td>S</td>
<td>HT</td>
<td>HT</td>
<td>HT</td>
<td>HT</td>
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<td>R</td>
</tr>
<tr>
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<td>37</td>
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<td>43</td>
<td>44</td>
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</tr>
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<td>Altitude</td>
<td>593</td>
<td>588</td>
<td>550</td>
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<td>830</td>
<td>768</td>
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<td>S</td>
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<td>S</td>
<td>S</td>
<td>R</td>
<td>R</td>
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<td>R</td>
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<td>58</td>
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<td>60</td>
</tr>
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<td>Altitude</td>
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<td>626</td>
<td>615</td>
<td>602</td>
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<td>525</td>
<td>555</td>
<td>598</td>
<td>632</td>
<td>642</td>
<td>590</td>
</tr>
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<td>R</td>
<td>R</td>
<td>R</td>
<td>R</td>
<td>R</td>
<td>R</td>
<td>R</td>
<td>S</td>
<td>HT</td>
<td>S</td>
<td>HT</td>
<td>S</td>
<td>HT</td>
<td>R</td>
</tr>
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<td>64</td>
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<td>73</td>
<td>74</td>
<td>75</td>
</tr>
<tr>
<td>Altitude</td>
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<td>543</td>
<td>467</td>
<td>428</td>
<td>428</td>
<td>446</td>
<td>453</td>
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<tr>
<td>Type</td>
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<td>S</td>
<td>S</td>
<td>S</td>
<td>S</td>
<td>S</td>
<td>S</td>
<td>HT</td>
<td>HT</td>
<td>HT</td>
<td>S</td>
<td>HT</td>
<td>S</td>
<td>HT</td>
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</tbody>
</table>

87
Table 5.2: Parameters measured during YOGAM used for the assessment presented in this paper. For every parameter it is indicated a) how raw data was treated to obtain the location bin values, b) how individual parameters are connected to other parameters and c) how they eventually were transformed in this study to become normally distributed (sqrt = square root). N: Number concentration, S: Surface area concentration, V: Volume concentration. Numbers in brackets indicate size ranges (in nm). \( N_{\text{tot}} \) and \( N_{\text{bkg}} \) values were derived from condensation particle counter measurements (CPC TSI CPC3025, D>3 nm), while the rest of the N, S, and V based parameters were obtained from SMPS (scanning mobility particle size) and OPC (optical particle counter) measurements, see text and Bukowiecki et al. (2002b).

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Raw data time resolution</th>
<th>Treatment</th>
<th>Dependencies</th>
<th>Transformation</th>
</tr>
</thead>
<tbody>
<tr>
<td>N(&lt;30)</td>
<td>3 min average</td>
<td>-</td>
<td>-</td>
<td>log10</td>
</tr>
<tr>
<td>N(30-80)</td>
<td>3 min average</td>
<td>-</td>
<td>-</td>
<td>log10</td>
</tr>
<tr>
<td>N(80-140)</td>
<td>3 min average</td>
<td>-</td>
<td>-</td>
<td>log10</td>
</tr>
<tr>
<td>N(140-310)</td>
<td>3 min average</td>
<td>-</td>
<td>-</td>
<td>log10</td>
</tr>
<tr>
<td>( N_{\text{tot}} ) (OPC)</td>
<td>6 s average</td>
<td>-</td>
<td>sqrt</td>
<td>log10</td>
</tr>
<tr>
<td>( N_{\text{tot}} ) = CPC(mean)</td>
<td>1 s average</td>
<td>-</td>
<td>-</td>
<td>log10</td>
</tr>
<tr>
<td>( N_{\text{bkg}} ) = CPC(background)</td>
<td>1 s 5% percentile</td>
<td>-</td>
<td>-</td>
<td>log10</td>
</tr>
<tr>
<td>S(&lt;30)</td>
<td>3 min average</td>
<td>~ ND^2</td>
<td>log10</td>
<td></td>
</tr>
<tr>
<td>S(30-80)</td>
<td>3 min average</td>
<td>~ ND^2</td>
<td>log10</td>
<td></td>
</tr>
<tr>
<td>S(80-140)</td>
<td>3 min average</td>
<td>~ ND^2</td>
<td>log10</td>
<td></td>
</tr>
<tr>
<td>S(140-310)</td>
<td>3 min average</td>
<td>~ ND^2</td>
<td>log10</td>
<td></td>
</tr>
<tr>
<td>( S_{\text{tot}} ) (OPC)</td>
<td>6 s average</td>
<td>~ ND^2</td>
<td>sqrt</td>
<td></td>
</tr>
<tr>
<td>V(&lt;30)</td>
<td>3 min average</td>
<td>~ ND^3</td>
<td>log10</td>
<td></td>
</tr>
<tr>
<td>V(30-80)</td>
<td>3 min average</td>
<td>~ ND^3</td>
<td>log10</td>
<td></td>
</tr>
<tr>
<td>V(80-140)</td>
<td>3 min average</td>
<td>~ ND^3</td>
<td>log10</td>
<td></td>
</tr>
<tr>
<td>V(140-310)</td>
<td>3 min average</td>
<td>~ ND^3</td>
<td>log10</td>
<td></td>
</tr>
<tr>
<td>V1 = V(&lt;1000)</td>
<td>3 min average</td>
<td>~ ND^3</td>
<td>sqrt</td>
<td></td>
</tr>
<tr>
<td>V2.5 = V(&lt;2500)</td>
<td>3 min average</td>
<td>~ ND^3</td>
<td>sqrt</td>
<td></td>
</tr>
<tr>
<td>V10 = V(&lt;10000)</td>
<td>3 min average</td>
<td>~ ND^3</td>
<td>sqrt</td>
<td></td>
</tr>
<tr>
<td>( V_{\text{tot}} ) (OPC)</td>
<td>6 s average</td>
<td>~ ND^3</td>
<td>sqrt</td>
<td></td>
</tr>
<tr>
<td>DC</td>
<td>1 s average</td>
<td>-</td>
<td>sqrt</td>
<td></td>
</tr>
<tr>
<td>CO</td>
<td>1 s average</td>
<td>-</td>
<td>log10</td>
<td></td>
</tr>
<tr>
<td>Altitude (Alt)</td>
<td>1 s average</td>
<td>-</td>
<td>log10</td>
<td></td>
</tr>
<tr>
<td>Pressure (Press)</td>
<td>1 s average</td>
<td>~ Alt^{-1}</td>
<td>log10</td>
<td></td>
</tr>
<tr>
<td>Temperature (temp)</td>
<td>1 s average</td>
<td>-</td>
<td>-</td>
<td></td>
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<tr>
<td>Relative Humidity (RH)</td>
<td>1 s average</td>
<td>-</td>
<td>log10</td>
<td></td>
</tr>
<tr>
<td>Global Radiation (GR)</td>
<td>1 s 95% percentile</td>
<td>-</td>
<td>-</td>
<td></td>
</tr>
</tbody>
</table>

Based on the focus of interest of this study, we calculated several comprehensive integrated sum parameters for different size ranges from the size distribution data (see Table 5.2). The result of the above procedure is a data set consisting of a [parameter x location bin] matrix for every measuring day. A summary of measuring days selected for YOGAM, including meteorological conditions, is given in Table 5.3. Although the YOGAM campaigns also included measurements made during spring and summer 2001, they were not used for ANOVA and PCA due to problems with SMPS and DC measurements (high signal scattering due to sampling problems and calibration problems, respectively). Summer data for the rest of the measured parameters (\( N_{\text{tot}} \), \( N_{\text{bkg}} \), CO) are however considered on other occasions in this paper and are mentioned in the specific context.
Table 5.3: Overview over the YOGAM measuring days discussed in this study. Summer 2001 data (5 measuring days) were not used for this study except for CO due to problems with SMPS and DC measurements. Temperature and global radiation represent daily averages plus standard deviation of the day-time mean (temperature) and 95% percentile (global radiation) values measured with the mobile laboratory.

<table>
<thead>
<tr>
<th>Date</th>
<th>Day type</th>
<th>Temperature (°C)</th>
<th>Global Radiation (W m⁻²)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Autumn 2001</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>11.10.01</td>
<td>Weekday</td>
<td>12.9 ± 2.6</td>
<td>300 ± 114</td>
</tr>
<tr>
<td>14.10.01</td>
<td>Sunday</td>
<td>15.6 ± 3.0</td>
<td>320 ± 92</td>
</tr>
<tr>
<td>31.10.01</td>
<td>Weekday</td>
<td>14.4 ± 1.7</td>
<td>214 ± 132</td>
</tr>
<tr>
<td>05.11.01</td>
<td>Night</td>
<td>4.6 ± 1.0</td>
<td>-</td>
</tr>
<tr>
<td>06.11.01</td>
<td>Weekday</td>
<td>5.9 ± 1.1</td>
<td>138 ± 92</td>
</tr>
<tr>
<td>Winter 2001/02</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>28.01.02</td>
<td>Weekday</td>
<td>9.9 ± 1.1</td>
<td>214 ± 102</td>
</tr>
<tr>
<td>29.01.02</td>
<td>Weekday</td>
<td>5.1 ± 2.1</td>
<td>156 ± 52</td>
</tr>
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<td>29.01.02</td>
<td>Night</td>
<td>1.2 ± 2.0</td>
<td>-</td>
</tr>
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<td>30.01.02</td>
<td>Weekday</td>
<td>6.8 ± 3.3</td>
<td>218 ± 90</td>
</tr>
<tr>
<td>03.02.02</td>
<td>Sunday</td>
<td>8.6 ± 3.1</td>
<td>254 ± 100</td>
</tr>
<tr>
<td>Spring 2002</td>
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<td></td>
<td></td>
</tr>
<tr>
<td>22.04.02</td>
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<td>10.7 ± 2.8</td>
<td>510 ± 130</td>
</tr>
<tr>
<td>23.04.02</td>
<td>Weekday</td>
<td>13.1 ± 2.3</td>
<td>528 ± 136</td>
</tr>
<tr>
<td>25.04.02</td>
<td>Weekday</td>
<td>12.2 ± 2.9</td>
<td>480 ± 180</td>
</tr>
<tr>
<td>26.04.02</td>
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<td>14.5 ± 1.6</td>
<td>314 ± 214</td>
</tr>
<tr>
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<td>15.5 ± 2.5</td>
<td>626 ± 90</td>
</tr>
<tr>
<td>16.05.02</td>
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<td>18.8 ± 3.3</td>
<td>612 ± 96</td>
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<td>17.05.02</td>
<td>Weekday</td>
<td>22.1 ± 2.8</td>
<td>624 ± 80</td>
</tr>
<tr>
<td>30.05.02</td>
<td>Night</td>
<td>10.0 ± 2.0</td>
<td>-</td>
</tr>
<tr>
<td>02.06.02</td>
<td>Sunday</td>
<td>18.0 ± 2.0</td>
<td>640 ± 100</td>
</tr>
</tbody>
</table>

5.3 ANOVA TESTS– DOES DAY-TO-DAY VARIATION EXCEED SPATIAL VARIATION?

In our previous case study (Bukowiecki et al., 2002) we showed that on a specific measuring day the background particle number concentration in our testing area differed by up to more than one order of magnitude between urban and rural areas. Taking all the data from the whole year into account, the question arises how this urban/rural variation is quantitatively related to the day-to-day variation due to different meteorological conditions in the Zürich area. Figure 5.2 shows a date vs. location contour plot for the 5% percentile (background) values of the total particle number concentration. It is clearly seen that rural and urban regions, but also locations influenced by heavy traffic, show different levels throughout the year (horizontal stripes). However, there are days/periods in which the overall particle background concentration is much higher than during other days or periods, exceeding the regional variation.
Fig. 5.2: Seasonal and spatial particle background variation for the Zürich (Switzerland) area. A contour plot of the particle background number concentration (D>3 nm) is shown, calculated with the 5% percentile of the CPC total particle number concentration (see Bukowiecki et al, 2002b). The x-axis represents the days selected for YOGAM measurements (including spring and summer 2001), while the y-axis depicts a morning and afternoon loop along the YOGAM route (in chronological order).

To better examine the influence of both daily weather conditions and local pollution characteristics on the measured parameters, Figure 5.3 shows box plots for the measured levels of \( N_{\text{bkg}} \), \( N_{\text{tot}} \), \( N(80–140) \), \( N(<30) \), active surface area and CO, separated both by date (daily averages over all locations) and location (location bin averages over all dates). Before interpreting the plot, analysis of variance (ANOVA) was performed for additional quantification, i.e. to examine whether the variation of the above average values was significant for date and location. A two-way factorial layout with replicates was applied, using the SPLUS 6.0 software (Insightful Inc., Seattle, Washington) with variables that were transformed to be normally distributed according to Table 5.2 (see Chambers and Hastie, 1992; Voss, 2000). F-values were calculated for both factors (date and location) to test the null hypothesis. For an acceptable null hypothesis, F-values are close to 1 and indicate that the variance between different groups of concentration levels (e.g. the variance of the daily averages) is approximately equal to the variance within all the individual concentration levels (i.e. the variance of the entire sample population). F>>1 thus indicates that the variance (i.e. the effect on the signal) between the level groups is significantly larger than the sample population variance.

The ANOVA showed that for all the selected parameters the variance both in date and location was significant (on a 0.01 level for F-statistics, probability \( p(F)<0.001 \)). Furthermore, both ANOVA and the box plots in Figure 5.3 reveal that for \( N_{\text{bkg}} \) \( (F_{\text{date}}=73.5, F_{\text{location}}=4.21) \), \( N_{\text{tot}} \) \( (F_{\text{date}}=265, F_{\text{location}}=21.7) \), the active surface area \( (F_{\text{date}}=197, F_{\text{location}}=17.5) \) and \( N(80–140) \) \( (F_{\text{date}}=152, F_{\text{location}}=25) \) the variation in date exceeded the
variation in location. For these parameters, the ANOVA model also quantitatively confirms the qualitative finding drawn from Fig. 5.2. For $N(<30)$ ($F_{\text{date}}=36.0$, $F_{\text{location}}=16.7$) and CO ($F_{\text{date}}=19.5$, $F_{\text{location}}=11.4$), the spatial variation is more similar to the day-to-day variation. It is suspected that this is due to the regularly observed formation of primary ultrafine particles with a short lifetime (see Introduction) in heavy-trafficked areas, and due to the long atmospheric lifetime of CO, respectively, as it will also be further discussed in Sects. 5.4 and 5.5. Conclusively, Figure 5.4 illustrates the variation of the selected pollutants in the YOGAM area. The upper plot shows the deviation of the particle background number concentration from the annual average in the YOGAM area. Depending on the daily weather condition, the curve is shifted up or down, maintaining a similar shape (Fig. 5.4, lower panel). On average, a clear differentiation for urban, rural and heavy-trafficked areas is recognized on a per-route base. As shown in the bottom plot, the signal scattering (i.e. the absolute day-to-day variance) is basically constant for all location bins. This is also supported in the ANOVA by an insignificant interaction between the date and location factor ($p(F) >> 0.05$ for all parameters).

![Box plots for measured concentration levels]  

**Fig. 5.3:** Box plots for the measured concentration levels of $N_{\text{bkg}}$, $N_{\text{tot}}$, $N(80-140)$, $N(<30)$, active surface area and CO during the YOGAM days (see Table 5.3), separated both by date (daily averages over all locations) and location (location bin averages over all dates). Box = median, 25% percentile, 75% percentile; □ = mean; x = minimum/maximum. Error bars represent standard deviation.
Before analyzing seasonal averages of the above parameters we investigated how well the measuring days selected during YOGAM could be considered as representatives for the corresponding seasons, since the meteorology of the selected days possibly differed from the seasonal average and rainy days were entirely excluded from the YOGAM measurements. From two official monitoring sites that are operated by the Zürich city authorities and located at different locations in downtown Zürich, PM10, PM2.5 and CO values were available for comparison with the YOGAM mobile measurements. In Fig. 5.5, PM10, PM2.5 and CO mean values (weighted per day) estimated from mobile laboratory measurements in downtown Zürich (typically 15 min in the morning and one hour at noon on every measuring day, plus one 24-h period in every season) are compared to the corresponding parameters measured at the stationary measuring sites. For mobile YOGAM data, PM10 and PM2.5 were estimated from V10 and V2.5, respectively, assuming a particle density of 1.7 g cm\(^{-3}\). This is only a rough approximation, since bulk material density, particle shape and ambient humidity have a large influence on the exact value (Hand and Kreidenweis, 2002).
Fig. 5.5: Comparison of PM10, PM2.5 and carbon monoxide measurements made by the YOGAM mobile laboratory with measurements performed by the official Zürich city monitoring program at two Zürich downtown locations. Mean values are shown here, which did not relevantly differ from the corresponding median values. On each YOGAM day, the mobile laboratory was used for short-term stationary measurements at Zürich-Wiedikon, where also one of the two monitoring sites is located. PM10 and PM2.5 for the YOGAM mobile measurements were estimated from V10 and V2.5 using a particle density of 1.7 g cm⁻³ (see text). A one-way ANOVA was performed to find significant differences between the considered mean values. A star above the bars denotes a significant difference (on a 0.05 level) between the 24-h seasonal mean and the 24-h mean of the YOGAM days. Equally, a circle denotes a significant difference between the YOGAM 24-h and midday means, while an "x" denotes a significant difference between the midday stationary and mobile lab measurements.
Main characteristics seen in Figure 5.5 are:

- **Stationary measurements, seasonal (24-hour) means vs. YOGAM days (24-hour):** For PM10 (and also the available PM2.5 data), the selection of measuring days was only significantly representing the seasonal 24-hour mean for summer, while the selection of campaign days led to significantly higher seasonal median values for the other seasons (especially in autumn). For CO, the selection of days was not significantly representative for the seasonal 24-hour mean for any of the seasons, although the mean values are similar for summer and spring.

- **Stationary measurements, YOGAM 24-hour means vs. YOGAM midday means:** The measured mean values were significantly different from each other for most of the parameters and seasons, reflecting that a short midday episode is in most cases not representative for the entire diurnal variation, which is strongly influenced by rush hour or nighttime stagnation episodes. For PM10 (and PM2.5) the midday means were higher than the 24-hour means, while mean diurnal CO concentrations were lower during midday episodes.

- **Stationary vs. mobile measurements, comparison of YOGAM midday data:** The (partially parked) mobile YOGAM mean data for CO, PM10 and PM2.5 did not statistically differ from the corresponding stationary midday means (except for spring), although the mean values appear considerably different in the plots. This is due to the smaller sampling population for the midday mean values, yielding a larger variance and a smaller F-value in F-statistics (see above).

Overall, the selected YOGAM measuring days overestimated seasonal means during 2001 and 2002, especially for autumn and winter. This possibly reflects the fact that only days without rain were selected for YOGAM measurements. Given the complex measuring situation, the midday Zürich downtown mobile measurements agreed reasonably well with the corresponding stationary measurements. Figure 5.6 shows the seasonal variation of the above parameters (plus V10, V2.5, N(30–80) and N(140–310)), resolved by location category (rural, suburban, urban and heavy-traffic areas) as defined in Table 5.1. Roughly, CO and most number based aerosol parameters (N) on the one hand and V10, V2.5 and the active surface area on the other hand show similar seasonal trends. According to the estimation of seasonal representation described in the previous paragraph, winter data are too high for the first group (CO, N), while the second group (V10, V2.5, active surface area) primarily overestimates the autumn data. On average, rural (R) and suburban (S) areas showed lower concentration levels than urban (U) and heavy-traffic (HT) regions for all considered parameters except N(<30). Overall, higher levels were found during autumn and winter for the size range D<310 nm, for V10, 2.5 and for the active surface area. In contrast, winter and spring dominated the seasonal variation of N_{str}, N_{bkg} and CO.
Fig. 5.6: Seasonal variation of $N_{\text{tot}}$, $N_{\text{bkg}}$, $N(<30)$, $N(30-80)$, $N(80-140)$, $N(140-310)$, V2.5, V10, active surface area and carbon monoxide, resolved by location category (R: rural, S: suburban, U: urban, HT: heavy-traffic areas, see Table 5.1 and Figure 5.1). Mean values are shown, with bars representing one standard error of mean. Due to SMPS and DC measurement problems no summer data are available except for $N_{\text{tot}}$, $N_{\text{bkg}}$ and CO.
5.4 PCA – EXPLORATORY DATA ANALYSIS

Principal component analysis is first of all a data reduction technique (see e.g. textbooks by Jolliffe (1986) or Mardia et al. (1979)). Figuratively, it extracts the directions in which a cloud of data points is maximally stretched, i.e. has a maximal variance. The most relevant information of the data set (J variables with K observations) is contained in these directions (i.e. principal components, in the following termed PCs). The PCs represent orthogonal and therefore independent linear combinations $PC_i$ of the J original variables $v_j$ (Eq. 5.1):

$$PC(i) = \sum_{j=1}^{J} b_{ij} \cdot v_j$$  \hspace{1cm} (5.1)

where $b_{ij}$ are the component loadings and indicate how strongly a specific original variable $v_j$ contributes to $PC_i$, and $v_j$ is the original variable. PCs are found by calculating the eigenvectors and corresponding eigenvalues of the correlation matrix formed by the input data. The projection of the original data on the eigenvectors defines the PCs, and the eigenvalue of every eigenvector indicates the contribution of the specific PC to the total data set variance. By definition, there are $J-1$ principal components, with the first ones containing the most relevant information. Taking only these PCs, the original data set can be stored and compressed with a lower amount of variables, and the original data can be restored with only a minor loss of information.

For the YOGAM data, PCA was individually performed for the [location bin × measured parameter] matrix of every measuring day showing no data gaps, using the SPLUS 6.0 software. This strategy of analyzing single days individually was selected because an annual analysis of all the data is already covered by the previous section and would therefore possibly yield redundant information. The goal was rather to obtain individual "footprints" for every day, telling more about the influence of e.g. meteorological conditions on the spatial and daily variation of the pollutants. From the input matrix, the correlation matrix was calculated. Both original data and data transformed to normality (see Table 5.2) were tested as input for PCA. No significant changes in the loading pattern were observed, so we decided to use the original data to avoid interpretation artifacts due to distortion of the original data. The signal-to-noise ratio was larger than 3 for all variables, so no down-weighing of noisy variables had to be taken into account (Paatero and Hopke, 2003). A further issue regarding our input data is the fact that although several parameters in our input matrices are not in linear relationship, they are in a square relationship to each other (especially the N, S and V variables). Testing the influence of the number of dependent parameters in the input matrix on the PCA results again showed that the PCs and their loading patterns did not relevantly change. A change occurred however in the relevance of the individual PCs, i.e. the eigenvalues of the components decreased with a decreasing number of dependent parameters. With a minimal set of parameters, different criteria for evaluating the relevance of PCs (see PCA textbooks) suggest that mainly the two first PCs are relevant. Overall, it was therefore decided to use the full set of variables for the further qualitative analysis of the first two principal components. With this analytical design, the first PC explained $60 \pm 5\%$ of the total variance, whereas the second PC accounted for $15 \pm 5\%$. Respective values for the further PCs 3 and higher were lower.
than 10%. Standardized component loadings $c_{ij}$ (Eq. 5.2) and the standardized values of PCs, $x_{ijk}$ (Eq. 5.3) are the most useful parameters for a qualitative PCA analysis:

$$c_{ij} = \frac{b_{ij}}{\sqrt{EV_i}} \quad (5.2)$$

$b_{ij}$: loading value of PC for variable $v_j$; $EV_i$: eigenvalue of PC.

$$x_{ijk} = \sum_{j=1}^{J} \frac{v_{ij}(k) - \bar{v}_j(k)}{s(v_j)} \cdot c_{ij} \quad (5.3)$$

$v_{ij}(k)$: $k$-th value of variable $v_j$; $s(v_j)$: standard deviation of variable $v_j$.

Figure 5.7 shows the annual average of the first principal component, along with its loading pattern. Obviously, the loading pattern for the first component shows relatively little variation throughout the year (see standard deviation bars). All loadings except for global radiation, altitude and temperature have positive values. The parameters that are contributing most to the first PC are those in the middle of the considered size spectrum, i.e. $N,S,V(80–140)$ or $N,S,V(140–310)$, as well as CO and the active surface area. At the same time they showed a minimal contribution to PC2 (loading values <20% of the maximum PC2 values). This suggests that this component represents a general degree of pollution. The standardized PC1 (lower graph in Fig. 5.7) shows high values in urban regions and regions with heavy traffic and low values in rural areas far away from anthropogenic activity. This leads to the conclusion that the largest variation in our daily data sets is caused by the degree of anthropogenic influence on the respective measuring locations.

![Normalized first principal component PC1 and corresponding loading pattern](image)

**Fig. 5.7:** Normalized first principal component PC1 (bottom graph) and the corresponding loading pattern (top graph). The average plus standard deviation of the individual days is shown and thus represents an annual average. Variable names and location classifications are given according to Tables 5.1 and 5.2.
In contrast to PC1, PC2 showed no uniform loading pattern throughout the year. Since N, S, V(80–140) or N, S, V(140–310) hardly contribute to PC2 (see above), other factors than anthropogenic influence had to be found. To reveal similarities in the loading patterns of PC2, a cluster analysis was performed. Both for PC1 and PC2 the loading values of N, S and V differed by less than 10% within the particle size ranges 7–80 nm, 80–310 nm and 310 nm – 10 µm. Therefore, average values $A_{7-80}^{N,S,V}$, $A_{80-310}^{N,S,V}$ and $A_{310-10000}^{N,S,V}$ were used for cluster analysis of the PC2 loadings. The input for the cluster analysis was a [parameter x date] matrix consisting of the PC2 loading patterns, with the 12 parameters CO, active surface area, $N_{a} / N_{bkg}$, $A_{7-80}^{N,S,V}$, $A_{80-310}^{N,S,V}$ and $A_{310-10000}^{N,S,V}$, altitude, pressure, temperature, relative humidity and global radiation for the 19 YOGAM measuring days (matrix dimension 12 × 19). A hierarchical tree with euclidean distances (Fig. 5.8) was obtained using a divisive clustering algorithm (Kaufman and Rousseeuw, 1990). A clear split into two main branches (A and B) is seen, while branch B is divided in two major sub-branches (B1 and B2) on the second highest hierarchical level. Within these three categories (A, B1 and B2) we searched for meteorological/geographical variables that were different in the three individual cluster categories. Figure 5.9 shows that despite a few outlier days global radiation seems to be a main divider for category A and B, and that the wind speed at high altitudes is significantly split by all three categories (0.05 level significance in F-test statistics). In contrast, temperature is statistically only insignificantly different, although temperatures appear to be highest in category A and lowest in category B1. In categories B1 and B2 the main wind direction was SW (> 80%), while the prevailing wind direction for category A was NE and SW in an approximately 1:1 ratio.

![Fig. 5.8: Cluster analysis hierarchy tree for the 19 PC2 loading patterns obtained by individual PCA for every YOGAM measuring day. Every individual loading pattern contained 12 parameters (see text). A divisive clustering algorithm based on euclidean distances was used. A, B1 and B2 represent main branches, splitting the data into three categories.](image-url)
Concluding this section, the following statements and questions arise from the PCA and cluster analysis:

- Within one day, the distance to anthropogenic pollution sources caused the largest variation (65%) in the measured pollutant parameters. This contribution to the total data variance was in all cases larger than influences from meteorology (on a one-day base). In the selected area, most of the locations that are least influenced by anthropogenic activity are located at higher altitudes.

- Beside anthropogenic activity, meteorological conditions are suspected to explain further 15% of the total pollutant variation. Namely differences in global radiation and in the wind speed at high altitudes split the YOGAM days into different categories, each possibly reflecting a particular meteorological situation. In this case it is expected that particle number size distributions will show differences for these individual categories.
5.5 USING PCA RESULTS AS INPUT FOR FURTHER DATA ANALYSIS

As stated in the previous section, anthropogenic air pollution can statistically be assigned to high levels of particles in an intermediate size range (80–310 nm) and high CO levels. For further analysis, this knowledge was then used to have a more specific look into the original data set. Indeed, it is already known from gas phase chemistry that CO is a good indicator for anthropogenic activity. Furthermore, we already showed in Bukowiecki et al. (2002) that the particle number concentration in the size range 80–140 nm is strongly connected to anthropogenic activity. PM10 or PM2.5 in areas surrounding an urban region are further parameters often discussed in this context (see Introduction). To carry on the discussion of the previous section's findings, the YOGAM database (see Sect. 5.2) was therefore used to classify data in the two following ways.

5.5.1 Location-dependent Pollution

For all database entries (i.e. 1 morning and 1 afternoon value per date and location, except location bins 1–9) of N(80–140), V2.5 (representing PM2.5) and CO, the percentile within the individual parameter was calculated. Categorizing these percentiles by location and parameter yielded an average percentile for every location and every parameter. Figure 5.10 shows this average percentile for every location bin and parameter, in chronological order according to the YOGAM route. Additionally, the altitude profile is shown. It is confirmed that most of the locations that are least influenced by anthropogenic activity are located at higher altitudes. The only exceptions are locations influenced by busy main roads. The relationship between the percentiles and the inverse altitude is almost linear for all three parameters ($R^2 = 0.6\pm0.1$).

![Fig. 5.10: Location-attributed average percentiles for pollution by CO, N(80-140) and V2.5 (see text). The x-axis represents the YOGAM route in chronological order and shows classifications according to Table 5.1. Additionally, the altitude profile of the YOGAM route is shown.](image-url)
5.5.2 Event-based Pollution

To study the influence of meteorological parameters, a classification of the individual measurements (in the following termed events), rather than a classification per location bin was considered to be reasonable. Again, the percentile of every single value was calculated individually for N(80–140), V2.5 and CO. In contrast to above, the average of the percentiles over the three parameters was then formed for every date and location in the database. These average percentiles per event were assigned to one of 5 categories: Category 1 included average percentile values of 0–20%, category 2 20–40%, category 3 40–60%, category 4 60–80% and category 5 80–100%. In this way, high-pollution events would fall into category 5, while clean-air events were assigned to category 1. Figure 5.11 shows annual mean and median SMPS particle number size distributions for the individual categories. There is a remarkable difference between the median and the mean distributions especially for category 5, indicating that extreme situations within this category strongly influence mean distributions. Here, extraordinarily high number concentrations of ultrafine particles are found, which were regularly observed in the morning hours on a route stretch near a busy freeway (location bin numbers 4 and 5 in Table 5.1). This level of primary ultrafines is typical for freeways (Kittelson et al., 2001; Zhu et al., 2002) and is much larger than for other, non-freeway urban conditions that statistically were more frequent during YOGAM. This is also reflected in the median size distribution, which is less influenced by freeway situations. The trend from categories 1 to 5 shows, beside an increase in the integrated number concentration and the number concentration in the combustion aerosol accumulation mode, an especially noticeable increase in ultrafine number concentration. This confirms that the formation of primary ultrafines was enhanced in situations of high anthropogenic (and especially traffic-related) air pollution. There is however no evidence from these data that a large number concentration of accumulation mode particles, which shortens the lifetime of ultrafine particles due to higher coagulation rates, suppresses nucleation of primary ultrafines.

![Fig. 5.11: SMPS number size distributions for the event-based pollution categories defined in Section 5.5.2. Both median and mean distributions are shown. The distributions are based on the whole-year YOGAM data set.](image-url)
Figure 5.12 shows temperature-resolved mean and median number size distributions for category 5 and confirms the previous findings in literature stating that the formation of primary ultrafine particles is enhanced at cold temperatures (Abdul-Khalek et al., 2000), as it is seen both in mean and median number size distributions. The differences in the mean and median distributions can be assigned to the same reasons as discussed for Fig. 5.11.

Fig. 5.12: Temperature-resolved SMPS number size distributions of using all YOGAM database entries assigned to pollution category 5 (see text). Both median and mean distributions are shown. The average number of individual distributions per temperature category is 150-200. GR: Global radiation.

Figures 5.13 and 5.14 show particle number size distributions resolved by cluster categories A, B1 and B2 (see Sect. 5.4) for the pollution categories 5 and (1,2), respectively. Additionally, the size distributions are split into morning and afternoon cases. OPC size distributions are included in graphs. The slight discontinuities in the combined SMPS and OPC number distributions are likely to result from the fact that in the OPC the individual particles are classified according to their light scattering behavior, which depends on the particle size, morphology and refractive index. Since the OPC was calibrated with spherical Latex particles, the observed shift towards smaller diameters is most probably due to the different refractive index and complex morphology of the measured particles in the range 300–1000 nm. In Fig. 5.13, presenting the highest pollution event category (downtown Zürich and morning freeway episodes), the striking difference in the morning median and mean distributions once more suggests an occurrence of heavy primary (directly traffic-related) ultrafine particle formation during strongly polluted morning events, enhanced by cold temperatures (comparable to Fig. 5.12). This phenomenon is strongest for category B1 (mainly cold winter days) and weakest for category A (mainly spring days), but clearly occurs in all cluster categories. In
the afternoon distributions no evident differences between median and mean distributions are observed. In all cases, especially in category A, a concentration decrease in the 80–140 nm size range is seen. This is usually caused by increases in the mixed boundary layer height in the afternoon.

Fig. 5.13: SMPS (7-310 nm) and OPC (0.3–10 µm) median and mean particle number size distributions measured during YOGAM during events with high anthropogenic pollution (event category 5, see Section 5.5.2). Distributions are resolved by categories A, B1 and B2, which differentiate main types of meteorological conditions during YOGAM (see text). A: high global radiation, low wind speed at high altitudes; B1: low global radiation, medium wind speed at high altitudes; B2: low global radiation, strong winds in high altitudes.
Fig. 5.14: SMPS (7–310 nm) and OPC (0.3–10 μm) median and mean particle number size distributions measured during YOGAM during events with low anthropogenic pollution (event categories 1 and 2, see Section 5.5.2). Distributions are resolved by categories A, B1 and B2, which differentiate main types of meteorological conditions during YOGAM (see text). A: high global radiation, low wind speed at high altitudes; B1: low global radiation, medium wind speed at high altitudes; B2: low global radiation, strong winds in high altitudes.

Figure 5.14 shows the corresponding plots for data in the lowest pollution categories (1 and 2), mainly found at rural, elevated areas (see also Fig. 5.10). For cluster category A (mainly spring days with high global radiation), a remarkable difference between median and mean distributions is seen for the afternoon distributions, which does not occur that obviously in the corresponding morning distributions and the entire rest of the cluster.
categories. This might be an indication that secondary ultra-fine particles occurred in low polluted areas under these conditions, triggered by higher photochemical activity. Furthermore, these particles are probably not primary because they are found in the afternoon at higher temperatures than in the morning. From the size of these particles \( (D \approx 20 \text{ nm}) \) we conclude that nucleation took place several hours before the mobile van entered the area of interest in the afternoon (typically at 2:30 pm). Similar to Fig. 5.13, concentrations in the 80–140 nm size range decrease from morning to afternoon, in this case suggesting that the rural locations were influenced by pollution also in the morning. Due to vertical mixing and dilution the concentrations decreased throughout the day. Category B2 (low global radiation and strong winds at high altitudes) is characterized by extraordinarily low number and surface area concentrations for particles larger than 300 nm, yielding low values of \( S_{\text{tot}} \) and \( S(\text{OPC}) \). This indicates a generally clean atmosphere, associated with the high wind speeds from the west with a low residence time over the continent, and possibly resulting from precipitation on the previous hours/days causing below-cloud scavenging of large particles. The third category, B1 (low global radiation, cold temperatures), shows low concentration levels for large particles in the mornings (see also \( S_{\text{tot}} \) and \( S(\text{OPC}) \)) but a large increase in the afternoon. At the same time there is a rather high number concentration (compared to the other situations) for both the median and mean distributions in the ultrafine size range in the mornings, which decreases in the afternoon. Daily morning concentrations of \( N(<30) \) and CO were correlated in this category, and the morning average temperature was low (7.5°C). This suggests that the observed ultrafine particles were primary.

5.6 SUMMARY AND CONCLUSIONS

It was the goal of this study to obtain an integral picture on the annual variation of fine and ultrafine aerosol levels in the Zürich area with the help of mobile measurements. We already showed earlier that mobile measurements are useful for short-term air pollution investigations that allow investigating and distinguishing between day and night situations but also between urban and rural areas within the same experiment involving a single mobile laboratory. Using appropriate multivariate statistics the same has been shown in this study to be possible also for day-to-day investigations. Overall, the total particle background number concentration was lowest at elevated rural sites. The annual average of the particle background covering all area types was 25000±20000 cm\(^{-3}\) (mean ± standard deviation, \( D>3 \text{ nm} \)). In downtown Zürich, the annual background concentration level was 35000±30000 cm\(^{-3}\), while the corresponding value for rural areas was 15000±12000 cm\(^{-3}\). This agrees with the ranges that we presented in our previous YOGAM case study. It has been shown with Principal Component Analysis (PCA) that this trend was always true within one measuring day, and that \( N(80–140) \), \( V2.5 \), carbon monoxide and the active surface area are good indicators for the level of anthropogenic air pollution. Analysis of Variance (ANOVA) showed that the spatial (urban vs. rural) concentration variation was significantly smaller than the day-to-day and seasonal variation for \( N_{\text{tot}} \), particle background number concentration, active surface area and \( N(80–140) \), while it was more similar only for \( N(<30) \) and CO. Thus, meteorology governs the major annual variance of fine and ultra-fine particulate air pollution in the selected area and exceeds the spatial pollution variation. Therefore, it is for example suggested for epidemiological studies to relate health effects not only to an exposure location type, but also to the...
influence of weather conditions at a specific location. Based on PCA and cluster analysis it has also been shown that primary (directly traffic-influenced) ultrafine particles regularly occurred in highly polluted areas, with an increased formation potential at cold temperatures, which was typically the case during winter inversion episodes. Ultrafine number concentrations along a freeway stretch were consistently much higher (usually >80000 cm$^{-3}$ on average) and more regularly observed than in other urban area types. These observations agree well with previous literature. A suppression of nucleation has not been observed for high concentrations of combustion accumulation mode aerosol. There was a weak evidence for secondary (anthropogenic or biogenic) ultra-fines in clean rural areas in the afternoons of warm and sunny days, mainly in spring. Their occurrence was however generally low, and number concentrations were considerably lower than for primary ultrafines. Nucleation events characterized by a "banana" shape of size distribution contour plots, as for example described by (Boy and Kulmala, 2002b), were not captured by this experiment, due to the mobile approach in this complex terrain.

These findings lead us to the conclusion that, although the selection of days was not representative for entire seasons in this study, the performed mobile measurements were suitable for pollutant assessments to obtain good information on spatial and day-to-day variability. For aspects concerning spatial resolution on a relatively short time scale (<1 day), an experimental design using a mobile measurement may even be more appropriate than a network of stationary measuring sites.

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REFERENCES


In this thesis two different experiments involving mobile pollutant measurement laboratories have been described. It has been a major scope to evaluate mobile experiment types with respect to their potential to complement current state-of-the-art experimental designs. First of all, the ready-to-use flexibility of mobile laboratories stood out to be the probably largest advantage of a mobile laboratory. Within both projects described in this thesis there have been valuable side opportunities for additional easily performable short-studies with the mobile laboratory, not only within the scope of the project goals, but also for third parties. Especially environmental and other federal agencies appreciated the rapid availability of the PSI and UMN on-road laboratories. For example, the Minnesota Department of Transportation (MNDOT) funded a mobile laboratory study in 2000, in which nanoparticles on Minnesota highways were investigated (Kittelson et al., 2001). Similarly, the PSI mobile laboratory was used for monitoring ambient levels of aerosols and trace gases in the Mesolcina and Leventina valleys (Southern Switzerland) during and after a two-months closing of the Gotthard road tunnel due to a heavy road accident, to study the effect of changed traffic routes through the Alps on ambient pollutant levels (BUWAL, 2002). Beside flexibility, lower costs for equipment can be considered as a further general advantage of mobile measuring setups for spatially resolved studies, since only one set of instruments is needed instead of a whole network. For example, the total costs for material (van plus equipment) was approximately 700000 Swiss Francs (450000 Euros) for the Swiss mobile laboratory. Thereof, the major fraction was used for instruments, so an equally equipped network of measuring stations would have resulted in drastically larger material costs. Nevertheless, the consumption of time and personnel resources is higher for on-road experiments. Beside a driver paying attention to traffic, additional personnel were needed in most cases to survey the scientific part of the experiments, depending on the degree of automation of the measurements.

The chase experiment performed in the United States showed that measurements of engine exhaust under real-world conditions are a necessary and non-negligible addition to laboratory studies in today’s engine emission research. In the next years it will be important for atmospheric scientists to continue the promotion of this knowledge to the automotive industry, to optimize emissions of new engines with respect to future, doubtlessly stricter particle emission regulations. The U.S. project has in this context illustrated a novel possibility to link laboratory studies to on-road emission verification. It is conceivable for the near future that car manufacturers will have to come up with new strategies for real-world verification of their laboratory emission test procedures. The experiments described in this thesis however show that significant work on the instrument development side is still necessary. On-road exhaust emission measurements typically involve highly transient signals that only can be tracked by fast instrumentation with a time resolution around one second. This is feasible with an increasing number of monitoring instruments currently used in research (e.g. condensation particle counter type instruments or diffusion charging sensors), but most of these instruments lack an official and legal accreditation for national and international quality standards (as for example current monitors for PM10 and PM2.5).
The PSI study showed that mobile measurements are suitable for long-term pollutant assessments to obtain good information on spatial variability and reasonable information on the temporal variability. For aspects concerning spatial resolution they may be even more appropriate than a network of stationary measuring sites. Thus, a mobile laboratory is a valuable complement to monitoring networks. Critical points for a mobile assessment as described in this study are the representation of seasonality by the selection of measuring days and a careful definition and planning of test conditions (route, departure times etc.) and handling of artifacts (self-contamination etc.). Data analysis is overall more demanding than for a network of monitoring stations. With appropriate advances in instrument development (improvement of time resolution, legal accreditation) and method development (further system automation) the regular use of mobile laboratories for monitoring ambient air pollutant concentrations is a valuable option for atmospheric scientists and possibly also for regulating agencies.

Finally, this thesis aimed at gaining further insight into the processes and meteorological conditions that lead to observed levels of fine and ultrafine particles. Relating the findings of this thesis and recent findings in literature to the ongoing debate on adverse health effects of fine and ultrafine particles, one general conclusion is that despite a somewhat clearer picture about formation and composition of ultrafine particles, the question about their degree of possible adverse health effects is still rather far from being satisfyingly answered. In areas influenced by anthropogenic activity, ambient fine and ultrafine particles in the D = 80 - 140 nm size range are generally characterized by an insoluble inorganic (soot) core, covered by condensed organic and inorganic material. Recent toxicological literature points out that the insolubility of these cores and the oxidizing potential of the surface material are likely to be relevant parameters for triggering adverse health effects in the human airways. Furthermore, the particles are relatively persistent in the ground-near atmosphere (in the order of hours to days) and reach large parts of urban and suburban populations in pronounced concentration levels. This thesis also showed that the day-to-day variation in ambient concentrations of both fine and ultrafine particles clearly exceeds the average level differences between urban and rural areas, suggesting that meteorology has to be taken into account for population exposure studies.

In contrast, the situation is different for primary nanoparticles (directly traffic-related, D <50 nm, mainly consisting of hydrocarbon and a minor fraction of sulphuric acid and water). It is currently still debated whether they are negligible with respect to health effects in the human airways or not, due to their rather high volatility and their low lifetime (in the order of minutes). Although these properties are suspected to reduce the harm potential of primary nanoparticles and ultrafine particles, number concentrations have been shown to be extraordinarily high on and near freeways, resulting in an increased exposure for persons living or working in such areas (see also studies on ambient aerosol penetration into buildings, e.g. by Hussein et al., 2002).

For secondary ultrafine particles (biogenic or indirectly traffic-related) even more unknowns exist. They are usually more water-soluble than primary ultrafines. From an exposure point of view, they are most probably not problematic because they tend to have a rather low occurrence. Future studies will have to gain more insight into the composition of ultrafine particles assigned to this category.
Overall, this study supports that future regulation of emissions and ambient aerosol concentrations will be required to not longer be solely based on mass measurements, as it is mostly the case today. Taking into account all the findings from ambient aerosol research and health effect studies, other parameters like particle number concentration, surface area concentration and chemical composition will have to be considered for establishing future regulation standards.

REFERENCES


Figures A1 – A 21: Additional technical illustrations of the MOSQUITA (Measurements of spatial quantitative immissions of trace gases and aerosols), PSI’s mobile pollutant measurement laboratory. Further general information is also available at http://lac.web.psi.ch.

Figures A22 – A42: A selection of pictures, showing different areas and locations along the YOGAM (Year of Gas phase and Aerosol Measurements) route:

Figures A43 – A52: Further illustrations (YOGAM public relation, link to other projects)
Figs. A1, A2: The PSI mobile pollutant measurement laboratory MOSQUITA (Measurements of spatial quantitative emissions of trace gases and aerosols) on its way in the Zürcher Oberland. The compact size of the IVECO daily transporter (length 5.1 m; width 2 m; height 2.6 m; max. gross weight 3.5 tons) was suitable also for measurements on small roads.

Fig. A3: Racks for gas phase measurements (left rack) and power supply (right rack). For total power consumption of typically $1.6 \pm 0.2$ kW while driving, a second alternator was built into the van engine system. With this setup, the running van motor delivered 2.8 kW of power, which was stored in two 12V/110Ah batteries. These batteries served as buffer in case of short-time power interruptions (up to ½ hour) and were connected to two sinus inverters (90% efficiency), yielding 2 x 720 W with 220V and 2 x 100 W with 12 V available to operate the measuring equipment.

Fig. A4: Interior of the MOSQUITA, seen through the open rear door. The rack for aerosol measurements was accessible from the van rear and right-hand side. To remove the heated air caused by the power consumption of the instruments, the interior of the van was air conditioned.

Fig. A5: Cockpit view of the MOSQUITA, showing control displays for the power supply system (A) and the auxiliary ventilation tube (B) which blows additional conditioned air backwards to the instrument racks. Additionally, a video camera (not seen here) was installed in the cockpit, recording the traffic situation in front of the mobile laboratory. These videotapes were important during the data analysis process, since they helped much for the interpretation of the measured signal curves.

Fig. A6: Roof equipment of the mobile laboratory. (A): Aerosol inlet tip, (B): Inlets for gas phase measurements, (C): Pyranometer for global radiation measurements, (D): Humidity and temperature sensors (wind protected), (E): Wind direction measurements, (F): Global Positioning System (GPS), (G) and (H): Kr-85 source and Differential Mobility Analyzer for SMPS measurements. All devices were accessible by a ladder attached to the van rear door and a walking platform on the roof.
Fig. A7: Aerosol rack with running instruments. To be able to control the proper operation of the instruments in the aerosol and gas phase racks while driving, it was possible for the YOGAM personnel to be seated on the blue seat (including safety seatbelts).

Fig. A8: Real-time visualization of the measured parameters. The shown laptop was connected to a data acquisition board (DaqBook 260, IOTECH Inc., USA), managing the acquisition of analog and digital output signals from the gas phase and aerosol racks. An application based on LabView 5.1 (National Instruments Inc.) was programmed to store and process the collected data on the local hard drive of the laptop. For most instruments a value was saved every second. With this setup, the van personnel could observe data acquisition on-line anytime during the drives. After every measuring day, the collected data were saved to the PSI IT network.

Fig. A9: Aerosol inlet tip. To catch the ambient air while driving before it was affected by the own van exhaust, and to minimize turbulence caused by the van front, the main inlet was located above the van front end, at a height of 2.35 m. The aerosol inlet and flow system dimensions were designed such that laminar flow was prevailing. The conical inlet (1 cm diameter at the entrance) enabled isokinetic sampling at 50 km/h (14 m s\(^{-1}\)) driving speed, reducing the air velocity in the sampling system to 0.5 \(\pm\) 0.1 m s\(^{-1}\), which is close to the highest flow velocity possible for laminar flow under these conditions (Flow Reynolds number Re \(\sim\) 1800).

Fig. A10: Inside the van, the main sampling air stream was slowed down in a cylinder to a constant laminar flow velocity of 0.06 \(\pm\) 0.02 m s\(^{-1}\). For further distribution of the sampling air to the individual instruments, different inlet tips were mounted inside the distribution cylinder. These tips were adapted to each individual instrument flow rate, still enabling isokinetic sampling. The time delay of the sampling air between the main inlet tip and the distribution cylinder was 10 \(\pm\) 3 seconds.

Fig. A11: Heavy-duty blower (Marine Blower, JABSCO Inc., USA), providing constant flow through the aerosol inlet system (see Figs. A9, A10).
Fig. A12: The Ultrafine Condensation Particle Counter (CPC, UCPC 3025, TSI Inc. USA) has been found to be suitable for stand-alone use in mobile applications. To prevent instrument damage from vibration shocks while driving, shock absorbers plus additional rubber foam layers were installed between the rack shelves and the instrument. Since peak number concentrations for urban on-road measurements often exceed 200000 cm$^{-3}$, and the upper detection range of this instrument is 100000 particles per cm$^3$, a clean-air dilution system was designed for the CPC, yielding a 1:4 to 1:8 dilution of the CPC sampling air. A recalibration of the clean-air dilution flow and the resulting dilution ratio was performed in regular intervals.

Fig. A13: The diffusion charging sensor (LQ1-DC, Matter Engineering AG, Switzerland) sampled from the aerosol distribution cylinder and was especially suitable for fast tracking of highly transient traffic exhaust signals.

Fig. A14: Aethalometer (AE-10, Magee Scientific Inc., UK), including automatic filter tape advancement system.

Fig. A15: Optical Particle Counter (OPC, DustMonitor 1.108, Grimm Inc., Germany). An extra sampling air branch-off was designed for the OPC (10 cm after the aerosol inlet transfer line entered the van interior), to keep the sampling line for coarse mode particles (1-20 µm) short and to prevent particle losses by gravitational settling. With the selected setup, losses for particles with D = 2.5 µm were calculated to be < 2 %, < 10% for D = 6 µm and < 20 % for particles with D = 10 µm. The OPC was calibrated with latex spheres by the manufacturer twice during YOGAM. Although the OPC measures particle diameters up to 25 µm, particle diameters > 10 µm were not analyzed with this setup due to the described sampling losses.

Fig. A16: The Betameter (Eberline FH-64-IR) sampled inlet air from the aerosol distribution cylinder. Before entering the instrument, the sampling air passed a cyclone with a 2.5 µm cutoff and 30 cm of heated steel tubing, to measure dry PM2.5.
Fig. A17-A21: The SMPS (Scanning Mobility Particle Sizer, consisting of a Kr-85 source (see Figures A17, A18 A), a differential mobility analyzer (DMA, DMA3071; TSI Inc., USA, see Figures A17, A18 B) and a condensation particle counter (CPC, CPC 3010, TSI Inc., USA, see Figure A20) was located on the van roof and branched off its sampling air (1 lpm) from the main air stream already before the transfer line entered the van. A mixing volume (steel vessel) of 1 l was implemented upstream the SMPS, to smooth the incoming air over a 1-minute interval. The sheath and excess air flows of the DMA(10 lpm) were handled in a closed-loop arrangement, in which the flow was kept constant with a pump and a mass flow controller (see Figure A21 A, B). To remove flow pulsations caused by the pump, the sheath air was appropriately overpressurized with a restriction valve downstream of the pump (see Figure A21 C). Before entering the DMA, the sheath air passed a copper coil (see Figures A17, A18 C), to become adapted to ambient temperature. This setup had the advantage of a large flow stability and an identical composition of the sheath and sampling air. The monodisperse aerosol exiting the DMA was rapidly transferred to the CPC 3010 (located directly under the van roof) in a stainless steel sampling line of 30 cm in length. With this entire outdoor setup, the measured aerosol was kept at ambient temperature and humidity during the entire scanning mobility process, preventing volatilization of water and other highly volatile aerosol compounds during the measurement. Since the upper particle size limit was 310 nm, isokinetic sampling was not a critical issue for the SMPS. Size calibration of the SMPS was performed using monodisperse Latex spheres with D = 79 nm. Sheath air and aerosol flows were monitored daily.
Figs. A22-A26: Zürich-Wiedikon, one of the official air pollution monitoring sites operated by the Zürich city authorities (white container, see http://www.zueri-luft.ch for details). Due to its vicinity a Swiss main traffic route (Nationalstrasse A1), this location is strongly influenced by both local and long-distance traffic. On every YOGAM measuring day the PSI mobile laboratory performed one hour of stationary measurements (usually around noon) next to the official monitoring site, to compare jointly measured parameters (e.g. PM2.5, CO and O₃). During these periods, the van batteries were externally fed and recharged with 380 V from the Swiss electricity network via a voltage transformer.
Figs. A27-A30: Typical suburban traffic around Zürich (Figure A27: Kemptthal, Figures A28, A29: Regensdorf, Figure A30: Aathal). These locations often showed the highest pollution levels in the entire region.
Figs. A31-A34: Low-altitude rural areas (Figures A31-A33: Greifensee; Figure A34: Bertschikon).
Fig. A35

Fig. A36

Fig. A37

Fig. A38

Figs. A35-A38: Impressions from rural areas along the YOGAM route. These route stretches usually showed a minimal amount of traffic. In spring, rapeseed (see Figure A38) was omnipresent.
Figs. A39-A41: Bachtel, the highest elevated location along the YOGAM route (950 m a.s.l.)

Fig. A42: Agricultural traffic was a major source of artifacts in rural areas. Emissions from a single agricultural vehicle typically overloaded several of the aerosol and gas phase instruments during the 10-15 seconds during which the mobile laboratory caught its exhaust plume.
Figs. A43-A48: The MOSQUITA was used on several occasions to impressively illustrate ambient air pollution to the public. Real-time concentrations of a selection of gas phase and aerosol pollutants were shown and discussed directly on a screen. Figures A43 and A44: “Zürcher Festival des Wissens”, Zürich main station, April 2001; Figures A45 and A46: “EnergieTag” at PSI, May 2001; Figures A47 and A48: Open day at the ETH Physics Department, ETH Hönggerberg, May 2002.
Figs. A49, A50: The MOSQUITA in action during the project CHAPOP (Characterization of High Alpine Pollution Plumes). Pictures were taken in August 2001 in the Upper Leventina Valley (Southern Switzerland). For further information see: http://lac.web.psi.ch

Figs. A51, A52: The University of Minnesota mobile emission laboratory (MEL) was constructed to compare laboratory diesel engine emissions (obtained during dynamometer, i.e. test bench experiments) to corresponding emissions from real-world situations. The MEL was used during on-road truck-chase experiments, in which the diesel exhaust plume of the followed truck was captured and analyzed several seconds after its emission from the exhaust stack. The laboratory was installed in a cargo container that was mounted on a platform hauled by a tractor. A 3.6 m aluminum boom above the cab of the tractor transferred the sampled aerosol to a distribution manifold in the interior of the MEL. A flow-regulating vane pump and a large bypass flow for the instruments maintained constant suction at the inlet of the boom. For further information see: http://www.me.umn.edu/divisions/mel
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