PROCEEDINGS OF THE THIRD COLLOQUIUM ON PARTICULATE AIR POLLUTION AND HUMAN HEALTH

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I. INTRODUCTION

Robert F. Phalen, University of California, Irvine

Perspective

This Colloquium was the third in a series that brought together a diverse group of research scientists, regulators and other individuals interested in the effects of inhaled particulate air pollution on human health. Each colloquium had objectives that were responsive to prevailing needs.

First Colloquium (Irvine, CA, January, 1994)

- Assemble the relevant central scientific experts.
- Define issues and uncertainties relating to epidemiological associations between low levels of particulate matter and adverse health outcomes.
- Air the diverse perspectives.
- Establish communication across the involved scientific disciplines and between the regulatory and regulated communities.
- Influence active research programs in order to promote improved coordination of efforts.

Second Colloquium (Park City, UT, May, 1996)

- Expand the participation of researchers to include additional disciplines.
- Update the research progress and debate the uncertainties.
- Clarify the significant gaps in knowledge.
- Encourage and improve collaborations across disciplines.
- Influence active research programs in order to improve coordination of findings.

Third Colloquium (Durham, NC, June, 1999)

- Focus on the uncertainties and research priorities that were identified by the Committee on Research Priorities for Airborne Particulate Matter of the National Research Council (NRC) in their report, "Research Priorities for Airborne Particulate Matter: I. Immediate Priorities and a Long-Range Research Portfolio" (National Academy Press, Washington, DC, 1998).
- Update the research knowledge base and assess important findings.
- Improve communication and coordination across the many relevant scientific disciplines.
- Influence active research programs and new researchers in order to improve their efforts.
- Facilitate publication of emerging research in support of the U.S. EPA's criteria document review on Particulate Matter.

Announcement of the planned Third Colloquium on Particulate Air Pollution and Human Health generated both intense interest and a substantial response from researchers; eventually 171 abstracts of papers were submitted for inclusion in the program. The Program Committee (listed below) decided that all of the accepted research papers would be poster presentations, organized into five non-concurrent sessions. Each session, attended by all participants, focused on questions based on the NRC Committee's report. Each session began with two brief invited

platform papers in order to provide a "perspective" on the session question, and attendees then visited the session posters. After poster viewing, a discussion led by the session chair was held between the attendees and an expert panel selected to represent varied disciplinary expertises and perspectives. Following the discussion, an invited speaker provided an "integrative summary" of the session. A sixth session, also with "perspectives" speakers, a panel-attendee discussion and an "integrated summary" speaker completed the colloquium. The questions and topics addressed by the sessions were as follows (chairs are in parenthesis).

- Session 1: What are we breathing and how can it best be characterized? (Ronald Wyzga)
- Session 2: What properties of particulate matter are responsible for health effects? (Jonathan Samet)
- Session 3: What are the biological mechanisms underlying adverse health effects? (Kevin Driscoll)
- Session 4: What improvements in dosimetry and extrapolation modeling will provide for better evaluation of human health effects and risk assessment? (Robert Phalen)
- Session 5: Who is susceptible to particulate matter and why? (Mark Utell)
- Session 6: Integrative summary of the colloquium. (David Bates)

In addition to covering the main question/topic addressed in each session, attendees were not discouraged from raising new issues, expressing concerns, or posing challenges to the assumptions implicit in the views presented.

All of the authors of posters, the invited speakers, and the session chairs were encouraged to submit their material for publication in these proceedings; in addition, all attendees were invited to submit a 1-page contribution to these proceedings. Presenters were also permitted to submit their papers for peer-review and possible publication in one or more special issues of the journal *Inhalation Toxicology*. The contributions to these proceedings have not been peer-reviewed, and thus, may differ from those accepted by the journal.

These proceedings comprise the program (Section II), commentaries submitted by session chairs and invited speakers (Section III), papers presented in the five poster sessions (Sections IV-VIII), a report of a satellite pre-colloquium workshop on "Risk Assessment and Risk Management of Ambient Air PM" (Section IX), brief comments from attendees (Section X), and a summary of the colloquium evaluations that were filled out by the attendees.

Brief Summary of Presentations and Discussions

It is not practical to summarize all of the significant results of the Colloquium; the material that follows captures its diversity in temporal order and flavor. Sections III through IX of this report contain additional detail. The question of what people actually inhale was a major issue especially since most people spend most of their time indoors, where variable factors such as air turnover, air conditioning, air "cleaning" and human activity can modify the air quality. Little is known about the "personal cloud" from which people breathe, especially for those segments of the population that are presumed to be most sensitive to the effects of air pollutants. The list of potentially important air pollutants/characteristics is large and growing. The list includes particulate matter (PM) mass, PM surface area, particle size, metals (both soluble and insoluble

forms), acids, organics, sulfates and nitrates, inorganic carbon, ultrafine particles (diameter 0.1 micrometers and less), peroxides, biological aerosols, and co-present gases, such as CO, O_3, NO, NO_2 and SO_2. Also, environmental co-stressors, including temperature extremes and infection epidemics, were included in discussions. The lack of information on the nature and size distributions of biological aerosol components was stressed, especially since such components are known to have significant health effects and they may be present even in very small particle size fractions. Also, the significance of complex mixtures of air pollutants to human responses was identified as largely unknown. The relationships between sources and air pollutants in the breathing zones of people were acknowledged to be complex and highly variable in space and time. In some locales for example, while urban airborne particulate mass has decreased over the years, particle number per unit volume of air has steadily increased. Another complication that was mentioned is that human subject exposure history may be a factor in determining responses, along with PM characteristics, co-stressors and underlying subject health status.

Epidemiology was frequently discussed at the colloquium. The effects of errors in exposure estimates and the difficulties in separating out the effects of PM constituents that co-vary, such as ultrafine particles and CO, were identified as important topics for additional study. Epidemiological studies that test hypotheses regarding effects of metals, biogenic components and coarse particles were identified as needed, as were investigations that address childhood asthma. It was noted that the "usual suspects" for sensitive subpopulations, such as the elderly, children, those with influenza, asthma and cardiopulmonary diseases, paints a picture that is too simplistic. Who is susceptible not only depends on the health effects being evaluated and the level and length of exposure, but probably also on factors that place affected individuals in the extremes of the distributions of sensitivity and exposure.

Research relating to the potential mechanisms for the health effects of PM was a major subject of discussion. The components of the susceptibility of humans and animal models include dosimetry; relative sensitivity of tissues; amount of functional reserve; and unique pathophysiologic mechanisms. It was noted that dosimetry efforts are hindered by lack of knowledge of the important PM characteristics. Laboratory animal models of human disease have been developed over the past decades and new ones are emerging. Just considering rodents, models exist for bronchitis, emphysema, fibrosis, allergic asthma, senescence, immaturity, pulmonary vasculitis, hypertension, cardiomyopathy, coronary insufficiency, infections, dietary deficiencies, genetic abnormalities and other conditions. Although the proper utilization of such models, and their applicability to affected humans in PM studies, are still problematic, such models (including non-rodents) were considered to be essential for hypothesis driven mechanistic studies of the effects of particulate air pollution. Among the missing models are, for example those for sleep apnea and models that mimic the effects of very long-term low level exposures. In such exposures adverse effects may slowly develop along with some benefits of exposure (induction of defenses, for example). Such models must have human-like toxicokinetics and physiological responses that relate to the duration or exposure.

The presentations and discussions brought out many observations and questions as well as recommendations for future research. The epidemiological associations between PM measures and adverse health outcomes have been consistently seen (many places, many times, and by many investigators), yet the hypothesized "suspects" (potential victims and potential PM related

culprits) are disturbingly numerous. Also, new research has uncovered surprises, such as the potential extrapulmonary effects of ultrafine particles and the possible adverse effects involving normal defense mechanisms of the respiratory tract. The relationships between acute responses and chronic responses are obviously important and very poorly understood. At one extreme, acute responses were seen as leading to chronic disease, and at the other extreme, they were deemed as potentially essential for affording protection from adverse chronic outcomes. Dose is certainly an important factor, but also is genetic predisposition, and the lifetime exposure/response history. Is the failure to respond to PM inhalation also a cause for concern? The size of the susceptible population pool was suggested as being under 1% of the population, and variable in time due to variations in weather, respiratory tract infection rates and other factors. To unscramble these uncertainties, both hypotheses-driven as well as exploratory studies were seen as indicated. Also, the combined strengths of both disciplinary research and cross-disciplinary research were seen as needed to identify and understand the linkages between environmental PM exposures and human health.

At this time, no single particle size fraction can be said to be the major culprit; ultrafine particles, $PM_{2.5}$ and even coarse-mode particles will require future examination. Even within these largely accepted size modes, enormous variations in composition and physical characteristics (solubility, hygroscopicity and surface characteristics are examples) exist both in outdoor and in indoor air. It was noted that chemists can measure more substances in the air than most people can imagine, so what to focus on was identified as a significant problem, rather than analytical sensitivity. The characteristics of PM that are important from the perspective of cells of the body (in contrast to the perspective of scientists) are as yet poorly understood, so advising the chemists as to what to measure was seen as a challenge.

Some still ask: "Do the particles really do it?; Do they do it alone?; and if so, which ones do it?" The bulk of PM mass in the urban atmosphere may not be directly emitted, but it may be produced by secondary processes (reactions). It was noted that an important group, experts on sources and transformation of contaminants, was under-represented at the colloquium. If the sources of air pollution are also important to people (electric power, transportation food production, construction, manufacturing, cooking, etc.) then the question of finding an acceptable level of adverse effects arises. Alternative, non-PM related, potential explanations for the epidemiological associations should also continue to be pursued. Resolving PM/health questions was described as especially pertinent because many of the sources of PM air pollution are important to preserving human health.

It is clear that research on the health effects of PM is in a phase of rapid development and exciting discovery. If, as was offered at the general summary, the measure of progress is the evolution of new questions, then we are making excellent progress in understanding the effects of PM on human health!

Acknowledgements

First and foremost the sponsors who made the essential funding commitments deserve credit. The major sponsor, with respect to funding, planning and hard work was the U.S. EPA. It was

clear from the outset that the EPA supported as complete and as thorough a colloquium as could be conducted. Other significant essential contributing sponsors included the American Petroleum Institute, the Health Effects Institute, the Electric Power Research Institute, the California Air Resources Board, Florida Power and Light Company, and the Ford Motor Company. Additional help was provided by The National Institute of Environmental Health Sciences, the American Association for Aerosol Research, the NYU School of Medicine's Department of Environmental Medicine, the UCI Department of Community and Environmental Medicine, the UCI and UCLA Centers for Occupational and Environmental Health, and the journal *Inhalation Toxicology*. The organizing committee was Richard Schlesinger (chair), Daniel Costa, Robert Devlin and Robert Phalen. Their key staff were Toni Moore (NYU) and JoAnn Fuller (EPA). The Program Committee was Robert Phalen (chair), Maria Costantini, Daniel Costa, Robert Devlin, Douglas Dockery, Terry Gordon, Carol Henry, Philip Hopke, Petros Koutrakis, George Malindzak, Frederick Miller, Gunter Oberdörster, Shankar Prasad, Jonathan Samet, Richard Schlesinger, Mark Utell, John Vandenberg, and Leendert van Bree. Yvonne Bell (UCI) was the key staff person. The editor of *Inhalation Toxicology*, Donald Gardner was a strong supporter and advisor to the colloquium.

The invited speakers, panelists and session chairs included Hillel Koren, John Vandenberg, Richard Schlesinger, Ronald Wyzga, Petros Koutrakis, Jack Spengler, Harriet Burge, Glen Cass, Judith Chow, George Thurston, Jonathan Samet, Philip Hopke, Kevin Dreher, Lester Kobzik, Eric Wichmann, Bert Brunekreef, Kevin Driscoll, Mark Frampton, Robert Devlin, Kenneth Donaldson, Andrew Ghio, John Godleski, Joseph Brain, William Bennett, Frederick Miller, W. Michael Foster, Chong Kim, Joachim Heyder, Mark Utell, Daniel Costa, Anthony Frew, Terry Gordon, C. Arden Pope III, Joel Schwartz, Leendert van Bree, David Bates, Douglas Dockery, Morton Lippmann, Judith Graham, Daniel Greenbaum, Roger McClellan and Joe Mauderly. The authors of posters contributed the essential substance of the colloquium; they and their research groups are gratefully acknowledged.

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II. COLLOQUIUM PROGRAM

Saturday, June 5, 1999

6:00 – 8:00 p.m. **Welcoming Reception**

Sunday, June 6, 1999

7:30 – 8:30 a.m. **Continental Breakfast**

8:30 – 9:00 a.m. **Opening Remarks**

Welcome
Robert Phalen, Irvine, CA

Introduction and Statement of the Problem
Hillel Koren, Research Triangle Park, NC
John Vandenberg, Research Triangle Park, NC

Overview of Meeting Format
Richard Schlesinger, Tuxedo, NY

SESSION 1: What are we breathing and how can it best be characterized?

Chair: Ronald Wyzga, Palo Alto, CA

9:00 – 9:30 a.m. **Perspectives on the Research Issue**
Petros Koutrakis, Boston, MA
Jack Spengler, Boston, MA

9:30 – 11:00 a.m. **Poster Viewing**

11:00 – 12:30 p.m. **Discussion**

Panel Members:
Harriet Burge, Boston, MA
Glen Cass, Pasadena, CA
Judith Chow, Reno, NV
Paul Lioy, Piscataway, NJ
Petros Koutrakis, Boston, MA
Ronald Wyzga, Palo Alto, CA

12:30 – 12:45 **Integrative Summary of Session 1**
George Thurston, Tuxedo, NY

12:00 – 2:00 p.m. **Lunch**

SESSION 2: What properties of particulate matter are responsible for health effects

Chair: Jonathan Samet, Baltimore, MD

2:00 – 2:30 p.m.	**Perspectives on the Research Issue** Richard Schlesinger, Tuxedo, NY Philip Hopke, Potsdam, NY
2:30 – 3:30 p.m.	**Poster Viewing**
3:30 – 5:00 p.m.	**Discussion** Panel Members: Kevin Dreher, Research Triangle Park, NC Philip Hopke, Potsdam, NY Lester Kobzik, Boston, MA Richard Schlesinger, Tuxedo, NY Erich Wichmann, Munich, Germany
5:00 – 5:15 p.m.	**Integrative Summary of Session 2** Bert Brunekreef, Wageningen, the Netherlands
7:00 p.m.	**Colloquium Dinner**

Monday, June 7, 1999

7:30 – 8:30 a.m.	**Continental Breakfast**

SESSION 3: What are the biological mechanisms underlying adverse health effects?

Chair, Kevin Driscoll, Cincinnati, OH

8:30 – 9:00 a.m.	**Perspectives on the Research Issue** Mark Frampton, Rochester, NY Robert Devlin, Research Triangle Park, NC
9:00 – 10:30 a.m.	**Poster Viewing**
10:30 – 12:00 p.m.	**Discussion** Panel Members: Robert Devlin, Research Triangle Park, NC Kenneth Donaldson, Edinburgh, UK Mark Frampton, Rochester, NY Andrew Ghio, Research Triangle Park, NC John Godleski, Boston, MA
12:00 – 12:15 p.m.	**Integrative Summary of Session 3** Joseph Brain, Boston, MA
12:15 – 2:00 p.m.	**Lunch**

SESSION 4: What improvements in dosimetry and extrapolation modeling will provide for better evaluation of human health effects and risk assessment?

Chair: Robert Phalen, Irvine, CA

2:00 – 2:30 p.m.	**Perspectives on the Research Issue** William Bennett, Chapel Hill, NC Frederick Miller, Research Triangle Park, NC
2:30 – 3:30 p.m.	**Poster Viewing**
3:30 – 4:30 p.m.	**Discussion** Panel Members: William Bennett, Chapel Hill, NC W. Michael Foster, Baltimore, MD Chong Kim, Research Triangle Park, NC Frederick Miller, Research Triangle Park, NC Gunter Oberdörster, Rochester, NY
4:30 – 4:45 p.m.	**Integrative Summary of Session 4** Joachim Heyder, Munich, Germany

Tuesday, June 8, 1999

7:30 – 8:30 a.m.	**Continental Breakfast**

SESSION 5: Who is susceptible to particulate matter and why?

Chair: Mark Utell, Rochester, NY

8:30-9:00 a.m.	**Perspectives on the Research Issue** Arden Pope, Salt Lake City, UT Daniel Costa, Research Triangle Park, NC
9:00 – 10:30 a.m.	**Poster Viewing**
10:30 – 12:00 p.m.	**Discussion** Panel Members: Daniel Costa, Research Triangle Park, NC Anthony Frew, Southampton, UK Terry Gordon, Tuxedo, NY Arden Pope, Salt Lake City, UT Joel Schwartz, Boston, MA Leendert van Bree, Bilthoven, the Netherlands
12:00 – 12:15 p.m.	**Integrative Summary of Session 5** Mark Frampton, Rochester, NY
12:15 – 1:30 p.m.	**Lunch**

SESSION 6: Integrative Summary of the Colloquium

Chair: David Bates, Vancouver, BC, Canada

1:30 – 3:00 p.m.

Perspectives
Douglas Dockery, Boston, MA
Morton Lippmann, Tuxedo, NY
Judith Graham, Research Triangle Park, NC

Discussion
Panel Members:
Douglas Dockery, Boston, MA
Judith Graham, Research Triangle Park, NC
Daniel Greenbaum, Boston, MA
Morton Lippmann, Tuxedo, NY
Roger McClellan, Research Park, NC

General Summary
Joe Mauderly, Albuquerque, NM

3:00 – 3:15 p.m. **Closing Remarks**
Daniel Costa, Research Triangle Park, NC
Robert Devlin, Research Triangle Park, NC

SATELLITE MEETINGS

Pre-Colloquium Workshop (Saturday afternoon, June 5th)
A workshop on "Risk Assessment and Risk Management of Ambient Air PM," sponsored by the USEPA and RIVM (the Netherlands), will be held on Saturday afternoon.

USEPA PM Supersites Program Discussion Meeting (Monday evening, June 7th)
The USEPA has organized a discussion session to foster interaction among a spectrum of scientific disciplines having interest in applying to the USEPA's Supersites Program. Further information about this meeting can be obtained from the following web sites:
http://www.epa.gov/ttn/amtic/supsites.html; http://www.epa.gov/ncerqa/rfa/

III. SESSION SUMMARIES AND COMMENTARIES

The Particulate Whodunit: Introductory Remarks for Integrative Summary Session

David V. Bates

Professor Emeritus of Medicine
Department of Health Care & Epidemiology
University of British Colombia
Vancouver, BC, Canada

I have headed these remarks "The Particulate Whodunit" because our efforts to understand the basic science behind the epidemiological findings have had all the elements of a whodunit. So the first question might be: "Was there a body?" This took up most of the time of the First Colloquium in Irvine, California. Most observers, but not all, would feel that the possible confounders of the time series studies had now been eliminated, though the longitudinal data sets require further analysis. Where have we got to now? It is clear from the 160 posters at this meeting that we are at the stage of having too many suspects. Fine particles seem capable of eliciting a wide range of responses; there are some who believe that the metal content may be critical in the toxicity, and others who do not feel that this conclusion is definitive. There is no doubt that diesel particles are capable of inducing pulmonary inflammation and of enhancing the effects of a subsequently administered allergen.

Indeed, we have now reached a stage when we can declare unequivocally that most of us are living in an environment which will enhance the effects of allergens, since ozone, NO_2 and particles independently can do this – and the fact that these often exist together or are encountered sequentially makes it even more likely that this explains the aggravation of asthma which everyone is documenting.

We might also ask: "What have been the surprises?" I think that it is remarkable that the low level inhalation of ambient particles is capable of causing systemic effects. These range from effects on the heart rate, on heart rate variability, to mobilization of neutrophils from the bone marrow. Although such observations do not constitute a direct link to explain mortality, they nevertheless indicate that the effects of such inhalation are not limited to the lung, as many of us would have supposed to be the case.

We often talk of the importance of integrating knowledge from different fields – indeed the title of this session is an "integrative summary." We have seen in the posters some examples of this, and one outstanding contribution from the EPA group in Chapel Hill was the experimental study of particles collected from the Utah Valley. You will recall that Arden Pope's first paper was the observation that respiratory admissions of children to hospital in the Utah Valley fell dramatically when the Geneva Steel mill was on strike. By extracting particles from the filters at that time the EPA group found that both in rats and in humans the influx of inflammatory cells after administration was similar in the particles form the years when the mill was operating, but virtually absent in the particles from the year in between when it was closed. Furthermore, the histology of the rat lungs showed clearly that what was induced was an acute bronchiolitis – precisely the clinical diagnosis in the children admitted to hospital when the mill was operating.

In trying to move forward, we must recognize that we are dealing with the impact of complicated systems on complicated clinical situations. Diesel emissions are complicated; urban air is complex as Glenn Cass showed us on the first day; and PM2.5 is not a simple substance. But pneumonia in the elderly, and states of congestive heart failure, and the variety of what is loosely termed "asthma" should remind us that these syndromes are also complicated. We should not be surprised that the full understanding of the interaction of the one on the other will stretch our ingenuity and also possibly our resources.

Integrative Summary of the Third PM Colloquium

Morton Lippmann

Nelson Institute of Environmental Medicine
NYU School of Medicine
Tuxedo, NY

Abstract

Research on human exposure to ambient air particulate matter (PM) reported on at the Third PM Colloquium indicates that the field is now moving beyond descriptive reports that focussed largely on gravimetric concentrations of PM in ambient air and in other microenvironments, and their associations with indices of short-term changes in rates of mortality and morbidity. There is now a welcome shift in emphasis toward a more detailed analysis of PM exposures and dosimetry in terms of size-segregated PM fractions (PM_{10}, $PM_{2.5}$ and ultrafines) and their chemical constituents, as well as toward biological response measures. Such responses shed light on the underlying mechanisms that account for both short- and long term responses to ambient air PM and copollutants on the respiratory tract, the cardiovascular system, and immune function. Through both the formal presentations of research findings and the opportunities provided for more informal discussions of mutual interests, this Third Colloquium has enhanced opportunities for collaborative research that may be able to clarify the chain of events leading from pollution in the ambient air to adverse impacts on health and longevity.

Introduction

Research on human exposure to ambient air particulate matter (PM) and its health effects has intensified since the second PM Colloquium (Lee and Phalen, 1996) in Park City, UT, as evidenced by the increased number and range of papers presented at this Third Collquium, as well as by the great increase in the number of registrants. While it is not possible to fully review all of the new information presented at the Colloquium and its significance, I hereby attempt to summarize some of the notable developments that I, as one longtime observer, consider noteworthy and potentially important.

The presentation that follows is largely in bullet form. The references cited are papers presented at the Colloquium.

Some Notable Developments Since 2nd PM Colloquium

Research interest and opportunity to compete for research funds can do wonders for advancing basic and applied research on PM exposures and their health effects.

1. There have been significant advances in technical means of conducting:

   - Size-selective personal exposure assessments.
   - Real-time measurements of $PM_{2.5}$ components, including semi-volatile species.
   - Measurements of concentrations of PM components of toxicological concern on air sampling filters.
   - Measurements of composition of individual airborne particles.
   - Exposure assessment surveys of populations on a sound statistical basis.
   - Controlled exposures to concentrated ambient PM.
   - Controlled exposures to laboratory generated exposure atmospheres intended to represent ambient PM components of toxicological concern.

2. Epidemiological studies have become more sophisticated, and informative regarding roles of PM components, regarding:

   - Different roles of $PM_{10-2.5}$, $PM_{2.5}$, and $PM_{0.1}$ (ultrafine particles).
   - Different roles of PM components on various disease endpoints, i.e., mortality and morbidity for various categories of respiratory and cardiovascular diseases.
   - Relative influences of PM components and co-pollutant gases.

4. **Controlled human and human cell exposure studies to materials from ambient PM offer exciting new prospects for elucidating PM-related disease processes.**

   - Human and rat lung instillations of Utah Valley PM10 filter extracts before, during, and after steel mill closing, and consistency of findings with published epidemiology findings (Ghio et al., 1999a).
   - Differential response to instilled Fe_2O_3 depending on surface properties (Lay et al., 1999).
   - Responses of human volunteers to the inhalation of fresh diluted diesel engine exhaust (Sandström et al., 1999).
   - Differential responses of human peripheral blood to silica, diesel PM, and urban PM (Zussman et al., 1999).
   - Demonstrated ability to expose human volunteers to concentrated ambient PM of varying composition has potential to resolve critical issues (Gong et al., 1999; Ghio et al., 1999b).
   - Ambient concentrations of PM correlated with human heart rate variability (Pope et al., 1999).

5. Controlled animal and in-vitro exposure studies continue to be difficult to interpret in relation to effects indicated by epidemiologic studies, especially for:

   - Responses seen only at very high dose levels.
   - Those responses seen only in healthy young animals.
   - Responses that are dependent on mechanisms or metabolic pathways not known to be relevant to low dose human exposures.

6. Disease mechanism oriented research has produced some new techniques, approaches, hypotheses, and models that can be expected to provide "keys" to unlock the mysteries of adverse responses to low-dose PM and pollutant gas exposures among small percentages of large populations. Some of the research reported at this Colloquium that looked most promising to me include:

   - Cardiac function changes to urban PM exposures.
   - Biomarker development for oxidant stress (Hooper et al., 1999; Lay et al., 1999).
   - Macrophage and tissue responses to peroxide in aerosols (Hooper et al., 1999).
   - Evidence for significant and rapid translocation of inhaled ultrafine particles to other organs (Finch et al., 1999).
   - Enhanced responses to concentrated ambient PM in infected animals (Zelikoff et al., 1999).

7. Controlled animal inhalation exposure studies are needed that are explicitly designed to elucidate mechanisms and dose-response relationships for the pulmonary and cardiovascular effects occurring in significant excess among humans exposed to elevated PM, especially for:

   - Concentrated ambient PM with and without pollutant gases.
   - Compromised animal models that may represent susceptible human subpopulations.
   - Examining the influence of number, surface, and mass concentrations of materials found in ambient air in $PM_{10-2.5}$, $PM_{2.5}$ and $PM_{0.1}$ size ranges.

8. Alternative approach (paraphrasing Dr. J. Brain's Integrative Summary of Session 3 on the biological mechanisms underlying adverse health effects). Use arbitrary control level of 65 $\mu g/m^3$ (or was it m.p.h.?).

9. Dosimetry research results represent excellent updates and needed refinements of lines of particle deposition research in human lungs that were advanced significantly in the 1960s and 1970s. Extensions of lines of earlier research on particle retention, especially long-term retention and translocation, are also needed.

Conclusions

The Third PM Colloquium in Durham, NC provided an opportunity for a large part of the world's research community that is engaged in cutting-edge research on PM to meet and share their findings and plans for future investigations. This opportunity to meet and discuss research should help them focus their ongoing and future research projects on the most critical data gaps

and should also lead to more collaborative efforts and programs. The Colloquium's Organizing Committee clearly deserves a great deal of credit for the evident success of this Third PM Colloquium.

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Summary Of The Third Colloquium On Particulate Air Pollution And Human Health, Durham, North Carolina, June 6-8, 1999

An Evolution Of Perspectives

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This colloquium, the third since the beginning of the series in 1994, attracted over 350 participants who presented 152 posters of original work grouped into 5 sessions, each of which were accompanied by 3 integrative platform presentations, comments by panelists, and discussion from the floor. The meeting was highly successful, which was not a foregone conclusion considering the current proliferation of meetings, sessions within meetings, workshops, hearings, and committee activities focused on particulate matter (PM).The meeting was very well-attended, facilitated no doubt by its strategic siting at a readily-reached venue. The meeting was very timely, roughly coinciding with the initial stages of the next PM Criteria Document, the awarding of 5 new EPA PM research centers, and broad speculation about the impacts of a recent court decision on present and future regulatory strategies (U.S. Court of Appeals, 1999). The meeting was very well-organized, with its success wisely relying more on stimulation by a smorgasbord of individual presentations than on one's ability to maintain attention during plenary presentations.

I witnessed the proceedings in a contemplative mood, borne not only of the noble desire to truly understand where all this effort is leading us, but also by the assigned responsibility to offer summary comments to the restive crowd in the final moments of the meeting. I became impressed with the notion that the gauge of our progress is not only the volume of useful information we produce, but also the evolution of the questions we are asking. The success of scientific endeavor probably consists 80% of asking the proper questions and only 20% of finding patrons for our work, conducting the work diligently, and communicating it fluently. Yesterday's concepts often do not provide a sound basis for tomorrow's hypotheses, and many of today's concepts may be doomed to the same fate. It is critical then, to distill what we are learning from what we are doing. To that end, a few examples of the evolution of our questions since the first colloquium in 1994 are presented as encouraging evidence that we are indeed learning. In each case, the emerging approach to framing the issue is contrasted with the manner in which the issue might have been framed in 1994.

1. **What are the critical information gaps?" vs. "What do we know about PM?"** In 1994, much of the debate centered on whether or not the statistical associations between ambient PM levels and adverse population health effects were fact or artifact. The proceedings were summarized in two volumes of *Inhalation Toxicology* (Phalen and Bates, 1995a; 1995b). Results of clinical and animal studies were presented, but there was not yet a coherent, and certainly not coordinated, body of research focused on

questions selected by the contemplation and consensus of leaders in the field. Moreover, it was apparent that there had been insufficient communication among atmospheric, epidemiological, and laboratory health scientists. The word, "particle" was often the only commonality among the diverse studies examined for hints of answers to the questions; "do they really do it?"; "which ones do it?"; and "how could they do it?". Clearly, greater focus and selectivity were needed to make the best use our limited funding and array of scientific talent and techniques.

Today, PM research is being shaped by the analytical planning efforts of several organizations, among which in the U.S. alone are EPA, NIEHS, NAS/NRC, HEI, NARSTO, and several states, universities, industry associations, and independent research organizations. A considerable overlap in composition among the planning groups has facilitated a *de facto* coordination, even though no effective, formal, comprehensive coordinating effort has yet developed. Similar activities have occurred in other countries. The most widely touted set of research recommendations is that developed by the NAS/NRC Committee on Research Priorities for Airborne Particulate Matter, under contract to EPA at the direction of the U.S. Congress (NRC, 1998). These recommendations describe and prioritize research needs under 10 topics encompassing key information gaps related to PM composition, exposure, dose, mechanisms of effect, and susceptible subpopulations, and provide researchers and research managers with a useful tool for sharpening research focus.

The reviews and discussions since 1994 have also acted in another way to improve our conceptualization of the PM problem. It has become clear that no single unifying hypothesis regarding PM characteristics, exposure, co-exposures, dose, response, or susceptibility is likely to explain the PM-health relationship. There is a broader realization that we face a extremely complex task, there is not likely to be any single revolutionary breakthrough in our research effort.

2. **"What are the important composition and size characteristics?" vs. "Which particles do it?"** Although the diversity of airborne particles has long been recognized, the statistical links between simple measures of particle mass and health outcomes tended to focus attention on over-simplified concepts of particle size and composition. Progress is being made in framing questions based on more accurate concepts of physical-chemical characteristics. For example, great strides have been made in determining the bulk composition of individual particles; ie, the portion of mass or volume composed of different materials. Discussion between biologists and atmospheric scientists, however, is now focusing attention on the fact that this approach falls short of telling us how the respiratory tract "perceives" particles. A cell must respond to the surface, not the interior, of poorly-soluble particles. Although reactive fractions or surface coatings may comprise a minority of the particle mass, cells may only "see" those components.

Progress is also being made in dispelling the widely-held myth that deposition, and thus perhaps risk, is precisely linked to particle size. We had a good understanding in 1994 of the general relationship between particle aerodynamic or diffusional size and fractional deposition in different regions of the respiratory tract. However, several important facts

have often been overlooked, particularly outside the particle dosimetry community. First, the relationship between size and location of deposition is one of probability; indeed, some 10 μm and larger particles do penetrate to alveoli. While it is true that smaller particles on average generally penetrate deeper than larger particles, the mass dose of the fewer larger particles to the deep lung could exceed that of the small particles. Second, path length and ventilatory preference differ markedly among ventilating units of the lung. A given particle type might cause a problem in a minority of "susceptible" ventilating units at a level where average deposition data would suggest the particle should not be a problem. Third definitions of "PM_{10}", "$PM_{2.5}$", etc, are widely, but erroneously, thought to exclude particles larger than the indicated size. We are making some progress, at least among the technical community, in stating more accurately that the indicated size is the functional diameter of 50% collection efficiency, and portions of the larger particle populations are also included in the collected mass.

3. **"What processes produce the particles?" vs. "Which source emits the culprits?"** In 1994, epidemiological information had linked ambient particle mass to adverse health outcomes, and most speculation about attribution of health burden to sources concerned particles directly emitted from sources such as vehicles, power plants, smelters, fireplaces, etc. Although the impacts of those sources remain an important issue, it is becoming more broadly realized that most of the fine ambient PM (eg, $PM_{2.5}$) is not emitted from any source, but is formed in the atmosphere from materials emitted from man-made or natural sources as gases or vapors. It is also becoming more broadly appreciated that the amount and composition of PM in an air mass can change markedly in both amount and composition with time and movement. For example, as parcels of air move eastward from Los Angeles, they pass over a small area with a high concentration of dairies that generate ammonia. The particulate composition of the air reaching Riverside often differs markedly from that of Los Angeles due to the "bloom" of ammonium nitrate particles over the dairies (Joe Norbeck, University of California, Riverside, personal communication, May, 1999).

4. **"What is the role of co-factors?" vs. "How do we sweep away the confounders."** In 1994, and during the ensuing years preceding promulgation of the new PM standards in the U.S., most of the large number of epidemiological studies showing statistical associations between ambient PM and health dealt with other pollutants as "confounders" to be eliminated mathematically or by experimental design in order to explore, or perhaps prove, the causality of PM. It is becoming more broadly acknowledged that co-exposures to other pollutants, as well as other factors, undoubtedly work together with PM to cause some, or perhaps all, of the effects. A significant contribution was the re-analysis sponsored by HEI (HEI, 1997) which demonstrated in a formal way the implausibility of isolating an independent effect of PM. It is a significant advancement that today, the question is more frequently, and more plausibly, framed as "how does PM contribute to the adverse health impacts of dirty air?" After all, nobody ever breathed only one pollutant at a time!

5. **"To what extent can animals model features of human susceptibility?" vs. "What is the best animal model?"** Indications that the effects of PM are manifested primarily in

certain subpopulations, together with the difficulty of eliciting adverse responses in young, normal laboratory animals exposed to ambient levels, have placed a premium on the development and use of animal models of enhanced susceptibility. Spontaneous or artificially-induced animal conditions having features of human cardiorespiratory aging or abnormalities have long been used, and investigators have long debated the relative merits of different models. Much of this debate in past years centered on defining the "best" model, presumably that which most successfully modeled the entire human condition. Because animals differ from humans in anatomy and physiology, it follows that no animal can completely mimic all features of a human condition. Animal conditions can model selected features of human conditions, however, and most animal models have utility when properly used and when the results are properly qualified. There is a growing recognition that it is inappropriate to assume that any animal model accurately reflects the totality of a human condition, and that investigators (and reviewers of papers) have important responsibilities to select the most representative model for the specific hypothesis being addressed, and to discuss the limits of extrapolation of results to humans when reporting the work.

6. **"How do variations in dose, response, and reserve contribute to variations in susceptibility?" vs. "What is the list of susceptibles?"** The mandate in the Clean Air Act to consider sensitive subpopulations, and epidemiological data showing temporal associations between short-term increases of PM and cardiorespiratory deaths in elderly subjects and increased morbidity in people with respiratory disorders, have focused attention on identification of subpopulations having the greatest susceptibility. In the past, descriptions of the suspected health impacts of air pollutants have often included a "litany of susceptibles" encompassing children, the elderly, and people with lung disease, sometimes whether or not the presumptions were founded in actual data. Aside from the excitatory value of invoking concern for children (as one example), there are indeed several rationales, and some data, supporting hypotheses that children may be of special concern, and the issue of susceptibility is rightly assigned a high priority. At the same time, there are rationales, and some data, suggesting that children, and their developing lungs, are not always at increased risk and may even constitute a resilient population.

Today, one can sense a growing tendency to frame the susceptibility question in a more precise manner. To wit, there is a distribution of susceptibility among the population, and individuals might be in the upper portion of that distribution because of greater than average dose, greater or different than average response, or lesser than average reserve with which to cope with exposures that all receive. Increased dose may derive from location (exposure), volume of respiration relative to size, or anatomical features enhancing deposition or reducing clearance. Increased response may derive from the stage of development or senescence of organ systems or genetic or acquired variations in responses from the molecular to the organism levels. Reduced reserve may derive from the immaturity, senescence, or damage of defense mechanisms, or from concurrent conditions that draw upon the body's normal functional reserve. If the young, the old, or the infirm are indeed "susceptible" it is because of one or more of these factors, and it is the factors we must model and study, not just the general population category. Moreover, there is growing realization that many responses in even "normal" individuals (ie, not

among the presumed susceptible subpopulations) likely result from local "susceptibility" due to one or more of the above factors.

7. **"Can we eliminate any hypotheses" vs. "What are the plausible hypotheses?"** Much effort in 1994 and since has focused on generating plausible hypotheses regarding the existence, nature, magnitude, and mechanisms of health impacts of airborne PM. This "range-finding" exercise has generated numerous lists of hypotheses that have helped to broaden thinking and facilitate cross-disciplinary communication. As the PM research effort fully hits its pace, it will be necessary to shift an increasing portion of our attention to determining whether any of our hypotheses might be eliminated. It is, of course, possible that all currently hypothesized factors and mechanisms are correct under some circumstances and contribute in part to the total risk. It is both inevitable and desirable that even more hypotheses will be generated as we become more knowledgeable. It is likely, however, that the objective, rigorous testing of hypotheses and continuing critical review of our knowledge will allow us to focus on a limited number of the most important risk factors.

8. **"How can we use information?" vs. "How can we generate information?"** As the burgeoning PM research effort unfolds, a huge amount of information will be developed. Much of the past concern has focused on the many ways in which we might generate this information. Today, one can sense more thought, and sometimes concern, about the manner in which this information will actually be organized, analyzed, communicated, and used in an effective and timely manner. This is a sign of wisdom.

Conclusions

As one compares our knowledge regarding the health risks from ambient PM, the nature and magnitude of our research effort, and the evolution of our questions, there is no doubt that we have made considerable progress since the first Colloquium in 1994. Of course, we certainly should have, considering the resources that have been directed toward the effort. As illustrated by the above examples, it is encouraging to note that our questions are developing positively in focus and sophistication. However, as one considers these examples, another important reality becomes clear. In many cases, our progress is not so much in our knowledge per se, but rather in our greater communication of knowledge across disciplinary lines. Cross-disciplinary and inter-organizational communication and coordination must be a hallmark of our collective PM research effort in order to make the most effective progress in appropriately protecting public health in the face of high stakes and competing demands.

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What Are We Breathing and How Can it Best be Characterized?

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The opening session of the Colloquium, which addressed the issues of defining and characterizing relevant PM exposures, consisted of introductory and summary talks, poster viewing, and a discussion between the audience and an expert panel. The platform presentations and expert panel members' comments tended to point to areas in need of new research, while the 50 posters documented recent advances in knowledge. This commentary highlights some of the information that was presented.

Several speakers emphasized that understanding "personal exposures" is a key to uncovering who might be affected by PM inhalation, under what circumstances they might be affected, and what pollutant sources (or atmospheric chemical processes) might be producing the effects. Jack Spengler (Boston, MA) commented that the average person spends 87% of their time indoors, that air conditioning can greatly reduce the penetration of outdoor PM into the indoor air, and that as the number of people in a room increases, so do the pollutant levels. Also, O_3-generating "air cleaners" can greatly increase the ultrafine particle count indoors. He pointed to several areas in need of further research: chemical characterization of indoor PM; the toxicology of indoor PM; emission source characteristics; infiltration and turnover rates for air contaminants indoors; and how human activities modify indoor PM exposures. Petros Koutrakis (Boston, MA) stated that the "personal cloud" is largely composed of coarse-mode (>2.5 μm aerodynamic diameter) particles, and that the greatest differences in outdoor vs. indoor PM is expected in the wintertime. Koutrakis called for additional research on defining actual exposures (both personal and community), better chemical and temporal characterizations of exposures, and uncovering the factors that produce subject variability in PM exposures; such research will require improvements in methodology. Harriet Burge (Boston, MA) emphasized the serious lack of understanding of exposures to biological aerosols. She commented that pollen and spore levels are associated with asthma, hospitalizations and mortality. Burge remarked that a single inhaled ragweed pollen grain can produce symptoms in a sensitive person. Judith Chow (Reno, NV) indicated that there is also a need to improve the consistency among the many PM sampling methods that are commonly used. Glen Cass (Pasadena, CA) also emphasized the importance of biological aerosols as potentially significant confounders in epidemiologic studies of the effects of PM; for example, paved road dust has about 20 biological components. Cass also commented that many complete chemical analyses of environmental aerosols are already available and emerging, and the real challenge is what will be done with the large amount of data that is being generated. He saw the need to shift focus from individual PM components and move toward understanding mixtures of air pollutants and how specific sources contribute to these mixtures. Mike Lebowitz (Tucson, AZ) added that there is tremendous allergenic potential in $PM_{2.5}$ samples.

Summarizer George Thurston (Tuxedo, NY) raised some questions that must be better answered. What are the characteristics of PM that can and should be measured? How can ambient PM be

concentrated so that it can be studied toxicologically? How well do central site monitoring stations reflect personal exposures? Should there be greater emphasis on understanding the contributions of specific sources to PM exposures as opposed to the focus on PM characteristics alone?

Current research efforts, as evidenced by the posters, are only addressing some of the aforementioned problems. Several studies are looking at traffic, including diesel engine related, as a significant contributor to indoor and outdoor PM exposures. Data on indoor exposures in hospitals and homes are elucidating the roles of the specific activities of people as modifiers of PM exposures. Also, the currently accepted trimodal size distribution of urban aerosols is too simplistic to be universally applied; particle size change due to hygroscopic growth is more significant than has been previously appreciated. It is clear that the current research is raising additional important questions.

Even given the large number of relevant current studies, many gaps in knowledge exist. Details on personal exposures (with respect to chemistry, size distributions and variability) are still largely lacking. Information on peak exposures, where and when they occur and their chemistry, is nearly non-existent. Other than for traffic, specific sources are not well tied to human exposures. Also, the methods for characterization of particle surfaces are not very advanced, which is a problem when one considers that the particle surface is what initially contacts the cells of the respiratory tract. Although the current research efforts are largely on-track for contributing to understanding the consequences of PM inhalation, there are obviously many significant unresolved relevant problems.

Session 2: What Properties Of Particulate Matter Are Responsible For Health Effects?

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In recent years many properties of particulate matter in air have been suggested to be potentially responsible for the associations between particle mass in air (notably PM10) and various deleterious effects on health. Among these are:

1. Mass in different sizes; in particular, potency of respirable particles (PM2.5) vs. 'coarse mass' (the difference between PM10 and PM2.5)
2. The number of particles in the air and the surface area of particles; notably, it has been suggested that the number of ultrafine, sub-100 nm particles in the air, which carry very little mass, might be a more relevant attribute than the total respirable or inhalable mass.
3. The chemical composition of the particles; candidate substances with specific biological mechanisms are, among others:
   a. transition metals and valence state
   b. acidity
   c. biogenic components such as pollen (fragments), bacterial endotoxin and mould components
   d. reactive PAHs, and Elemental Carbon or 'soot' related to diesel exhaust in particular

Last but not least, the question to what extent associations between PM and health variables are confounded by gaseous pollutants remains an issue of some concern.

In Session 2 of the symposium: "What properties of particulate matter are responsible for health effects?" many although not all of the above issues were discussed.

1. **PM2.5 vs. Coarse Mass, CM.** The results of the previously published analyses out of the six cities study (Schwartz, JAWMA) suggested that CM was not a predictor of daily mortality, in contrast to PM2.5 which was. New studies conducted in the Los Angeles Basin (S.K. Van Den Eeden, et al., *A Parallel Time-Series Study of Air Pollution in the Los Angeles Air Basin)* and Mexico City (D. Loomis, et al., *Stronger Effects of Coarse Particles in Mexico City*) suggested stronger effects of CM than of PM2.5 on mortality, however. A study conducted in Chili, presented in session (L.A. Cifuentes, *Daily Mortality by Cause and Socio-Economic Status in Santiago, Chile*), on the contrary, found stronger effects of PM2.5 than of CM. A laboratory study from Taiwan (L.C. Chen, et al., *Composition of Ambient Particulate Matter as Determinant of Cellular Response*) showed that the cellular response to particles was dependent on particle size (fine particles eliciting a stronger response on an equal mass basis) only for particles collected near busy roads, not for particles collected elsewhere The discussion suggested

that the CM in places such as Mexico City may contain many of the noxious substances that are prominent in PM2.5 in other places, possibly due to industrial emissions. It was also mentioned that the one city that did show CM effects in the Six Cities study, Steubenville, may have such characteristics as well. It seems clear that CM cannot be discarded as predictor of daily mortality in certain areas, and more work is needed to define where CM is a problem and where it may not be.

2. **Ultrafine particles.** One experimental study (K. Donaldson, et al., *Inflammation Caused by Ultrafine Carbon Black Particles is Independent of Transition Metals or Other Soluble Components*) showed that the inflammatory effects of ultrafine carbon black were independent of the transition metal content. Another showed that the ultrafine fraction of size-fractionated ambient PM elicited a stronger production of granulocyte-macrophage colony stimulating factor by human bronchial epithelial cells than larger particles (J. Reibman, et al. *Effect of Size-Fractionated Ambient PM on Release of GM-GSF by Human Bronchial Epithelial Cells*). This may be important in explaining acute effects of ambient PM on asthma. A study design was presented from Austria (H. Hauck, et al., *AUPHEP On The Way. Austrian Project on Health Effects of Particulates*) that included long-term ambient monitoring of ultrafine and other particle size fractions. Other epidemiological studies on ultrafine particles are currently underway in Europe, focusing on daily mortality in Erfurt, Germany (Wichmann) and on acute cardio-respiratory responses in elderly patients in Helsinki, Finland, Erfurt, Germany and Amsterdam, the Netherlands (Pekkanen). The discussion emphasized the problems associated with exposure assessment to ultrafines in epidemiological studies, as still not much is known about spatial variability, indoor/outdoor number concentration ratios, relationships between ambient monitoring and personal exposure etc.

3a. **Transition metals and valence state.** Transition metals continue to raise attention as active ingredients of the PM container. Epidemiological data to support that transition metals at realistic ambient concentrations are related to health endpoints are still largely lacking, the evidence continues to come mostly from experimental studies. One rat instillation study (J.A. Hotchkiss, et al., *Residual Oil Fly Ash (ROFA)-Induced Pulmonary Inflammation and Mucous Cell Metaplasia in Rats Correlates with Leachable Vanadium Content*) showed that inflammation and mucous cell metaplasia associated with residual oil fly ash was related to the leachable Vanadium content. A human experiment (C. Solomon, et al., *Airway Cytokine Expression as a Function of Chemical Composition of Inhaled Metal Particles*) showed that ZnO at 20 mg/m^3 but not MgO at 52 mg/m^3 was able to elicit an increase in several airway fluid cytokines as measured in induced sputum. The discussion emphasized the potential importance of valence state (Fe^{+++} vs. Fe^{++} for instance) and of the solubility of relevant compounds at target sites such as epithelial lining fluid.

3b. **Acidity.** Recent epidemiological studies from the U.S. and Canada such as the 24-cities study point to Particle Strong Acidity (PSA) as a PM attribute closely related to health indicators such as lung function and chronic respiratory symptoms. A long-term exposure study in healthy dogs (J. Heyder, et al., *A Longitudinal Study with Dogs Exposed to an Acid Aerosol*) could not demonstrate such effects in an experimental setting, raising questions about the adequacy of the animal model (healthy vs. compromised) and

exposure conditions (PSA alone or in ambient mixtures with various co-pollutants). An epidemiological study from North-East U.S. cities (R.C. Gwynn, et al., *Health Effects of Primary and Secondary PM Components in Two New York State Metropolitan Areas*) found closer associations between daily mortality and sulfate as an indicator of acidic secondary PM than with the Coefficient of Haze as indicator of primary carbon soot.

3c. **Biogenic components such as pollen (fragments), bacterial endotoxin and mould components.** There was relatively little attention in the Symposium for this class of components. A study from Seattle (S.H. Moolgavkar, et al., *Air Pollution, Pollens and Hospital Admissions for COPD in the Seattle Metropolitan Area*) found tree pollen concentrations as well as ambient carbon monoxide to be more closely associated with daily COPD admissions than ambient PM.

3d. **Reactive PAHs, and Elemental Carbon or 'soot' related to diesel exhaust in particular.** An experimental study reported at the Symposium (M.C. Madden, et al., *Ozonation of Diesel Exhaust Particles Affects Lung Responses*) found that the toxicity of diesel exhaust particles (DEP) was enhanced by prior exposure of the particles to ozone. Such interactions have not been well studied epidemiologically; re-analysis of existing databases having data on both PM and ozone may provide indications of whether such interactions can be shown at ambient concentrations, and with human health data as well.

The issue of confounding by (or interactions with) gaseous co-pollutants remains on the table. A meta-analysis presented at the Symposium (D.M. Stieb, et al., *Acute Effects of Ambient Air Particles and Gases on Mortality: Preliminary Results of a Meta-Analysisabstract 144*) suggested that it is very hard to separate effects of ambient PM from those of gaseous co-pollutants, except ozone, the correlation of which with PM is often sufficiently low to establish their independent effects. A study from the Netherlands (E. Buringh, et al., *Is SO_2 a Causative Factor for the PM Associated Health Risks in the Netherlands?*) investigated associations between SO_2 and daily mortality at different levels of exposure and found the effects to be stronger (per unit concentration) at lower levels; then the study showed that in geographic areas with low levels, the effects were in fact smaller (per unit) than in areas with high levels, suggesting that SO_2 in this case is a surrogate rather than an active ingredient. Such analyses circumvent the co-linearity that often exists between PM and gaseous co-pollutants.

What Properties of Particulate Matter are Responsible for Health Effects?

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This session, "What properties of particulate matter are responsible for health effects," addresses one of the current, critical issues related to airborne particulate matter and health. Answering this question was one of the topics given priority by the National Research Council's Committee on research priorities for particles (NRC 1998). Research on this topic is needed not only to advance understanding of mechanisms underlying observed health effects, but also to guide control strategies.

In carrying out research on this topic, we face a challenging array of possibilities for investigation, as defined by health effects and potentially relevant properties of particles (Table 1). Virtually every cell in this array has been given some credence by informed conjecture or initial observations. The spectrum of hypotheses implied by the table is broad, ranging from non-specific, e.g., particles have general toxicity regardless of characteristics, to far more focused, e.g., cardiac toxicity arises from transition metals. The presentations in this session of the colloquium covered this spectrum and are illustrative of toxicologic and epidemiologic approaches being used to test hypotheses related to particle characteristics.

The rationale for research directed at toxicity-determining characteristics of particles is evident. The Environmental Protection Agency regulates particle mass concentration only; the 1997 promulgation of both PM_{10} and $PM_{2.5}$ standards acknowledges that biologically relevant lung doses are determined by particle size. However, airborne particles are inherently a mixture, with some of the defining characteristics given in Table 1. Unfortunately, for both investigators and regulators, the characteristics of particulate matter typically vary over time, with sources and meteorology, and within regions. This complex heterogeneity is potentially a barrier to testing highly focused hypotheses, using experimental models of exposure to ambient particles or epidemiological approaches. Incorporating such heterogeneity into regulatory limits may also not be possible.

In testing hypotheses concerning particle toxicity, we will need strong evidence concerning a particular hypothesis, equivalent to one cell in Table 1, in order to favor that hypothesis over the alternatives. Both observation and experimental data are most informative when a highly specified hypothesis is tested against some plausible alternative. An example is a clinical trial (a controlled and randomized experiment) carried out to test the efficacy of one treatment -- perhaps a new drug -- against a control often the already-standard treatment. The trial is designed to gather data to compare the new treatment against the alternatives. For particle characteristics, this relatively straightforward experimental scenario is replaced by the need to test multiple, competing and not necessarily exclusive, hypotheses. In fact, strong prior evidence

has not yet accumulated for most of the specific hypotheses corresponding to the cells of Table 1.

Consequently, scientific researchers face an extraordinarily challenging task in gathering data, whether by experiment or observation, to address the question that titled this session. Which hypotheses should be explored initially? What type of evidence is needed to favor one hypothesis over alternatives? While the urgency of answering the overall question is acknowledged, insufficient consideration has been given to the two complementary questions listed above.

Research is being carried out energetically on specific hypotheses related to toxicity of particulate matter. Work presented at this session is illustrative. Experimental studies addressed vanadium content and inflammation (Hotchkiss), transition metals and toxicity of carbon black (Donaldson), size and elemental composition (Chen), and acid content (Heyder); the scope of the epidemiologic studies was equally broad: ultrafine particles (Hauck), coarse particles (Loomis), biogenic aerosols (Moolgavkar), and acidity (Gwynn and Stieb). The rationales for these particular hypotheses are uncertain and we lack an overall strategy for directing investigative attention towards particular hypotheses. As always, we leave initiative to the research community, but a higher level of oversight may be warranted. We also need periodic syntheses of the evidence to determine which hypotheses can be set aside and which merit further research.

My second question, "What type of evidence is needed to favor one hypothesis over alternatives," has received little explicit discussion, even though study designs should be based around obtaining appropriate data for testing specific hypotheses. The researcher's dilemma is obvious; if several hypotheses have equal prior credibility, e.g., cardiac effects reflect ultrafine mass or transition metal content, how should experiments be designed to test these hypotheses against each other, or against the composite of alternatives? Epidemiologists face the same challenge but cannot manipulate exposures, except through judicious selection of study locales.

The general criteria and processes for evaluating information will also be challenged as we grapple with whether the evidence supports the conclusion that one or more specific characteristics of particles determine toxicity. These processes have included using criteria for causality, such as those used in the Surgeon General's reports, and the process of expert synthesis used by the Environmental Protection Agency through its development of a criteria document and staff paper with review by the Clean Air Scientific Advisory Committee (CASAC). We should continue to refine our approaches for synthesizing data, just as we continue to expand the data base on air pollution and health. Lacking both the adequate evidence and a process for summarizing it in a policy-relevant fashion, we may be unable to answer the question "What properties of particulate matter are responsible for health effects?"

Table 1

1. CHARACTERISTIC	*Response*				
	2. CARDIOVASCULAR DISEASE	**Acute Respiratory Infection**	**Chronic Obstructive Pulmonary Disease**	**Asthma**	**Morbidity**
Mass					
Size					
Metals					
Acidity					
Organics					
Biogenic PM					
Sulfate/Nitrate					
Peroxides					
Elemental C					
Other Pollutants					

Properties of Ambient PM Responsible for Human Health Effects: Coherence Between Epidemiology and Toxicology

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Over the past few years, epidemiological studies have found consistent associations between air pollution, including indices of particulate matter (PM), and adverse health outcomes. These studies have been conducted in various geographic locations and have involved a range of populations. While the consistency of the findings and the presence of an apparent dose-response relationship provides a strong argument for causality, epidemiological studies can only conclude this based upon inference from statistical associations. Toxicological studies, which involve controlled exposures in laboratory settings, are attempting to provide some plausibility for a role of ambient PM in this association, by examining the relationship between certain physiochemical characteristics of ambient PM and biological responses. Thus, the question at hand is whether there is any consistency between results of epidemiological and toxicological studies, i.e., coherence. This can be addressed in terms of two approaches, namely mechanistic plausibility and dosimetric plausibility between characteristics of PM and health effects noted in epidemiological and toxicological studies.

In terms of dose, there is little coherence between epidemiological and toxicological studies. While the former show association of increased mortality/morbidity with PM at low ambient concentrations, even with acute exposure, the latter show associations of biological responses with PM atmospheres, both concentrated ambient PM and PM surrogates, only at much higher than ambient levels. This may be due, at least in part, to the small sample sizes generally used in controlled exposure studies compared to the large populations generally examined in epidemiological evaluations. The apparent lack of coherence is also evidenced by the fact that epidemiological health outcome associations appear to be exposure concentration dependent, while a number of toxicological studies with concentrated ambient PM have often shown no obvious relationship between exposure concentration and response. This latter observation may be the result of differences in composition of ambient PM on different days, and the fewer number of days involved in toxicological studies compared to those examined in epidemiological studies.

There is a growing body of data which is providing some degree of mechanistic plausibility for epidemiological health outcomes. Some of these are shown in Table 1. In addition, there are a number of commonalities between epidemiological and toxicological studies in terms of specific components of ambient PM which may be responsible for adverse health effects. Some of these are summarized in Table 2. There are certain caveats. For example, repeated exposures to ambient PM on different days do not always yield the same results in the same laboratory; this may be due to differing characteristics of pollution on different days. In addition, similar exposures in different species or animal model of compromised humans do not always yield the same results; this may reflect differences in susceptibility.

Table 1. Mechanistic Plausibility: Coherence Between PM-Exposure Associated Health Effects from Epidemiological and Toxicological Studies

Epidemiological Health Endpoints	Toxicological Health Endpoints	
	Concentrated Ambient PM	Specific PM Components
↑ Hypertension/↑Stroke	Δ Homeostasis (e.g., peripheral blood diffs.)	Δ Blood Coagulation Factor: UF Carbon ↑ Platelets, WBC: Diesel Exhaust (whole)
↑ Ischemic Heart Disease/ ↑ Heart Attack	Δ Heart Rate Variability Δ EKG Wave Form Segments	↑ Arrhythmia Incidence: ROFA
↑ Acute Respiratory Infection (e.g. acute bronchitis, pneumonia)	↓ Mø ROI Production ↓ BALT Δ Pulmonary Cytokine Profile	↓ Mø ROI Production: Ammonium Sulfate Δ Pulmonary Cytokines: Metals
Exacerbation of COPD, Asthma	--	↑ Airway Reactivity: H^+ Δ Mucociliary Function: H^+
↑ Respiratory Symptoms Δ Lung Function Indices	--	Pulmonary Inflammation: UF Metals Δ Pulmonary Cytokines: Metals

Table 2. Currently Hypothesized PM Physiochemical Properties Related to Biological Responses

	Response	
PM Characteristic	Epidemiology	Toxicology
mass concentration	associated with health outcomes	associated with biological responses
particle size	relative association with health outcomes often related to size mode (FP, CP, UF, etc.)	different biological responses noted with different size modes
metals	Utah Valley -- effects from steel mill related to metals	ROFA: effects related to metals
acidity	some evidence for H^+ association with health outcomes	various biological responses
organics	association of PM with lung cancer, possibly due to carcinogenicity of organic fraction	known mutagens/carcinogens
biogenic PM	possible association with health outcomes	generally allergenic
sulfate/nitrate salts	association with some health outcomes (markers for H^+)	generally not very toxic at low concentrations
peroxides	?	high levels may produce biological effects
elemental C (soot)	?	mutagenic/carcinogenic/irritant

Inhaled Particle Dosimetry: Session Commentary

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Abstract

The Third Colloquium on Particulate Matter and Human Health addressed the roles that inhaled particle dosimetry plays in understanding the potential health risks of human populations exposed to particulate air pollution. Nineteen papers, including posters, were presented that addressed particle deposition and clearance in both humans and laboratory animals. The effects of age, gender and illness were addressed as well as ultrafine particles and correlations between particle deposits and tissue pathology. The papers and related discussions also illuminated some important gaps in knowledge such as: the accuracy of dosimetry predictions for individuals; the under representation of susceptible populations; the movement of deposited particles to non-lung tissues and organs; and the accuracy of extrapolations across species. Although current dosimetric information is useful for understanding the effects of particulate air pollution several unsolved problems remain.

Introduction

It is well understood in toxicology that "the dose makes the poison" (Paracelsus – 16^{th} century) and inhaled particles are no exception. The session question addressed by 16 posters, 3 platform papers and a general discussion at the Third Colloquium on Particulate Matter (PM) and Human Health (Durham, NC, USA, June 6-8, 1999) was: "What improvements in dosimetry and extrapolation modeling will provide for better evaluation of human health effects and risk assessment? Plenary speaker Joachim Heyder emphasized the power of aerosol dosimetry when applied to individuals, as opposed to groups. Heyder observed that in aerosol inhalation studies with dogs, those animals that responded were those with the greatest doses. Heyder recommended a focus on "individual dosimetry," because individual responses are most often the crux of toxicological problems. Plenary speaker Frederick Miller chose to focus on three fundamental uncertainties relating to PM dosimetry. First, the particle property (or properties) most closely tied to potential adverse health outcomes has (have) not been identified: candidates include particle number, surface area, volume and mass. Second, regional doses within the respiratory tract are still poorly understood. Third, the important adverse effects of inhaled particles have not been well elucidated. From the observations of these speakers it is clear that dosimetry has much to offer, and that it faces substantial challenges in relation to the question addressed by the session.

Recent Findings

Aside from the major advances over the past 50 years in understanding the phenomena of inhaled particle deposition and clearance, some recent achievements were presented at the

colloquium. (Authors of papers are given in parentheses.) Three papers addressed airways disease. Two modeling papers indicated that airflow-obstructed lungs can be expected to have increased particle deposition as well as increased heterogeneity of deposits within the respiratory tract (T.B. Martonen, R.A. Segal and C.S. Kim; and J.S. Brown, D. Crawford-Brown and W.D. Bennett). Experiments with inhaled radiolabeled 5μm mass median aerodynamic diameter particles in patients with obstructive airways disease indicated that in comparison to healthy controls, the patients, in fact, exhibited increased deposition, and that poorly ventilated regions had both the highest deposition and the fastest clearance (J.S. Brown, K.L. Zeman and W.D. Bennett).

Three papers addressed residual particles in autopsy lungs. Examination of 43 (of a collection of 117) autopsy lungs (Hispanic males 16-73 years of age from CA) for pathologic changes and particle deposits indicated that fibrosis, muscle hypertrophy and inflammation (especially in the proximal respiratory bronchioles) were positively correlated with indices of mineral dust retention (M.G. Menache, K.E. Pinkerton, F.H.Y. Green, E.B. Bahne and M.B. Schenker). Total particle content (minerals and carbon) measured in digested autopsy lungs from Mexico City and Vancouver residents correlated positively with 3-year mean PM_{10} levels in the two cities; PM_{10} was higher in Mexico City as was lung particle loading (M. Brauer, B. Stevens, S. Vedal, C. Avila-Casado, T.I. Fortoul and A. Churg). Similarly, mineral analyses of particles recovered from dogs and people in Mexico City produced correlations between elemental composition of particles from lungs and those in fugitive dust and fly ash particles, indicating the promise of eventually linking specific sources to lung burdens (J. Gallagher, J. Inmon, G.L. Calderon, F. Blanchard, R. Kellogg, J. Scott, L. Stettler, J. Lewtas, A. Levine and A.K. Prahalad).

Ultrafine, UF, (diameter 0.1 μm and less) particles were studied in inhalation experiments with both rats and humans. In rats, inhaled ultrafine radioactive Ag particles indicated that silver was dissolved in blood, but that focal accumulations (of grains in autoradiograms) were seen in lung and liver (G.L. Finch, K.J. Nikula, E.B. Barr, J.C. Seagrave, M.B. Snipes, C.H. Hobbs and J.L. Mauderly). Whether or not the accumulations were formed in the rats livers after transport, or transported there as intact particles is an important issue. In human studies, UF particles of 0.04μm diameter had greater deposition efficiencies in females (n=11) than in males (n=11), but larger UF particles (0.08 and 0.10μm diameter) had similar gender-related deposition; UF particles of 0.06μm diameter had marginally greater deposition in females (P.A. Jaques and C.S. Kim). Doses per unit airway surface area was greatest in large airways for UF (and fine and coarse) particles in both men and women; women tended to have greater deposition efficiencies of UF (and coarse) particles than did men (C.S. Kim, S.C. Hu, P. Jaques, J. Ding, and P. DeWitt; S.C. Hu and C.S. Kim).

Body size will affect both airway size and specific ventilation (volume of air breathed per unit of body mass), thus age-related effects on particle dosimetry can be expected. Studies of 2 μm diameter particle deposition in subjects aged 7 to 35 years found that children had a higher rate of particle deposition normalized to lung surface area than did adults and adolescents. The investigators attributed the difference to increased specific ventilation in relation to lung size instead of differences in age or body height (W.D. Bennett and K.L. Zeman). In a modeling study comparing the deposition of 1 μm aerodynamic diameter particles in a 22-month old vs. an

adult, the infant had a predicted 38% relative increase in deposition (C.J. Musante and T.B. Martonen).

A multiple path (airway) particle deposition model for rats and humans was used to indicate significant differences in particle deposition among the lobes for both species; the model also indicated that UF particle deposition was high, but confined to relatively few acini (R. Subramaniam, J.I. Freijer, B. Asgharian, F.J. Miller, F.R. Cassee, L. van Bree and P.J.A. Rombout). The computational model was used successfully in predicting the deposition of inhaled cadmium chloride particles of various sizes in experimentally-exposed rats. The rats lungs were also evaluated toxicologically, and preliminary results failed to show a particle size effect on biochemical changes as determined by analysis of bronchoalveolar lavage samples (F.R. Cassee, A.J.F. Boere, L. van Bree, P.H.B. Fokkens and J.I. Freijer). Clearance of insoluble radioactive sulfur colloid particles deposited directly into the bronchi (via bronchoscope and breathhold) of anesthetized dogs (N=5) was studied. Sublobar segments differed in initial clearance rates of the particles, but clearance appeared to be complete in all of the studied regions by 24 hours (W.M. Foster, K. Macri, S. McCulloch, T. Myers and A.N. Freed). Finally, airflow patterns in a transparent replica of the human nasal cavity was examined using a particle laser velocimetry technique: the complex geometry produced very complex flow patterns having regions of flow separation, reverse flows and stagnation (J.T. Kelly, L.M. Hopkins, A.S. Wexler, and A.K. Prasad).

The above papers clearly do not represent all of the research activity in particle dosimetry, but they illustrate the types of studies that are being conducted in response to the questions surrounding particulate air pollution; these papers should be considered to be only samples of current relevant research. On the other hand, each of the papers made one or more useful contributions to the understanding of inhaled particle dosimetry.

Uncertainties

The above papers, along with similar research in the literature, not only represent recent advances in understanding the dosimetry of inhaled particles, but they also show that gaps in knowledge tend to overwhelm what is known. A complete analysis of dosimetry related uncertainties is not feasible, so a sampling will have to suffice. For the purposes of understanding particulate air pollution, uncertainties exist with respect to the following issues.

- Particle deposition and clearance requires much more study in diseased/abnormal humans and laboratory animals. The diseases and conditions of interest are numerous and include asthma, upper and lower respiratory tract infections, sleep apnea, emphysema, fibrosis, respiratory tract cancer, edema and congenital abnormalities of the airways. The currently used laboratory animal models of diseased humans represent a special challenge for dosimetry as such models are not only varied, but they are often produced by unusual and extreme treatments. Species differences in structure and function further complicate comparative dosimetry considerations.

- Particle clearance and translocation to sites beyond the airway surfaces requires more emphasis. Where and why insoluble particles accumulate, and how diseases/abnormalities

influence those processes is a large area for investigation. This is an especially crucial topic for ultrafine particles, as they may have significant access to sub-epithelial tissues in the respiratory tract, and they may translocate intact to organs such as the heart, blood vasculature, brain, kidney and liver. Accumulation of insoluble particles in such locations may have adverse consequences that are relevant to particulate air pollution. Conversely, knowledge of which accumulations are benign is also important.

- Although some dosimetry information is available related to differences in body size and gender, this knowledge is incomplete, especially in relation to particle clearance, accumulation and potential transport to non-lung tissues. This issue is compounded by possible differences in the effects of disease conditions in the very young and the very old compared to typical adults. The extent to which non-anatomical gender differences (such as hormonal and immunological) influence dosimetry is important for study.

- Correlating particle dosimetry and toxicologic responses is an area that has just begun to be investigated. The relevant characteristics of particles, such as number, surface, volume and mass that produce adverse responses is a part of this issue, as is the significance of prior exposures (which may produce tolerance or sensitization).

- Species differences in dosimetry and their implications for understanding human risks requires more study. Clearly, a large fraction of our knowledge of the effects of particulate air pollution must come from laboratory animal studies. Both confident extrapolations, and understanding mechanisms of action require additional dosimetry research.

- How well dosimetry models work for individuals is largely unknown. There is a need to validate all aspects of dosimetry, including regional deposition and clearance phenomena, for individual people and laboratory animals. Techniques for such studies are available, but they have yet to be adequately exploited.

- Realistic air pollution, which includes complex particles and particle/gas mixtures require study. The real-world is more complex than what has been examined in dosimetry investigations. Real aerosols include particles that are hygroscopic, contain organic and inorganic components, and have properties that may significantly modify breathing patterns and airway structure. Real-world activities involve unusual breathing patterns as well as co-stressors (thermal and emotional for example) that may alter the dosimetry and effects of inhaled particles.

As expected, the uncertainties related to dosimetry are substantial, and clearly not all can be investigated thoroughly. Therefore, judgement, careful planning, and increased interactions across relevant disciplines will all be essential if dosimetry research is to make important contributions in the near term. The time for such contributions is at hand, because there is currently an appreciation for the importance of dosimetry in providing for a better evaluation of the human health effects of particulate air pollution.

How May The Dosimetry Of Inhaled Particles Play A Role In The Observed Mortality/Morbidity Associated With PM10?

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Particulate air pollution has been linked to acute increases in mortality/morbidity primarily in the elderly, children and those with preexisting cardiorespiratory disease. While these individuals may be predisposed to acute toxic effects, they may also receive an increased dose of particulate matter to their lungs or other body organs compared to healthy, young adults. The dose of inhaled particulate matter is a function of both 1) deposition on lung surfaces as well as 2) clearance from those surfaces. Either or both processes may be altered in susceptible populations, leading to an enhanced dose.

Particle deposition in the lung is a function of multiple factors, including particle size, breathing patterns, and airway geometry. In the healthy lung, it is clear that for a given breathing pattern, total deposition efficiency of particles increases as particle size increases from 0.5 um to 10 um mass median aerodynamic diameter (MMAD) (1). Similarly, deposition efficiency increases as particle size decreases from 0.5 um to ultrafine 0.01 um particles. Minimal deposition efficiency occurs in the 0.1 to 1.0 um range where particles are most buoyant, i.e. following flow streamlines in and out of the lung. It is important to remember, however, that many ambient particles in this size range are hygroscopic, growing to larger sizes as they enter the respiratory tract, enhancing their deposition efficiency (2).

For a given particle size, total deposition may vary as a function of breathing pattern (1, 3). In general, an individual who achieves a given minute ventilation with a slow, deep breathing pattern (i.e. slow rate of breathing and large tidal volume) deposits a greater fraction of particles per breath than one who breathes more rapid and shallow. Variation in breathing pattern between healthy subjects (age 18-80) has been shown to influence variability in fine particle deposition (4). On the other hand, age per se, does not appear to influence deposition efficiency of fine particles in adults (4).

Several investigators (summarized by Schlesinger (5)) have shown that total deposition efficiency is greater for nose vs. mouth breathing for particles larger than 1um MMAD. The filtering capacity of the nose may act to protect the lung from high concentrations of airborne particulates. Intersubject variability in nasal vs. oral breathing, especially as occurs during exercise, may also influence variability in total deposition within the lung. Children, who generally spend more of their time exercising than adults, are likely to receive an increased dose of inhaled particles to their lungs from both the increased ventilation associated with exercise as well as a lesser contribution of nasal ventilation.

Changes in airway geometry, especially associated with obstructive lung disease, may have a dramatic effect on total deposition efficiency. Bennett et al (6) showed that patients with chronic obstructive pulmonary disease (COPD) receive on average 2.5 times the deposited dose at rest of

their age-matched healthy cohort. The deposited dose in COPD increased (as much as 5 times normal) with increasing airway obstruction (as determined by airway resistance measures). While much of the dose increase was attributable to the airway narrowing in these individuals, some of the increase (about 50% on average) was due to their increased resting minute ventilations compared to healthy individuals. Furthermore, patients characterized as more chronic bronchitic, rather than emphysematous, had the greatest increase in total deposition. The enlargement of peripheral airspaces associated with emphysema tended to decrease total depositon efficiency.

Regional deposition of particles in the lung may also vary with particle size, breathing pattern, and airway geometry. Sites of deposition shift to more proximal airways as particle size increases from 0.5 to 10 um (7,8) and recent studies (data presented by Kim et al at the colloquium (8)) suggest that a similar shift towards proximal airways occurs as particle size decreases in the ultrafine range (0.1 to 0.04 um). As a result of this shift in deposition site, particles will be concentrated over a much smaller airway surface area (8,9), enhancing local tissue doses in the lung several fold. Enhanced flow rates, such as occurs during exercise, shifts fine and coarse particle deposition towards more proximal airway surfaces (10, 11). Again, this may be especially relevant for comparing doses between children and adults, the former spending more time at exercising ventilation rates. As a result, the local airway tissue doses of inhaled particles may be several fold greater in children compared to adults. Finally, the regional deposition patterns in COPD patients are very nonuniform in the lung, i.e. "hotspots" associated with airway deposition (e.g. data by Brown et al presented at the colloquium (12, 13). It's likely that the increased total deposition of fine particles seen in these patients (6) is associated with enhanced bronchial airway deposition, again greatly enhancing dose per surface area on these airway surfaces.

Once deposited on an airway surface a number of factors affect its clearance from the lung, including site of deposition, particle solubility, and epithelial integrity. The latter may in turn be affected by inflammation associated with airway disease and/or co-pollutant exposures. Insoluble particles will tend to clear more rapidly by mucociliary clearance if they deposit more proximally (i.e. closer to the mouth) in the bronchial tree. Because larger particles tend to deposit more proximally, they would be expected to clear the lung more rapidly (7). There is limited data however on the kinetics of ultrafine particle clearance from human airways.

A number of investigations have shown that insoluble particles clear much more slowly from the lungs of COPD patients than from healthy lungs (14), at least 1/2 the rate of normal clearance on average. This occurs despite the fact that, due to their obstructive lung disease, particles tend to deposit in more proximal airways in these patients. The slowed clearance in COPD further enhances particle dose in these patients compared to healthy subjects. While smokers also show a slowed clearance of insoluble particles (15), they also exhibit a speeding of clearance for soluble particles (16. This is likely due to a disruption of epithelial integrity which, on the one hand, retards mucociliary clearance, but also allows a more rapid movement of soluble constituents across the epithelial surface into the interstitium and blood stream. Co-pollutants such as ozone also enhance movement of soluble particles across the epithelium into the bloodstream (17). Rapid movement of toxic particle constituents into the bloodstream may

translate into extrapulmonary effects, i.e. such as cardiac effects suggested from epidemiological and animal studies.
Clearance rates of insoluble or soluble particles have been little studied as a function of age, especially in children. Exercise has been shown to enhance both mucociliary clearance rates (18) as well as transepithelial transport rates of soluble particles (19). While the former acts to reduce dose to airway tissue, the latter effect is to enhance transport into the blood stream. Once again, these effects may apply more to children who spend more of their daily routine exercising.

Based on the available information summarized above, it appears that altered dosimetry in susceptible individuals likely plays a role in the observed mortality/morbidity associated with PM10. The enhanced total deposition, the shifting of particle deposition towards the larger airways, and the slower mucociliary clearance rates in COPD results in a many fold (10-100 times) increase in airway tissue dose compared to normal. The role of exercise 1) to shift particle loads to bronchial airways with smaller surface area and 2) to induce more rapid movement of soluble components into the bloodstream may be more pronounced in children who spend more time exercising than adults. Certainly biological factors, e.g. pre-inflammed airways in COPD or asthma, also may contribute to effects in the susceptible populations , i.e. a different dose response curve than healthy adults, but dosimetry factors may also act to place these susceptible populations at a higher dose on their respective dose-response curve.

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Session 5: Who is Susceptible to Particulate Matter and Why?

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Session Summary: Who Is Susceptible To Particulate Matter And Why?

It is clear that individuals in the population respond in different ways and to different degrees. The number of epidemiologic and toxicologic studies focusing on "susceptibility" to particulate matter has escalated over the past few years. The National Research Council Report ("Research Priorities for Airborne Particulate Matter", 1998) identified "Susceptible Subpopulations" as one of 10 research priorities. The report emphasized that individual levels of susceptibility are "influenced by individual variations in physiology, behavior, exposure, biological mechanisms, host factors, exposures to co-pollutants, and the biologically effective dose". Genetic factors will undoubtedly be shown to substantially determine susceptibility. Toxicological, epidemiological, and clinical data indicate that asthmatics, children, elderly, and individuals with pre-existing cardiac and respiratory diseases are especially susceptible to particulate matter. The "susceptibility" session of the Third Colloquium on Particulate Matter and Human Health provided an excellent opportunity to review, discuss, debate and evaluate the recent thinking and research on this critical topic.

OBSERVATIONS ON SUSCEPTIBILITY

With regard to the issue of individual susceptibility to particulate matter, two points are obvious: 1) human variability and diversity dictate that responses to toxic exposures will vary among individuals; and 2) frail health status likely confers increased susceptibility to an environmental insult. Human beneficence, and The U.S. Clean Air Act, mandate that air pollution standards be established to protect susceptible populations. However, the issue of susceptibility to particle exposure presents particular difficulties in fulfilling this mandate: mortality apparently occurs in response to particle exposure at very low mass concentrations, and the nature of the toxin(s), and the mechanisms of injury involved, are largely unknown.

Helpful perspectives on the key issues were provided by Drs. Arden Pope and Dan Costa. They set the stage for this session with examples of the usefulness and limitations of epidemiological and animal exposure studies, respectively. A total of 31 posters were then presented dealing with almost the entire spectrum of susceptibility issues, including age, gender, smoking, allergy,

asthma, COPD, infection, co-pollutant exposure, airway inflammation, cardiac disease, hypertension, and genetics. The panel discussion following poster viewing raised a number of important issues, and served to remind us of some lessons already learned.

First, susceptibility for a given health effect may not confer susceptibility to a different health effect. Perhaps the most striking example is ozone: individuals who experience the greatest reductions in lung function with exposure are not necessarily more likely to experience airway inflammatory effects. With regard to particle exposure, there is likely to be more than one important health effect, and more than one reason for susceptibility. The mechanisms contributing to respiratory mortality may differ from those responsible for excess cardiovascular mortality.

We tend to talk about susceptibility as if it were a single entity; if it were, all we would need to do is find out who and how. In reality, there are likely to be a myriad of health effects of particle exposure (i.e., symptoms, lung function decrements, airway inflammation, infection, cardiac effects, etc.), with a number of susceptible populations for which mechanisms and susceptibility factors differ. Our work is ahead of us.

IS IT ALL DOSIMETRY?

One way in which diverse effects may be linked or related is by considering the critical aspects of dose: effect depends upon dose to the critical organ, tissue, or cell.

Issues of dosimetry, when taken broadly in this way, are complex, and include the following:

Intake
Deposition in the respiratory tract
Airways distribution ("Hot Spots")
Airway Clearance
Airway Permeability
Systemic distribution
Critical organ/tissue/cell

The concept of dose may also be considered at the sub-cellular or molecular level. In other words, the critical factor may be the degree to which particle-cell interaction leads to signal transduction and gene expression, which will in turn depend upon bioavailability of particle constituents (i.e., metals), particle-receptor interactions, etc. Although considering dosimetry in this way may provide conceptual benefits, the complexities remain. What individual characteristics determine dose at the cellular and sub-cellular level?

Is It All Gene Polymorphisms?

The degree to which genetic susceptibility determines responses to environmental pollutants remains an issue of debate and investigation. Identifying genes, loci, linkages, and polymorphisms that confer susceptibility to particle effects may provide tools both for identifying and modifying susceptibility. This approach may also provide clues to heretofore unknown mechanisms or diseases that confer susceptibility. However, the complexity and variability of the human genome, and the likelihood that many health effects involve changes in the expression of multiple genes, make the task daunting.

AN EXAMPLE OF THE PROBLEM

Several of the posters, and much of the discussion during this session, dealt with the apparent cardiovascular effects of particle exposure which have been suggested by epidemiological studies. It became clear during this session that it is difficult to think about who is susceptible when we don't know what is happening. From a clinical perspective, there are at least four possibilities or questions that have been considered in the literature and at this meeting:

1. Is there a direct cardiac effect of particle exposure? Penetration of very small particles or their reaction products into the systemic circulation could induce inflammatory cytokine expression in the myocardium, resulting in a myocarditis or epicarditis, or progression of coronary artery disease. These changes could cause the observed increases in heart rate, changes in heart rate variability, and contribute to congestive heart failure and arrhythmias.

2. Are observed cardiac effects caused by pulmonary consequences of particle exposure? The heart and lungs are intimately linked; chronic obstructive pulmonary disease may be accompanied by pulmonary hypertension and right heart failure (cor pulmonale). Exacerbation of airway obstruction or reduction in oxygen transport would be expected to worsen the right heart failure.

3. Are cardiac effects secondary to systemic effects of particle exposure? Airway inflammation may be accompanied by an acute phase response, with increases in blood viscosity and coagulability that may persist for days. Such changes could precipitate coronary events in individuals with coronary artery disease.

4. Do cardiac effects occur only in individuals with severe underlying heart disease, such as coronary artery disease, congestive heart failure, myocardial infarction? If so, is the particle-induced event precipitated by a respiratory insult (hypoxia, increased pulmonary artery pressure), a systemic insult (increased blood viscosity), or a direct cardiac effect?

We need to keep in mind that not all measurable effects of particle exposure represent adverse health effects. For example, it is unknown whether a small increase in heart rate observed in association with an increase in PM_{10} is a marker for adverse cardiovascular events.

Where Do We Go From Here?

The nature of the questions being asked are forcing investigators to broaden their horizons, and to become multidisciplinary. Suddenly pulmonary toxicologists and epidemiologists are scrambling to understand cardiac epidemiology, heart rate variability, and cardiorespiratory reflexes. Cardiologists are being asked to help design studies to answer these questions. Human clinical and field studies are beginning to focus on potentially susceptible populations.

As we work to answer the important questions, the following caveats and suggestions emerged from this session.

1. Animal Models: Compromised animals used in research are indeed "animal models", and are not models of human disease. They are most useful in dissecting mechanisms of injury which may be applicable to human disease and particle health effects. It is important to "know your model"; in other words, know the physiological and pathological manifestations of the animal disease, in order to better understand particle effects.

2. Human Studies: Just as the animal toxicologist must know his model, so the clinical investigator must know his subjects. Both healthy and compromised subjects must be carefully selected and characterized, and care must be given to appropriate definitions of diseases and classification of disease severity.

3. Epidemiological Studies: We need to understand the potential relationships between "markers" of effect, such as heart rate, heart rate variability, airway inflammation, blood fibrinogen, viscosity, etc., and adverse outcomes. This will likely involve more collaboration and interaction between epidemiologists, toxicologists, and clinicians.

Some Summary Comments on the Third Colloquium

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After revisiting the proceedings of the first two colloquia, it seems clear that progress has been made on some issues while others have been largely neglected. Lessons learned and acted upon, together with the corollary gaps, include:

1. Even if one's primary interests center on particulate matter (PM), in epidemiology it is necessary to also consider a full suite of co-pollutants. As Doug Dockery so aptly put it during his summary, "It's not just $PM_{2.5}$" and "not all particles are alike." Given these realizations, problems that remain include:

1.1 Because regression results tend to become unstable when multiple pollutants are included simultaneously, all 2- or 3-pollutant combinations must be investigated.

1.2 The relative measurement errors and their distributions affect how PM components and co-pollutants interact. Collinearity among actual exposures is generally unknown.

1.3 There are several conflicting ways to depict the regression results for a given interacting pollutant as "strongest."

1.4 Complementary components of PM such as (fine, coarse), (carbon, non-carbon), or (SO_4^{2-}, non-SO_4^{2-}) have rarely been studied in joint regressions. Overlapping measures such as PM_{10} or $PM_{2.5}$ are more difficult to interpret in terms of control strategies.

1.5 Personal exposure studies have tended to focus on PM rather than on confounders.

1.6 Mechanistic studies have not tried to focus on mixtures.

2. Exposure and mechanistic studies are essential for causality; many more such studies have begun since the 2nd Colloquium. However, the two disciplines are largely unconnected:

2.1 A substantial portion of the mechanistic studies is focused on potential causal agents for which no exposure data are available and for which substantive exposures to the most susceptible individuals are unlikely. These include residual oil fly ash (ROFA) and acid aerosols; personal exposures to ultrafine particles have not been studied.

2.2 Exposure studies have identified sulfate (as opposed to H^+) as an agent that may represent outdoor fine particles, but no mechanistic scenarios include sulfate per se.

2.3 The regulatory focus is on exposures to particles of "outdoor origin," but this distinction cannot be made for gaseous co-pollutants. Further, until specific types of harmful PM have been identified, there can be no assurance that harmful particles are not emitted or re-suspended indoors. Thus, total combined exposures remain unknown.

3. Differences in PM dosimetry according to health status have long been well known, yet they have not been applied to epidemiology. For example, Bill Bennett pointed out that substantially more PM deposits (locally) in the lungs of COPD patients; could this factor alone be responsible for the higher observed dose-response functions for COPD deaths? Is this also true for gases?

4. Measurement error was identified as a critical factor for epidemiology in the 2nd Colloquium; this lesson is beginning to take hold, and some data are beginning to appear. However, no comprehensive protocol has been developed to allow corrections to be made to the extant epidemiology, and sensitivities of dose-response functions to measurement error have rarely been explored empirically. Further, the effects of measurement error on the implied shapes of dose-response functions have not been taken seriously, especially with regard to setting ambient standards. The apparent absence of thresholds may thus be an artifact.

The overarching scene at this juncture is thus one of complexity. No single pollutant or PM component can be blamed for all of the observed health responses and few (if any) may be exonerated. PM research has succeeded in getting the attention of the environmental community; it is now important to follow through with objective and coordinated research.

IV. EXPOSURE/CHARACTERIZATION-RELATED PAPERS (SESSION 1)

Fraction of $PM_{2.5}$ Personal Exposure Attributable to Urban Traffic: A Modeling Approach

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ABSTRACT

Personal exposure to fine particles ($PM_{2.5}$) in a non-smoking adult population has been characterized in Grenoble, France, in the framework of the European EXPOLIS study. The objective of this paper is to assess the fraction of the $PM_{2.5}$ personal exposure attributable to urban traffic emissions. Volunteers (n=40) carried a personal exposure monitoring case and filled in questionnaires on their outdoor and indoor environments, as well as time-activity diaries (15 min. resolution), during 48 hours (working days). Workplaces and places of residence were classified in 2 categories using a Geographic Information System (GIS) : the atmospheric environment of some volunteers is best represented by PM ambient air monitors located in urban background sites ; others by monitors situated close to high traffic density sites (proximity sites). A partial least squares regression model estimated the $PM_{2.5}$ personal exposure (average=36.6 $\mu g/m^3$; standard deviation=23.4 $\mu g/m^3$) as a function of time spent in proximity (at work, home or commuting), PM_{10} ambient air levels during the same days, and several confounders (passive smoking and indoor sources of particles). Six scenarios of "proximity" and "background" environments were accommodated, according to traffic intensity and road distance, in a sensitivity analysis ; the best fitted model had a R^2=0.7. Personal $PM_{2.5}$ exposures predicted by this model for different segments of the study population were compared to the background personal exposure, thus providing an estimate of the additional contribution of time spent near traffic sources. On average (% time spent in proximity=16.3 ; proximity scenario defined as the area located less than 50 m from a street with a traffic intensity greater than 20,000 veh/d), the $PM_{2.5}$ personal exposure attributable to traffic equals 30%. For the lower tercile of the population, this contribution is 26% ; for the upper tercile, it is 45%. A very influential parameter of this modeling estimation is the proportion of background ambient air particulate concentrations associated with traffic emissions. Based on local night-time / day-time concentration ratios, a 20% proportion has been derived and used for these results. In the literature, this parameter ranges from 10% to 60%, yielding a proportion of personal exposure attributable to traffic proximity between 20% and 60%, and high exposure situations reaching 60 to 75%. While these estimates are based only on winter data, they are in agreement with other results published in the literature. This modeling approach might be applied to other metropolitan situations, insofar as local data are used to assess the influence of traffic emissions on background ambient air PM_{10} concentrations.

INTRODUCTION

Studies of personal exposure to air pollutants are numerous (Janssen et al., 1998 ; Jantunen et al., 1998 ; Monn et al., 1997 ; Wallace, 1996 ; National Human Exposure Assessment Survey, 1995). To date, most epidemiological studies on air pollution and health are based on indirect exposure characterization using air quality monitoring network levels (Katsouyanni et al., 1997 ; Quénel et al., 1995).

Recently, fine particles ($PM_{2.5}$: less than 2.5 μm in diameter) have drawn great attention in air pollution personal exposure studies. The health impact of $PM_{2.5}$ has been shown to be significant in epidemiological studies ; this is a different health impact from PM_{10} (diameter less than 10 μm) (Peters et al., 1997 ; Wilson et al., 1997 ; Lipfert et al., 1997 ; Schwartz et al., 1996).

Moreover, sources of pollutants, including particles, have evolved during the last decades. Industrial emissions have decreased because of regulatory constraints while mobile sources of pollutants have increased, particularly in urban areas. As a result, urban traffic may constitute a major part of urban populations' exposure to several air pollutants (Airborne particles expert group, 1999 ; Comité de la prévention et de la précaution, 1997). Fine particles are mainly anthropogenic, resulting from combustion processes such as traffic exhausts which generate soot, or urban heating in winter. Atmospheric photochemistry may also be an important source of fine or ultra-fine particulates in summer, natural sources are a smaller contributor of fine particles by comparison with their coarse fraction (Quality of Urban Air Review Group, 1996).

In this context, the objective of this paper is to assess the fraction of $PM_{2.5}$ personal exposure which is attributable to urban traffic emissions. To do so, $PM_{2.5}$ exposure of an adult urban population was characterized with personal monitors and related to indoor sources of particles, time-activity patterns of the study participants and ambient air surveillance data, using statistical modeling.

MATERIALS AND METHODS

Materials

The study took place in Grenoble, capital of the French Alps, from 1996 to 1999. It was carried out in the framework of the European study EXPOLIS (Exposure distribution of adult urban populations). Forty volunteers were selected in summer 1996, 40 in winter 1997 and 20 in summer 1998. They were 20-60 years old, non smokers, living and working in Metropolitan Grenoble, and commuting with different means of transport. This paper focuses on the winter phase data for reasons that are developed in the discussion.

Each volunteer filled in questionnaires on his (her) life environments (at home, at work and commuting) as well as a detailed (15 minute resolution) time-activity diary. A number of variables were collected : heating system at home and at work, number of persons living/working with the volunteer, passive smoking, cooking exposure etc. The EXPOLIS study protocol has been described elsewhere (Jantunen et al., 1998).

Volunteers carried a personal monitoring case (PM-case) during 48 h. (working days). When they stayed without moving in an indoor environment for a long period (office, home etc.), volunteers were instructed to lay the monitoring case on a chair / table close to them. The PM-case included a portable pump (Buck Inc., flow of 4 l/min.) and a cyclone (Gussman Kenny, cut off point : 2.5 µm) ; particles were collected on Teflon filters (2 µm porosity) which were deionised (Multistat EI-RN) and weighed on a micro-balance (Mettler MT5).

Ambient air PM_{10} levels (TEOM technology) are monitored continuously by the Grenoble Air Quality Network (ASCOPARG). Most European towns do not monitor $PM_{2.5}$ as EU legislation only requires PM_{10} to be characterized. A Geographic Information System was used to classify the volunteers' places of residence and of work into 2 categories : the atmospheric environment of some volunteers can be best represented by PM ambient air monitors located in urban background sites ; others by monitors situated close to high traffic density sites (proximity sites). Each volunteer was characterized by a percent of time (including time at home, at work and commuting) spent near traffic. Definition of traffic proximity depends on the distance (D) from the place of residence to the nearest street and on traffic

density of the specific street (T). Several definitions of "proximity" were accommodated (D being 50, 100, or 200 m. ; T being 10,000 or 20,000 veh/d), in order to perform a sensitivity analysis, with the fraction of time spent in proximity depending on each of the 6 scenarios. While commuting, a subject was classified as being in a "proximity situation".

Model construction

Hypothesis 1 : the PLS model

A partial least squares (PLS) regression model estimated the $PM_{2.5}$ personal exposure (dependent variable, $[PM_{2.5}]$) as a function of time spent at a proximity location (tprox), PM_{10} ambient air levels during the same days at the background and the proximity sites (respectively PM_{10back} and PM_{10prox}), and several confounders, chosen after review of the literature on personal exposure to particles :

$$[PM_{2.5}] = a.\ [PM_{10prox}\ .\ tprox] + b.\ [PM_{10back}.\ (1\text{-}tprox)] + \Sigma c_i\ confounder_i + constant \qquad (1)$$

Equation 1 can also be written as following :

$$[PM_{2.5}] = [a.\ PM_{10prox} - b.\ PM_{10back}].\ tprox + (b.\ PM_{10back} + \Sigma c_i\ confounder_i + constant) \qquad (2)$$

Consider a hypothetical population with no indoor exposure (confounders set to 0). Equation 2 simplifies to :

$$[PM_{2.5}]' = (a.\ PM_{10prox} - b\ PM_{10back}).\ tprox + (b.\ PM_{10back} + constant) \qquad (3)$$

or : $[PM_{2.5}]' = A.\ tprox + B$

where A is the increase in personal exposure associated with a unit increase of life time close to traffic (in $\mu g/m^3$) ; B is the background exposure level (in $\mu g/m^3$).

For any time tprox, the relative crude contribution of traffic exposure is :

$$F = A.\ tprox\ /\ (A.\ tprox + B) \qquad (4)$$

Hypothesis 2 : Influence of the traffic-related PM_{10} at the background site and corrected attributable personal exposure

If one assumes that the background level B, considered as homogeneous across Metropolitan Grenoble, is independent from traffic sources, then F (as written in equation 4), is the correct value for the contribution of traffic to personal exposure. That is probably not the case and a

corrected fraction F' was developed, according to the following hypotheses : (1) at the traffic proximity site, what is measured by fixed monitors is the sum of the true background level ($PM_{10realback}$) and of traffic-related pollution ($PM_{10traffic}$) ; (2) at the background site it is the true background pollution ($PM_{10realback}$) plus a fraction directly attributable to traffic ($k.PM_{10traffic}$) due to dispersion of fine particles. These hypotheses are translated into equation 5 :

$$[PM_{2.5}]' = tprox.\ (PM_{10traffic} + PM_{10realback}) + (1-tprox).\ (PM_{10realback} + k.PM_{10traffic}) \quad (5)$$

which is also written :

$$[PM_{2.5}]' = [(1-k).\ PM_{10traffic}].\ tprox + [PM_{10realback} + k.\ PM_{10traffic}] \quad (6)$$

$$\text{or } [PM_{2.5}]' = [(1-k).tprox + k].\ PM_{10traffic} + PM_{10realback}$$

where $[(1-k).tprox + k].\ PM_{10traffic}$ is the PM_{10} traffic-related exposure and ($PM_{10realback} + k.PM_{10traffic}$) is the new B value.

The relative weight of traffic-related PM_{10} at the Grenoble background site was determined comparing the day (7 am - 10 pm) and night (11 pm - 6 am) PM_{10} ambient air concentrations at the same place during one month and a half in summer (1/6 - 11/7/96) and two months in winter (10/1 - 9/3/97).

From equations 3 and 6, it can be written that $PM_{10traffic} = A / (1-k)$. As a result, F', the « true » fraction of $PM_{2.5}$ personal exposure attributable to traffic is :

$$F' = F + [(A.k / (1-k)) / (A.tprox + B)] \quad (7)$$

RESULTS

Descriptive results

The $PM_{2.5}$ personal exposure in winter (N subjects = 34) was on average 36.6 $\mu g/m^3$ (standard deviation=23.4 $\mu g/m^3$). The PM_{10} ambient air levels, during the same days at the urban background site, was 36.7 $\mu g/m^3$ on average (s.d.=15.4 $\mu g/m^3$). Figure 1 displays the correlation between the 2 variables (R = 0.46, p = 0.006). The corresponding urban proximity site mean PM_{10} concentration was 43.4 $\mu g/m^3$ (s.d.=19.8 $\mu g/m^3$), with similar correlation (R=0.44, p=0.009).

The main characteristics of the volunteers for the first summer phase have been described elsewhere (Boudet et al., 1998). Winter volunteers had very similar social-demographic characteristics : more than half of the people have participated in both phases. Descriptive statistics for the percent of time spent in proximity are displayed in Table 1, given the six scenarios of proximity (based on the criteria of distance D and of traffic density T). Averages of time spent in proximity for the whole study population range from 16.3% (s.d.=26.8%) to 49.1% (36.1%) according to these scenarios. The percent of time spent in proximity increases with the distance between the place of location and the street, which is expected.

Local data analysis at the background urban site showed that the PM_{10} levels during the day was 20% greater than those during the night. This result was identical in summer and in winter. Thus, the proportion of traffic-related particles at the ambient site was set to 20% for the Grenoble situation.

Model variables selection

Predictive variables included in the model were : (1) PM_{10} background site ambient air level (PM_{10back}), (2) PM_{10} proximity site ambient air level (PM_{10prox}), (3) time spent in proximity, (4) passive smoking (smoke), (5) gas heater (gas) and (6) chimney. Among the 34 studied volunteers, 18 had a gas heater at home and 4 had a chimney. The average duration of passive smoking during the 2 days of personal monitoring was 95.7 minutes (s.d. = 241.0 min). Sixteen acknowledged exposure to environmental tobacco smoke at home or at work. The correlation matrix between these explanatory variables is displayed in Table 2.
Equation 1 is expanded below for the following proximity scenario : D < 50 m and T > 20 000 veh/d ; the corresponding model R^2 is 0.7.

$$[PM_{2.5}] = 1.01\ ([PM_{10prox}].[tprox4]) + 0.61\ ([PM_{10back}].(1-[tprox4]) + 0.04\ [smoke] + 10.97\ [gas] + 18.94\ [chimney] - 1.78 \quad (8)$$

Equation 3 determines the $PM_{2.5}$ ambient personal exposure as a function of time spent in proximity. Figure 2 suggests that the study population might be composed of 2 subgroups, but the number of individuals in each group is too small to make a conclusion. As an illustrative example, Figure 3 describes in detail the determination of F (equation 4) for one

individual (spending 44% of time in proximity) from the EXPOLIS population. F' (equation 7), the "true" fraction of personal $PM_{2.5}$ exposure attributable to traffic for this individual (relative weight of traffic-related PM_{10} at background site = 20%, based on the Grenoble day/night ratio at this site) is 46.2% for this volunteer.

Table 3 shows the average crude and "true" fractions (based on the entire sample) of personal $PM_{2.5}$ exposure attributable to traffic for the set of 6 proximity scenarios (all run with the relative weight of traffic-related PM_{10} on the background site=20%), with the corresponding model R^2: the best fitted model is for a proximity scenario defined by D < 50 m and T > 20,000 veh/d (R^2=0.7). The effect of varying the relative weight of traffic-related PM_{10} at the background site (with a range between 10 and 60%, based on the literature data) was also assessed. The fractions of personal exposure attributable to traffic proximity are provided on average for the entire study sample, and summarized in Table 4.

Figure 4 displays the results of a sensitivity analysis according to the relative weight of traffic-related PM_{10} at the background site ; the definition of the proximity is set to the best fitted scenario (D<50m ; I>20,000). In this figure, the attributable fraction of personal exposure is calculated for the whole study population along with two subgroups : the 1st and 3rd terciles of the distribution, based on the fraction of time spent in proximity. When this parameter varies between 10 and 60%, the average attributable fraction of personal exposure ranges between 20 and 60%. In the Grenoble situation, where this weight was found rather low, equal to 20%, the corresponding average fraction is 30%, with an interval defined by the 1st and the 3rd population terciles ranging between 26 and 45%.

DISCUSSION

The main results of this study are the following : (1) In the Grenoble study population, the average fraction of the $PM_{2.5}$ personal exposure attributable to traffic proximity is 30 %, with an interval comprised between 26 and 45% (1st and 3rd terciles of the space-time activity distribution of the study population). (2) A sensitivity analysis shows great variations of this estimation, with the average fraction of personal exposure varying between 20 and 60%, when the relative weight of traffic-related PM_{10} at the background site ranges between 10 and 60% ; this is the most sensitive parameter in the model. (3) There are great disparities of this

attributable personal exposure fraction according to the time-space activity profiles of the population, with tercile extremes between 20 to 75%.

$PM_{2.5}$ continuous ambient air measurements are scarce, to date, in European countries, the air quality standards relative to particles deal with PM_{10} or black smoke. As a result, the only data which could be compared with the $PM_{2.5}$ personal exposure results in Grenoble are PM_{10} ambient air levels during the same days of personal measurements. This is a weakness of our modeling approach, although the correlations between the winter phase $PM_{2.5}$ personal exposures and the corresponding PM_{10} ambient air levels at the urban background (R=0.46) or the traffic proximity sites (R=0.44) were substantial. When direct $PM_{2.5}$ ambient air surveillance values will be available routinely, this approach may be used with less uncertainty. Ambient air $PM_{2.5}$ concentrations are more evenly distributed across metropolitan areas than PM_{10} (Boudet et al., 1999 ; Wilson et al., 1997 ; Burton et al., 1996). A local study showed that, in winter and at the urban background site, the proportion of PM_{10} represented by $PM_{2.5}$ was about 33% (s.d. 12%) ; for the proximity site it was 42% (s.d. 12%).

This modeling was only accommodated for the winter period because, in summer, no correlation was found between the $PM_{2.5}$ personal exposures and the PM_{10} urban levels ($p>0.15$), due to the great homogeneity of personal $PM_{2.5}$ and ambient air PM_{10} values. More data are needed to assess this effect of season. Given the variable correlation between PM_{10} and $PM_{2.5}$ concentrations across and within cities, our results cannot be extended to summer situations without verification.

PLS (Partial Least Squares) regression was used in our model rather than regular linear regression because it tolerates some residual correlation between the model variables, and thus is more robust (Tenenhaus, 1998 ; Hoskuldsson, 1988). It is also more convenient for the case of a high number of variables and a small number of individuals. Adjustment variables included in the model were chosen upon the literature data (Monn et al., 1997 ; Wallace et al., 1996). Major indoor $PM_{2.5}$ sources are environmental tobacco smoke and gas heater or cooker, which were included in our model. Once the model is built with these indoor sources variables, the traffic apportionment estimation can be undertaken setting the specific indoor sources to 0 (i.e. assuming no passive smoking nor gas appliance or chimney at home / work). The $PM_{2.5}$ penetration rate from outdoor sources to indoor environments has been shown close to 1 (Wallace, 1996). Hence, although most of the time is spent indoors (around 90% of the time, in winter, for the EXPOLIS sample), the exposure contribution of $PM_{2.5}$ coming from

outdoors is important when studying a non smoking population. Now, the relative weight of traffic on this virtual population with no indoor source exposure is clearly an overestimation for the true general population.

One possible confounder in our modeling approach that was not considered, due to lack of data, is the impact of urban heating in the winter : it is related to population density, which is greater, in Grenoble, in the proximity area than about the background area. Further, our modeling approach assumes linearity of the percent time at proximity - fraction of personal exposure relationship, a feature which needs to be verified for extreme ranges of the distribution.

How the proximity is defined is not very influential on the average fraction of $PM_{2.5}$ personal exposure attributable to traffic (maximum : 10% variation between the proximity scenarios). On the other hand, this fraction ranges from 20 to 60% when the relative weight of traffic-related PM_{10} at the background site is set to vary from 10 to 60%. This is a crucial parameter which depends heavily on the background monitor site characteristics. The literature data on this matter are scarce. A recent report (Airborne particles expert group, 1999) estimated this relative weight for 17 British urban background sites, both during winter and summer periods, using the high correlation between PM_{10} and CO (which is a good traffic emissions tracer). In winter, it ranged between 15 and 68% ; in summer, between 8 and 52 %, with great day-to-day variability. When the modeling selected days with the highest PM_{10} / CO daily correlations, this fraction was enhanced between 66 to 79%. Our Grenoble data, based on night- to day-time PM_{10} ratio in winter, lay at the lower end of this distribution. Given the high sensitivity of the model results to the relative weight of traffic-related PM_{10} at the background site, local data should be used in order to apply this model to other situations than Grenoble. Several clues to assess this fraction can be used, such as (1) studying the correlation between CO (or NO_x) and particles at the background site, or (2) comparing night and day PM levels. Another important determinant of the attributable fraction of personal exposure is the time-space profile of the population : the difference between the estimated fractions for the first and third terciles of the population distribution relative to time spent in proximity environments lies between 20 and 75%.

An air inventory of the different emission sources of particles estimated the fraction of primary PM_{10} particulates attributable to traffic as about 80%, on average, in London (QUARG, 1996). Tracers of traffic exhausts were also used in the same report to assess the fraction of $PM_{2.5}$ or PM_{10} attributable to traffic exhausts accounting that 98% of CO and 90% of NO_x are attributable to urban traffic in Metropolitan areas. On this basis, the ambient air $PM_{2.5}$ fraction attributable to traffic exhausts amounted to 41% using NO_x as a tracer, while the PM_{10} fraction ranged from 66 to 78% using CO as a tracer. These estimates showed seasonal variability : the PM_{10} fraction attributable to traffic was greater in winter than in summer. The authors explained this seasonnality as the result of the photochemical formation of secondary PM_{10} (ammonium sulfates and nitrates), which occurs mostly in summer. Subjects living around a high density street in the Netherlands have a personal exposure to PM_{10} higher than those living far away (Janssen, 1998). Chen et al. (1998) reached the same conclusion after having studied spatial variations in atmospheric particles in Taipei (Li C.S., 1994).

CONCLUSION

This paper proposes a methodology to assess the fraction of $PM_{2.5}$ personal exposure attributable to traffic exhausts. Applying this approach to literature data, this attributable fraction lies between 20 to 60%, on average, with subgroups of the population incurring attributable personal exposures in the range of 60 to 75%. In Grenoble, where ambient air at background locations is little influenced by traffic, this fraction was estimated about 30% on average (1^{st} and 3^{rd} study population tercile distribution = [26 ; 45%]), in an adult non smoking population, with no specific indoor source of particles. They match the scarce data found in the literature. Extrapolation to other urban situations is possible insofar as the relative weight of traffic-related PM_{10} ambient air concentrations at the background site is determined locally. The model results are very sensitive to this parameter while the definition of proximity of life environments to traffic emissions is less influential.

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Figure 1 : Correlation between $PM_{2.5}$ personal exposures ($\mu g/m^3$) and PM_{10} ambient air levels ($\mu g/m^3$) among the EXPOLIS volunteers (n=34, Grenoble, winter 97).

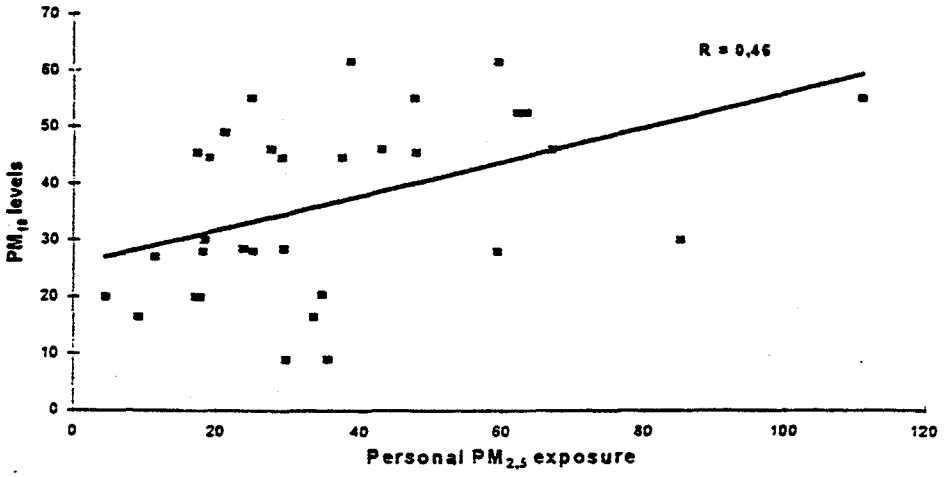
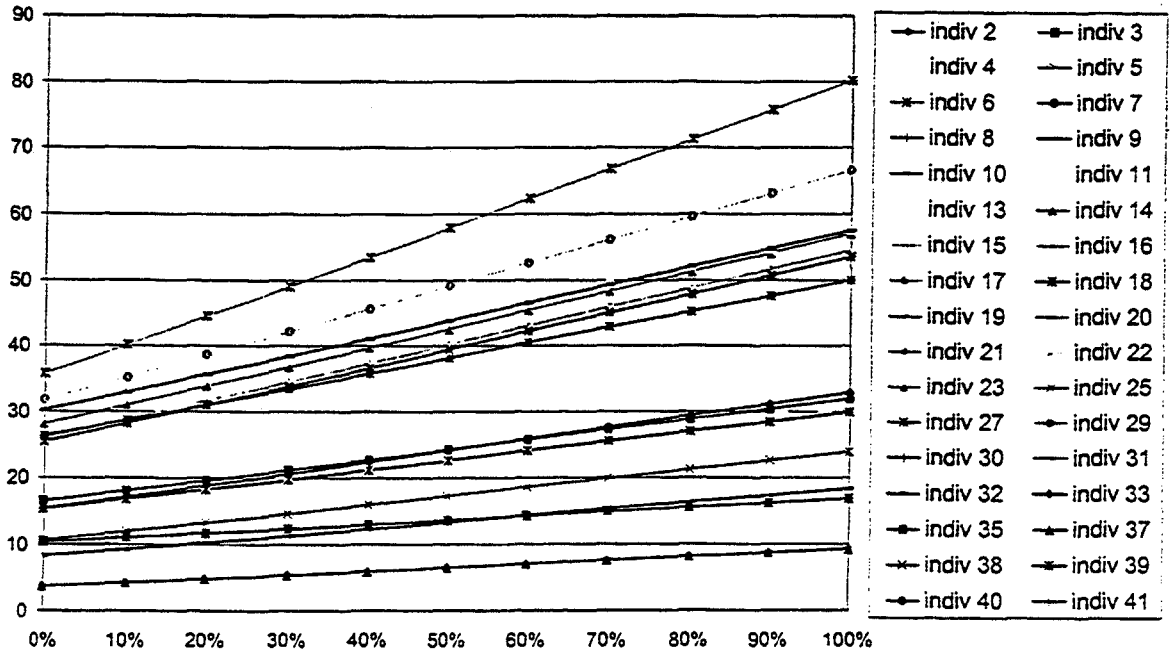


Figure 2 : $PM_{2.5}$ personal exposure (as given in equation 3*, in $\mu g/m^3$) for each individual, depending on the time spent in proximity (tprox4, in %)



* see Materials and Methods

Figure 3 : Graphic determination of the fraction F for one volunteer spending 44% of his time in proximity, using the PLSR model

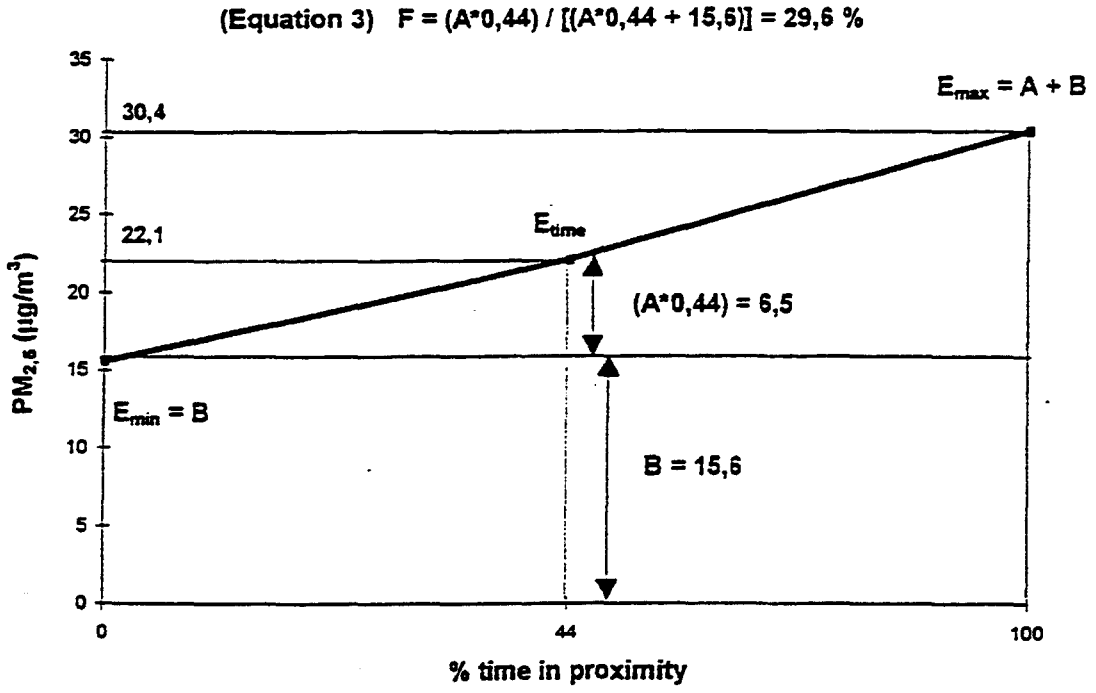
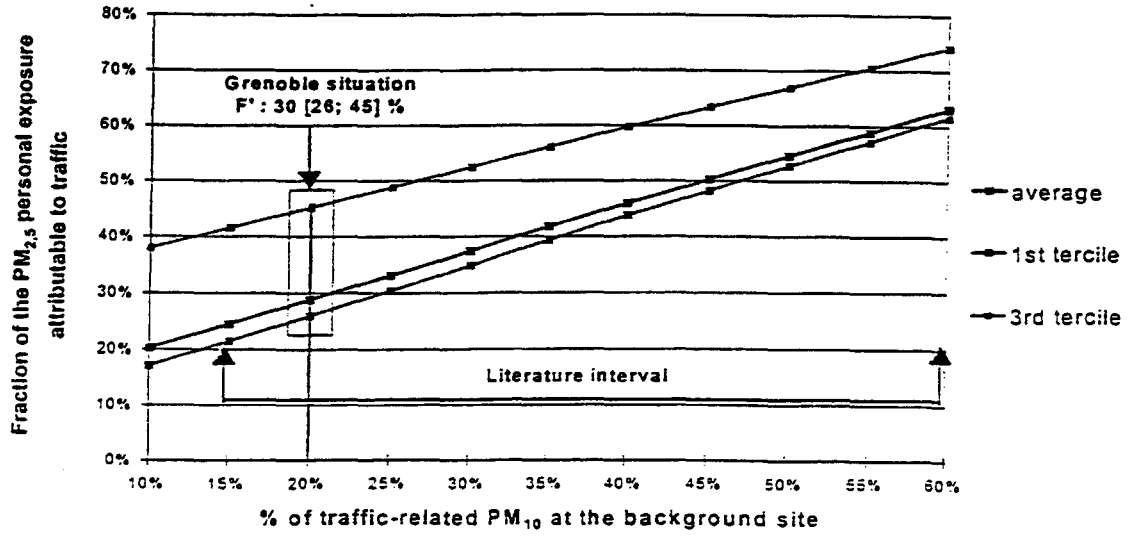


Figure 4 : Sensitivity analysis - $PM_{2.5}$ personal exposure attributable to traffic according to the relative weight of traffic-related PM_{10} at the background site *



* Proximity scenario : D < 50 m ; T > 20,000 veh/d

Table 1 : Descriptive statistics for the fraction of time spent in proximity, and Pearson correlation with personal $PM_{2.5}$ exposure, according to 6 scenarios of proximity

Proximity criteria (tprox)	Average (%)	s.d.	R *
(1) < 50 m ; > 10,000 veh/d	30.6	34.6	0.27[a]
(2) < 100 m ; > 10,000 veh/d	37.4	36.6	0.28[a]
(3) < 200 m ; > 10,000 veh/d	49.1	36.1	0.28[a]
(4) < 50 m ; > 20,000 veh/d	16.3	26.8	0.48[c]
(5) < 100 m ; > 20,000 veh/d	20.2	30.1	0.38[b]
(6) < 200 m ; > 20,000 veh/d	23.7	32.5	0.41[b]

* Pearson correlation coefficient between time spent in proximity and $PM_{2.5}$ personal exposures.

[a] $p < 0.15$

[b] $p < 0.05$

[c] $p < 0.01$

Table 2 : Correlation matrix between the variables included in the model (Equation 1) *

Correlation	(PM_{10prox} × tprox4)	$PM_{10back.}$ × (1-tprox4)	smoke	gas	chimney
PM_{10prox}× tprox4	1	-0.49	0.04	-0.11	0.15
$PM_{10back.}$ × (1-tprox4)	-0.49	1	-0.05	-0.02	-0.24
smoke	0.04	-0.05	1	0.06	-0.13
gas	-0.11	-0.02	0.06	1	-0.02
chimney	0.15	-0.24	-0.13	-0.02	1

* see Materials and Methods

Table 3 : Fraction (F) of personal $PM_{2.5}$ exposure attributable to traffic, according to the proximity definition, and corresponding model R^2 *

Definition of time spent in proximity	R^2 (%)	Average F [a] (%)	Average F' [b] (%)
(1) < 50 m ; > 10,000 veh/d	60.1	14.4	31.7
(2) < 100 m ; > 10,000 veh/d	59.2	15.4	31.9
(3) < 200 m ; > 10,000 veh/d	58.5	19.8	35.7
(4) < 50 m ; > 20,000 veh/d	**65.0**	**11.6**	**28.8**
(5) < 100 m ; > 20,000 veh/d	63.8	13.2	30.1
(6) < 200 m ; > 20,000 veh/d	60.7	11.2	26.7

* based on the % of traffic-related PM_{10} at the background site = 20%

[a] and [b] : crude proportion (F), and corrected proportion F' [see Materials and Methods]

Table 4 : Average fractions of $PM_{2.5}$ personal exposure attributable to traffic exhausts (%), according to definition of proximity and to the relative weight of traffic-related PM_{10} at the background site

weight of traffic-related PM_{10} at background site (%)	T > 10,000 veh/d			T > 20,000 veh/d		
	D<50m	D<100m	D<200m	D<50m	D<100m	D<200m
0	14.4	15.4	19.8	11.6	13.2	11.2
10	23.1	23.7	27.8	20.2	21.6	19.0
20	31.7	31.9	35.7	28.8	30.0	26.7
30	40.4	40.0	43.7	37.4	38.5	34.5
40	49.0	48.3	51.7	45.9	47.0	42.2
50	57.7	56.5	59.7	54.5	55.4	50.0
60	66.4	64.7	67.6	63.1	63.9	57.8

* Model validity limit : weight of traffic-related PM_{10} at background site ≤ 60%

Analysis of Light- and Heavy-Duty Diesel Vehicle Particulate Emissions and Some Implications for Public Health

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Introduction

As the scientific community continues to scrutinize the effects of particulates on public health, the contribution of diesel vehicles to the overall particulate burden is receiving more and more attention. There is increasing evidence that diesel particulate emissions are likely to have an adverse effect on humans, but a direct link to specific diseases or mortality has not yet been established. The potential relationship between diesel particulate matter (PM) and chronic human health disorders has recently been discussed by Bradow (1982), McClellan (1987), Westerholm and Egebäck (1994), Koren (1995), Frew and Salvi (1997), and Carraro et al. (1997), as well as by others. However, there are no reports based on direct laboratory results involving humans, and even epidemiological findings are few in number.

Assuming they could be obtained, direct laboratory results on humans or related epidemiological findings would obviously be extremely beneficial in establishing the specific role that diesel particulate emissions play in the public health arena. However, there would still be unresolved problems as to how diesel vehicles operating in real-world settings actually affect general public health and to what degree. Moreover, it is not clear how such results would be "scaled up" to reflect the presence of hundreds or thousands of diesel vehicles operating in a given community; nor is it clear how such an effect might be isolated from other, potentially confounding, factors such as atmospheric or weather conditions.

There are additional challenging questions to be addressed. To obtain a clear understanding of the public health effect of diesel emissions in the broader particulate debate, it must first be possible to precisely distinguish the contribution of vehicles (the mobile source) from other sources, and then to be able to reliably allocate that contribution to various vehicle types—cars, trucks, buses, etc. Next, it must be possible to differentiate the diesel signature from that of other fuels (principally gasoline). Finally, it is necessary to know the actual (or projected) numbers of vehicles in use in a specific community, and the proportion of those vehicles that operate on diesel, in order for an appropriate upscaling to be undertaken—that is, the vehicle population must be well-known, which, in and of itself, is difficult to achieve.

The ability of the scientific community to determine the public health impact of diesel PM emissions is confounded by conflicting actions being taken in the political arena. On the one hand, the federal government is promoting air quality standards that would presumably mitigate the use of diesel fuel (at least in its current formulation). On the other hand, the use of diesel (presumably clean-burning diesel) as a transportation fuel is being actively promoted as a matter of national energy security

Yet another difficult aspect of the problem has to do with the general pattern of growth in the overall vehicle population, as well as societal changes that affect vehicle usage (service applications, driving patterns, etc.) and vehicle miles traveled (VMT). The size of a static vehicle population is hard enough to determine, much less one that is constantly growing and changing in character. In addition, the fact that there just are not that many diesel sedans currently operating, and that the ones that are in use are relatively old, makes it difficult to project what the diesel particulate contribution might actually be in the near future. Consequently, the present debate is leveled more squarely on heavy-duty vehicles, which are even more difficult to enumerate and the emissions of which are more costly (and more involved) to assess. All other things being equal, heavy-duty diesel vehicles emit proportionately more particulates than light-duty vehicles, but the vehicle population mix ten, twenty, or even fifty years from now might be entirely different from what it is today. Sustained growth in the number of light-duty diesel vehicles could

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substantially alter the mobile source particulate burden simply because there would be considerably more light-duty than heavy-duty vehicles on the road.

The Problem of Variability in Particulate Emissions

Many factors affect the reliability of urban air quality assessments—and hence projections of public health risk—and the situation is further compounded by data limitations. High-quality, real-world data on diesel PM emissions from vehicles in actual use, for example, is especially difficult to obtain in the amounts necessary to make truly informed decisions. Nonetheless, estimates of the particulate burden attributable to diesel vehicles are being more routinely promulgated, largely in response to the tightening federal air quality standards.

Many of the estimates are based on results obtained from relatively small numbers of vehicles; and the estimates themselves are frequently presented in terms of simple averages without regard to the associated variability. Estimates of all types of emissions obtained from vehicle testing studies are known to be imprecise; yet this imprecision is sometimes ignored or ill-treated. The level of PM emitted from vehicles in everyday use is undoubtedly more variable than commonly acknowledged by those responsible for collecting the data, and this lack of precision may go unrecognized by policy makers, the public, and health professionals alike.

Claims about the impact of vehicular PM emissions can be easily distorted (either pro or con) when simple averages (representing small numbers of vehicles) are reported, and when appropriate consideration is not given to sampling, experimental, and/or naturally-occurring variability. The lack of precision can lead to overstatement or understatement of the contamination levels, which when incorporated into urban air quality assessments, eventually plays out in projections of public health risk that may be incorrect. Ultimately, the consequences can be serious. If there is an overstatement of the public health risk, there will be an adverse economic impact attributable to the unnecessary costs of prevention and corrective action. If there is an understatement of the public health risk, the result may be higher-than-expected levels of chronic disease and mortality, not to mention the associated costs of health care.

Methodology

Achieving more reliable estimates of particulate emissions—and by extension, more realistic assessments of environmental and public health risk—is a fairly straightforward proposition. However, it does require testing of substantially more vehicles and/or the application of more sophisticated methods. An especially useful statistical method is the procedure known as analysis of variance (see, for example, Daniel, 1999), which facilitates a full accounting and partitioning of the total variability in a data set. In the statistical literature, the concepts of analysis of variance are mature and well known; but the methodology is not prominently employed by emissions and air quality professionals.

There are several benefits to using the analysis of variance approach. First, it provides for an adjustment in average values to account for small and/or unbalanced numbers of observations, and hence it accommodates a more direct comparison of average values. Second, it allows for discovery and treatment of the effects of all identifiable sources of variation. Finally, it facilitates a more complete assessment of precision through the computation of appropriate standard errors and statistical confidence bounds.

Analysis of variance is rooted in the principles of least squares, and it requires the specification of a linear statistical model that not only stipulates the sources of variation, but also identifies which sources are fixed and random. The technique can be easily coupled with other statistical techniques such as regression analysis to achieve a thorough and rigorous analysis of all available data.

Case Study: Particulate Emissions from Light- and Heavy-Duty Diesel Vehicles in the Denver Metropolitan Area

Analysis of variance was used to study PM data from light- and heavy-duty diesel vehicles randomly selected from those operating in the Denver metropolitan area from mid-1996 to mid-1997. The available PM measurements represent a combination of data from both types of vehicles. All data was collaboratively obtained in conjunction with the recent Northern Front Range Air Quality Study (Norton, et al., 1998). The data set is unique because so little in-use diesel PM emissions information is in existence, and virtually no other such data is available from

vehicles operating at altitude (note, however, that the experimental program was not designed to specifically test the effect of altitude). Vehicle recruitment, data collection, chemical analysis, and related details pertaining to the study are discussed in Cadle, et al. (1998), Coburn (1998), and Yanowitz, et al. (1999).

The data set consists of PM emissions obtained on 22 light-duty vehicles and 21 heavy-duty vehicles. The light-duty vehicles represent a variety of manufacturers, models, and transmission types, with model years ranging from 1979 to 1995. Mileage (actual odometer readings) on the vehicles at the time of emissions testing ranges from slightly less than 18,000 to more than 280,000. The light-duty vehicles in the study fleet are generally representative of the light-duty vehicle population operating in the Denver metropolitan area, although it is clearly difficult to obtain good representation with so few units. In this particular case, the number of light-duty vehicles in the study is primarily limited by access and availability.

Table 1. Number of heavy-duty vehicles and tests, by weight class and model year, on the HDT driving cycle under both hot start and cold start conditions.

Weight Class	Model Year	All Vehicles	All Tests	HDT Driving Cycle Only			
				Hot Start		Cold Start	
				Vehicles	Tests	Vehicles	Tests
Light	1993	1	5	1	2	1	1
	Subtotal	1	5	1	2	1	1
Medium	1987	1	7	1	3	0	0
	1988	1	7	1	3	1	1
	1989	2	17	2	5	1	1
	1991	1	8	1	3	1	1
	1993	2	11	2	5	1	1
	Subtotal	7	50	7	19	4	4
Heavy	1981	1	7	1	2	1	2
	1983	1	10	1	3	0	0
	1984	1	4	0	0	0	0
	1990	2	12	2	3	0	0
	1991	1	5	0	0	0	0
	1993	2	8	1	2	1	1
	1995	1	7	1	3	1	1
	Subtotal	9	53	6	13	3	4
Bus	1981	1	3	0	0	0	0
	1986	1	11	1	3	0	0
	1993	2	13	2	5	1	1
	Subtotal	4	27	3	8	1	1
All Classes	All Years	21	135	17	42	9	10

All the light-duty vehicles were emissions tested using the Federal Test Procedure (FTP) urban driving cycle. Some vehicles were tested in the summer of 1996, while others were tested in the winter of 1997. Tests were conducted by both the U.S. Environmental Protection Agency (EPA) and the Colorado Department of Public Health & Environment (CDPHE), and in some instances, one or both of the agencies tested vehicles more than once. All tests were conducted using chassis dynamometer simulation with the resident on-board fuel. In addition to PM, measurements were obtained on a full range of other emissions constituents and criteria pollutants. The total number of vehicles and total number of tests conducted, by weight class (sedans and light pickups; heavy pickups) and model year, are given in Coburn (1998).

The heavy-duty vehicles represent a variety of engine manufacturers and models, as well as different service applications (transit buses, snow plows, dump trucks, etc.). Engine certification model years range from 1981 to

1995, and mileage (since last engine rebuild) at the time of testing ranges from slightly more than 5,000 to more than 595,000. Again, the heavy-duty vehicles in the study fleet are generally representative of the heavy-duty diesel vehicle population operating in the Denver metropolitan area, although it is similarly difficult to represent that population with so few units. In this case, the number of vehicles is principally limited by the cost of the emissions test.

Heavy-duty vehicles were emissions tested using three different driving cycles: the Central Business District (CBD) cycle, the Heavy-Duty Transient (HDT) cycle, and the West Virginia Truck (WVT) cycle. Both "hot start" and "cold start" tests were performed. The Colorado Institute for Fuels and High-Altitude Engine Research at the Colorado School of Mines conducted all heavy-duty vehicle tests. Due to time and cost constraints, as well as physical operating limitations, not every vehicle was tested on all three driving cycles or under both starting conditions. Because these tests were conducted throughout the late winter and early spring of 1997, a test blend of commercially available wintertime fuel was used. In order to simulate vehicle speeds and operations, all tests were conducted with the vehicles mounted on a chassis dynamometer. Measurements on a full suite of emissions constituents were obtained, including PM, CO, NO_x, and THC. Table 1 presents the total number of vehicles and total number of tests conducted, by weight class (light heavy-duty, medium heavy-duty, heavy heavy-duty, and transit bus) and model year, as well as corresponding counts for the HDT driving cycle only (both cold- and hot-start conditions). For this study the HDT driving cycle for heavy-duty vehicles was considered to be most closely aligned with the FTP urban driving cycle for light-duty vehicles.

Statistical Analysis Results

From the analytical standpoint, a number of experimental factors were of interest. With regard to light-duty vehicles, it was desirable to know whether there was a difference between the particulate emissions results obtained in the summer and winter, whether test results produced by EPA and CDPHE were analogous, whether sedans and light pickups were distinguishable from heavy pickups, whether vehicles of different makes, models, and model years yielded higher or lower results, whether individual vehicles responded differently, and whether mileage was a significant contributor. From the standpoint of heavy-duty vehicles, the factors of interest included weight class, model year, driving cycle, start condition, service application, individual vehicle differences, and mileage.

Because of the relatively small size of the data set, as well as statistical confounding of the experimental factors, not all variables could be examined simultaneously; meaning that not all sources of variation could be isolated and estimated as adequately as desired. To underscore this situation, note the information presented in Table 2, which is a matrix of average PM emissions (in grams per mile), cross-tabulated by model year and weight class, for the heavy-duty vehicles tested on the HDT driving cycle under "hot start" conditions. The matrix indicates the number of vehicles per category as well as the number of tests conducted on each vehicle. Table 1 gives the impression that there is considerable data to be examined; but from the perspective of Table 2, the true sparseness of data is apparent.

Table 2 also provides some additional information. It succinctly illustrates the "between-vehicle" variation, and apart from differences in numbers of vehicles and tests, it indicates the degree of "among-weight class" variation (note the light heavy-duty and transit bus classes are represented by minimal numbers of vehicles). Further, Table 2 presents some evidence about the variability in particulate emissions among model years, although model year cannot be evaluated as a prevailing effect because some years in the period 1981-1995 are not represented in the data set.

A number of formal analyses of variance were performed to help extract as much information as possible from the data set. For the light-duty vehicle data, these analyses helped substantiate that test results obtained by EPA and CDPHE were not significantly different, on average, and that they could be pooled to increase the number of observations from which to compute average values. A similar result was obtained with regard to testing season—summer and winter test results were not found to be significantly different, on average, and they were also subsequently pooled. Finally, an analysis of variance indicated that sedans and light pickups did not exhibit significantly different average PM emissions, so those two categories of vehicles were combined. Sedans and light pickups were assumed to be a fixed, physically different category of vehicles from heavy pickups per EPA specifications.

Table 2. Matrix of average PM (g/mile) for heavy-duty vehicles, by weight class and model year, on the HDT driving cycle under hot-start conditions. Single digits in parentheses indicate the number of tests (observations) per average value. Double digits in parentheses indicate the number of vehicles per average, followed by the number of tests per average.

Model Year	Weight Class				All Classes
	Light	Medium	Heavy	Bus	
1981			3.25 (2)		3.25 (1;2)
1982					
1983			3.50 (3)		3.50 (1;3)
1984					
1985					
1986				0.65 (3)	0.65 (1,3)
1987		2.31 (3)			2.31 (1;3)
1988		1.80 (3)			1.50 (1;3)
1989		2.17 (2) 1.16 (3)			1.57 (2;5)
1990			1.46 (1) 3.90 (2)		3.08 (2;3)
1991		1.61 (3)			1.61 (1;3)
1992					
1993	1.58 (2)	0.98 (2) 1.18 (3)	0.72 (2)	0.73 (3) 0.73 (2)	0.98 (6;14)
1994					
1995			0.77 (3)		0.77 (1;3)
All Years	1.58 (1;2)	1.56 (7;19)	2.31 (6;13)	0.70 (3;8)	1.63 (17;42)

For the heavy-duty vehicle data, analysis of variance was used to assess the differences in average particulate emissions attributable to model year, driving cycle, and start condition. All were deemed to be statistically significant, thus preventing various categories of vehicles from being pooled. Weight class was again assumed to be a fixed, differentiating factor per EPA specifications. Other determinants, such as engine manufacturer and engine model were not found to be significant. Three principal factors—vehicle, model year, and weight class—accounted for almost all the variability in the data, irrespective of the combination of driving cycle and start condition under which measurements were obtained.

In addition to these results, analysis of variance was used to calculate the precision and 95% confidence intervals associated with various average values of PM. This is an important aspect of the analysis of variance approach, because it allows the total variability to be partitioned into individual components so that an appropriate level of precision can be computed. As previously noted, it also provides for adjustments to accommodate the imbalances in numbers of vehicles and tests, since it is precision (or variance) that is most affected by this problem.

Figure 1 is an example graph of the resultant average PM values (adjusted through least squares, where appropriate), and upper bounds of the associated 95% confidence intervals on those average values, that are determined from the analysis of variance computations. In particular, Figure 1 shows the results for medium heavy-duty vehicles tested on the HDT driving cycle under both hot and cold start conditions. Similar graphs can be prepared for all other vehicle weight classes—both light- and heavy-duty. There are two important features of this graph. First, the average PM emissions are considerably higher than would be allowed under federal particulate standards for diesel vehicles of this type. Second—and perhaps even more important—the respective confidence intervals are rather wide, and their lower bounds are negative. For each model year indicated in Figure 1, the margin of error on the estimated average value of PM is substantially larger than the average itself, irrespective of start condition, indicating very low precision of estimation. Further, the negative lower confidence bounds indicate that each

interval includes a value of zero. This suggests that there is little or no statistical evidence to conclude that average PM is really any different from zero—a disconcerting, but not surprising, result given the sparseness of data and the confounded nature of the experimental factors.

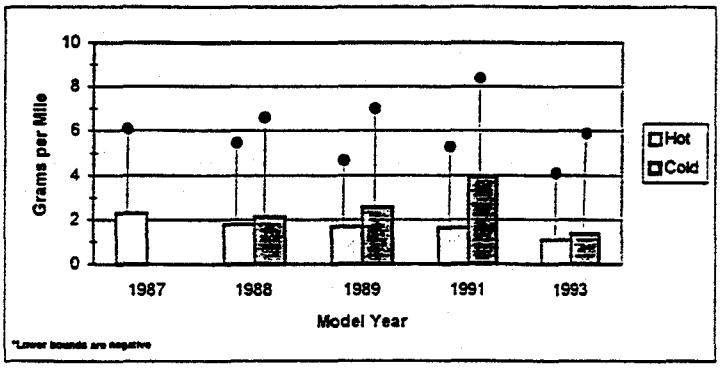

Figure 1. Adjusted PM averages and upper 95% confidence bounds, by model year, for medium heavy-duty vehicles tested on the HDT driving cycle under both hot and cold start conditions.

Discussion

Particulates emitted from diesel vehicles are a material part of the total particulate burden. Still, the exact mechanisms by which diesel particulates affect human health, and the degree to which they do so, are not well known or agreed upon. Current political and economic forces have the potential to substantially increase particulate output as a direct result of greater reliance on diesel as a transportation fuel. Consequently, it is imperative to have a precise understanding of the levels of particulates emitted by diesel vehicles in actual daily use so that reliable projections can be made of their impact on the public health of communities.

Unfortunately, average values of PM emissions are typically presented for various classes of vehicles without regard to their associated statistical precision. Single point estimates such as these can be misleading when the uncertainty of estimation is high and it goes unreported. In fact, this practice can be costly in terms of both human health risk and economic resources if such averages are misinterpreted or misrepresented. On the other hand, when properly computed and applied, the uncertainty in estimation can be used in a positive way to establish statistical bounds within which the true average PM emissions of a community's entire vehicle population is expected to lie. Though the resulting bounds may be extreme (owing to natural variability and/or inadequate sampling), they still yield a truer picture of the situation than average values alone.

Proper computation of the uncertainty in average PM emissions can be accomplished through effective use of the statistical technique of analysis of variance. Using this approach, it is also possible to determine the likely significance of various factors as contributors to PM emissions and as sources of variation, and to adjust comparative average values that are based on unequal numbers of vehicles and test results.

When diesel PM emissions measured on vehicles operating in the Denver metropolitan area during 1996 and 1997 were statistically analyzed using the method suggested here, they were shown to both exceed the federal standards, on average, and to be highly variable. Vehicle-to-vehicle differences, for example, constituted the most significant component of variance in the data, and this was true for both light- and heavy-duty vehicles. These findings suggest that typically reported average values of PM emissions are not sufficient indicators, by themselves, of the level of contamination.

The statistical methodology applied to the Denver case study was not routine, although the data were typical of the kinds that arise in similar investigations. The analysis was hampered by the limited number of vehicles and tests, a situation which is often encountered (particularly when considering diesel PM emissions). Nonetheless, it was possible to extract a number of important results. For the heavy-duty vehicles in particular (which emit more PM on

a mass basis than light-duty vehicles), newer-technology engines produced significantly lower average PM emissions; average emissions measured on the three driving cycles were significantly different (as a general rule, Avg. $PM_{WVT} \leq$ Avg. $PM_{HDT} \leq$ Avg. PM_{CBD}); cold start PM emissions were significantly higher, on average, than hot-start emissions; and transit buses had lower average PM emissions than anticipated. Some of these outcomes were previously hypothesized, but they had not actually been demonstrated in a formal study of this kind.

In the future, substantially more vehicles will need to be tested in order to achieve estimates having the levels of precision necessary to support human health risk projections. Better vehicle recruitment strategies to insure the necessary numbers of vehicles are obtained, better sampling designs to insure proper coverage and characterization of the overall vehicle population, and better experimental designs aimed at identifying and controlling sources of variation are needed. In addition, experimental designs will have to be constructed in such a way to allow effects such as atmospheric conditions and altitude to be formally tested. Such improvements will be necessary to obtain sufficient high-quality data irrespective of enhancements in fuel and engine technology.

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Exposure Of Chronic Obstructive Pulmonary Disease (COPD) Patients To $PM_{2.5}$ And Sulfate: Relationships Between Personal And Ambient Levels

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Abstract

Most time series studies of particulate air pollution and acute health outcomes assess exposure of the study population using fixed site outdoor measurements. Here we evaluate the relationship between ambient particulate concentrations and personal exposures of a population expected to be at risk of particle health effects. Sixteen subjects (non-smoking, ages 54 - 86) with physician-diagnosed COPD wore personal $PM_{2.5}$ monitors for seven 24-hour periods, randomly spaced approximately 1.5 weeks apart. Sampling was conducted within the Vancouver metropolitan area during April-September 1998. Time-activity logs and dwelling characteristics data were also obtained for each subject. Daily 24-hour ambient PM_{10} and $PM_{2.5}$ concentrations were measured at five fixed sites spaced throughout the study region. Sulfate (SO_4^{2-}), a marker of ambient combustion-source particulate, was measured in all $PM_{2.5}$ samples.

The mean personal and ambient $PM_{2.5}$ concentrations were 18 $\mu g/m^3$ and 11 $\mu g/m^3$, respectively. The mean personal to ambient concentration ratio of all samples was 1.75 (range: 0.24 to 10.60) for $PM_{2.5}$, and 0.75 (range: 0.09 to 1.42) for sulfate. Regression analyses were conducted on pooled data and for each subject separately. Ambient concentrations were expressed either as an average of the five values obtained for each day of personal sampling, or the concentration obtained at the site closest to each subject's home. Personal sulfate was more highly correlated with all ambient measures than $PM_{2.5}$. All pooled analyses resulted in lower correlation coefficients (Pearson's r) than the median correlation coefficient of individual regressions. The median correlation between personal and average ambient $PM_{2.5}$ concentrations was 0.48 (range: -0.68 to 0.83). Using sulfate as the exposure metric, the median Pearson's r between personal and average ambient concentrations was 0.96 (range: 0.66 to 1.0). Use of the closest ambient site did not improve the median correlation of the group for either $PM_{2.5}$ or sulfate. Inclusion of time-activity and dwelling characteristics data did not result in a predictive regression model for $PM_{2.5}$ personal exposure (R^2: 0.27). The model for sulfate was predictive (R^2: 0.82) as personal exposures were largely explained by ambient levels.

These results indicate a relatively low degree of correlation between personal exposure and ambient $PM_{2.5}$ that is not improved by assigning exposure to the closest ambient monitor. The correlation between personal exposure and ambient concentration is high, however when using sulfate as a marker of outdoor combustion-source particulate.

Introduction

The focus of this study is the assessment of exposure to particulates for a population expected to be at risk of particle health effects.

In time series studies of particulate air pollution, fixed site outdoor measurements are common exposure measures. If ambient measurements correlate poorly with personal exposures over time, exposures would be misclassified and lead to bias.

Studies of personal exposure to particulate matter have demonstrated increased personal exposures compared to ambient concentrations. Excess personal exposure has been attributed to proximity to particle-generating sources and indoor activities. Additionally, spatial variability in ambient concentrations may contribute to misclassified exposures.

Sulfate (SO_4^{2-}), a marker of outdoor combustion-source particulate, has been suggested as a better exposure metric than either PM_{10} or $PM_{2.5}$ due to high correlation between personal and ambient concentrations. In comparison to PM mass, the sulfate component penetrates efficiently indoors, exhibits less spatial variability and has no major indoor sources.

While most exposure studies have focused on healthy adults, epidemiologic studies have demonstrated that certain health-compromised groups are more susceptible to the effects of particulate air pollution. Exposures of susceptible individuals may differ from the healthy population, for example, due to reduced mobility.

Objectives

- To determine the correlation between personal and ambient measures of PM_{10}, $PM_{2.5}$ and SO_4^{2-} over time for a population susceptible to particle health effects.
- To determine the extent to which various activities and housing characteristics influence personal exposures of the study group.
- To determine whether ambient data obtained at the closest site to subjects' homes or ambient data averaged over multiple sampling locations is the best indicator of personal exposure.

Methods

- Study population:
  - 16 subjects (7 male, 9 female)
  - ages 54 – 86 (mean age: 74)
  - current non-smokers, nor living with smokers
  - physician-diagnosed moderate COPD ($FEV_1 < 0.75$ L)
- Personal Sampling:
  - Seven 24-hour sampling sessions per subject (total observations = 106) spaced randomly throughout study period, at least 1.5 weeks apart
  - $PM_{2.5}$ Personal Exposure Monitor (MSP Corp.) with 6" aluminum inlet at 4 L/min
  - 24-hr time-activity logs
  - Dwelling characteristics questionnaire
- Ambient Sampling:
  - 24-hour measurements collected on each day of personal sampling
  - PM_{10} (TEOM) and $PM_{2.5}$ (Harvard Impactor at 4 L/min)
- $PM_{2.5}$ filters analyzed for mass (gravimetric) and SO_4^{2-} (ion chromatography)

Results

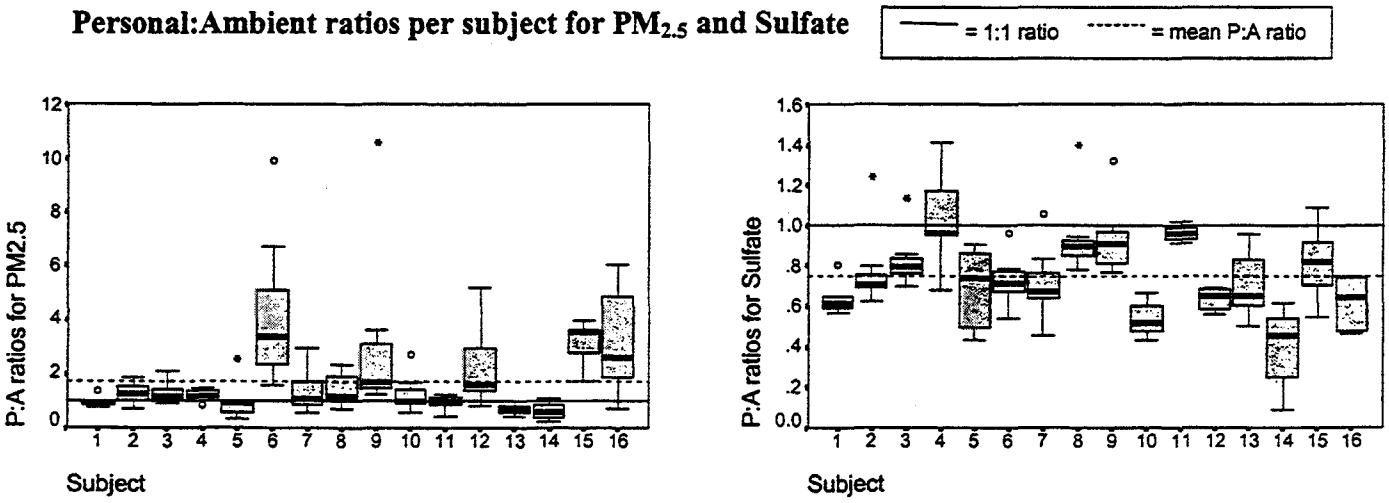
1. Descriptive Statistics

		Particulate Concentrations ($\mu g/m^3$)			
		n	Mean	sd	Range
Personal	SO_4^{2-}	106	1.5	0.9	0.2 – 4.7
	$PM_{2.5}$	106	18.2	14.6	2.2 – 90.9
Ambient*	SO_4^{2-}	90	1.9	0.9	0.4 – 5.4
	$PM_{2.5}$	90	11.4	4.1	4.2 – 28.7
	PM_{10}	90	18	7	6 - 51

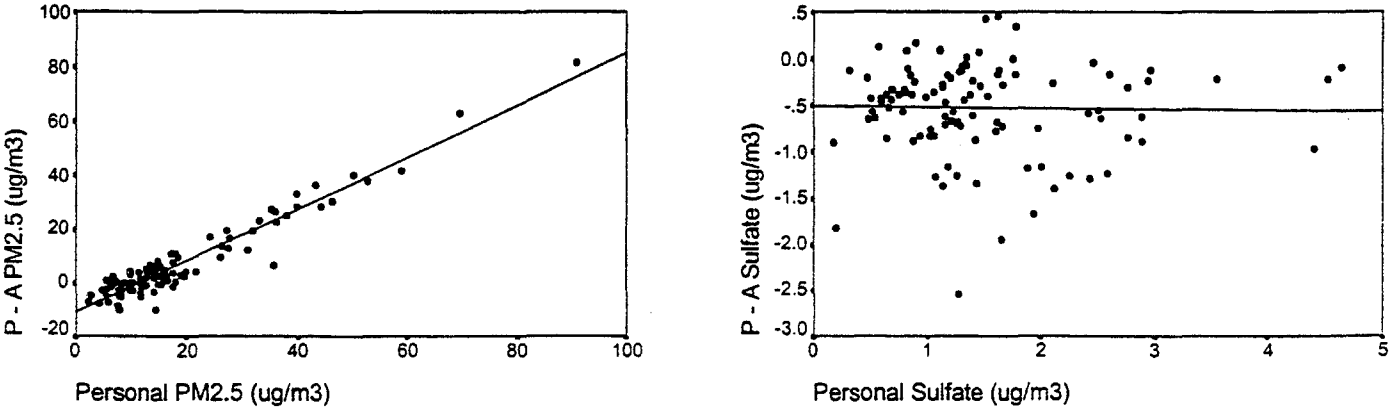
* Average concentrations from 5 outdoor locations for each day of personal sampling

2. Differences Between Personal And Ambient Levels

Personal:Ambient ratios per subject for $PM_{2.5}$ and Sulfate



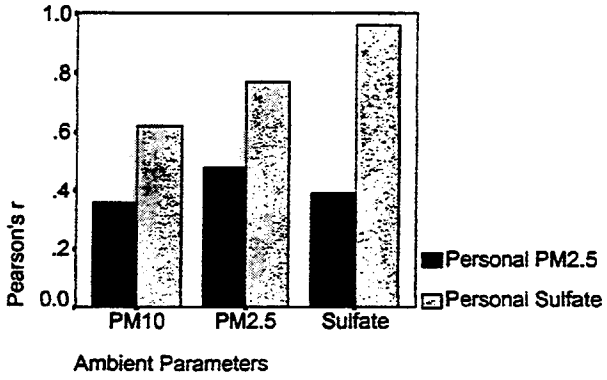
Is the difference between personal and ambient concentrations dependent on level of personal exposure?



3. Correlation Between Personal And Ambient Levels

Which ambient parameter is the best indicator of personal exposure?

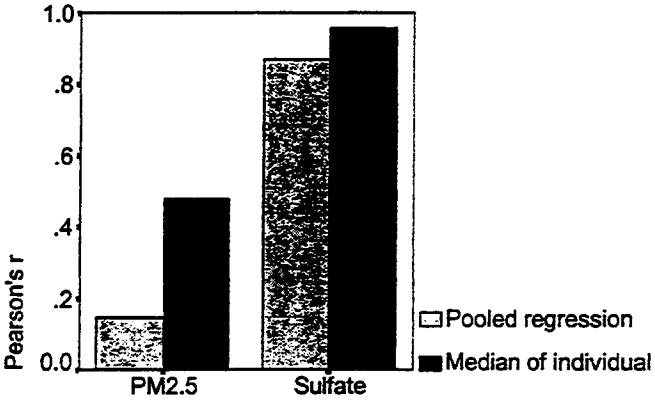
Median correlation coefficients from regressions (N=16) between ambient PM_{10}, $PM_{2.5}$ and



sulfate and personal $PM_{2.5}$ and sulfate

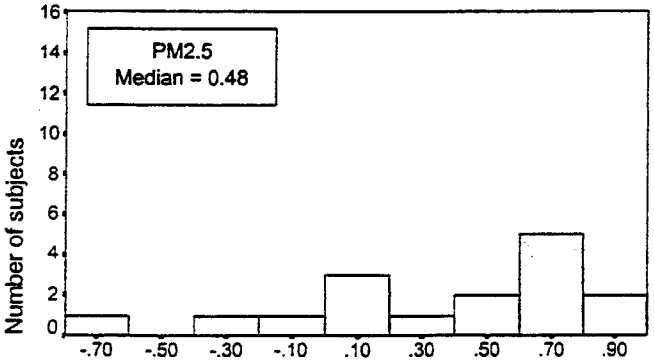
Pooled analysis vs. individual regressions:

Pooled r and median correlation of individual regressions between personal and ambient $PM_{2.5}$ and sulfate

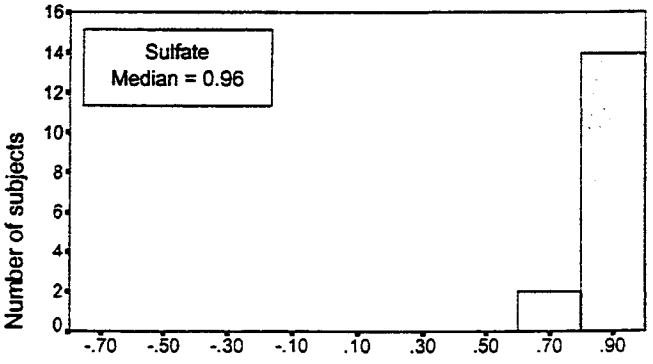


Correlation between personal and ambient measures over time:

Individual Pearson's r values for all 16 subjects

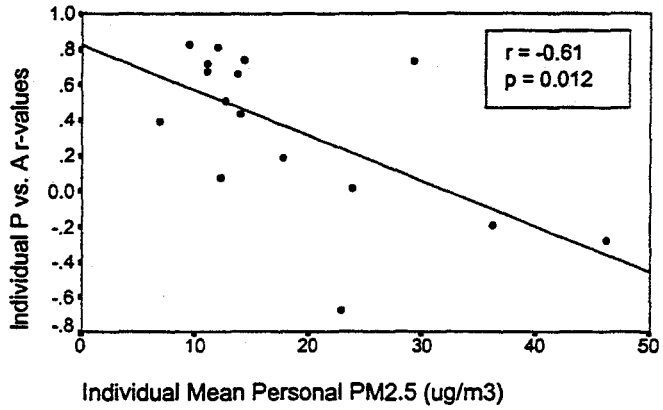


Individual Pearson's r-values for P vs. A PM2.5



Individual Pearson's r-values for P vs. A Sulfate

Are correlations for $PM_{2.5}$ dependent on level of personal exposure?

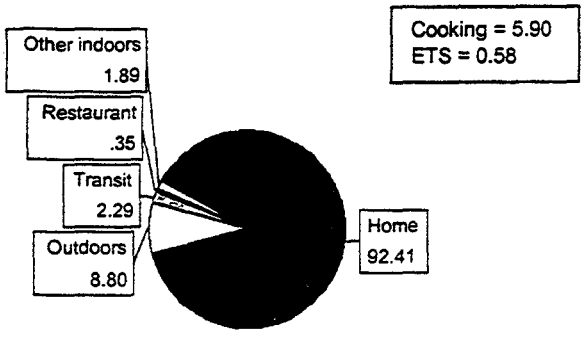


4. Personal Exposure Regression Models

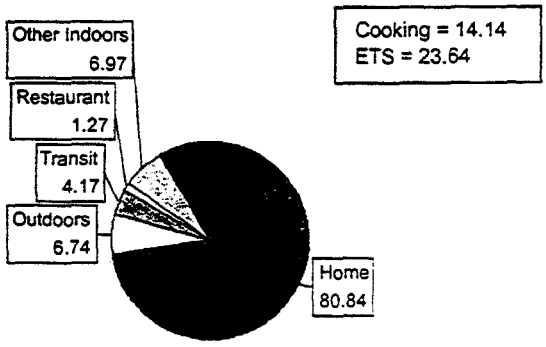
$PM_{2.5}$ ($R^2 = 0.27$):	House volume (m^3)**
	Ambient $PM_{2.5}$ ($\mu g/m^3$)**
	% of time spent near ETS*
	% of time spent at home
	% of time spent cooking
SO_4^{2-} ($R^2 = 0.82$):	Ambient SO_4^{2-} ($\mu g/m^3$)**
	House volume (m^3)**
	% of time spent outdoors**
Non Significant Variables:	Road distance, Open windows
	Building type, # of rooms
	Carpeting, Range hood use

** $p<0.05$; * $p<0.1$; ▲ pooled data

Time-activity variables (% of day)



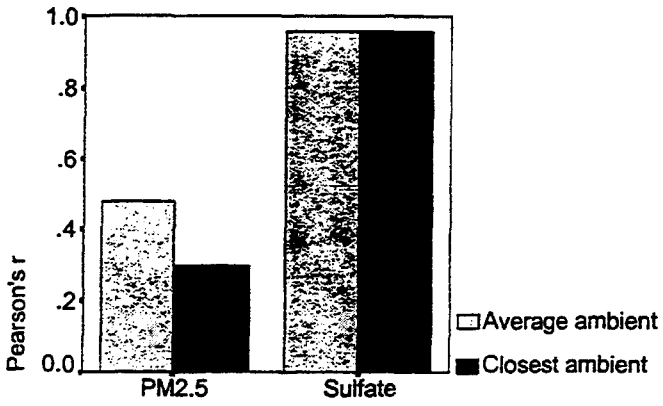
COPD Study Population



Retired (age 65+) Reference Population[1]

5. Use Of Data From Closest Site To Subjects' Homes

Median correlation coefficients of personal vs. average ambient and personal vs. closest ambient for $PM_{2.5}$ and SO_4^{2-}



Range of correlations between individual ambient sites:

PM_{10}, r (0.64 - 0.95)
$PM_{2.5}$, r (0.54 - 0.78)
SO_4^{2-}, r (0.80 - 0.95)

Conclusions

- There was a moderate correlation between personal exposure and ambient $PM_{2.5}$ over time (r = 0.48). Correlations were low for individuals with high personal exposures. The correlation between personal exposure and ambient SO_4^{2-} over time was much higher (r = 0.96).

- Pooled data gave lower correlation coefficients than the median of individual regressions, suggesting exposure misclassification is a greater concern for cross-sectional as opposed to time series study designs.

- Correlations were not improved by assigning exposure to the closest ambient monitor or by use of time-activity and dwelling data.

- Personal $PM_{2.5}$ exposures were higher than the ambient. The difference between personal and ambient levels increased as personal exposures increased. Personal SO_4^{2-} exposures were lower than ambient levels, but increased as ambient levels increased.

- The COPD patient study population had considerably different time-activity characteristics than the general retired population, suggesting that health-compromised individuals have different exposure characteristics.

Implications

- Ambient measurements are not good surrogates for personal $PM_{2.5}$ exposure.

- Ambient measurements using SO_4^{2-} as the exposure metric could be acceptable due to high correlation between personal and ambient measures and as SO_4^{2-} has been correlated with health effects in epidemiologic studies.

Limitations

- Small study population
- Relatively low ambient concentrations with little variability
- Low variability in time-activity data due to large amount of time spent at home

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STATISTICAL CHARACTERIZATION OF THE DIAMETER AND SHAPE OF AIRBORNE PARTICLES AT AN URBAN LOCATION USING SCANNING ELECTRON MICROSCOPY

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Particles in the air are characterized not only by their effective diameters but also by their shape. Electron microscopy provides detailed information about individual particles, their diameter and shape. Following image analysis, statistical methods can then be used to describe diameter and shape distribution. Using during a measuring campaign at the location this technique indicates the interestingly constant behavior of the diameter and the shape factor distribution.

INTRODUCTION AND AIM OF THE STUDY

It is only very recently that attention in the field of airborne pollutants has been focused on very fine particles. At present, the measurement of PM2.5 (particles < 2.5 µm) is widely discussed and used. The different categories of diameter (TSP, PM10, PM4, PM2.5) are selected for a number of reasons, with pragmatic choice being based on the inhalation and exhalation properties of the human respiratory system, as well as technical problems in measuring and sampling particles. Most of the methods used to study small particles in the air use techniques which describe different types of effective diameters. For example, impactors measure the effective aerodynamic diameter, while DMAs (differential mobility analyzers) measure the mobiltities of particles which are then used to conclude the diameters of hypothetical spherical particles. These methods enable the properties of the particle population or fractions to be described. Other methods determine the properties of individual particles (e.g. Berghmans et al., 1994; Jambers et al. 1995; Noble and Prather, 1996). Imaging procedures principally allow individual particles to be studied.

Particles in the air are characterized not only by their effective diameters but also by their shape. Electron microscopy methods can deliver more detailed information about the morphology of small particles down to the nanometer range. Scanning electron microscopy was often used for larger particles (e.g. Brown et al., 1995; Hunt et al., 1992) as well as for smaller particles (e.g. Colbeck et al., 1990; Eggenberger et al., 1994; Franck and Herbarth, 1999; Fruhstorfer and Niessner, 1994; Maynard and Brown, 1992). Because of the vacuum in the microscope tube, only dry particles remain completely unchanged. This study use the results of scanning electron microscopy (SEM) for the statistical description of these particles.

MATERIALS AND METHODS

For this study we sampled particles at a site in the city of Chemnitz. We chose a square located in the city center which is surrounded by mostly 4 - 5 – story buildings and crossed by two busy roads. The measurements were carried out in November 1998 at the mean temperatures, wind speeds and at atmospheric humidities listed in Table 1. The sampling time was approx. 1 h. We used a non-selective sampling inlet with a 7° opening. The orifice diameter was selected depending on the wind speed to allow nearly isokinetic sampling conditions (only negligible positive or negative acceleration of the air flow). The covering density of the filters by particles was gauged using the sampling time. Sampling was performed on nucleopore filters with pore diameters of 0.45 µm and a diameter of 47 mm. The sampling rate was ~1.5 m^3/h. The resulting face velocity was ~19 cm/s. A square with similarly heavy traffic in Leipzig was used by way of comparison. Although the measuring conditions were similar, this square is not as densely surrounded by buildings and has a broad opening facing onto a railway line. The Leipzig measurement is a typical example selected from 4 similar measurements on 4 days in this city.

TABLE 1. Ambient Weather Data During the Study Period

City	Date	Time	Humidity (%)	Temperature (°C)	Wind Speed (m/s)
Chemnitz	11/10/98	13:50 – 15:00	79.7	11.3	1.0
Chemnitz	11/11/98	11:10 - 18:10	78.4	6.0	2.0
Chemnitz	11/19/98	14:15 – 15:15	66.9	-0.9	1.1
Chemnitz	11/19/98	19:50 – 20:30	86.9	-2.5	1.2
Chemnitz	11/20/98	02:00 – 03:00	89.3	-2.3	1.0
Leipzig	03/05/98	09:00 – 10:00	84.1	6.9	0.76

The samples were covered by sputtering with gold and viewed under an EM912 microscope equipped with an digital scanning attachment for scanning electron microscopy (LEO). We usually took 5 images at magnification M1,000, 5 – 10 at M5,000, and 10 or more at M10,000. If necessary we also used M20,000 and more images at low particle density on the filter to improve the statistics.

The particles were detected using an image analysis system (SIS). These results were exported to a spreadsheet calculation program for a magnification-dependent weighting of the abundance of various particle fractions. The statistical description was carried out using StatSoft's STATISTICA software.

The mean diameter used is the average of eight diameters determined for the particle each at 22.5° rotation. This may result in the neglect of interstices of the irregular shape of larger particles and in the overestimation of the mass fraction of these particles. The large amount of information concerning shape necessitated using rather simple parameters to describe the shape. We used the

shape factor, which is defined as the ratio between the actual area of the particle in the microscopic projection and the area calculated from the perimeter of the particle in the projection ($f = 4\Pi A/p^2$).

Soot particles were identified by their electron microscopic image. The successfulness of this procedure was tested by EDX measurements. Other particles were removed from the population detected. These particles were untagged and soot particles remained. The subsequent evaluation scheme was the same as explained above for all particles.

RESULTS AND CONCLUSIONS

Figure 1 shows a typical overview of a sample collected by day but outside the rush hour. It contains a high number of particles, which can mostly be identified as soot particles (Fig. 2). Fig. 3 shows that in fact the great majority of the very small particles are soot particles. However, larger soot particles were also found, as can be seen in Fig. 4.

The night-time concentration of particles is much lower (Fig. 5), although the close-ups show that soot particles are still present (Fig. 6).

Interestingly, the distribution of the different particle diameters remained stable in various measurements at the same place at different times during the measurement campaign (Graph 1). The mean temperature varied at these measurements from – 2.5 °C to + 11.3 °C, the mean atmospheric humidity from 66.9 % to 89.3 % and the mean wind speed from 1 m/s to 2 m/s. The wind speeds measured were too low to whirl up significant amounts of dust from the ground at the location. The number of particles is significantly smaller during the night (Graph 2). The particle diameters measured differ between Leipzig and Chemnitz, with the percentage of particles < 100 nm being significantly smaller in Leipzig. Both the shape factor and the diameter behave similarly in a nearly constant manner (Graph 3). The distribution of various shape factors in Chemnitz was always similar with the exception of night-time measurements. The difference found in these night measurements is characterized by fewer chain-like particles, perhaps because of the fewer number of finer particles available for agglomeration and the presence of less traffic during the night. The distribution of shape factors in Leipzig differs significantly, showing the highest abundance at middle shape factors.

The distribution of the diameters of soot particles determines the distribution of the particle population as a whole (Graph 4). The non-soot particles have a smaller percentage of particles with a diameter less than 250 nm. Because traffic is heavy at both squares, the number of soot particles is higher than of non-soot particles. The shape factor of soot particles differs significantly from that of the non-soot particles (Graph 5). The larger the soot particles, the smaller is the shape factor (Graph 6) because of the tendency for larger particles to be formed by chain-like or irregular agglomerations of smaller particles. The hygroscopicity of diesel combustion particles is low and they exhibit a much smaller restructering with condensational growth than other carbon particles

(Lammel and Novakov; 1995). Soot particles age after leaving the vehicle exhaust pipe. Typical diameters as measured by DMA vary from 25 to 300 nm (Rickeard, 1996). We found more than 50% of particles in the range from 100 to 250 nm. In contrast to Rickeard et al (1996), in Chemnitz there are fewer soot particles with smaller diameters, which may be accounted for by agglomeration processes occurring after leaving the exhaust.

More particles with smaller mean diameters were found in Chemnitz than in Leipzig (Graph 7). The percentage of medium shape factors is higher in Leipzig than in Chemnitz (Graph 8).

The rough evaluation of mass using the mean particle diameters and regarding the particles as bulk material delivers reasonable mass fractions (Graph 9), albeit with the risk that the mass of larger particles is overestimated. Graphs 9 and 10 show that although the small particles account for a low percentage of the mass, they make up a much higher proportion in numerical terms. This illustrates the importance of the discussion of whether reducing particle number or particle mass is more relevant to protect human health (e.g. Oberdörster et al., 1995).

Conclusions:

- The results confirm that this method delivers a very detailed picture of the particulates in the air.
- As expected, the number of fine particles (< 1µm; < 500 nm) is much higher than of the larger ones.
- The day-to-night change of particle load (number and type) can be seen by this method.
- Soot particles constitute the majority of the non-volatile particles.
- The distribution of the particle diameters and of the particle shape factors shows a interestingly high constancy over the measurement campaign, which may be accounted for by the rather stable source spectrum and a rather low influence of other parameters.

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Chemnitz	11/19/98	19:50 – 20:30	86.9	-2.5	1.2
Chemnitz	11/20/98	02:00 – 03:00	89.3	-2.3	1.0
Leipzig	03/05/98	09:00 – 10:00	84.1	6.9	0.76

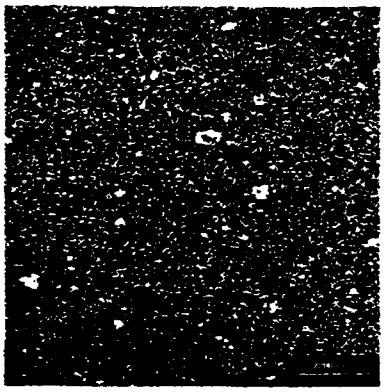


FIGURE 1. *Particles on a nucleopore filter, SEM, overview (daytime, outside the rush hour)*

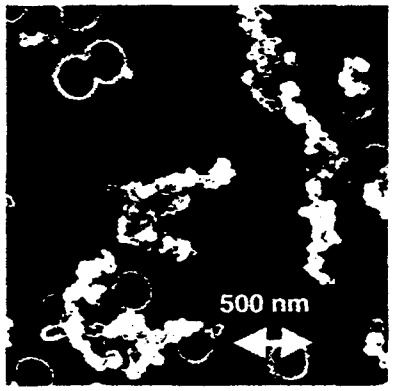


FIGURE 2. *Soot particles from the exhaust of a diesel car*

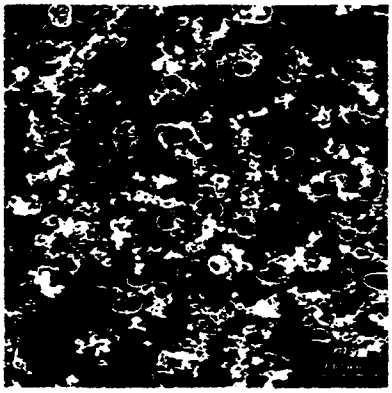


FIGURE 3. *Close-up (daytime, outside the rush hour)*

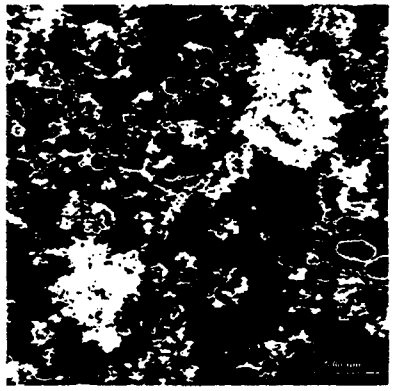


FIGURE 4. *Close-up (daytime, outside the rush hour)*

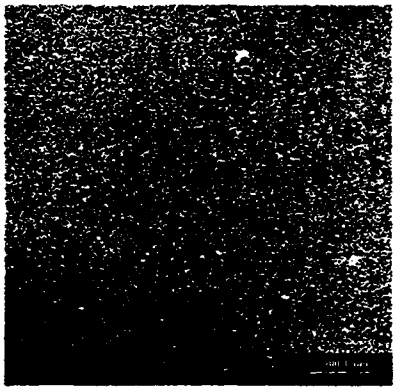


FIGURE 5. *Overview (at night)*

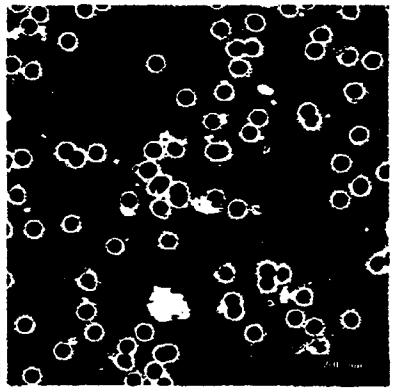
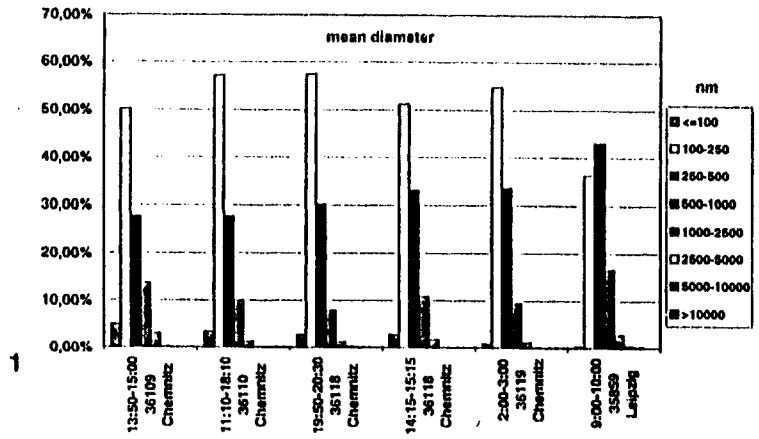


FIGURE 6. *Close-up (at night)*

Graphs

1: percentage of particle diameters
2: number of particle diameters (arbitrary units)
3: percentage of particle shape factors
4: number of particle shape factors (arbitrary units)
5: percentage of diameters of soot and non-soot particles
6: percentage of shape factors of soot and non-soot particles
7: percentage of diameters of soot particles in Chemnitz and Leipzig
8: percentage of shape factors of soot particles in Chemnitz and Leipzig
9: mass concentration of different particle fractions
10: number concentration of different particle fractions



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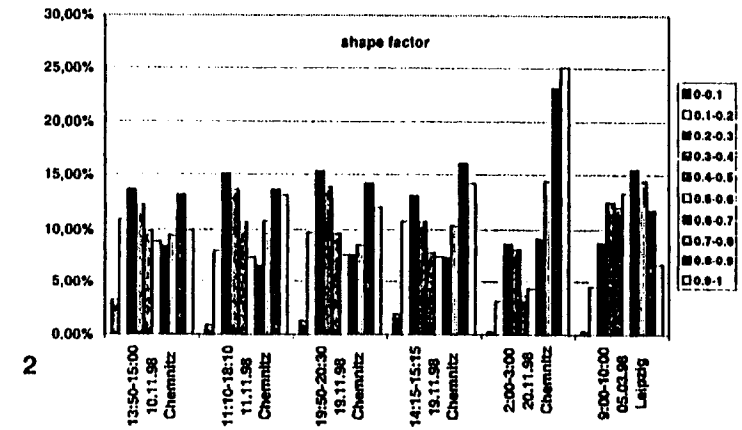

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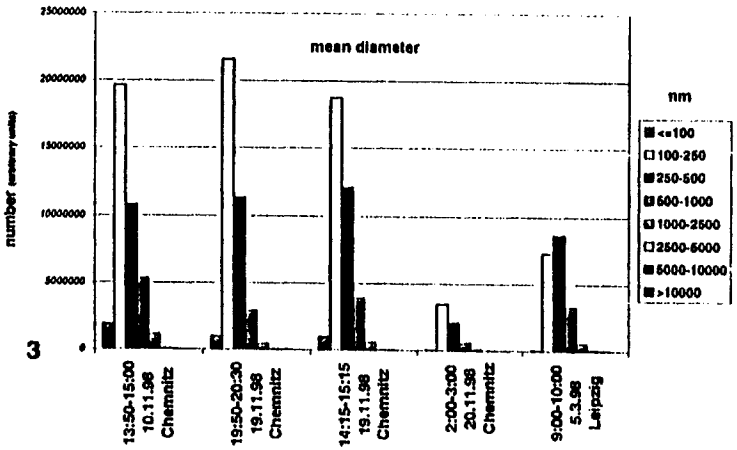

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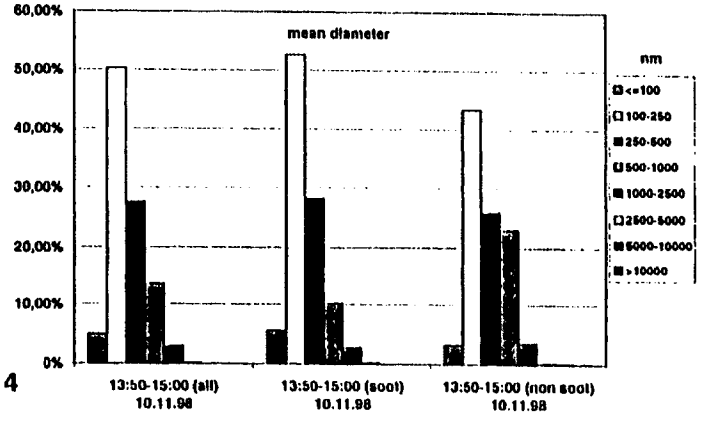
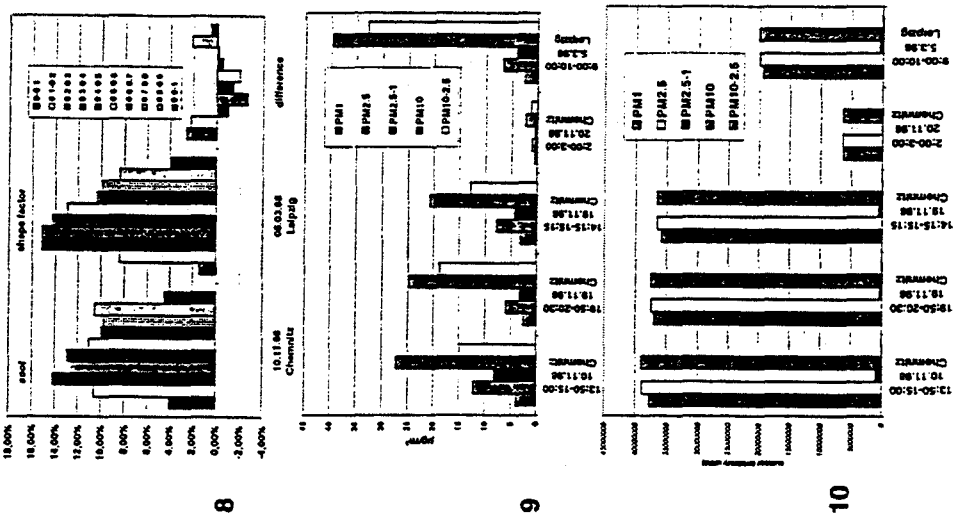
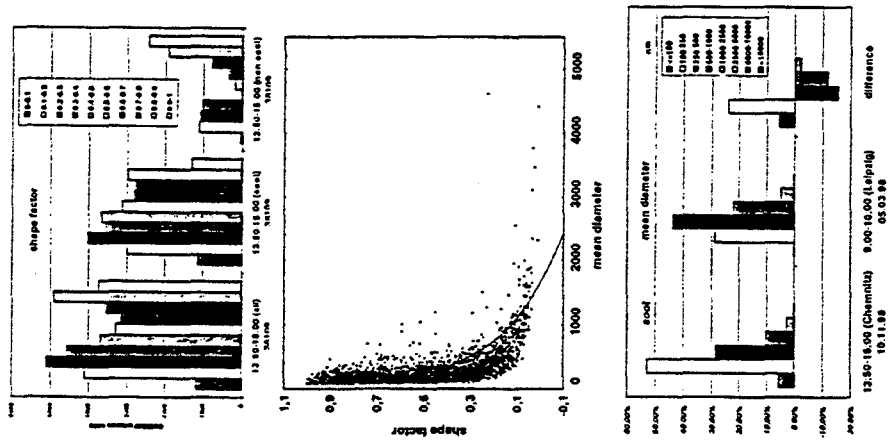


4

GRAPHS 1, 2, 3, 4





GRAPHS 5, 6, 7, 8, 9, 10

Development and Validation of a High Volume Low Cut-Off Inertial Impactor (HVLI)

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ABSTRACT

A low cut-off high volume conventional impactor was designed. This sampler uses a slit-shaped acceleration jet and operates at 1100 L/min. The impaction substrate is polyurethane foam. The impactor collection efficiency was characterized using polydisperse particles, and the 50% size cut-off was 0.123 µm. Losses within the sampler were also characterized and were less than 20%. The use of polyurethane foam (PUF) as a substrate has the following advantages over previously used substrates: a) PUF has a very high particle collection efficiency over a large range of particle sizes, even under conditions of heavy particle loading, as compared to other impaction substrates such as flat plates and thin porous membranes, which typically are subject to significant bounce-off and re-entrainment; b) no oil or grease coating is required, so potential interferences of impurities within such coatings are avoided when chemical, biological, and toxicological tests are performed on the collected particles; c) the PUF itself is chemically inert, minimizing interference with any of these tests; d) because of the high flow of 1100 L/min, a large amount of particles can be collected in a short period of time on a relatively small surface of substrate, facilitating recovery of the collected particles for the different tests; and e) large amounts of particles can be collected on a relative small collection surface and easily extracted with small amounts of water or organic solvents. This method will be suitable for the collection of large amounts of particles for toxicological studies and analysis of organic aerosols, which is not possible with other high volume samplers that utilize large filtration surfaces.

INTRODUCTION

Conventional inertial impactors have been used to classify ambient particles according to their diameter (Pierce and Katz, 1975; Milford and Davidson, 1985; Venkataraman *et al.*, 1994). The performance of conventional impactors has been studied extensively, and their behavior and characteristics can be predicted quite accurately (Marple and Liu, 1974, Marple et al., 1993). Other types of samplers have been also designed and developed. The virtual inertial impactor technology was designed to eliminate problems of bounce-off and re-entrainment and allows the collection of larger particulate mass (Marple and Chien, 1980). Virtual impactors can also be used to concentrate particles for inhalation studies (Sioutas et al., 1995a,b). One limitation of virtual impactors however, is the lack of complete separation of particles for sizes below the cut point. This results in a mixture of concentrated coarse particles and unconcentrated fine particles in the minor flow of the impactor and high losses of particles having diameter close to 50% cut-off point (Marple and Chien, 1980; Chen et al., 1986). A different type of conventional impactor was developed which has a rotating stage design, the micro-orifice uniform deposit impactor (MOUDI; Marple et al., 1991). With the MOUDI, it is still possible for bounce-off and re-entrainment losses to occur, since several layers of particles are accumulated during sampling. Furthermore, multiple jet interactions can deteriorate the performance of the impactor, affecting both the cut-point and internal losses (Fang et al., 1991).

The type of impaction substrate that is used depends on the species and chemical analysis to be performed (Spurny K.R., 1998). In addition, the collision of a high momentum particle with the collection surface or with previously collected particles has different possible outcomes: a) the particle is collected (with absorption of the energy by the substrate); b) the substrate does not absorb the energy, and the particle bounces-off of the surface and re-entrains into the airstream; c) energy is transferred to a previously collected particle, which is then re-entrained into the air stream or; d) the coarse particle breaks apart and some of the pieces are re-entrained into the air stream (Sehmel et al., 1978; Wall et al., 1990; John et al., 1991; 1993). To overcome these problems, the collection substrate can be saturated with a sticky substance, such as oil or grease. However, the use of oil or grease-coated substrates has

significant limitations for collection and analysis of ambient particles including: a) the sample is contaminated by components of such substances; and b) the collection efficiency of substrate depends on the amount of particles collected (Reischl and John, 1978; Pak et al., 1992, Tsai and Cheng, 1995; Biswas and Flagan, 1988).

Polyurethane foam (PUF) is manufactured by polymerization of ethyl carbamate (H_2N-C(=O)O-CH_2CH_3) under high pressure and temperature. Several types of polyurethane foam (SUPELCO, Supelco Park, Bellefonte, PA) are widely used to collect the gas phase of semi-volatile organic compounds downstream of a filter (Patton et al., 1992; Hawthorne et al., 1992; Kavouras et al., 1999). However, due to the relatively large pore sizes, PUF is not suitable as media to quantitatively collect smaller ambient air particles by filtration with sample air passing through. Although such porous foams in parallel or in series were recently suggested as pre-selective inlets to filter sample air, they had problems of bounce-off losses of solid particles (Chen et al., 1998). However, because of their large pores and the relatively low overall density, these materials may be suitable as impaction substrates for conventional impactors. These porous materials present negligible particle bounce-off and re-entrainment losses because particles can impinge onto the substrate with a possible gradual decrease of particle velocity.

EXPERIMENTAL SECTION

Design and description of the high volume low cut-off point impactor (HVLI)

Figure 1 shows the high-volume low cut-off point impactor (HVLI). It consists of a 2.5 μm cut-point size-selective inlet connected through a transition section, to a slit-nozzle conventional inertial impactor, which operates at a flow of 1100 L/min. The one-stage impactor uses polyurethane foam as the collection substrate and is shown schematically as well as in a photograph in Figure 2. Two closely spaced slit-shaped acceleration jets (13.97 [L] x 0.03 [W] cm) are used, with a theoretical 50% cut-off point of 0.10 μm at a flow of 550 L/min each ($\sqrt{Stk} = 0.50$; Re = 9319) (Hinds W.C., 1982). Particles with sizes

below the impactor cut-off point can be collected on a filter downstream of the impactor. The collection substrate, located directly below the acceleration jet, is a piece of polyurethane foam (Merryweather Foam, Barbarton,Ohio; density: 0.019 g/cm^3) with dimensions of 32.00 [L] by 0.63 [W] by 0.63 [H] cm. The distance between the acceleration nozzle and impaction substrate is 0.08 cm, corresponding to a S/W ratio of 2.6 (ratio of the jet-to-surface distance, S, to the nozzle width, W).

HVLI Validation Tests

The objectives of these validation experiments were to: (i) determine the size cut-off point and losses of the impactor and (ii) investigate the properties of the polyurethane foam as impaction substrate. In order to perform these tests over the entire size range of fine and coarse particles (<10 μm), two different measuring instruments were used to measure the number concentration and size distribution of particles upstream and downstream of the impactor system. For particle sizes from 0.02 to 0.5 μm, the Scanning Mobility Particle Sizer (SMPS) (Model 3071A, TSI Inc., St. Paul, MN) equipped with a Condensation Particle Counter (CPC) (Model 3010, TSI Inc., St. Paul, MN) was used. For 0.5 to 10 μm, the Aerodynamic Particle Sizer (APS) (Model 3310A, TSI Inc., St. Paul, MN) was used. Ambient samples were collected using a prototype sampler and two Harvard Impactors (HI) in order to investigate the collection efficiency of HVLI under real conditions. Finally, the organic background of PUFs was identified using gas chromatography/mass spectrometry analysis.

Methodology for particle measurements at low pressure

Both the SMPS and the APS require measurements of sample air at very close to atmospheric pressure. However, in order to achieve the small size cut-off of about 0.10 μm, the pressure drop across the slit-nozzle acceleration jet is about 0.25 atm. Thus, under normal operating conditions, it would be impossible to make measurements downstream of the impactor system with these instruments. However, a simple technique was employed which made it possible to overcome this problem using a low flow vacuum pump, which draws air from an isokinetic probe attached downstream of the sampler. The output flow of the

vacuum pump was at atmospheric pressure. There was a concern about the effect that particles generated by the pump or lost within the pump had on number concentration and size distribution of laboratory-generated particles. The vacuum pump that was used is a linear motor-driven free piston pump (Model VP, MEDO Inc., Hanover Park, IL). The operating principle of this pump minimizes the generation of particles. An electromagnet drives the piston into and out of a cylinder, drawing air in through a one-way inlet spring valve and pushing sample air out through a similar valve. Because the pump flow can be adjusted by varying the power voltage, no additional valve (that could cause additional particle losses) is needed to control the flow rate (8.0 L/min).

To determine the artifact particles produced by the MEDO pump as a function of particle size, a high efficiency particle air (HEPA) filter was attached to the inlet of the pump, and measurements were made at the outlet using both the SMPS/CPC and the APS instruments. Since the HEPA filter completely removed all particles from room air, all particles measured at the pump outlet were generated by the pump. To determine the particle losses within the pump, test air containing polydisperse particles at atmospheric pressure was measured both with and without the MEDO pump in-line. Polydisperse particles were generated by nebulizing an aqueous suspension of 2-20 μm hollow glass spheres (density: 1.1 g/cm^3) (Polysciences, Inc, Warrington, PA) with a Retek Model X-70/N nebulizer, using filtered air at 7 psi. The aerosol was mixed with filtered room air to obtain test air.

Measurements upstream and downstream of the impactor system

The test air mixture of polydisperse glass spheres was passed into the top end of a vertical cylindrical duct (100 cm [L] x 15.24 cm [ID]) made of anodized aluminum. Additional filtered room air was also added at the top of the duct. Turbulence was induced near the top of the duct, using a rectangular plate, to assure uniform concentration downstream. The sampler was connected to the bottom of the duct. Alternate measurements were performed between an isokinetic probe in the duct, just upstream from the impactor system, and with a similar probe downstream of the impactor system. In each experiment, the concentration and size distribution of particles was measured for 10 minutes upstream, 10 minutes

downstream and then 10 minutes again upstream. This series of three tests was repeated twice for each experiment. Experiments were conducted on three different days, so collection efficiency and losses were measured a total of nine times. To measure losses of particles as a function of size, for components of the impactor system, measurements at the inlet and outlet of the slit impactor system without the impaction substrate in place were done.

Cleaning and analysis of PUF

The chemical background of the collection substrate is an important parameter to use in studying organic aerosol, with this sampler and PUF as collection medium. For this reason, pieces of polyurethane foam used in our experiments were sonicated with a series of high purity organic solvents: methanol, ethyl acetate, hexane and methylene chloride ("SupraSolv" grade, Merck, Darmstadt, Germany) for 1 hour. Furthermore, PUF pieces were ultrasonically extracted with 100 ml methylene chloride for 1 hour. The organic extract was concentrated and an aliquot of diazomethane was added for alcohols and acids derivatization. Finally, the extract was analyzed by using gas chromatography (HP 5890) /mass spectrometry (HP 5971) in electron and chemical ionization for *n*-alkanes, polynuclear aromatic hydrocarbons (PAH), alcohols, acids, polychlorinated biphenyls (PCBs), phenols and other functional organic compounds.

RESULTS AND DISCUSSION

Characterization of the low flow vacuum pump

Artifact particle concentrations generated by the low flow MEDO vacuum pump were found to be low and reproducible. The total particle number concentration for sizes 0.2 to 2.5 μm was 162 ± 24 particles/cm^3 when the pump was operating at atmospheric pressure and somewhat higher (185 ± 19 particles/cm^3) when operating under vacuum (0.25 atm). The number concentration of measured polydisperse particles

both upstream and downstream of the impactor system (3775 and 1782 particles/cm^3, respectively) were ten to thirty times higher than the concentration of pump-generated particles, thus the contribution of pump-generated particles was minor. The number distribution of pump-generated particles, as a function of particle diameter both under atmospheric pressure (1 atm) and vacuum (0.25 atm), for nine different experiments, is shown in Figure 4. The number concentration increased rapidly from 0.02 to 0.04 µm, where it reached a maximum. For larger sizes the concentration decreased, with a concentration of 2.0 particles/cm^3 at about 0.1 µm, thus a small number of particles between 0.1 and 2.5 µm was generated.

Substantial losses of particles were found to occur within the low flow MEDO pump. However, these losses varied little with the particle size. Figures 5A, 5B and 5C show number concentration (particles/cm^3) results for the mean of three different tests, measuring upstream (directly from the duct) and downstream (measuring after passing through the MEDO pump), for size ranges 0.2 to 0.7 µm and 0.7 to 2.5 µm, respectively (A,B) and the relative loss, as a percentage of the upstream concentration, as a function of particle size (C). Tests were conducted with aerosolized hollow glass sphere aerosols, using the SMPS, and the APS. The losses of particles from 0.02 to 0.2 µm varied from 50 to 60% of generated particles (C) but the size distribution did not change significantly (A,B). For sizes from 0.2 to 2.5 µm losses were higher and varied from 60 to 75% (C). This could be explained by the higher inertial forces of larger particles, which is more important inside the pump where the air trajectory changes rapidly.

Since the artifact particles generated by the MEDO pump were small and reproducible, and since the relative losses of particles, as a function of particle size were stable, and the distortion of size distribution was not significant, it was possible to make adequate corrections to the number and size distributions of particles sampled both at the inlet and the outlet of the inertial impactor, using this low flow vacuum pump.

Particle losses in the impactor housing

By comparing measurements at the inlet and outlet of the slit impactor system, the collection efficiency of the impaction substrate was determined. Particle losses were calculated by measuring the particle

penetration through the sampler from which impaction substrate was removed. The observed losses (without the substrate in place) were determined by comparing the measurements before the sampler (in the duct) and after the sampler (in the outlet connection of the sampler). Figure 6 shows the percent losses as a function of particle size. Losses for particles smaller than 1.0 μm were negligible; for sizes between 1.0 and 2.5 μm losses were approximately 10%. It was previously observed that losses through the acceleration nozzle are negligible (Sioutas et al., 1997) and it was expected that there would be significant losses in the outlet manifold, because of the highly turbulent flow in this area of the system. Since particles larger than the impactor's cut off point were collected on the polyurethane foam, these losses do not affect the concentrations of particles collected onto a backup filter downstream of the impactor. Corrections were made to the sampler output measurements, in order to accurately determine the substrate collection efficiency and the 50% cut-off point.

PUF substrate collection efficiency

For our studies, PUF (density 0.019 gr/cm^3; Merryweather Foam, Barberton, Ohio) was used. This type of polyurethane foam was selected because of its low blank levels of major water-soluble and organic pollutants. Also, preliminary tests have shown negligible interferences for biological and toxicological studies (Salonen et al., 1999). Finally, this type of polyurethane foam has anti-static properties, which will inhibit the built-up of electrostatic charge during sample collection and storage. Figure 7 shows, the collection efficiency curve for the slit-nozzle system with the PUF impaction substrate. The size cut-off curve is sharp and the 50 % cut-off point (d_{50}) is 0.123 μm The experimental d_{50} is slightly higher than the theoretical value (0.10 μm). However, the collection of particles with diameter from 0.12 to 2.5 μm using high flowrates is challenging because of bounce-off and re-entrainment losses affect the performance of the sampler. The use of polyurethane foam eliminates these artifacts and thus the characteristics of the impactor are stable for longer sampling periods.

Field Validation Tests

Field tests were conducted to evaluate the performance of the impactor. A slit $PM_{0.123}$ slit-impactor downstream of a $PM_{2.5}$ size selective inlet was used. The dimensions of acceleration nozzles were 5.84 (L) x 0.03 (W) cm. The collection rate was 230 L/min. The dimensions of polyurethane foam substrate were 6.60 (L) x 0.60 (W) x 0.30 (H) cm. Different S/W ratios (2.31 and 3.08) were tested. Sampling was also performed using the Harvard impactor (with oil-impregnated porous stainless steel substrate). This impactor has a size cut-off of 2.5 μm and operates at 10 L/min. Particulate matter was collected on a Teflon filter.

Three samples were collected for 24, 48 and 72 hours. The polyurethane foam substrates were ultrasonically extracted with five (5) ml of ultra-pure H_2O for ninety (90) minutes. Teflon filters were wet with 50μl of ethanol prior to be ultrasonically extracted with five (5) ml of ultra-pure H_2O for twenty minutes. The extractable material was analyzed for sulfate anion (SO_4^{2-}) by ion chromatography.

As shown in Table 1, better agreement was observed when the S/W ratio was 3.08. In addition, sulfate concentrations measured by the Harvard impactor were similar to those measured with HVLI. In addition, the values of the ratio HVLI/HI are close to unit (0.88-0.99), indicated that HVLI can be used for collection by impaction of ambient particles.

Laboratory Capacity Tests

Tests were performed to examine the collection efficiency of particles as a function of the total amount of particles collected. The results of these tests were used to determine the maximum loading (capacity) below which the high collection efficiency curve of the impactor remains unchanged (Figure 8). The collection efficiency curve did not change for the first 5.50 hours (330 minutes). For longer times, there are decreasing efficiencies for collection of particles between 1.5 to 2 μm.

The mass concentration of generated particles was 5 mg/m^3, thus for a flow of 15 L/min, and a sampling period of 330 minutes, the total collected mass is 30.4 mg. Note that 24.75 mg is the capacity for an

impactor using a flow of 15 L/min, with an accelerator slit length of 0.38 cm. For a much higher flow of 1100 L/min the estimated capacity of the corresponding substrate using a slit length of about 27.94 cm is 1.81 gr. Therefore, for a high ambient PM_{10} concentration of about 100 $\mu g/m^3$ the sampler can be used to collect ambient particles for a sampling period of more than a week.

Organic backgroung of PUFs

The organic compounds background of PUFs can be a limiting factor in using the PUF as a collection media for organics. PUFs were pre-cleaned, extracted using ethyl acetate, methanol, n-hexane and dichloromethane, and analyzed using GC/MS to determine blank values for a number of organic compounds. A gas chromatogram of the organic extract is shown in Figure 9. Polynuclear aromatic hydrocarbons and their oxygenated and nitrated products, and polychlorinated biphenyls were not identified in PUF extracts. In addition, phenols and other polar compounds were not detected. This suggests that PUF is suitable collection media for these compounds.

A series of phthalate esters (RT_1: 11.02 min; RT_2: 12.81 min; RT_3: 31.11 min; RT_4: 35.31 min; m/z:149,165) and n-saturated acids (C_{14} (RT: 16.61 min); C_{15} (RT: 18.0008 min); C_{16} (RT: 20.03 min) and C_{18} (RT: 24.03 min); m/z=74,87) were detected. The amounts of organic compounds detected in this organic extract were very low (~1 pgr). Lets assume an ambient concentration of C_{15}, which its ambient concentration is lower than the other acids, of 10 ngr/m^3. For a sampling period of 6 hours, the collected amount of C_{15} will be 3.96 µgr. This amount is two to three orders of magnitude higher than the amount of C_{15} detected in the PUF. Thus, the use of PUF as an impaction substrate does not interfere the analysis of organic aerosol.

CONCLUSIONS

A high volume inertial impactor has been developed. This impactor uses a slit-shaped acceleration nozzle

and an uncoated polyurethane foam as an impaction substrate/collection media. After particles are colected, they penetrate within the polyurethane foam. This results in the minimization of particle losses due to bounce-off and re-entrainment.

A major feature of this sampler is that it can be used for a wide range of sampling durations, from a few hours to a week or more. Short sampling periods are feasible because the sampler high flow rate (1100 L/min). The ability to collect a relatively large amount of particles in a short time is important for studies which focus on time resolved exposure and/or source apportionment studies. Long durations are feasible because of the high capacity of the collection substrate. Such long durations are sometimes required to achieve enough sensitivity for measurement of certain trace organics, and to collect sufficient quantities of particles for biological and toxicological analysis. One other important feature of this sampler is that polyurethane foam is chemically inert and non-toxic. Also, because particles are collected on a small impaction surface (20.16 cm^2), the extract volumes of solvent required for particle recovery are significantly smaller than for filter based samplers. Overall, the development of this new sampler will make it possible to collect large amounts of particles for chemical analysis and toxicological studies. This will enable us to improve our knowledge on particle physicochemical properties and their health effects.

ACKNOWLEDGEMENTS

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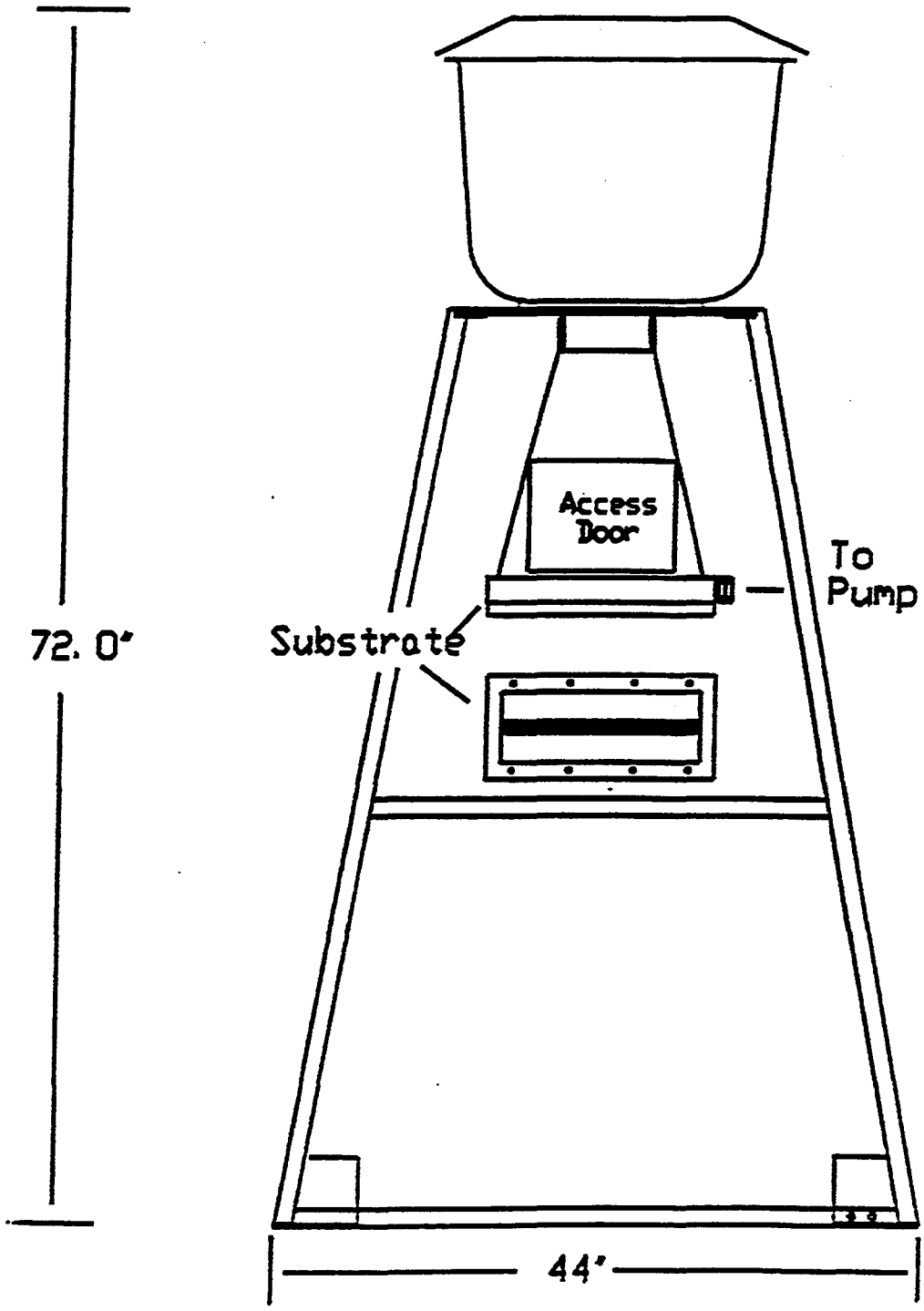
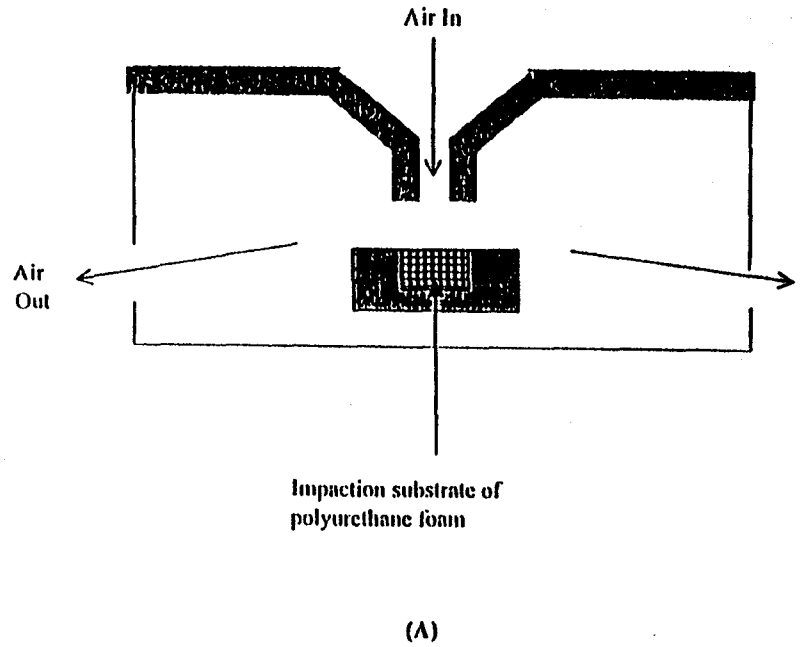
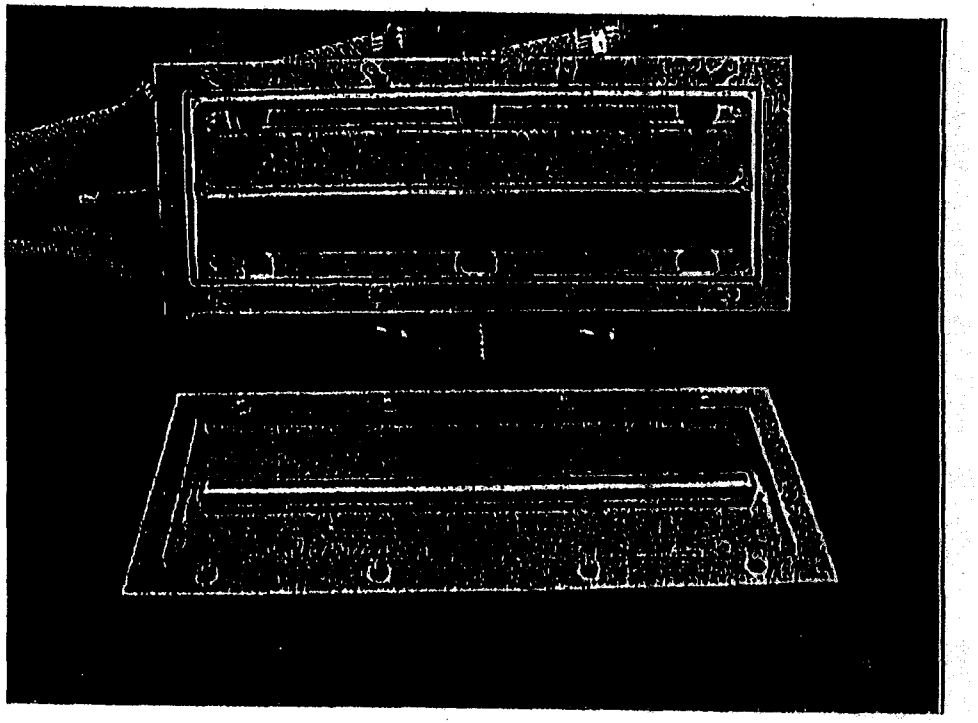


Figure 1: The High Volume Low Cut-Off Impactor (HVLI)



(A)



(B)

Figure 2: Schematic diagram (A) and photograph (B) of the High Volume Low Size Cut-Off Impactor (HVLI)

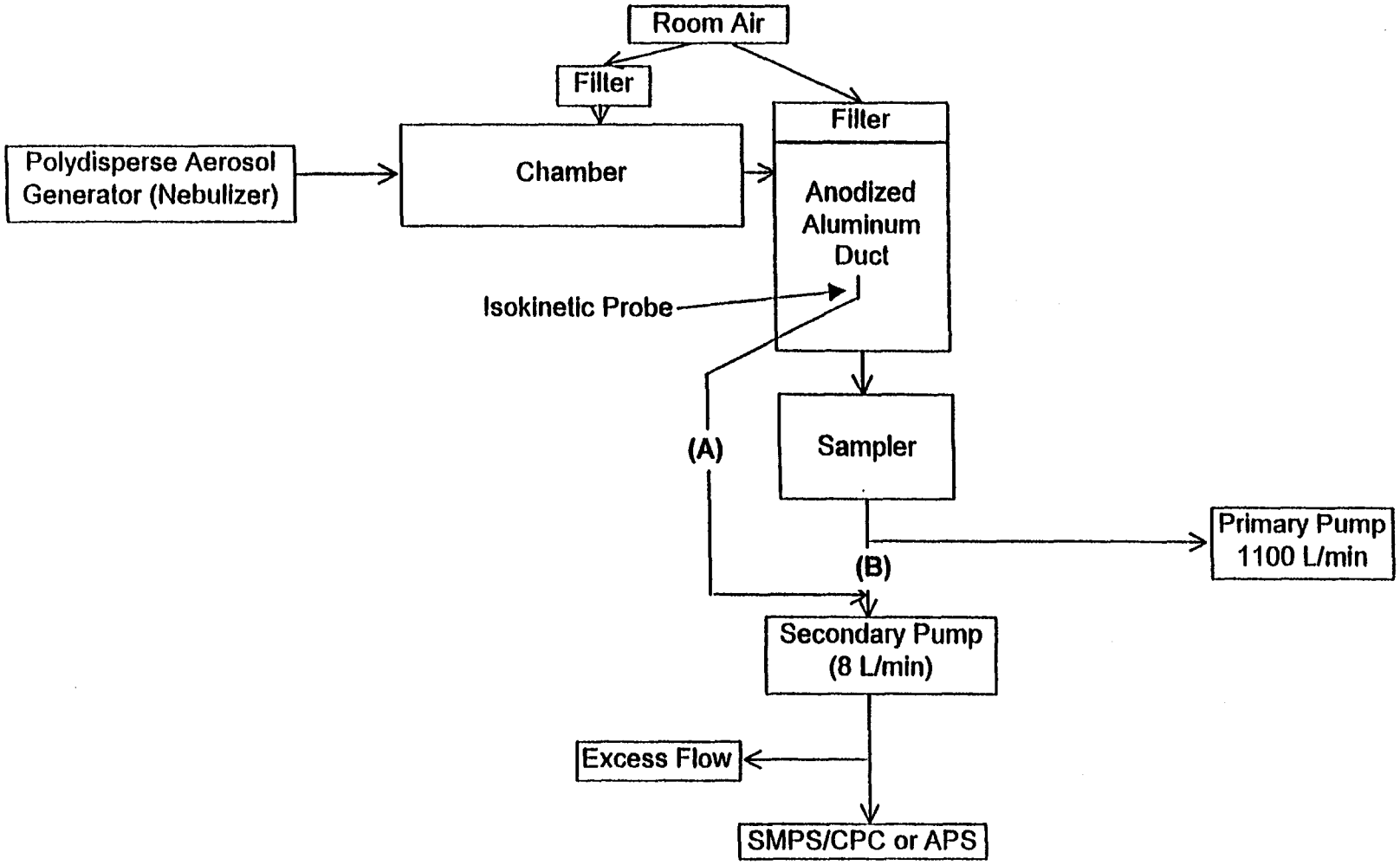


Figure 3: Impactor test experimental apparatus

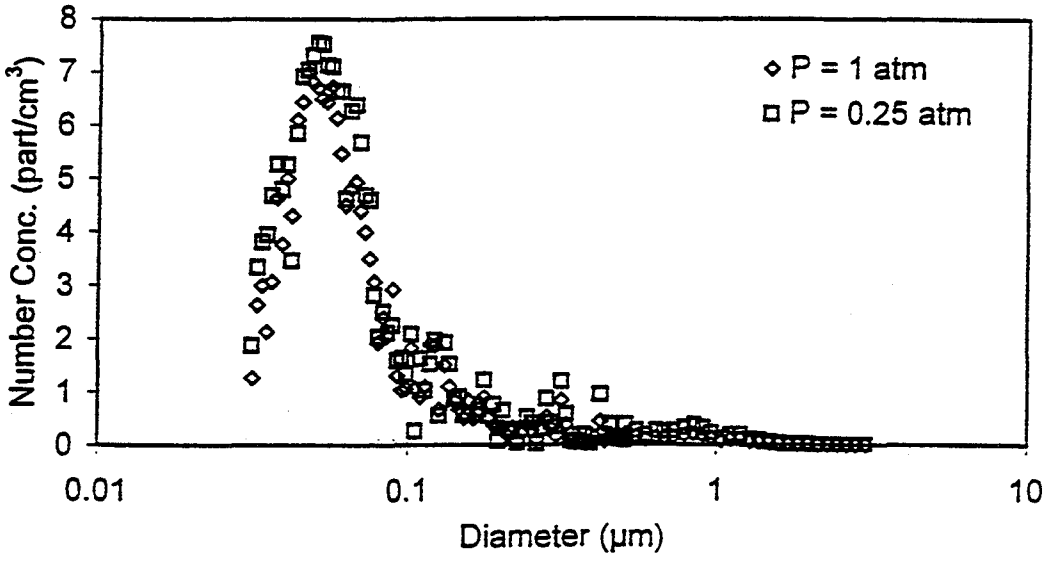


Figure 4: The number distribution of pump-generated particles under atmospheric pressure (1 atm) and vacuum (0.25 atm)

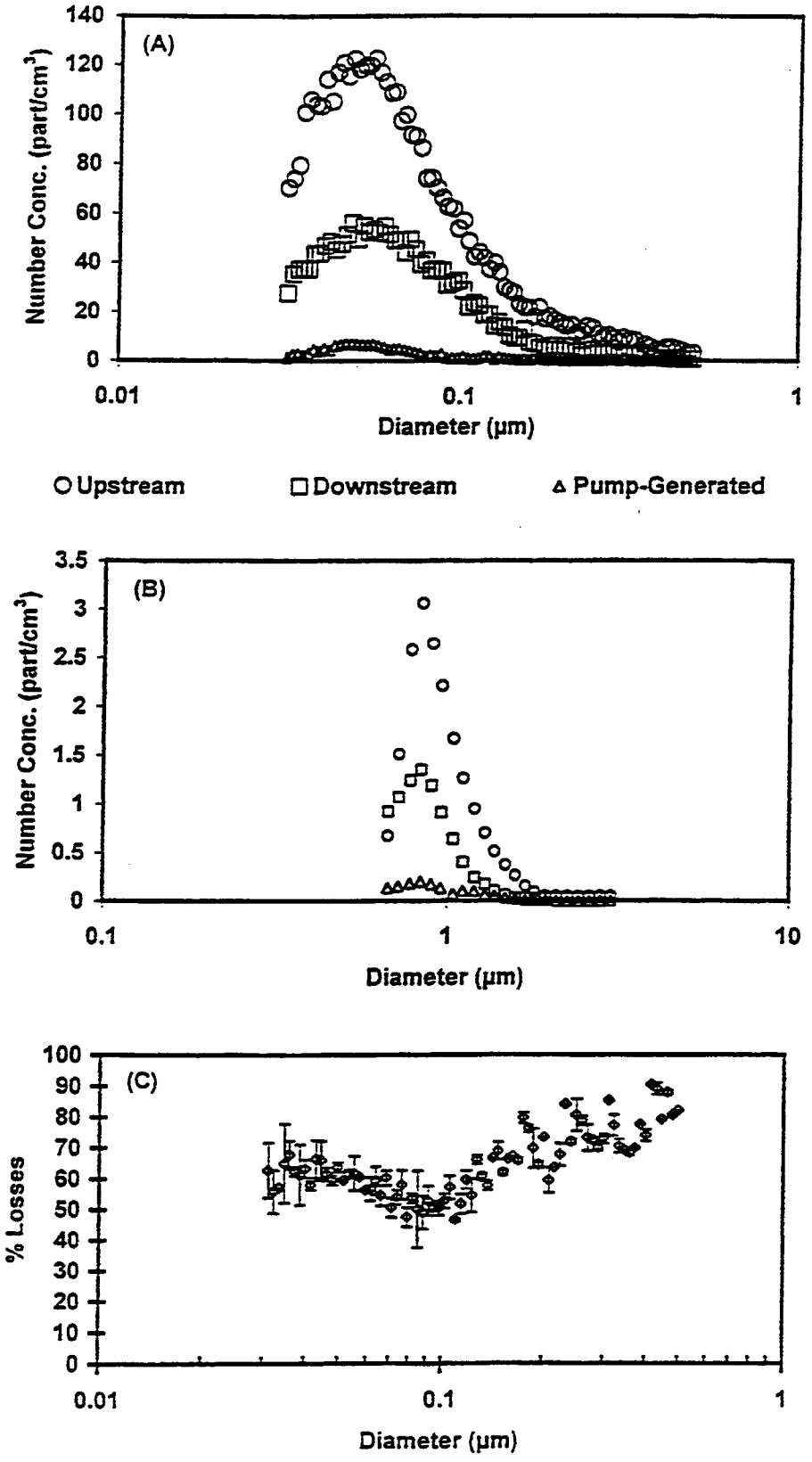


Figure 5: Losses of particles from 0.2 to 0.7 µm (A), from 0.7 to 2.5 µm (B) and as a percentage of upstream concentration (C) through the secondary pump

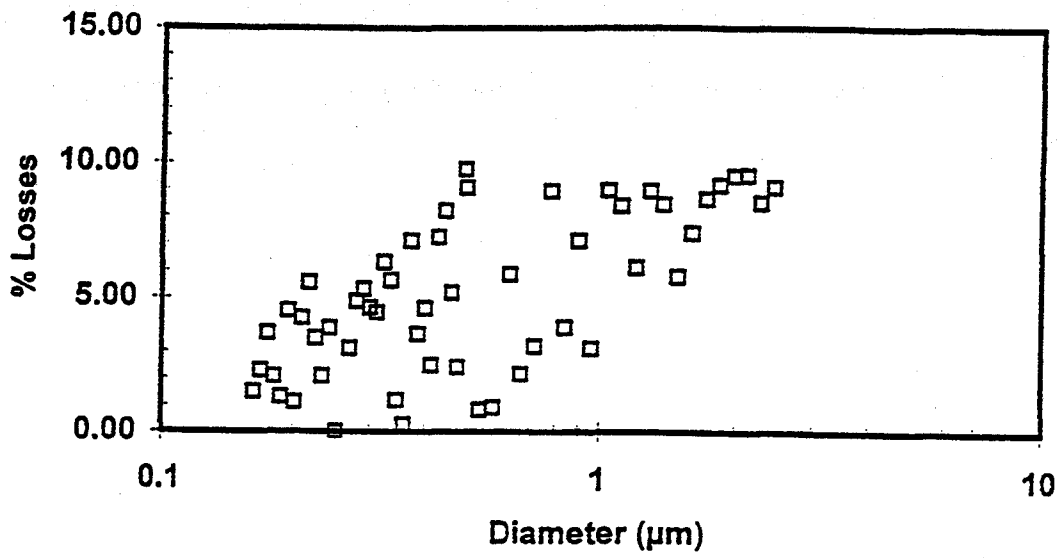


Figure 6: Percentage losses through the system

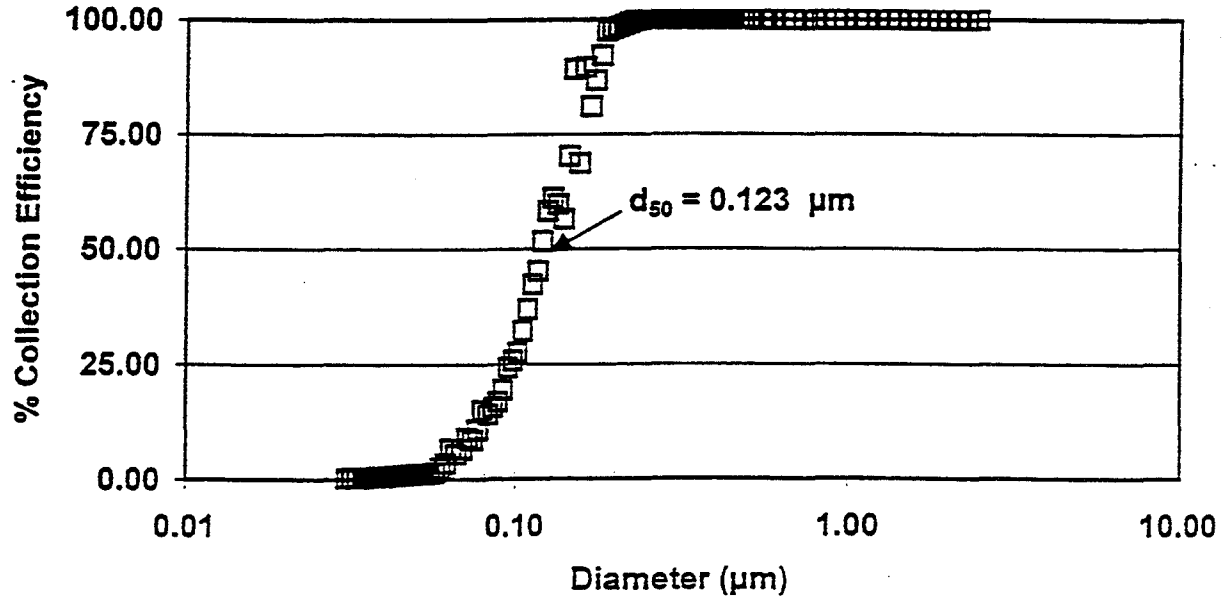


Figure 7: The collection efficiency curve for the slit shaped nozzle inertial impactor system with the polyurethane foam impaction substrate. The array denotes the 50% size cut-off point.

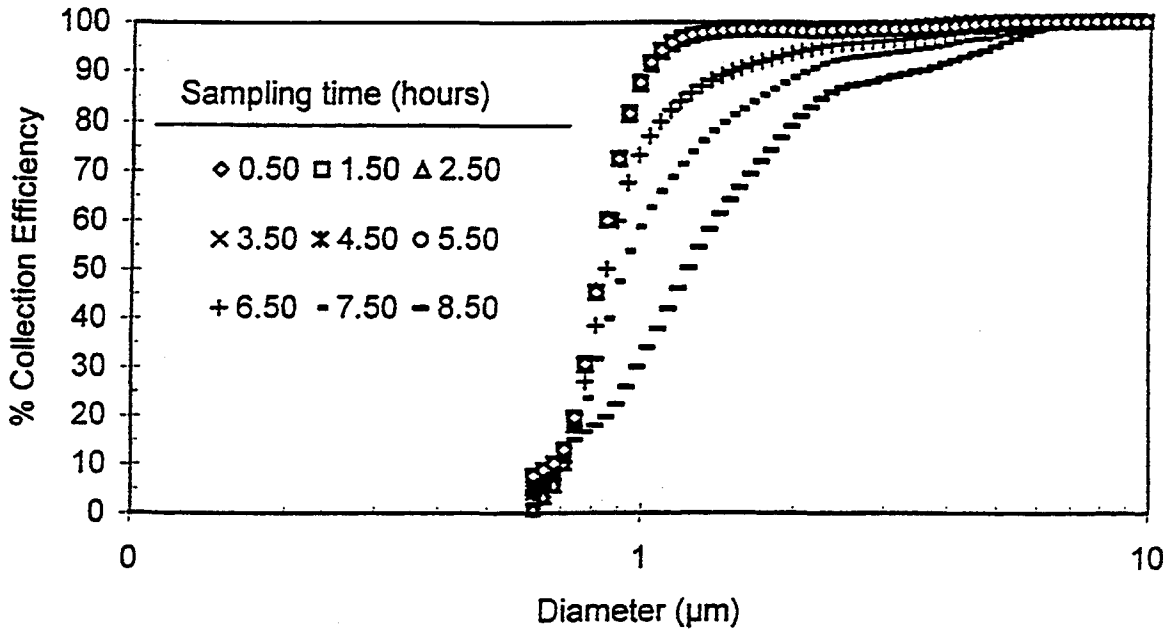


Figure 8: The collection efficiency curve for different sampling times from 0.50 to 8.50 hours

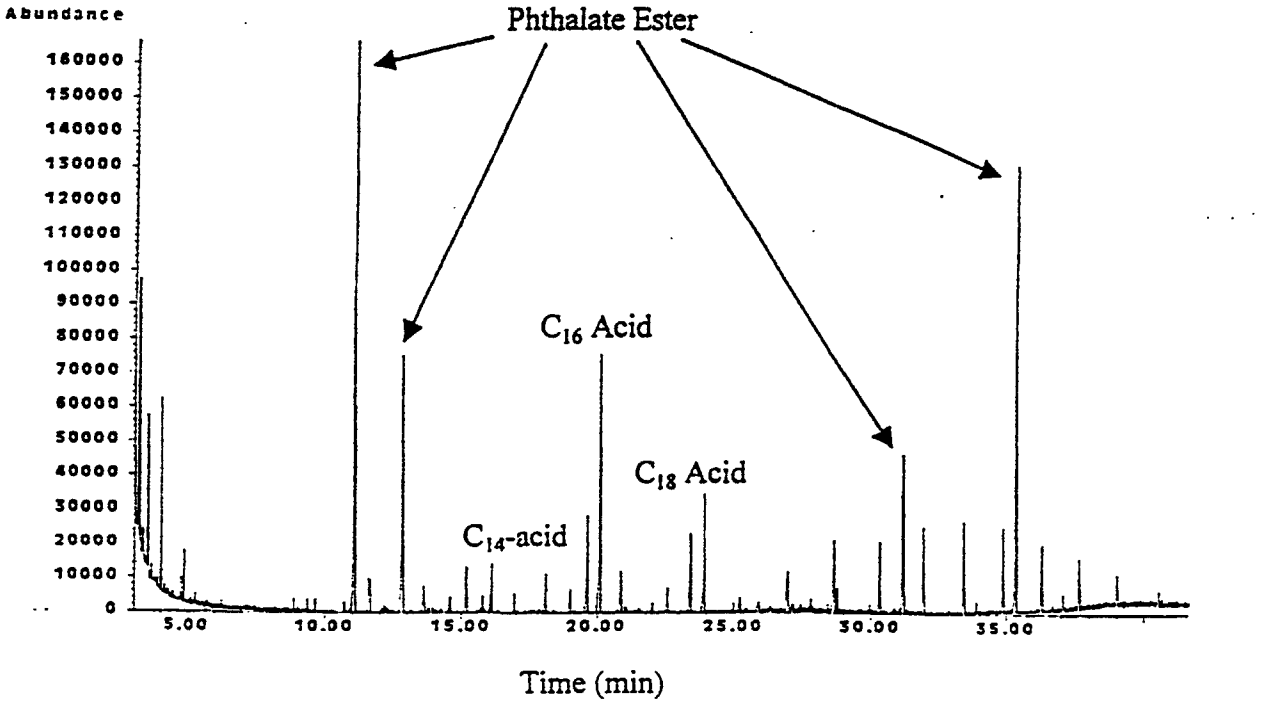


Figure 9: Gas chromatogram of polyurethane foam organic extract

Table 1: Concentration of sulfate measured with Harvard Impactors and HVLI at different S/W ratios

Sulfate Concentration ($\mu gr/m^3$)			
S/W Ratio	**Harvard Impactor (III)**	**High Volume Low ut-off Impactor (HVLI**	**HVLI/III Ratio**
2.31	5.36	3.52	0.66
3.08	2.98	2.56	0.86
S/W Ratio	**Harvard Impactor (III)**	**High Volume Low ut-off Impactor (HVLI**	**HVLI/III Ratio**
3.08	1.566	1.380	0.88
3.08	2.982	2.961	0.99
3.08	2.975	2.861	0.96

A NEW GENERATION OF PORTABLE COARSE, FINE AND ULTRAFINE PARTICLE CONCENTRATORS FOR USE IN INHALATION TOXICOLOGY

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ABSTRACT

This study presents the development of prototype portable coarse, fine and ultrafine particle concentrators. A single-round nozzle virtual impactor operating at an intake flow of 120 L/min is used to concentrate coarse particles (e.g., 2.5-10 μm) by a factor up to 40 depending on the minor flow rate. Fine and ultrafine particles are concentrated by first growing to super-micrometer sizes via supersaturation. This is accomplished by first drawing these particles over a pool of warm, deionized, distilled water to achieve saturation and then through a condenser that allows the particles to grow to super-micrometer size, followed by concentration in a virtual impactor. After concentration, particles are returned back to their original size distribution and relative humidity by removing excess moisture in a diffusion drier. The performance of these concentrators was evaluated using generated monodisperse particles as well as ambient air particles. Average concentration enrichment factors were 9.5, 20 and 37 for a minor flow of 12, 6, and 3 L/min, respectively. The average concentration enrichment based on particulate sulfate and nitrate was by a factor of 20 and 22.6, respectively. The HEADS sampler was used as the reference sampler. The enrichment values based on particulate nitrate indicate that no nitrate loss occurs during particle concentration enrichment. The concentration of particulate elemental (EC) and organic carbon (OC) was also evaluated, using the MOUDI as a reference sampler. The average concentration enrichment factors obtained for EC and OC were 20.4 and 21.6, respectively.

Our experimental results indicated that the enrichment in concentration is not dependent on particle size and chemical composition. Because of their compact size and high concentration efficiency, the concentrators described in this study are inexpensive and portable so can be moved easily to several locations over seasons that differ in PM chemical composition and source profiles.

INTRODUCTION

The National Research Council's Committee on Research Priorities for Airborne Particulate Matter (1998) has recognized appropriately the need for hypotheses-driven studies to investigate mechanisms responsible for adverse effects associated with ambient particulate matter (PM). Epidemiological evidence associating ambient particulate pollution with adverse health effects in humans is extensive (American Thoracic Society, 1996; Environmental Protection Agency, 1996). Nevertheless, fundamental uncertainty and disagreement persist regarding what physical and chemical properties of particles (or unidentified confounding environmental influences) influence health risks, what pathophysiological mechanisms are operative, and what air quality regulations should be adopted to deal with the health risks (Vedal, 1997). This lack of understanding reflects an inability of controlled laboratory investigations to detect effects of low levels of artificially generated particulates, which might support the epidemiological findings.

The recent development of ambient Particle Concentrators (Sioutas et al. 1995; Sioutas et al., 1997; Gordon et al., 1999) has made it possible to perform laboratory exposures with "real-life" ambient aerosols at increased (but still environmentally realistic) concentrations. Initial results suggest greatly increased toxic responses (as compared to these with artificial particles) and suggest that this type of exposure system may provide a useful method for assessing the health effects of ambient particles and for identifying specific risk factors and the means of controlling them (Godleski et al., 1996; Clarke et al., 1999). Current North American toxicity studies involving particle concentrators are being conducted in the Northeast, where the primary constituents of $PM_{2.5}$ are sulfate and organics (Spengler and Thurston, 1983; Burton et al., 1996). Similar studies in the West Coast of the U.S. have been initiated very recently and are rather limited in examining the effects of particles in the size range of 0.1-2.5 μm without targeting specific constituents of ambient PM.

Nevertheless, the currently available concentrators focus mainly on concentrating the accumulation mode of ambient PM (e.g., $PM_{2.5}$ without its ultrafine component), they are bulky, hence not easily transportable, and the concentration enrichment depends on particle size, with larger particles of the

accumulation mode being concentrated more effectively than smaller particles (Sioutas et al., 1997; Gordon et al., 1999).

Particle size and composition are two very important parameters in determining particle toxicity. There is a great need for PM toxicity studies that target specific chemical and/or physical PM properties, in their "real-life" state and at realistic levels. Such data are needed to address many of the most important air pollution-related health problems in the U.S., including non-cancer health effects, asthma, respiratory and cardio-pulmonary disease, and the role of particulate matter in human mortality.

The work presented in this paper discusses the development of a new generation of recently developed portable particle concentrators. These technologies, known as the California Particle Concentrators, maintain the concentrated particles in an airborne state and supply them to exposure chambers for human or laboratory animal inhalation studies. The Concentrators presented in this paper represent an extension of a prototype Ultrafine Concentrator developed by Sioutas et al (1999). In that system, ultrafine PM was first grown through condensational supersaturation to super-micrometer droplets, concentrated by means of a 1.5 μm virtual impactor and returned to its original size by passing through a diffusion dryer. The study by Sioutas et al (1999) focused on optimizing the design and operating parameters of that system, such as the saturator and condenser temperatures, to yield maximum obtainable concentrations of ultrafine particles. A successful pilot study utilizing a prototype Ultrafine Particle Concentrator to expose aged rats to selected components of ambient ultrafine particles has been completed (Kleinman et al., 1998). The study demonstrated significant cardiophysiological changes in 24-month old rats after exposure to ammonium nitrate and carbon particles having a 90 nm count median diameter. The observed changes were in the direction of those observed in humans with shock; i.e. depression of heart rate, blood pressure and blood delivery by the heart.

In this paper we discuss how this technology was extended to concentrate particles in the diameter range of 0.01-10 μm. The enrichment in concentration is determined experimentally as a function of particle size using monodisperse as well as polydisperse aerosols. In addition, detailed chemical characterization of the ambient and concentrated aerosols was performed. Comparisons between the mass, sulfate, nitrate, elemental and organic carbon concentrations of ambient and concentrated PM-2.5 aerosols are presented and discussed in detail.

Along with separating the particles from the majority of the air mass, the California Concentrators are capable of concentrating particles of discrete size groups. These groups could be Ultrafine Particles (<0.1μm), which are freshly generated particles, such as those generated by combustion, Fine Particles of any size sub-range between 0-2.5 μm and Coarse (>2.5 μm) particles. Due to their compact size and high concentration efficiency, these Concentrators are portable and will be deployed to several locations in California (including the first California Supersite at Fresno), over seasons that differ in chemical composition, source profiles and atmospheric chemistry. Thus, specific size ranges and chemical characteristics of concentrated ambient PM will serve as test aerosol to conduct specific hypotheses-driven animal inhalation toxicity studies.

METHODS

Description of the Coarse Particle Concentrator (CPC)

Particles in the Coarse Particle Concentrator (CPC) are drawn at 120 L/min through a 2-cm diameter inlet tube. A 0.8 cm ring, coated with silica grease, is inserted to the inlet to remove particles larger than approximately 10 μm. The design of this ring has been based on the experimental and numerical work by Muyshondt et al (1996) and Chen and Pui (1995) on particle deposition in abrupt (i.e., 90 ° angle) pipe contractions. The relationship between the fraction of particles depositing on the walls of the contracted part and particle aerodynamic diameter resembles that of conventional impactors. Particle deposition on the contraction can be predicted by means of the product $St(1- A_o/ A_i)$, where St is a modified Stokes number, defined as:

$$St = \frac{\rho_p U_i d_p^2 C_p}{9\mu d_o} \qquad (1)$$

where d_p, ρ_p, C_p are the particle diameter, density and slip correction, μ is the air viscosity, U_i is the velocity at the inlet of the contraction and d_o is the diameter of the contraction. A_o and A_i are the areas of

the ring and the inlet tube, respectively. The above dimensions of the contraction (e.g., ring) were chosen to yield 50% removal efficiency of 10 μm particles at a flow rate of 120L/min through the ring.

The CPC is a single-stage, round-jet nozzle virtual impactor (Figure 1a) with an acceleration nozzle diameter of 0.37cm and collection nozzle diameter of 0.56 cm. The virtual impactor has been designed to have a theoretical 50% collection efficiency cutpoint at about 1.5 μm when operating at an intake flow rate of 120 L/min. Depending on the desirable enrichment factor, the minor flow could vary from 3-12 L/min, resulting in concentration enrichment by a factor of 40 to 10, respectively.

The CPC was characterized in laboratory experiments using monodisperse fluorescent particles in the size range of 0.7-9 μm in aerodynamic diameter. Results from the characterization of the virtual impactor are shown in Figure 1b at three different minor flow rates, 3, 6 and 12 L/min, respectively. For particles having aerodynamic diameters in the range of 3 to 9 μm, the enrichment value is about 9, 20 and 36 (e.g., very close to the ideal enrichment values, defined as the ratio of the total-to-minor flow rate) and practically independent of particle size.

The CPC is also a component of the Fine and Ultrafine PM Concentrators described below, serving as the concentrator for the grown particles by super-saturation.

Description of the Fine Plus Ultrafine Particle Concentrator (F+UFPC)

This Concentrator is an extension of the prototype Ultrafine Concentrator described in detail elsewhere (Sioutas et al., 1999), and similar to the CPC, it operates at an intake flow rate of 120 L/min. Briefly, the aerosol is passed over a pool of warm deionized distilled water to achieve saturation. Subsequently, it is drawn through a condenser that allows the particles to grow to super-micrometer size. Particle enrichment occurs by drawing the grown particles through the Coarse Particle Concentrator (described above). The concentrated particles from the minor flow of the virtual impactor pass through a diffusion dryer to remove the excess vapor and return to their original size and relative humidity (Figure 2). The effect of parameters including vapor temperature in the saturator and minor-to- total flow ratio was investigated in order to determine an optimal configuration that concentrates ultrafine (e.g., 0.01-0.1 μm) particles with high collection efficiency, low losses and high concentration enrichment factor. Our experimental results identified saturation of the ultrafine aerosols at 35 °C and cooling to 25 °C as the optimum temperatures for operation of the Ultrafine Particle Concentrator. Lower temperatures either do not concentrate, or concentrate ultrafine particles less efficiently. Increasing the saturation temperature to 40 °C and cooling to 31 °C does not significantly improve the concentration enrichment. All of these experiments are described in detail by Sioutas et al. (1999).

Design and Evaluation of the Diffusion Dryers

The concentrated droplets are drawn through a diffusion dryer that removes excess moisture so that the grown particles return to their original size. The diffusion dryer consists of a cylindrical screen, 1.8 cm in diameter, placed in the center of a glass tube, 6 cm in diameter. Both glass tube and screen are 20 cm long. The inner space between the two tubes is filled with a desiccant to remove the excess water in the air stream.

Three different materials were tested as the desiccant used to dry the grown liquid particles:

1. Drierite: Anhydrous Calcium Sulfate ($CaSO_4$) with 3% cobalt chloride ($CoCl_2$) as indicator, 8 mesh; (W.A. Hammond Drierite Company LTD. Xenia, OH)
2. Desiccant; 99.6% SiO_2 as 100% indicating coat, 6-8 mesh (EM Industries, Inc. Gibbstown, NY)
3. Silica Gel; 100% plain SiO_2 6-12 mesh (Eagle Chemical CO., INC., Mobile, AL)

The purpose of these tests was to investigate whether these desiccants would reduce the aerosol RH at a given flow rate from 100% to less than 40% (e.g., crystallization point of most hygroscopic salts) to ensure that the concentrated fine or ultrafine PM is dry. Relative humidity was measured immediately downstream of the dryer with a temperature/relative humidity probe (Cole-Parmer® Model 37960, Cole-Parmer® Instruments Co., Vernon Hills, IL). Tests were conducted at an intake flow of 120 L/min and at two different minor flow rates (6 and 12 L/min, respectively). Experiments lasted for a period of 6 hours. Results from the diffusion dryer tests are shown in Figures 3a and 3b. Figure 3a shows that after the first hour of operation at 6 L/min, the Drierite material becomes saturated and cannot further remove any excess vapor. The RH of the concentrated aerosol increases from about 50% to 90% within 2 hours of operation. Both the EM SiO_2 as well as the silica gel desiccants maintain their vapor removal efficiency

over a 6-hour sampling period, with the silica gel reducing RH more effectively (e.g., to less than 40% over the entire 6-hour period) than the EM desiccant.

Figure 3b shows the vapor removal efficiency of the silica gel as a function of flow rate trough the diffusion dryer. As expected, the RH of the dried aerosol is lower at 6L/min (38-40%) than that at 12 L/min (55-60%) due to the longer time available for vapor diffusion to the dryer walls. Regardless of the minor flow rate, our tests identified silica gel as the optimum desiccant, and the rest of the F+UFPC evaluation was conducted using this material in the diffusion dryer.

Laboratory Evaluation of the Fine Plus Ultrafine Concentrator (F+UFPC)

The experimental setup for the characterization of the Fine Plus Ultrafine Particle Concentrator is shown in Figure 2. Monodisperse aerosols were generated by atomizing suspensions of ultrafine and fine particles using a constant output HEART nebulizer (VORTRAN Medical Technology, Inc., Sacramento, CA). Different types of suspensions were used, including monodisperse PSL fluorescent latex particles (size range 0.05-5 μm; Polysciences Inc., Warrington, PA) as well as monodisperse silica beads (particle size range 0.15 to 0.9 μm; Bangs Laboratories, Inc., Carmel, IN). Finally, ultrafine indoor air particles were used as the test aerosol. The generated PSL ultrafine aerosols were dried and neutralized and were drawn though the F+UFPC at 120 L/min. The dilution air in this series of tests was drawn through a HEPA filter to ensure that only particles generated by atomizing deionized water are counted by the CPC. The aerosol was mixed and saturated with water vapor at 35 °C, and subsequently drawn through the condenser. The temperature of the aerosol exiting the condenser was about 24 (± 1)°C.

The grown droplets were subsequently drawn through the Coarse Concentrator. Three different minor flow rates were tested, 3, 6 and 12 L/min, respectively (corresponding to theoretical enrichment factors of 40, 20 and 10, respectively). The TSI Condensation Particle Counter (CPC 3022, TSI Inc., St. Paul, MN) was connected immediately upstream of the saturator and downstream of the diffusion dryer (as shown in Figure 2) to measure the number concentrations of the original and concentrated aerosols.

Evaluation of the Fine Plus Ultrafine Concentrator Using Indoor Aerosols

In addition to laboratory experiments, the performance of the F+UFPC was evaluated in a field study, conducted indoors in the Aerosol Laboratory of the University of Southern California. The mass, sulfate and nitrate PM-2.5 indoor concentrations of the F+UFPC were compared to those measured by means of a collocated Harvard/EPA Annular Denuder Sampler (HEADS; Koutrakis et al., 1989). The HEADS operated at a flow rate of 10 L/min, and consisted of a conventional impactor inlet with a 50% cutpoint of 2.5 μm in aerodynamic diameter, a sodium carbonate-coated denuder to remove nitric acid from the air sample, followed by a 4.7-cm Teflon membrane to collect particles, and a sodium carbonate-coated glass fiber filter to collect nitric acid that volatilized from the collected PM on the Teflon filter.

A 4.7 cm Teflon filter (2 μm pore, Gelman, Science, Ann Arbor, MI) was placed immediately downstream of the diffusion dryer of the F+UFPC, which operated at a total flow of 120 L/min, of which 6 L/min was drawn as the minor flow. The Teflon filters were weighed before and after each field tests in a Mettler 5 Microbalance (MT 5, Mettler-Toledo Inc., Hightstown, NJ) under controlled relative humidity (e.g. 40-45%) and temperature (e.g., 22-24 degrees C) conditions, in order to determine the mass concentrations. Filters were weighed immediately at the end of each experiment as well as after a 24-hour equilibration time period. Laboratory and field blanks were used for quality assurance. Filters and filter blanks were weighed twice in order to increase precision. In case of a difference of more than 2 μg between consecutive weightings, a filter was weighed for a third time. The Teflon filters of the F+UFPC and HEADS as well as the glass fiber HEADS filter were then analyzed by means of ion chromatography to determine the concentrations of particulate sulfate and nitrate.

In addition to these tests, the indoor elemental and organic carbon (EC/OC) concentrations of the F+UFPC were compared to those determined using a modified Microorifice Uniform Deposit Impactor (MOUDI, MSP Corporation, Minneapolis, MN), described in more detail by Marple et al (1991). The MOUDI operates at 30 L/min and classifies particles in the following size intervals: < 0.1, 0.1-0.18, 0.18-0.3, 0.3-0.56, 0.56-1.0, 1.0-1.8, 1.8-3.2, 3.2-5.0, and 5.0-10 μm. For the purposes of our experiments, we only used the first two stages of the MOUDI and all particles smaller than 3.2 μm in aerodynamic

diameter were collected on a 3.7-cm diameter quartz filter (Pallflex Corp., Putnam, CT). A 4.7-cm diameter quartz filter (Pallflex Corp., Putnam, CT) was connected to the minor flow of the F+UFPC, immediately downstream of the diffusion dryer. The mass concentrations measured by the MOUDI and F+UFPC were determined gravimetrically using the same process described above. The EC/OC concentrations were determined by thermo-analysis. An aliquot of approximately 0.2 cm^2 from each filter was placed in a platinum boat containing MnO_2. The sample was acidified with a dilution of HCl and heated to 115 degrees C to remove the water and CO_2 (from sample carbonates). The boat was then advanced into a dual zone furnace where MnO_2 oxidized OC in the sample at 550 degrees C and EC at 850 degrees C. The CO_2 formed was converted to CH_4 for detection by a Flame Ionization Detector (FID). The analytical method is described in detail by Fung (1990).

The MOUDI instead of the HEADS was used to measure EC/OC concentrations because of its higher sampling flow rate, which allowed us to reduce the sampling time to 4-5 hours. The F+UFPC was used without any preselective inlet to remove particles above 2.5 or 3.2 μm. As it will be shown in the Results and Discussion section of this paper, particles larger than 3 μm are not concentrated by the F+UFPC because inertial deposition mechanisms remove these particles prior to reaching the virtual impactor.

RESULTS AND DISCUSSION

Laboratory Tests

Results from the laboratory evaluation of the Fine Plus Ultrafine Particle Concentrator are summarized in Figure 4 at three different minor flow rates (e.g., 3, 6 and 12 L/min). In all configurations, the major flow rate is adjusted to yield a total intake flow of 120 L/min. Hence, the maximum obtainable concentration enrichment factors for each configuration are 40, 20, and 10, respectively.

The concentration enrichment factors as a function of particle size, shown in Figure 4, are based on particle number concentrations measured upstream and downstream of the F+UFPC, and have been obtained using monodisperse aerosols in the size rage of 0.05-5 μm, except of the data corresponding to 0.025 μm particles. The enrichment values corresponding to 0.025 μm were obtained for indoor air particles, measured again by the Condensation Particle Counter (CPC 3022, TSI inc., St. Paul, MN). The count-based size distribution of ambient or indoor aerosols is dominated by particles smaller than 0.05 μm, peaking at around 0.02-0.035 μm (Whitby and Svendrup, 1980). We chose the size of 0.025 μm as an approximate number median diameter representing indoor aerosols, in order to include all of our experimental results in one graph.

Figure 4 shows clearly that the concentration enrichment corresponding to a minor flow rate of 3, 6 or 12 L/min does not depend on particle size for all particles smaller than 2 μm. The average concentration enrichment for ultrafine indoor air as well as monodisperse 0.05-2 μm PSL particles is by a factor of 9.5, 20 and 37, when the virtual impactor operates at a minor flow of 3, 6 and 12 L/min, respectively.

These concentration enrichment values are essentially identical to the maximum obtainable concentration factors. An important implication of these results is that no particle coagulation occurs during the concentration enrichment process. If any coagulation had occurred, the measured number concentrations downstream of the diffusion dryer (hence the enrichment factors) would have been substantially lower than the maximum obtainable values.

The concentration enrichment values decrease rapidly to 2 or less for particles larger than 3 μm in diameter. Inertial deposition mechanisms (most likely impingement on the surface of the water in the saturator) remove these particles before they reach the 1.5 μm cutpoint virtual impactor, where they would have been concentrated by the same factor as the rest of the aerosols. This is a desirable (albeit fortuitous) result, as it makes the use of a preselective PM-2.5 inlet to remove these particles from the air sample unnecessary.

Indoor tests

Results from the comparisons between the PM-2.5 mass, sulfate, nitrate, elemental and organic carbon concentrations determined using the F+UFPC and those using the HEADS or MOUDI are summarized in Tables 1-4, respectively. The total flow of the F+UFPC is 120 L/min, of which 6 L/min are drawn through

the collection nozzle as a minor flow, ideally containing all of the particles smaller than 2.5 μm, enriched in concentration by a factor of 20.

The first two columns in Table 1 show the PM-2.5 mass concentrations measured indoors by the HEADS or MOUDI (depending on the type of filter used) and the F+UFPC. The third column shows the values of the collection efficiency of the F+UFPC, defined as the ratio of the minor flow concentration of the F+UFPC to that of the HEADS or MOUDI, divided by 20 (i.e. the ideal enrichment factor). We employed this term to obtain an estimate of the fraction of the total particulate mass that was actually collected by the minor flow of the F+UFPC and thus account for particle losses (a similar definition of the collection efficiency of a concentrator has been employed by Sioutas et al., 1995; Sioutas et al., 1997 and Gordon et al., 1999). As the results in Table 1 suggest, a virtually perfect mass balance was obtained between the HEADS or MOUDI and the F+UFPC. The average collection efficiency of the F+UFPC was 1.01 (± 0.11), and the resulting concentration enrichment factor was 20.04 (± 2.2), both very close to the ideal values. It should be noted that there was no detectable difference (e.g., less than 4 μg) between the weights of the Teflon filter of the minor flow of the F+UFPC immediately at the end of each test and after the 24-hour equilibration period. This is another indication of complete water vapor removal by passing the particles through the diffusion dryer.

Table 2 shows the PM-2.5 concentrations obtained using the HEADS and F+UFPC. Similarly to the results based on mass concentrations, excellent agreement was obtained between the two samplers, with the average concentration enrichment factor being 20.04 (±3.6) and the average collection efficiency of the F+UFPC being 1.00 (± 0.18).

Table 3 shows the PM-2.5 nitrate concentrations measured by the HEADS and F+UFPC. The reported HEADS nitrate concentrations represent the sum of nitrate collected on both Teflon and glass fiber filters. The collection efficiency of the F+UFPC was on the average 1.13 (± 0.18), whereas the obtained concentration enrichment based on nitrate was 22.5 (±3.7). The somewhat higher efficiency and enrichment values than the ideal may be due to some uncertainty in the nitrate levels measured by means of the HEADS. This was due to the overall low nitrate levels that were measured indoors (e.g., less than 15% of the total mass concentrations), a rather surprising result, given the high particulate outdoor nitrate levels generally observed in Los Angeles. As the sampling flow rate of the F+UFPC was 120 L/min (e.g., 12 times higher than that of the HEADS), the F+UFPC nitrate concentration data are more robust. The generally low nitrate content of the indoor aerosol also explains the reason for obtaining a perfect mass balance between HEADS and F+UFPC, although only the Teflon filter of the HEADS was weighed. While some volatilization loss of ammonium nitrate from the Teflon filter of the HEADS sampler occurred (ranging from about 10% to as high as 55%), the very low nitrate levels did not contribute significantly to the overall mass concentrations and therefore did not affect the HEADS-to-F+UFPC comparison based on mass.

The results of Table 3 show conclusively that concentration enrichment though the F+UFPC occurs without any measurable loss of particulate nitrate, despite heating and saturation of the aerosol to about 35 °C. Ammonium nitrate dissociates to ammonia and nitric acid, with its dissociation constant increasing exponentially with temperature. However, the dissociation constant decreases sharply as the relative humidity (RH) exceeds 90-95% (Stelson and Seinfeld, 1982). For example, even at 50°C and at RH=95%, the dissociation constant of ammonium nitrate is approximately 7 ppb^2, which is the value of the dissociation constant at 18°C. Therefore, despite the increase in the aerosol temperature (which would have increased exponentially the value of the dissociation constant), saturation of the aerosol seems to prevent nitrate losses due to volatilization.

Results from the comparisons between the indoor PM-2.5 elemental and organic carbon concentrations determined using the F+UFPC and those by means of the MOUDI are summarized in Table 4. Similar to the results based on mass, sulfate and nitrate concentrations, excellent agreement was obtained between the F+UFPC and MOUDI EC concentrations, with the average concentration enrichment factor being 20.4 (±3.3) and the average collection efficiency of the F+UFPC being 1.02 (± 0.16). Good agreement was also obtained between the F+UFPC and MOUDI organic carbon (OC) concentrations. The overall concentration enrichment factor was 21.6 (± 6.4) and the average collection efficiency of the F+UFPC was 1.08 (± 0.32). It should be noted that the OC concentrations determined by means of either of the two samplers may be overestimated due to adsorption of gas-phase OC on the quartz filters or underestimated due to evaporation of volatile organic compounds from the quartz filters during sampling (Eatough et al., 1993). Positive sampling artifacts (i.e., adsorption) should be more

pronounced in the MOUDI than the F+UFPC because of the higher MOUDI flow rate (i.e., 30 L/min) compared to that of the minor flow of the F+UFPC (i.e., 6 L/min). Moreover, negative sampling artifacts (i.e., volatilization) would also be more pronounced in the MOUDI than the F+UFPC data. This is because of the higher flow rate and smaller size filter of MOUDI (3.7 cm) compared to those of the F+UFPC, both of which result in a higher pressure drop across its filter. The enrichment in concentration would also tend to reduce evaporative losses from the quartz filter of the F+UFPC. Recent studies showed that that nitrate losses from Teflon filter media could be virtually eliminated by placing the sampler downstream of a particle concentrator (Chang et al., 1999). The uncertainties introduced by the aforementioned artifacts may explain the somewhat higher standard deviation value obtained for the OC-based sampler comparison compared to those for the other species. The good overall agreement between the F+UFPC and MOUDI, however, suggests that these artifacts either negate each other or may not be significant under the specific conditions at which the experiments were conducted.

CONCLUSIONS

This study presented the development of prototype portable Concentrators, capable of enriching the concentration of particles in the range of 0-10 μm by a factor up to 40, depending on the output flow rate. These systems are compact in size, so that they can be easily transported in various locations in order to conduct primarily animal inhalation studies to concentrated PM, as these studies require lower output flow rates. The modular design of these concentrators, however, makes them readily adaptable to accommodate higher output flow rates that are desirable in conducting human exposure studies. This can be easily achieved by placing several single-nozzle virtual impactors in parallel.

Coarse PM (2.5-10 μm) are concentrated in a single-stage, round nozzle virtual impactor, operating at an intake flow of 120 L/min. Fine and ultrafine PM (F+UFP, smaller than 2.5 μm) are concentrated by first removing larger particles by impaction and then growing the remaining particles via supersaturation to super-micrometer droplets. The droplets are then concentrated using the same Coarse Particle Concentrator. Concentrated ultrafine and fine particles are returned to their original size by passing through a diffusion dryer using silica gel.

The experimental characterization of the F+UFPC showed clearly that the concentration enrichment does not depend on particle size or chemical composition. Volatile species such as ammonium nitrate are preserved through the concentration enrichment process under the laboratory conditions used in this study. Excellent agreement was found between mass, sulfate and nitrate concentrations measured by means of the F+UFPC and a collocated HEADS. Very good agreement was also found between the elemental and organic carbon concentrations determined using the F+UFPC and the MOUDI. Furthermore, the concentration enrichment based on particle counts showed clearly that no particle coagulation occurs during the enrichment process, for any of the three minor-to-total flow configurations tested.

The ability of the F+UFPC to enrich the concentrations of all particles in the fine mode (including its ultrafine particle component) enables inhalation toxicologists to conduct exposures to any selected sub-range of PM-2.5. For example, previous studies in California showed the presence of two sub-modes within the accumulation mode of ambient PM (Hering et al., 1997; John et al., 1990); one mode peaks at around 0.2 μm (consisting mainly of gas-to-particle reaction products, such as carbonaceous PM) and the other peaks at about 0.7 μm (mainly associated with hygroscopic PM such as ammonium sulfate and nitrate). Both modes have a geometric standard deviation of about 2 (John et al. 1990). By placing a conventional impactor upstream of the F+UFPC having a 0.3 μm cutpoint, inhalation studies could be conducted to ultrafine PM plus the elemental and organic carbon content of the accumulation mode, but without the majority of its sulfate and nitrate constituents. Similarly, a 0.15 μm conventional impactor would remove all but ultrafine PM from the air-sample, thereby resulting in an Ultrafine Particle Concentrator.

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TABLE 1. Comparisons Between the Mass Concentrations Determined Using the F+UFPC and the HEADS or MOUDI Using Indoor Air as the test Aerosol.

HEADS or MOUDI ($\mu g/m^3$)	F+UFPC ($\mu g/m^3$)	Collection Efficiency F+UFPC	Enrichment factor
		HEADS Experiments	
17.8	351.1	0.99	19.8
14.0	302.1	1.08	21.5
13.7	210.0	0.77	15.3
23.7	484.4	1.02	20.4
17.8	347.8	0.98	19.6
17.8	335.6	0.94	18.9
10.3	264.4	1.28	25.5
19.2	422.2	1.1	21.9
10.8	235.0	1.08	21.7
16.3	278.9	0.86	17.1
9.6	190.0	0.99	19.7
		MOUDI experiments	
10.93	235.20	1.08	21.5
16.1	334.4	1.04	20.7
18.3	324.4	0.88	17.7
25.9	496.7	0.96	19.1
25.5	420.0	0.82	16.4
33.9	666.7	0.98	19.7
19.4	398.9	1.03	20.5
55.6	1145.6	1.03	20.6
32.4	685.6	1.06	21.15
42.0	922.2	1.1	21.94
Average		**1.00**	**20.04**
S.D.		**0.11**	**2.22**

TABLE 2. Comparisons between Sulfate Concentrations Determined Using the F+UFPC and the HEADS Using Indoor Air as the test Aerosol.

HEADS ($\mu g/m^3$)	F+UFPC ($\mu g/m^3$)	Collection Efficiency F+UFPC	Enrichment factor
2.1	39.0	0.92	18.47
2.1	42.11	1.00	20.00
1.7	33.22	0.97	19.5
0.70	19.56	1.38	27.79
3.9	66.78	0.84	16.85
0.81	17.89	1.09	21.95
0.66	10.75	0.80	16.13
1.4	27.67	0.98	19.66
2.02	37.04	0.91	18.28
Average		**1.002**	**20.04**
S.D.		**0.18**	**3.62**

TABLE 3. Comparisons between Nitrate Concentrations Determined Using the F+UFPC and the HEADS Using Indoor Air as the test Aerosol.

HEADS ($\mu g/m^3$)	F+UFPC ($\mu g/m^3$)	Collection Efficiency F+UFPC	Enrichment factor
1.1	28.22	1.28	25.65
0.49	14.73	1.5	30.0
0.44	10.88	1.22	24.5
0.55	11.71	1.06	21.2
0.41	7.61	0.95	19.16
0.48	8.78	0.91	18.23
0.62	12.37	0.99	19.80
0.48	11.22	1.16	23.30
0.29	6.33	1.06	21.37
0.45	6.72	0.74	14.93
Average		**1.13**	**22.58**
S.D.		**0.18**	**3.71**

TABLE 4. Comparisons between Elemental and Organic Carbon Concentrations Determined by Means of the F+UFPC and the MOUDI Using Indoor Air as the test Aerosol.

Elemental Carbon				Organic Carbon			
MOUDI ($\mu g/m^3$)	F+UFPC ($\mu g/m^3$)	Collection Efficiency F+UFPC	Enrichment factor	MOUDI ($\mu g/m^3$)	F+UFPC ($\mu g/m^3$)	Collection Efficiency F+UFPC	Enrichmen factor
0.38	7.35	0.95	19.0	5.4	120.1	1.11	22.23
0.77	18.2	1.16	23.4	7.8	228.7	1.42	29.0
0.85	15.9	0.93	18.5	8.3	206.6	1.25	25.02
0.48	12.14	1.25	25.2	6.2	165.1	1.32	26.56
0.55	7.28	0.66	13.20	10.7	76.86	0.36	7.2
0.89	19.00	1.06	21.3	12.2	287.3	1.17	23.48
0.57	14.26	1.2	24.1	9.1	214.0	1.17	23.44
0.84	18.1	1.08	21.6	9.9	259.7	1.30	26.10
0.72	14.2	0.99	19.7	6.6	112.3	0.85	17.0
0.61	10.6	0.87	17.4	6.9	116.1	0.84	16.9
Average		**1.02**	**20.4**			**1.08**	**21.68**
S.D.		**0.16**	**3.28**			**0.32**	**6.43**

Figure 1a. Single-Nozzle Coarse Particle Concentrator

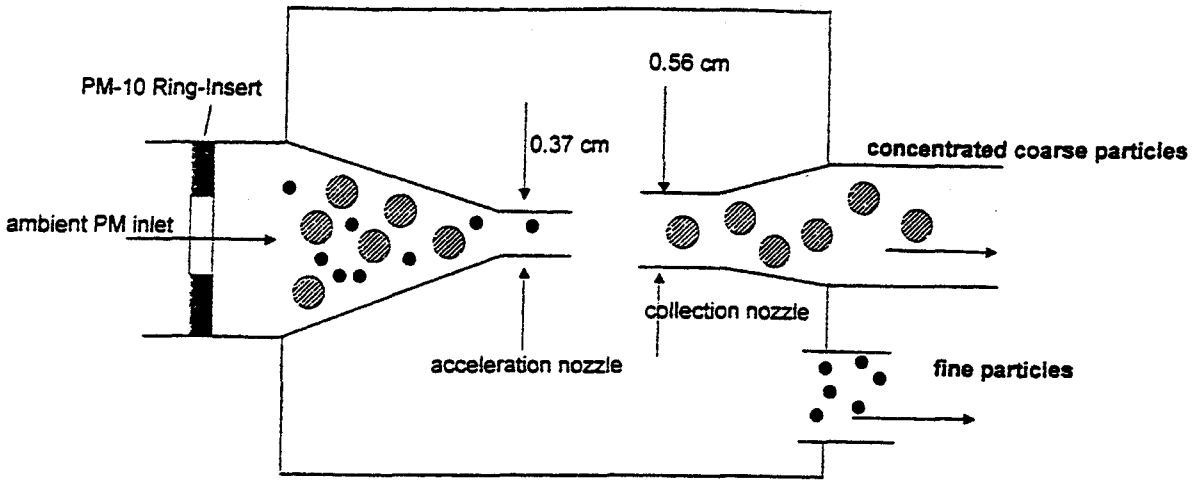
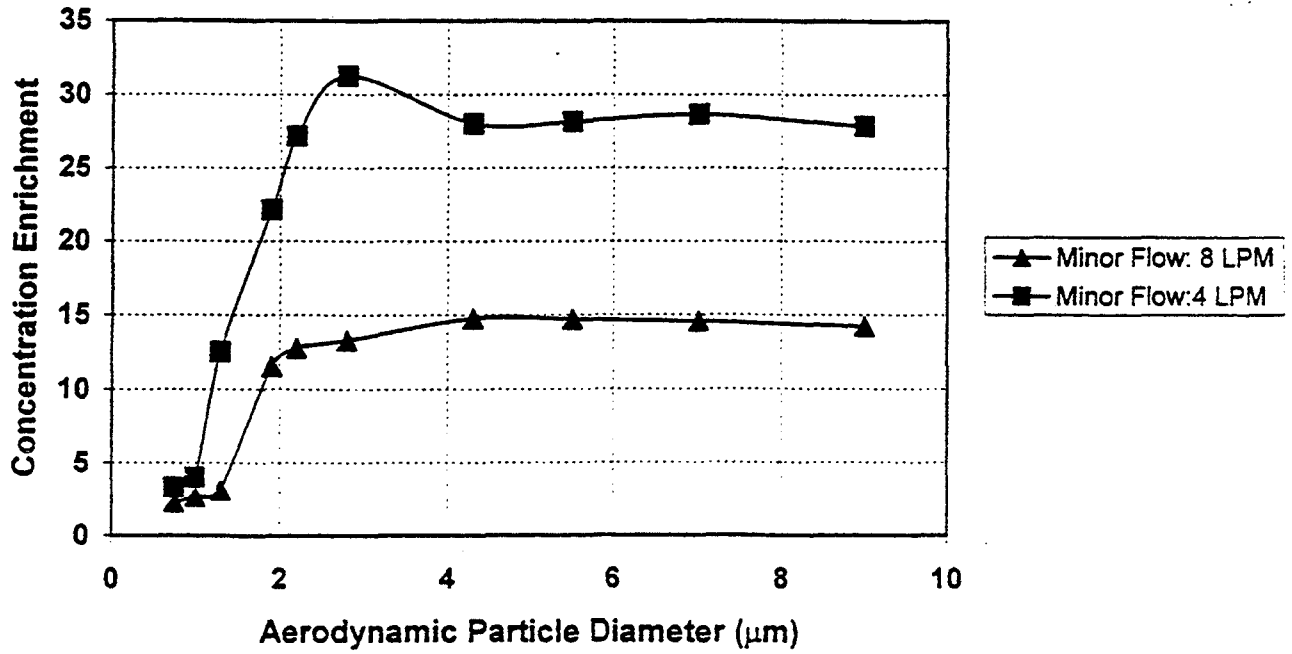


Figure 1b. COARSE PARTICLE CONCENTRATOR
Concentration Enrichment vs Particle Size



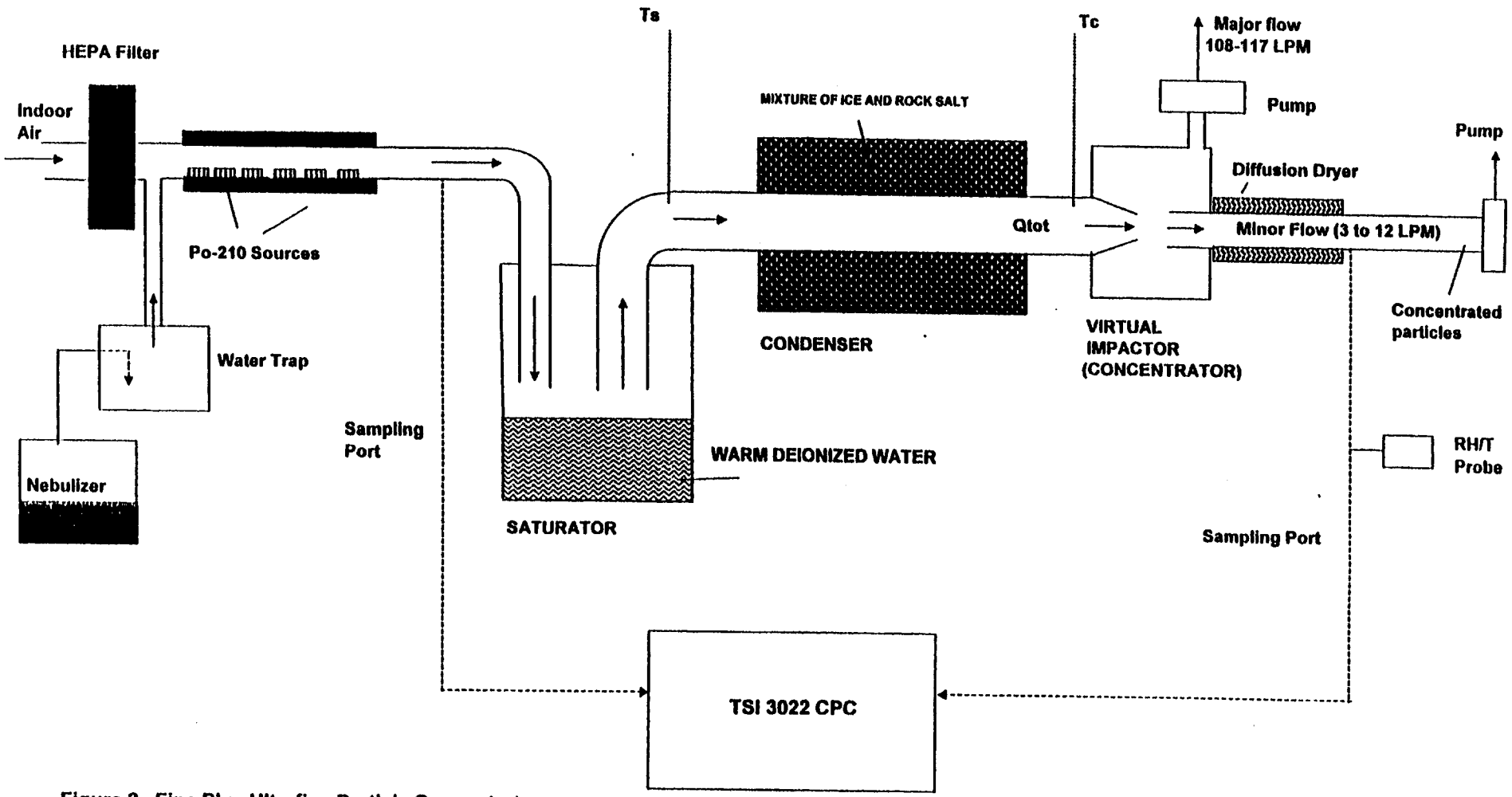


Figure 2. Fine Plus Ultrafine Particle Concentrator

Figure 3a. Performance of various Diffusion Drier materials at 6 LPM.

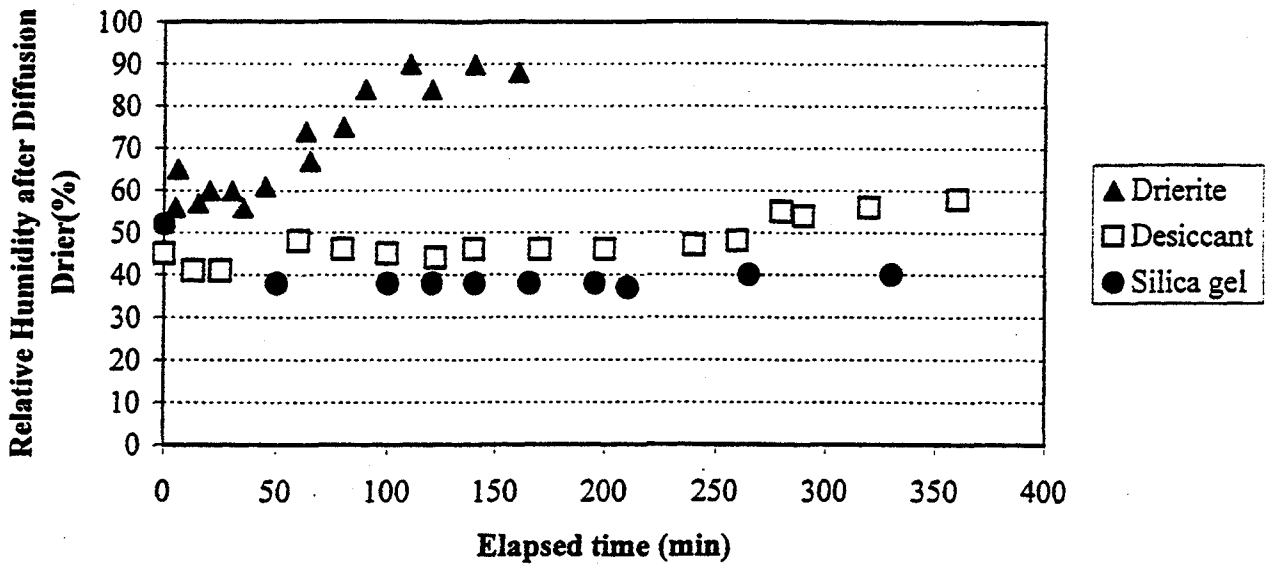


Figure 3b. Performance of Diffusion Drier with silica gel at different minor flow rates

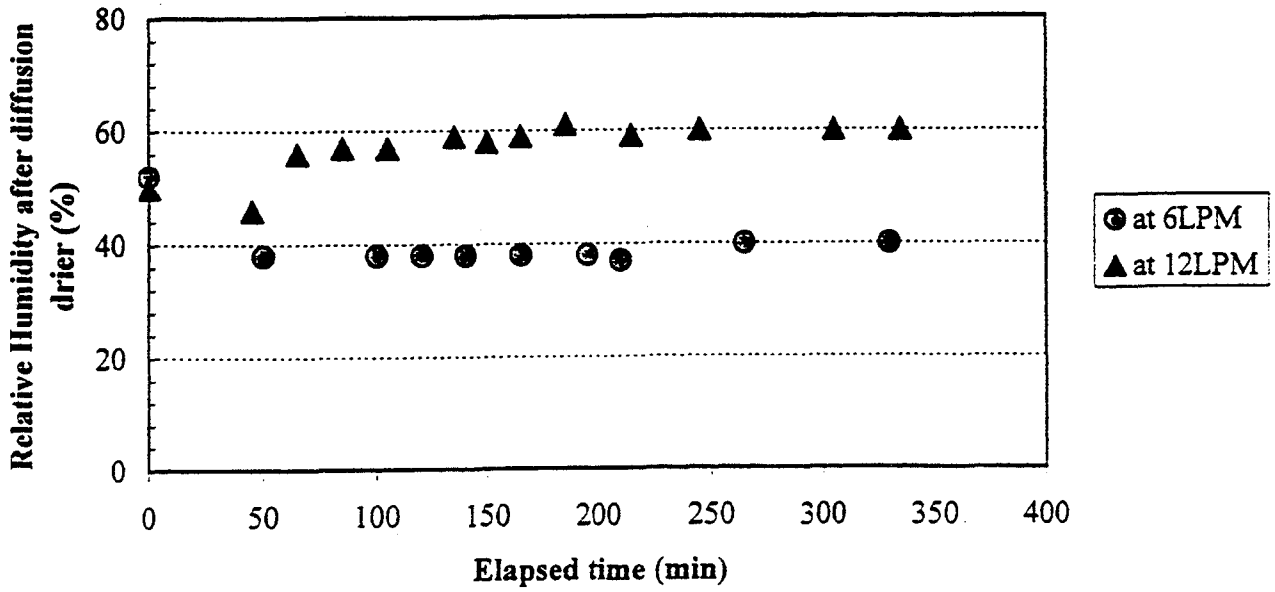
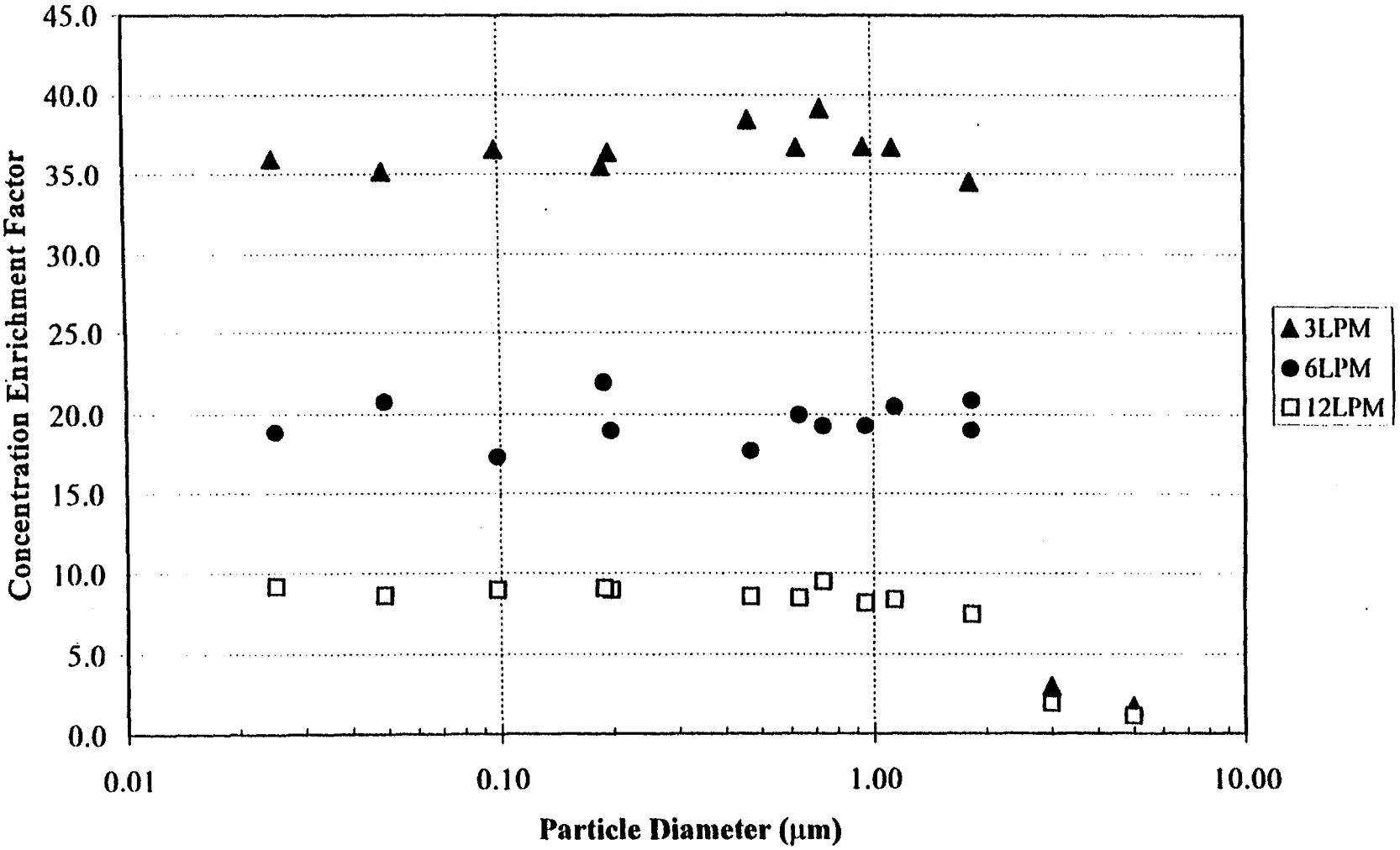


Figure 4. Characterization of the Fine + Ultrafine PM Concentrator Using Monodisperse Aerosols for 3 Minor Flows.
Total Intake Flow: 120 L/min



EXPOSURE ASSESSMENT FOR FINE AND ULTRAFINE PARTICLES IN AMBIENT URBAN AEROSOLS.

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Abstract

Background: Health effects of fine particles have been consistently characterized while the significance of ultrafine particles in quantifying exposures to ambient air pollution and in eliciting health effects remains unclear. We therefore compared available instruments to measure particle size and number distributions in ambient air and used them to characterize ambient air in three European cities.
Studies: 1) intercomparisons of three aerosol spectrometers to compare particle size and number distributions both in ambient air and in the laboratory 2) air pollution monitoring and aerosol spectrometry study in winter 1996/1997 in Germany, Finland and the Netherlands Results: 1) In the ambient side-by-side comparisons, the three aerosol spectrometers were very well comparable in total number concentrations and concentrations of ultrafine (0.01 - 0.1 µm) and accumulation mode (0.1 - 0.5 µm) particles. Number concentration of the coarse fraction (0.5 - 2.5 µm) were less comparable, which, however, added less than 2% to the total number concentration.
2) In the 3-cities winter study 1996/97, there was only a weak correlation between $PM_{2.5}$ and total number concentration or ultrafine number concentration in any of the three cities
Conclusions: Ultrafine particles can be measured reliably in ambient air with the three aerosol spectrometers used. Levels of ultrafine and fine particles are poorly correlated in European cities during the winter season. An ongoing epidemiological study aims at quantifying the effects of ultrafine and fine particles on cardiopulmonary endpoints in patients with coronary artery disease.

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Introduction

The most important air pollutants today in Western Europe, in terms of human health effects, are particulate matter, ozone, and NO_2. In particular, studies published since late 1970's have stressed the importance of thoracic particles (PM_{10}, particles with an aerodynamic diameter below 10 µm), which are associated with cardio-respiratory morbidity, mortality and declines in lung function.

Also the size distribution of particles is of crucial importance, as different size fractions of the particles have different chemical composition and are differentially deposited in the airways and lungs. However, today there is very little data on exposure to fine ($PM_{2.5}$, particles with an aerodynamic diameter below 2.5 µm) and ultrafine particles (particles smaller than 0.1 µm in diameter) in Europe, on the elemental composition of fine particulate matter in ambient air, and their health effects.

The goal of the project "Exposure And Risk Assessment For Fine And Ultrafine Particles In Ambient Air" supported by the European Union is to

1) Compare available aerosol spectrometers to measure continuously concentrations and size distributions of fine and ultrafine particles in urban atmospheres and also to compare them with commonly used particle measurement techniques and

2) improve knowledge of the human exposures in European cities to particulate matter of differing sizes. These results can be used to develop standards for air quality in Europe, for better and more efficient monitoring of air quality, and as a bases for designing control strategies to reduce the health effects associated with exposure to particulate matter in ambient air. The project is composed of three field works in ambient air and one in the laboratory on the comparability of the particle spectrometers and an air pollution monitoring study during winter 1996/97 in three European cities, Erfurt, Germany, and Helsinki, Finland and Alkmaar, the Netherlands.

Methods

Aerosol spectrometers

The German Mobile Aerosol Spectrometer (MAS) was described earlier (Brand et al., 1991,1992; Tuch et al., 1997, 1999). It consists of two different, commercially available, instruments. Particles in the size range from 0.01 µm to 0.5 µm were measured using a differential mobility analyzer (DMA, TSI model 3071) combined with a condensation particle counter (CPC, TSI model 3760). This set will be termed Differential Mobility Particle Sizer (DMPS) in the following. Particles in the size range from 0.1 µm up to 2.5 µm are classified by an optical laser aerosol spectrometer (LAS-X, PMS model LAS-X). To combine the spectral data weekly calibrations were performed by which the optical LAS-X was calibrated in terms of electrical mobility of the ambient aerosol particles (Tuch et al., 1997, 1999).

The Dutch Aerosol Spectrometer (DAS) consisted of two different, commercially available, instruments. Particles in the size range from 0.01 µm to 0.5 µm were measured using a Scanning Mobility Particle Sizer (SMPS, TSI model 3936). Particles in the size range from 0.1 µm up to 2.5 µm were classified by an optical laser aerosol spectrometer (LAS-X, PMS model LAS-X). The performance of this aerosol spectrometer will be described in due course (Khlystov et al., 1999; Mirme et al., 1999).

The Electrical Aerosol Spectrometer (EAS) was developed at the University of Tartu, Tartu, Estonia (Tammet et al., 1992; Mirme. 1994; Kikas et al. 1996; Tuch et al., 1999) and used by the Finnish group. The EAS measures the particle sizes in the range from 10 nm to 10 µm using two analyzers in parallel both being based on the measurement of electrical particle mobility. EAS utilizes unipolar diffusion charging in the size range of 0.01 - 0.5 µm in one analyzer and strong electrical field charging in the size range from 0.3 - 10 µm in the other analyzer, each made up of a series of electrometers determining the charge of particles of equal electrical mobility. Because of the spatial separation of the aerosol particles by the serial electrometers, all charges of all particles provide the entire distribution at the same time.

During the side-by-side intercomparisons each aerosol spectrometer provided an aerosol spectrum every 5-6 minutes. From each particle size distribution the integral particle number concentrations of the total spectrum and integrated particle number concentrations of selected size ranges were calculated. In this study hourly averages of total particle number concentrations ($NC_{0.01-2.5}$) and of particle number concentrations in size ranges 0.01-0.1 µm ($NC_{0.01-0.1}$), 0.1-0.5 µm ($NC_{0.1-0.5}$), and 0.5-2.5µm ($NC_{0.5-2.5}$) were used to characterize the ambient aerosol. An hourly average was considered valid if 66% of the data were available.

Side-by-side intercomparisons of aerosol spectrometers

Ambient aerosols

Three side-by-side intercomparisons of aerosol spectrometers were performed: two intercomparisons in Erfurt, Germany, during six weeks in spring 1996 (EAS + MAS only) and during three weeks in fall 1997 and one study in Petten, Holland, during ten days in summer 1996. In addition, a condensation particle counter (CPC, TSI model 3022) and a $PM_{2.5}$ Harvard impactor were used as an integral particle number concentration measuring counter and an integral particle mass determining instrument, respectively.

The Erfurt measuring site was located in a dwelling area two km from the center of the city and approximately 50 m east of a major road. The air pollutant mixture at this location was primarily influenced by traffic emissions and domestic heating. The aerosol spectrometers were placed either outside or in a van and the ambient aerosol was sampled through chimney 4 m above ground.

The measuring site in Petten was located at the campus of the Netherlands Energy Research Foundation 20 km away from the next city, 2 km away from the next village and about 100 m west of a major road and close to the sea shore of the North Sea. Therefore this intercomparison was considered to be predominantly an ambient rural aerosol. All three aerosol spectrometers, DAS, EAS and MAS, were located indoors and connected to a laminar flow chamber (airflow 600 l/min) with an outdoor inlet at a height of five meters above ground level. The ambient aerosol measurements were performed in June 1996 lasted in total 111 hours.

Laboratory aerosols

In Petten, Holland, also a side-by-side intercomparison of aerosol spectrometers was carried out using various laboratory test aerosols. Polydisperse test aerosols of ammonium sulfate, elemental carbon and sebacate oil in the ultrafine size range of 30 nm and 80 nm were generated in the laminar flow chamber (airflow 600 l/min) for the intercomparison.

Intercomparison of ambient aerosols in three European cities in winter 1996/97

In the winter 1996/97, particle number and size distributions were monitored with the aerosol spectrometers in three European cities (Alkmaar, Holland; Erfurt, Germany; Helsinki, Finland) for three and a half months. While Helsinki and Erfurt are large cities with several 100,000 inhabitants, Alkmaar has about 20,000 inhabitants. All three measuring sites were located inside the city at least 50 m away from a major road. In addition, total particle number concentrations were monitored with CPC's together with $PM_{2.5}$ and blackness of $PM_{2.5}$ filters. Data on gaseous pollutants and meteorological parameters were obtained from existing networks.

Results

Side-by-side intercomparisons of aerosol spectrometers

Ambient aerosols

The results of the first intercomparison of EAS and MAS in Erfurt, Germany, were described recently (Tuch et al., 1999). A manuscript is in progress to describe the results of the second Erfurt intercomparison on all three spectrometer (Mirme et al., 1999). Here we will first present detailed data of the short intercomparison of all three spectrometers in Petten, Holland and then also draw together the main results from the three intercomparisons.

Total number concentration in Erfurt during both intercomparisons was 2.5-fold of that observed Petten (Table 1). In Erfurt as much as 85-90% of the counted particles were observed in the ultrafine size range ($NC_{0.01-0.1}$), and about 10-15% of the counted particles were found in the lower fraction of the accumulation mode, 0.1-0.5 µm ($NC_{0.1-0.5}$), and very few particles in the upper

size range $NC_{0.5-2.5}$. In Petten the latter fraction is also very small, but $NC_{0.1-0.5}$ is about 30% and $NC_{0.01-0.1}$ is about 70% of the total number concentration.
Besides the large particle fraction $NC_{0.5-2.5}$ there is excellent agreement between the number concentrations determined by the three spectrometers and CPC. This is reflected in Table 2 which provides non-parametric Spearman rank correlation coefficients between the hourly geometric mean of the total number concentration $NC_{0.01-2.5}$ and those of all three size ranges for all three side-by-side intercomparisons. Although lower, also in the large particle fractions correlations between instruments were close to 0.8.
In Fig.1 the time series plot of hourly means of the total particle number concentration (0.01 - 2.5 µm) shows that all three spectrometers and a CPC followed concentration variations of the ambient air during the side-by-side measurements very well. Moreover the scatter plot of the integral particle number concentrations measured by the spectrometers versus the particle number concentration measured by the CPC (Fig. 2) indicates that the integral particle number concentrations derived from measurements with the DAS, EAS and MAS are comparable to those of an integral measuring instrument. Note the measuring principle of the CPC differs clearly from those of the three aerosol spectrometers which use the same measurement principle of electrical mobility for particles less than 0.5 µm but different concepts for larger particles.

Particle number concentrations in different size ranges: The time series plots of hourly means of the particle number concentrations of the three size ranges, 0.01-0.1 µm ($NC_{0.01-0.1}$), 0.1-0.5 µm ($NC_{0.1-0.5}$), and 0.5-2.5µm ($NC_{0.5-2.5}$) are given in Fig. 3a-c for all three spectrometers. All spectrometers indicate similar levels and variations of particle number concentrations of $NC_{0.01-0.1}$ and $NC_{0.1-0.5}$. This can also be seen by comparing the average levels over the period (Table 1) and the correlations between instruments (Table 2). There is good agreement between all the instruments in the variation of $NC_{0.5-2.5}$ (Fig 3c, Table 2). The average levels of $NC_{0.5-2.5}$ of DAS and MAS are also in good accordance but not between EAS and the other instruments (Fig 3c, Table 1). This relates to the fact, that DAS and MAS use both LAS-X optical particle spectrometers in this size range while the EAS measures electrical mobility of field-charged particles. Note, however that about 1% and less of the total particle number concentration is found in this size range.

Air pollution monitoring of ambient aerosols in three European cities in winter 1996/97

A manuscript is in progress which will describe the results of the ambient aerosol measurements in Alkmaar, Holland, and Erfurt, Germany, and Helsinki, Finland over the period of November 30, 1996 to March 13, 1997 (Ruuskanen et al., 1999). Here data are presented which show that there is only a poor correlation between $PM_{2.5}$ and the total number concentration for any of the three European cities. This is shown in Fig.4 which gives the non-parametric Spearman rank correlation coefficients between $PM_{2.5}$ and total number concentration $NC_{0.01-2.5}$.

Performance of the aerosol spectrometers: The ability of the instruments to continuously measure ambient aerosol under winterly weather conditions in remote measuring stations can be estimated by the fraction of valid measurement data. During the 3« months campaign 75%, 82% and 96% of hourly data were collected by DAS, EAS and MAS, respectively, and more than 80% of the hourly data by the CPC's in the three cities.

Laboratory aerosols

A manuscript is in progress which will describe the results of the laboratory comparison (Khlystov et al. 1999). As an example for the laboratory generated test aerosols size distribution spectra of two ultrafine ammonium sulfate ($NH_4(SO_4)_2$) aerosols integrated over a period of 45 min are shown in Fig. 5. Both aerosols - which represent an important fraction of the ambient aerosol - are sized equally by all three spectrometers. Also the total number concentration is similar between the three spectrometers with the exception of EAS for the large $NH_4(SO_4)_2$ aerosol which remains unclear but may be attributed to sampling line between EAS and the laminar airflow chamber.

Discussion

The DAS, EAS and MAS were successfully deployed in three side-by-side intercomparisons. They reliably recorded spectral number distributions as a function of the particle diameter and provided particle number concentrations of various size ranges of ambient fine particles. Based on the experience gained during the three side-by-side intercomparisons, operational procedures were developed which proved to be suitable for continuously measuring ambient urban air at remote measuring stations under winterly weather conditions during a 3« months measuring campaign in the winter 1996/97 without significant losses of data acquisition time due to instrumental failures.

The three side-by-side intercomparisons of the three aerosol spectrometers at Erfurt and Petten were performed during three different seasons of the year. While the ambient aerosol of Erfurt originates mainly from urban sources the Petten aerosol is more of a rural type and from the sea. Despite the variability of the ambient aerosols analyzed all three spectrometers followed the variations of the ambient aerosol in a similar manner and yielded almost identical results for total number concentration. These data - based on measurements of the electrical mobility or optical property of the aerosol particles - agreed very well with the total number concentration determined by the integral counting CPC. In addition, all three spectrometers followed the variations of the ambient aerosol in a similar manner and yielded almost identical results for particle number concentrations of particles with diameters < 0.5 µm. The good agreement was expected for ultrafine particles since all three spectrometers rely on the determination of the electrical mobility of the ultrafine particles. However, the good agreement for 0.1-0.5 µm particles is quite satisfying, since different measuring principles are used in DAS and MAS (optical properties) versus EAS (electrical mobility) in this size range. The good agreement is reflected in the very good correlation of the total number concentration $NC_{0.01\text{-}2.5}$ and of the number concentrations $NC_{0.01\text{-}0.1}$ and $NC_{0.1\text{-}0.5}$ for the size ranges 0.01 - 0.1 and 0.1 - 0.5 µm amongst the three aerosol spectrometers (Table 2). The size range 0.01 - 0.5 µm contains about 99 % of the total particles observed in the ambient air. Correlations between the instruments were lower in the size range 0.5 - 2.5 µm and EAS also measured clearly higher concentrations in this size range as compared to DAS and MAS. However, particles in this size range contribute to only about 1% to the total particle number concentration.

The laboratory-generated test aerosols reflect major compounds of the ambient aerosol: ammonium sulfate, elemental carbon and sebacate oil as an organic compound. They differed considerably in their optical, structural and morphological properties as well as in their chemical composition. Using these test aerosols of selected physico-chemical properties provided insight on the performance of the three aerosol spectrometers during the side-by-side intercomparison. As shown for the two ammonium sulfate aerosols all aerosol types used were reasonably well characterized by each of the spectrometers.

It is not surprising that there is poor correlation between the mass based $PM_{2.5}$ and the total number concentration in all three European cities during the winter season. The latter is maintained by the number of the ultrafine particles below 0.1 µm while $PM_{2.5}$ is dominated by particle larger than 0.3 µm. Ultrafine particles originate from local combustion type sources or photochemical reactions and are not long-range transported due to their dynamic behavior while particles in the accumulation mode originate from different sources, e.g. aged combustion-type aerosols which may or may not be long-range transported as well as dispersion-type aerosol particles like supermicron particles.

From the good agreement between the side-by-side intercomparisons it is deduced that the data obtained from the 3« months measurements in three European cities during winter 1996/97 can directly be compared. Based on these experiences epidemiological studies are already launched which will test whether there is an association between particle number concentrations of various size ranges of ambient urban aerosols and pulmonary and cardiovascular health effects. Ambient aerosol data and health outcome parameters obtained in different cities will then be combined for a meta-analysis in order to yield a broader view of ambient air quality and public health.

Acknowledgments

The study was done within the framework of the „Exposure and risk assessment for fine and

ultrafine particles in ambient air„ (ULTRA)-project. The project was funded by the EU ENVIRONMENT Programme Contract ENV4-CT95-0205.

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		Erfurt I	Spring 1996		Erfurt II	Fall 1997		Petten	Summer 1996
	N	Geom. Mean	Geom. Std.Dev.	N	Geom. Mean	Geom. Std.Dev.	N	Geom. Mean	Geom. Std.Dev.
Total number concentration									
CPC	798	24000	2.03	343	24900	2.01	83	10300	1.43
MAS	938	23000	2.04	382	21800	2.19	104	8740	1.46
EAS	926	23000	1.97	373	19800	2.2	107	10600	1.56
DAS		-.-	-.-	237	19400	2.22	51	8960	1.46
Number concentration in ultrafine fraction (0.01 – 0.1 µm)									
MAS	938	20000	2.20	382	18500	2.33	104	5300	1.65
EAS	926	19000	2.10	373	16900	2.31	107	6210	1.85
DAS		-.-	-.-	240	17200	2.25	89	6300	1.67
Number concentration in accumulation fraction (0.1 – 0.5 µm)									
MAS	938	2700	1.70	382	2590	2.19	109	3000	1.55
EAS	926	3500	1.73	373	2390	2.07	107	3770	1.36
DAS		-.-	-.-	358	2130	2.11	51	2940	1.38
Number concentration in coarse fraction (0.5 – 2.5µm)									
MAS	938	30	2.90	382	10.7	4.1	109	16.1	1.89
EAS	926	140	2.28	373	44	2.14	107	232	1.72
DAS		-.-	-.-	360	10.2	2.66	66	27.8	1.62

Table 1. Statistical characteristics of aerosol particle total and fraction number ($1/cm^3$) concentrations concentration. N is number of valid measurement hours.

Erfurt I Spring 1996	MAS	EAS	DAS	CPC
Total number concentration				
MAS	1	0.96	-.-	0.97
EAS		1	-.-	0.98
DAS			1	-.-
CPC				1
Ultrafine fraction				
MAS	1	0.95	-.-	
EAS		1	-.-	
DAS			1	
Accumulation fraction				
MAS	1	0.94	-.-	
EAS			-.-	
DAS			1	
Coarse fraction				
MAS	1	0.86	-.-	
EAS		1	-.-	
DAS			1	

Petten Summer 1996	MAS	EAS	DAS	CPC
Total number concentration				
MAS	1	0.91	0.86	.83
EAS		1	0.94	.98
DAS			1	.85
CPC				1
Ultrafine fraction				
MAS	1	0.91	0.88	
EAS		1	0.95	
DAS			1	
Accumulation fraction				
MAS	1	0.85	0.77	
EAS		1	0.87	
DAS			1	
Coarse fraction				
MAS	1	0.74	0.81	
EAS		1	0.79	
DAS			1	
Erfurt II Fall 1997	MAS	EAS	DAS	CPC
Total number concentration				
MAS	1	.99	.98	.99
EAS		1	.99	.98
DAS			1	.97
CPC				1
Ultrafine fraction				
MAS	1	0.98	0.98	
EAS		1	0.98	
DAS			1	
Accumulation fraction				
MAS	1	0.98	0.98	
EAS		1	0.99	
DAS			1	
Coarse fraction				
MAS	1	0.85	0.72	
EAS		1	0.81	
DAS			1	

Table 2. Non-parametric Spearman rank correlation of aerosol number concentrations in different fractions by three spectrometers, pairwise deletion of the data.

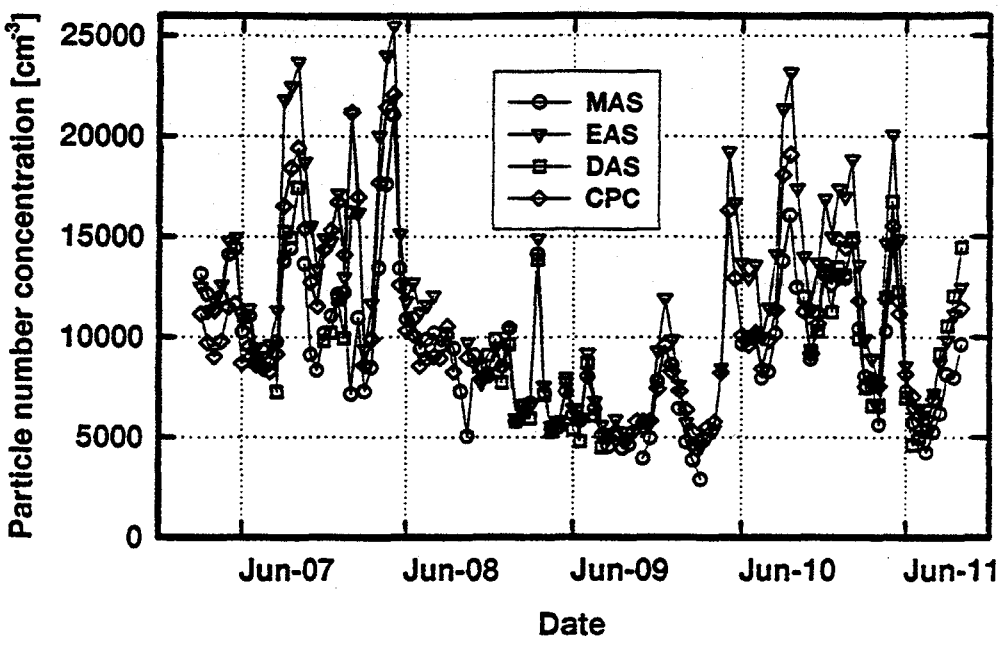

Fig. 1 Time series of mean hourly total number concentrations derived from DAS, EAS, MAS and CPC at Petten, Holland, in summer 1996.

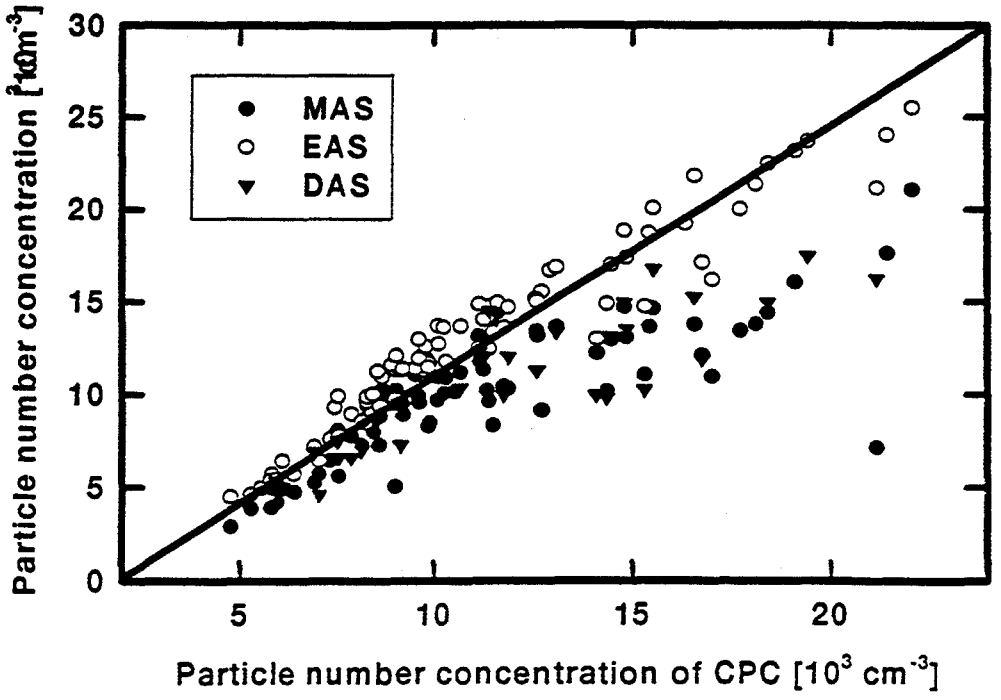

Fig.2 Scatterplot of DAS. EAS. ;MAS and second CPC of mean hourly total number concentrations versus mean hourly total number concentrations derived from first CPC at Petten, Holland. in Summer 1996.

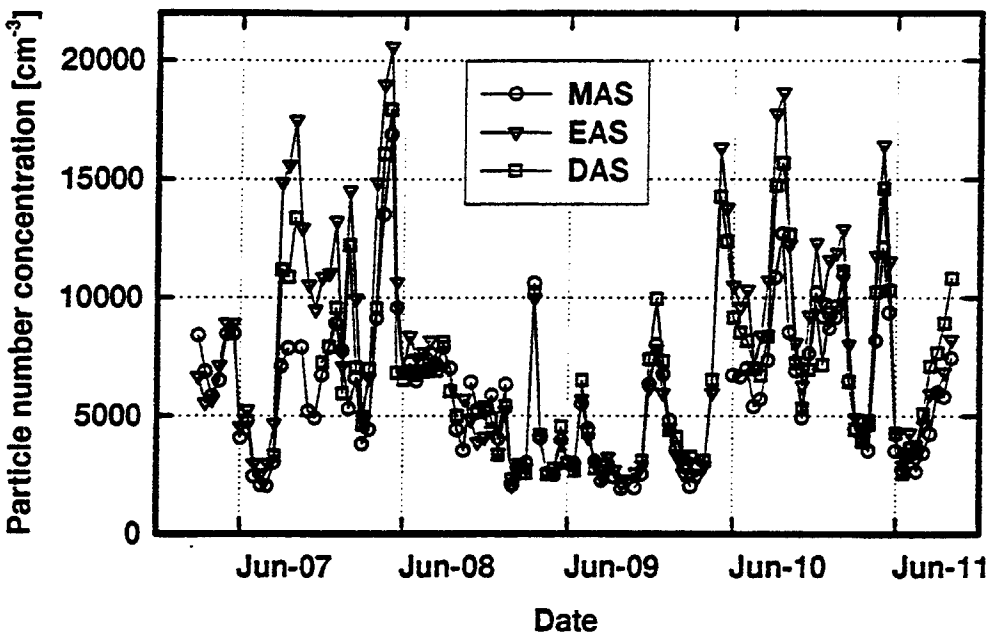

Fig 3a. Time series of mean hourly ultrafine particle (0.01 - 0.1 µm) number concentrations derived from DAS, EAS, MAS and CPC at Petten, Holland, in summer 1996.

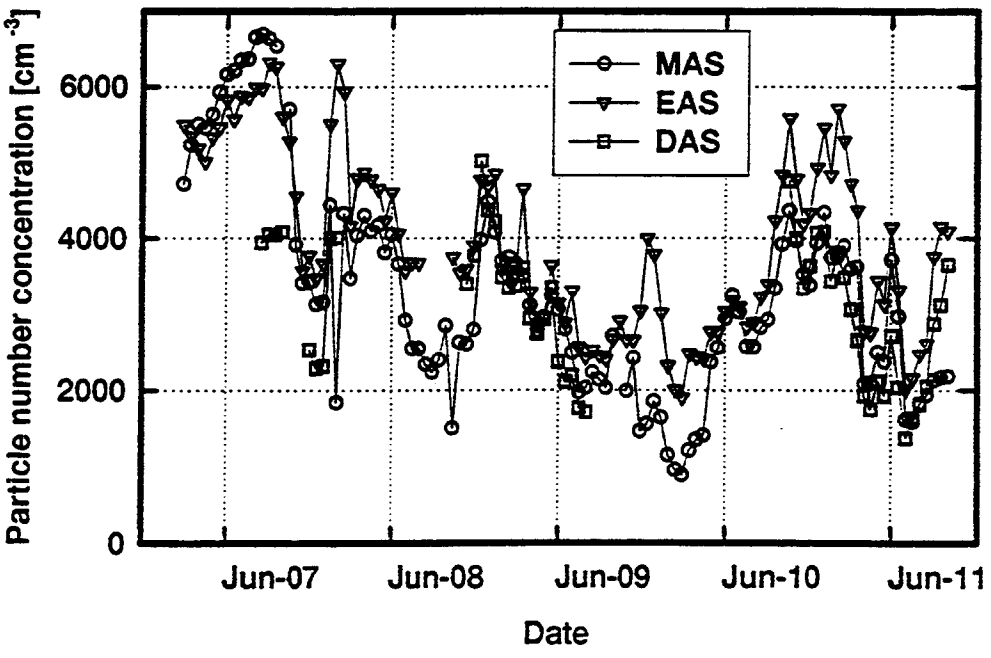

Fig 3b. Time series of mean hourly particle number concentrations in the accumulation mode (0.1 - 0.5 µm) derived from DAS, EAS, MAS and CPC at Petten, Holland, in summer 1996.

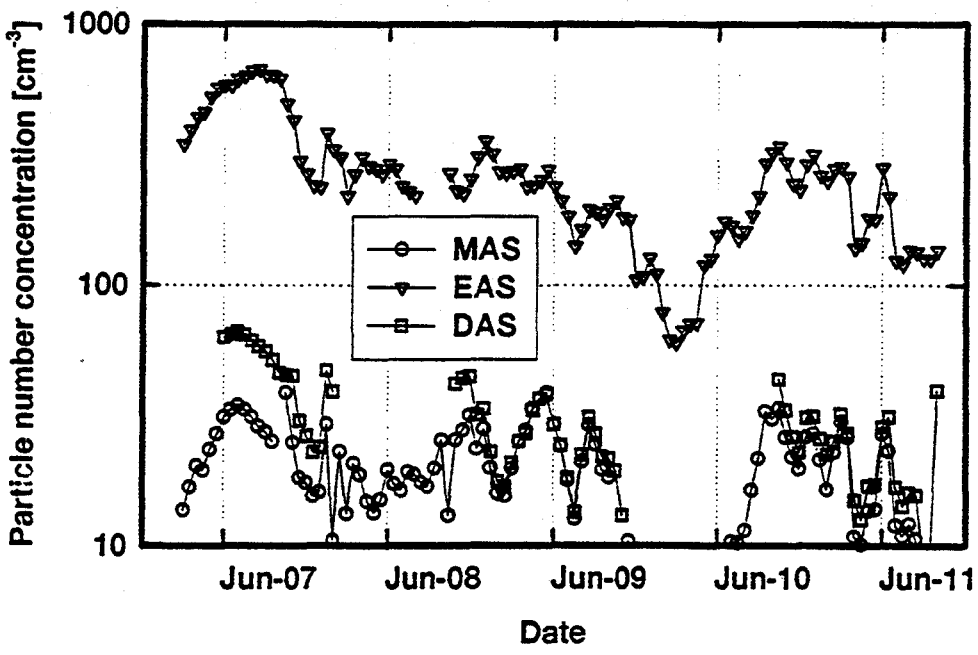

Fig 3c. Time series of mean hourly total coarse particle number concentrations (0.5 - 2.5 µm) derived from DAS, EAS, MAS and CPC at Petten, Holland, in summer 1996. Note logarithmic scale of number concentration.

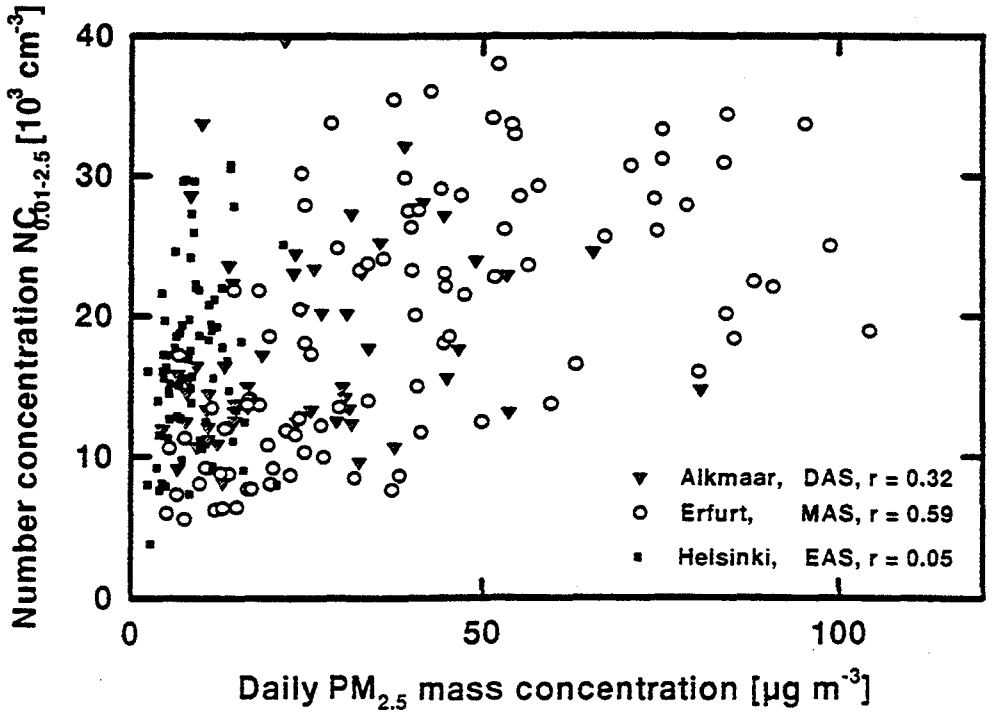

Fig. 4 Poor correlation between $PM_{2.5}$ and total particle number concentration $NC_{0.01-2.5}$ in the 3 cities of Alkmaar, Holland, and Erfurt, Germany, and Helsinki, Finland, during 3.5 months of the winter 1996/97. Non-parametric Spearman rank coefficients are given.

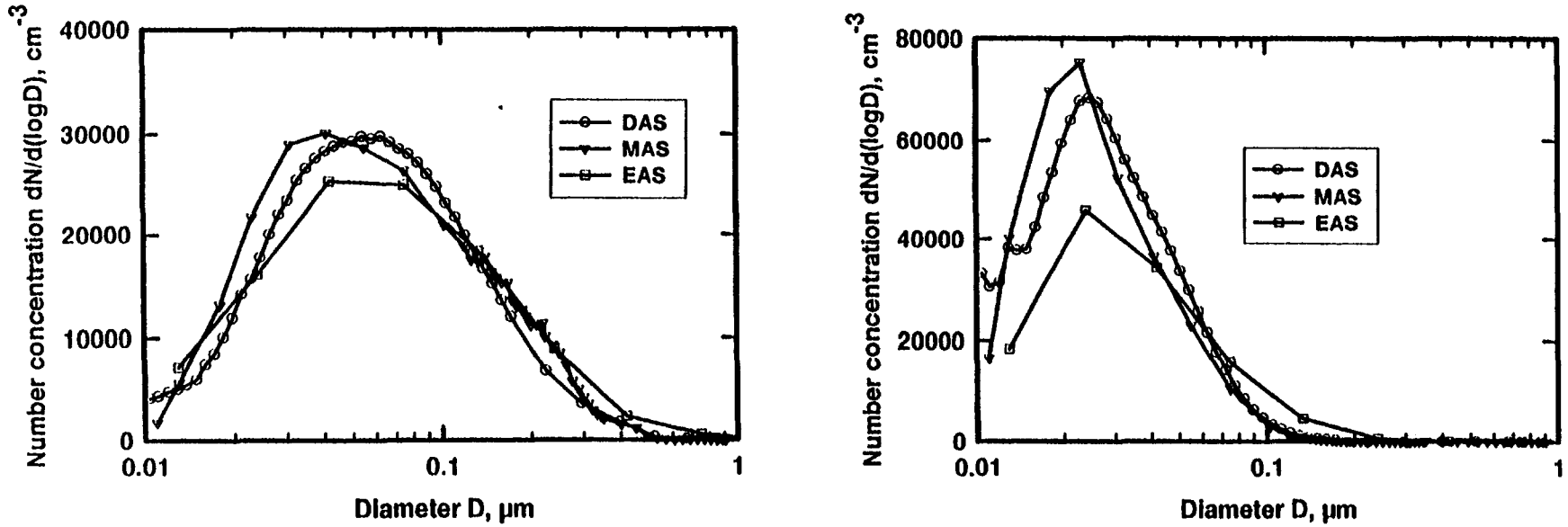

Fig. 5. Comparison of measured number size distributions for two ammonium sulfate aerosols using EAS, MAS and DAS. The nebulized ammonium sulfate concentration in distilled water was 2.5 g/l (left panel and 0.05 g/l (right panel).

The Application of an Optical Particle Counter and an Aethalometer to Define PM Exposures Scenarios inside Commuting Vehicles.

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ABSTRACT

A multipollutant, invehicle study was conducted in California to estimate commuter in-vehicle exposures, especially to PM, over 2-hour intervals. To more clearly define the sources of elevated $PM_{2.5}$, a 16 channel PMS LASX optical particle counter and a McGee Scientific continuous elemental carbon analyzer (Aethalometer) were used in tandem with a continuous CO analyzer and other PM integrated samplers. The LASX unit had been calibrated for optical response using California ambient and vehicular aerosols. The combination of near-real-time particle count by size and black carbon concentration, supplemented with CO data and video information from an onboard camera, greatly enhanced the ability to characterize elevated PM exposures and their sources.

Review of the data and video tapes from the 5 highest $PM_{2.5}$ commutes out of 29 total showed that even during trips on heavily traveled freeways, the emissions from the single vehicle immediately in front of the test vehicle could be substantial. The combined signature concentrations of a) elevated particle counts in the 0.15 – 0.30 μm size range, b) elevated elemental carbon, and c) minimal CO elevation were consistently identified on the video as resulting from poorly-tuned (smoking or odoriferous) diesel-fueled, heavy duty vehicles. Single high-emission vehicles (diesel or gasoline) in front of the test car accounted for as much as 30 – 50 % of the total $PM_{2.5}$ commute exposure. Well-tuned (especially alternative clean fuel) vehicles were essentially transparent to the monitoring system. Another key finding was that carpool lane usage in Los Angeles resulted in significant reductions of both pollutant concentrations and potential personal exposure.

INTRODUCTION

This report represents only a small part of a comprehensive study of pollutant exposures in vehicles.[1] The research was conducted with a pilot study in Sacramento, CA and the main study in Los Angeles, CA.

OBJECTIVES

The primary objectives of this paper were:

- Calibrate the aerosol sizing instruments with specific types of source aerosol using a high-flow differential mobility analyzer (DMA).
- Demonstrate particle count size distribution differences among leading vehicle types, focusing on heavy-duty diesels.
- Estimate particle count and elemental carbon distributions to invehicle concentrations while trailing behind selected vehicles.
- Estimate the influence of trailing distance on invehicle concentrations for elemental carbon from heavy-duty diesels
- Estimate concentration differences between carpool lane and noncarpool lane commutes.

EXPERIMENT DESIGN

The key elements of the experimental approach were:

- Calibrate the aerosol bins and response up to 2.5 μm with real ambient and vehicular aerosol using a high-flow DMA to classify the source aerosol.
- Construct and inside/outside sampling manifold system and calibrate it for line losses to permit single

analyzers to determine concentrations in both locations, cycling on a one minute schedule.

- Outfit a mobile test platform (sedan) with the continuous and integrated monitors (sampling near the driver's breathing zone), an associated data collection systems, and a video camera to record the driver's view and commentary.
- Use a laser distance meter at the front of the sedan to continuously determine the trailing distance from the vehicle in front of the sedan.
- Develop driving protocols that highlight the scenarios and leading target vehicles of interest; conduct simulated commutes on Sacramento (13) and Los Angeles (16) roadways.
- Collect 2-hour commute-average $PM_{2.5}$ (and other pollutant) samples to characterize the integrated commuting microenvironment concentrations.
- Conduct special commutes to allow a comparison of carpool versus noncarpool commutes.

VEHICLE DESCRIPTION

Inside sampling in the sedan was conducted at a location immediately behind the center of the front seat. All samplers with pumped systems were exhausted external to the vehicle. While this had some impact on the air exchange rate (AER), the total flow from these samplers was estimated to be less than 1 % of the through flow, based on measured AERs during commutes. Outside sampling required the use of a sampling line with high flow (16 lpm) to transport the air from near the base of the windshield to the distribution manifold. Large-bore solenoid valves were used to switch the air stream from inside to outside, controlled by a timed signal from the onboard laptop computer. Particle losses in the sample line were either compensated for or correction factors identified by comparing inside and outside counts with the sample line inside the car. Figure 1 shows the test vehicle.

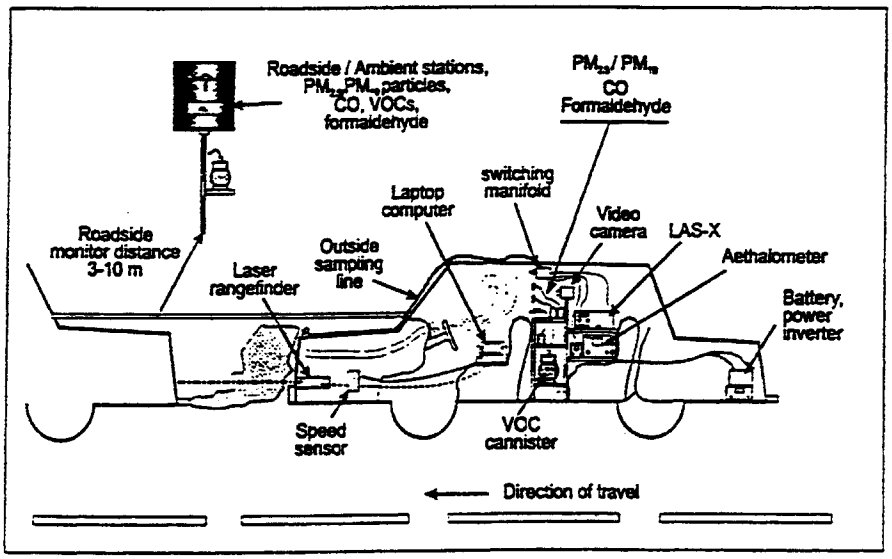

Figure 1. Stationary monitors and instrumented test vehicle.

OPTICAL COUNTER CALIBRATION

The LASX optical particle spectrometer counts and sizes aerosol particles between roughly 0.1 and 3 μm. Its sizing is based on the light-scattering properties of the aerosol and should vary from one type of particle to another. Use of a high-flow differential mobility analyzer for calibrating optical instruments has been described.[2] For this study, the LASX was calibrated using ambient aerosol in Berkeley, CA and vehicular

aerosol in a highway tunnel. Admittedly, a fraction of ambient aerosol is in the vehicular aerosol and vehicular aerosol in the ambient sample; the calibration procedure does use the majority aerosol from each source. In general, the ambient aerosol calibration is fairly close to the manufacturer's calibration, while the vehicular aerosol calibration is quite different. These calibrations are shown in Figure 2.

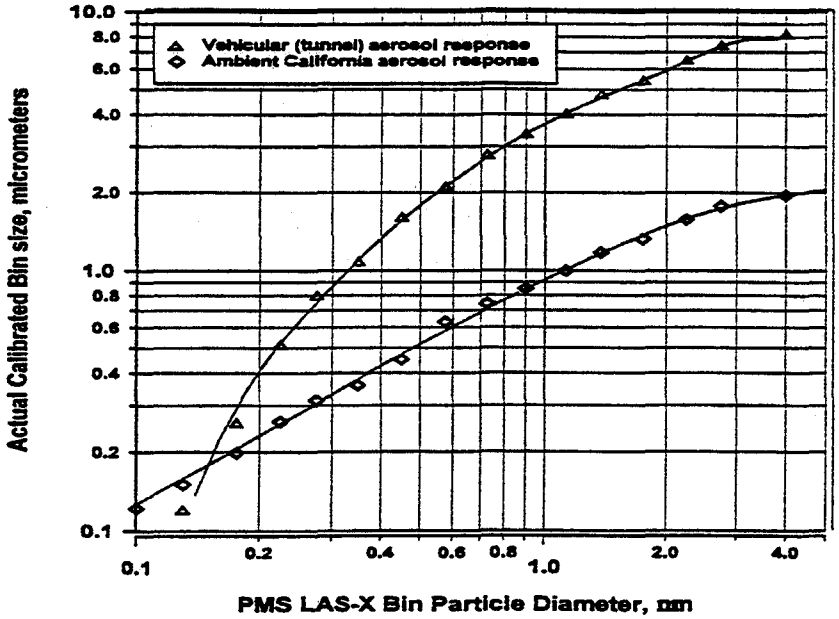

Figure 2. LASX calibration curves for ambient and vehicular aerosols.

The vehicular aerosol exhibits such different optical characteristics because 1) it contains much more light absorbing carbon than does the ambient aerosol, and 2) the particles are made of agglomerated chains of very small carbon spheres. This is inferred from measurements of the effective density of the particles, using the DMA to feed an aerodynamic particle sizer (APS). The effective density of the vehicular aerosol is about 0.7 g/cm^3 at 1 μm and decreases with diameter. The ambient aerosol exhibits a density of about 1.4 - 1.5 g/cm^3 with a slight increase as diameter increases.

COMMUTE 17

To illustrate the value of the test procedure, one commute was selected (number 17) comprising an afternoon, nonrush commute along an arterial street. During the commute, the instrumented sedan targeted several gasoline-powered cars and three city buses. Interestingly, although the buses appeared outwardly identical, each bus used a different fuel: ethanol, compressed natural gas, or diesel. Because each bus was identified by the driver-narrator on the video tape, the emissions from each could be easily distinguished. In addition, there were relatively long periods (up to 10 minutes) during which the trailing distance from a vehicle (CNG bus) gradually decreased. This provided an opportunity to gauge the effect of trailing distance on the emissions from an identifiable source. Figure 3 describes a partially annotated commute history for #17. Figure 4 shows the effect of trailing distance on the measured concentrations inside and outside the sedan.

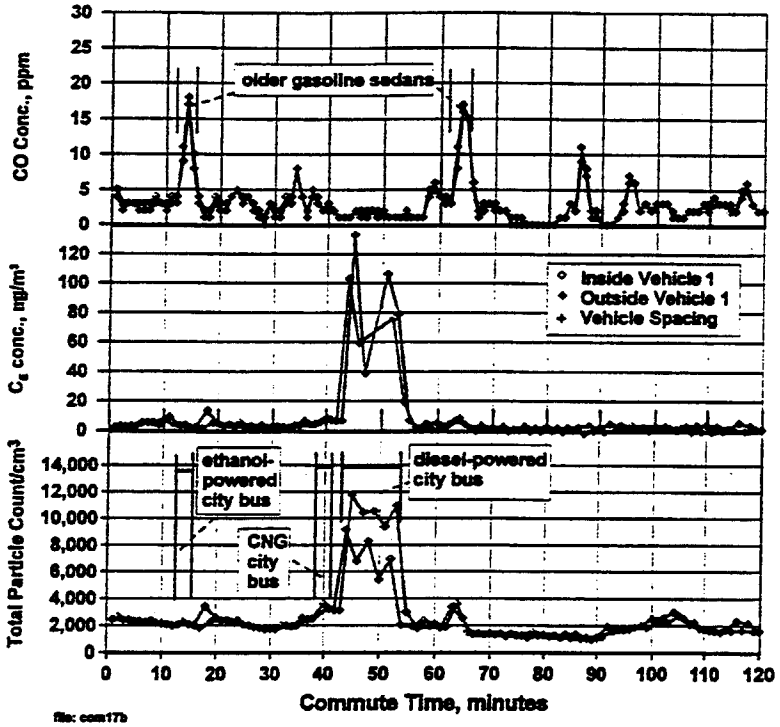

Figure 3. Continuous data for CO, elemental carbon (C_E), and Particle Count during a nonrush arterial commute.

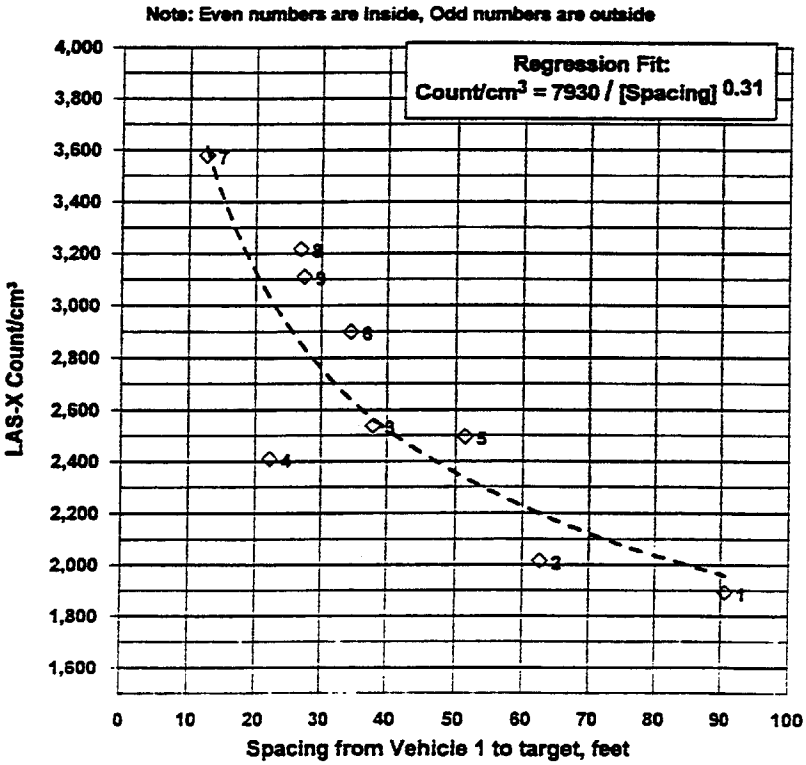

Figure 4. Particle count concentration vs. trailing distance, approaching CNG bus from behind.

The video record of the commute is valuable for verifying and explaining the measurements, as well as recording the descriptive comments of the navigator. As with most video images, still pictures do not convey the detail that can be seen when moving images are viewed. Figure 5 shows one frame of the commute, trailing behind the heavy-duty diesel bus.

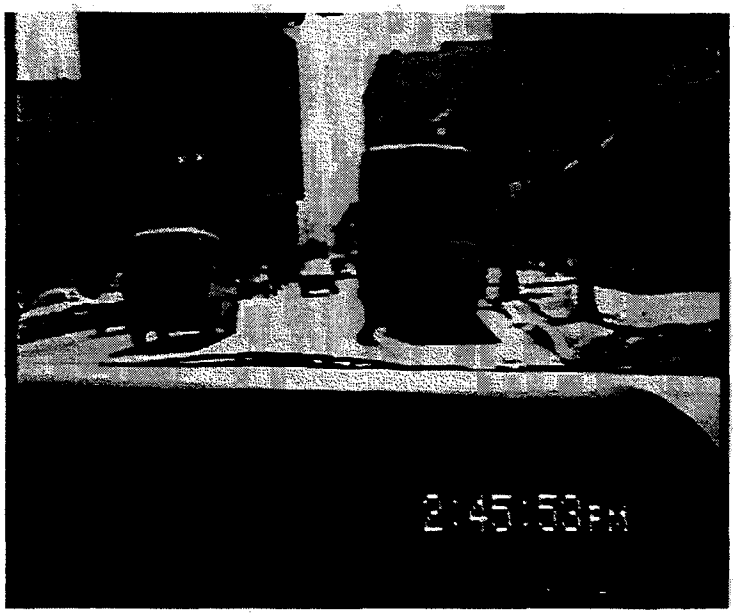

Figure 5. Video image from the commute 17 tape.

The LASX size distributions for several parts of the commute are plotted in Figure 6, using the ambient aerosol calibration for the instrument. The use of the ambient calibration is reasonable when there are no major sources of vehicular emissions in the "view" of the instrument. For most of the commute, this was true. Each of the traces, except for the heavy duty diesel bus trace, shows little minute-to-minute variation, and on the whole, the background, CNG bus, and ethanol bus traces are very similar in shape and magnitude. The heavy duty diesel bus shows a pronounced submicron peak in size, and the minute-to-minute variations are much larger, as the trailing distance varies in stop-and-go traffic. We interpret this to mean that the difference between the heavy-duty diesel bus trace and the average of the others is primarily due to diesel emissions and should be analyzed with the vehicular aerosol calibration. We show how the diesel peak would look using the vehicular aerosol calibration in Figure 6. The peak is shifted to a larger size and spread over a wider particle size range.

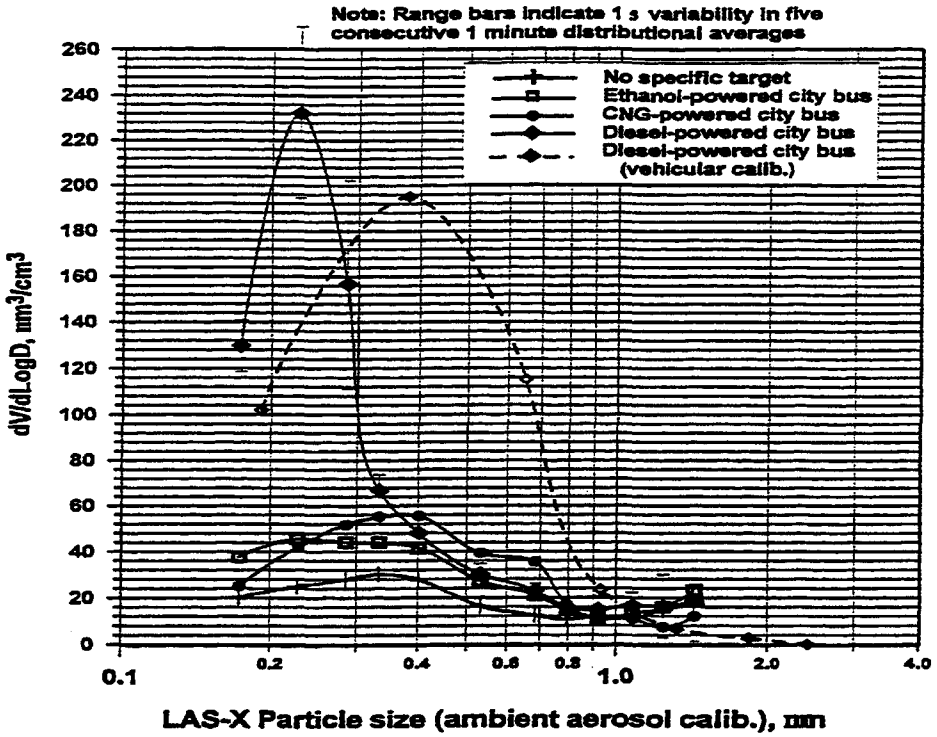

Figure 6. Volume size distributions along the commute.

SUMMARY OF SELECTED RESULTS

Throughout the project, it was found that particle concentrations within the sedan were lower than particle concentrations immediately outside the sedan, regardless of the high AERs on the commutes. This reduction appears to result from particle penetration losses occurring in the ventilation system of the car. On the other hand, gaseous pollutants were essentially the same concentration inside and out, suggesting little effect from the vent system. These trends for particle and gas integrated samples is shown in Figure 7.

Another interesting point was that carpool lane commutes in Los Angeles had distinctly lower concentrations of both particle and gaseous pollutants in rush hour traffic compared with noncarpool lane commutes. This occurred, even though the carpool lane was immediately adjacent to the congested, non-carpool lanes. In addition, the commute time in the carpool lane was roughly 30 percent lower than in the noncarpool lanes for the same distance traveled, resulting in even lower potential exposures for carpool-lane commuters. The concentration differences are shown in Figure 8. The ambient data from the nearest fixed-location sampling site, shows that metropolitan fixed-location measures may not adequately represent the concentrations occurring along the commute route.

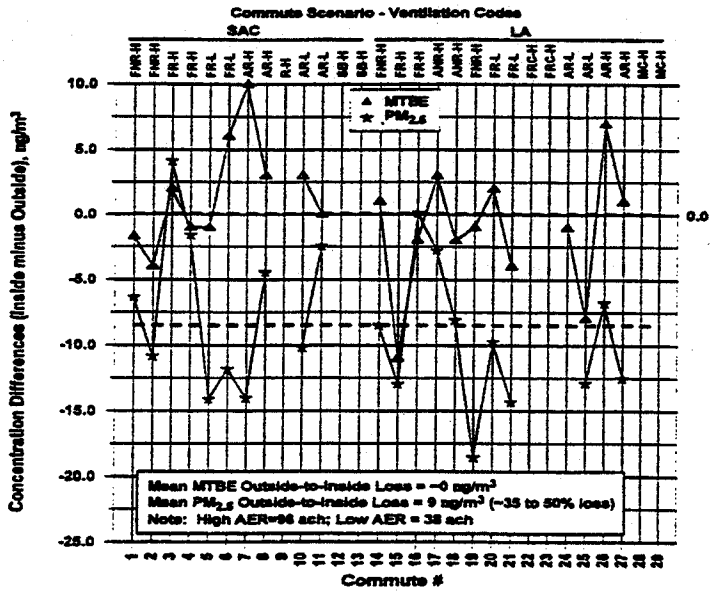

Figure 7. Comparison of inside and outside concentrations for gaseous MTBE and integrated $PM_{2.5}$ for all commutes.

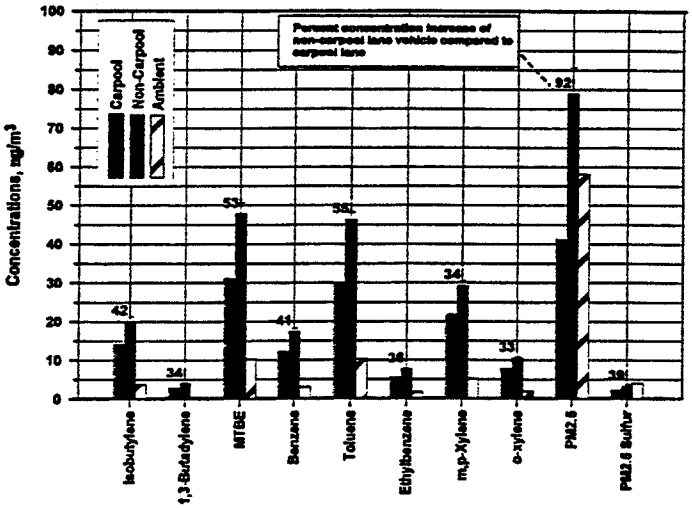

Figure 8. Comparison of carpool and noncarpool commute concentrations.

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Indoor And Outdoor PM10 And Associated Metals And Pesticides In Arizona

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Abstract

The National Human Exposure Assessment Survey study in Arizona (AZ NHEXAS) sampled trace metals in multi-media in & outside of 175 representative homes in Arizona. PM10 was collected using low-flow impactors indoors and out. Primary metals evaluated from monitoring of indoor and outdoor air were lead, cadmium, chromium, nickel, and arsenic. Secondary metals were also evaluated. They were analyzed them using GC-ICP/AA. Air concentrations of metals do not contribute appreciable amounts to total concentrations of metals, and none were above levels of concern. Measurements were made of selected pesticides (primarily chlorpyrifos and diazinon) from particulate matter (PM10) filters obtained indoors and outdoors. Indoor air pesticide exposures represent about 25% of the total exposure to these pesticides. The highest 10% of exposures were related to questions about pesticide usage, at home and work.

Introduction

PM10 and lead are regulated by National Ambient Air Quality Standards. Indoor PM10 and lead are known to contribute a large amount to total exposure to both (as mentioned in the EPA Air Quality Criteria Documents, 1986, 1992, 1996). In addition, other elemental metals can cause significant health effects. However, the population distributions of exposures to these metals in different media are unknown (Sexton et al., 1995). Inhalation of inorganic arsenic (As) is associated with respiratory, cardiovascular, neurological, teratogenic and carcinogenic effects (ATSDR, 1993a). Human exposure to cadmium occurs through ingestion and inhalation (ATSDR, 1997a). Smokers experience double the daily exposure of non-smokers to cadmium. Acute and chronic inhalation can result in damage to the lung including cancer, and chronic inhalation affects other organ systems. Chromium (III) and nickel are essential nutrients, but chromium VI and nickel exposures can cause adverse health effects; it is often assumed that total Cr can thus cause such adverse health effects. Among the sensitized, exposure to chromium or nickel provokes dermal and inhalation allergy, chronic bronchitis, and reduced lung function (ATSDR, 1993b, 1997b). Long-term inhalation of both metals is associated with an elevated risk of lung cancer (ATSDR, 1993b, 1997b). Daily exposure to all of these elemental metals is common.

Chlorpyrifos and diazinon, have widespread use (Lewis et al, 1988; Whitmore et al., 1994; Buckley et al., 1997). These organophosphate (OP) pesticides are known to have toxic endpoints and may have carcinogenic endpoints. OP insecticides accounted for one-third of all reported pesticide poisonings in the U.S. in 1990, and diazinon and chlorpyrifos accounted for 50% of the

OP reports (Kamrin, 1997). Acute toxicity from OPs involves acetylcholinesterase inhibition, with multiple organ system effects (Salem and Olajos, 1988). Low-dose chronic exposure can lead to the same effects, and other neurological symptoms (Kamrin, 1997).

The study is primarily concerned with residential exposures, using monitoring, questionnaire and time-activity pattern data, as part of an attempt to obtain population distributions of exposure, by media and total. The specific objectives of the overall study have been elucidated before (Lebowitz et al., 1995). In this paper, the focus will be on the efforts to document the occurrence, distribution, and some determinants of exposure to airborne PM10, metals and pesticides in the general population.

Methods

The National Human Exposure Assessment Survey (NHEXAS) study in Arizona employed a population-based probability design and contacted 1200 households (Lebowitz et al., 1995). Of these, 176 homes were targeted for intensive multimedia sampling. The study design, questionnaires employed, field and laboratory analytical techniques were previously presented. PM sampling (for metals and pesticides) was carried out at 4 L/min with a personal sampler pump (Model 224-PCXR8, SKC Inc.). Outdoor air was sampled to give an integrated 24-hr sample over a 3-day period using a timer for intermittent sampling. Indoor air was sampled in the same manner for an integrated 12-hr period over 3 days, and personal air was sampled similarly to give an integrated 8-hr sample over a one-day period. These schedules were sufficient to measure PM10, and metals in prior studies and in chambers. Personal, fixed indoor, and fixed outdoor air sampling for pesticides was accomplished using the URG-2000 sampler unit with 10 μm particle inlet, Teflon-coated glass fiber filter (25 mm diam., Pallflex T60A20), and polyurethane foam (PolyUrethaneFoam; 25 mm x 76 mm) sorbent (Gordon et al., 1999). Because of the small number of personal and outdoor air samples with detectable levels of pesticides, such sampling and analysis was discontinued during the course of the project. It was determined that the levels of pesticides outdoors had degraded (from UV and other meteorological phenomena) to the point of having mostly non-detects from outdoor air samples, and the personal air samplers were not sensitive enough for pesticides. PM_{10} air filters were weighed to calculate PM_{10} concentrations, x-rayed for metals and shipped to Battelle for analysis. Pb, Cd, Cr, Ni, and secondary metals were evaluated by Battelle using inductively-coupled plasma-atomic emission spectroscopy (ICP-AES). Detection limits, and Quality Assurance methods were provided previously (Lebowitz et al., 1995).

Results

For the 176 subjects, females were over-represented, and the study population contains one Hispanic for every two non-Hispanics (consistent for each gender and all age groups and consistent with the diennial census data (Robertson et al., 1999).

The proportion of time spent indoors at home was 77-80% for those <age 5 and >age 65 (the remainder being mostly outdoors; it was 63% for the others. Work or school time was 10-12% and transit was 5-8% for those 6-65.

The cumulative distributions of PM10 mass from impactor sampling are shown in Figures 1 (for outdoors) and 2 (for indoors); the 90th percentiles were 48.2 $\mu g/m^3$ and 81.7 $\mu g/m^3$, respectively.

Metals: Lead and cadmium went undetected in air. Indoor nickel, zinc and barium were detected in about 1% of the samples (with maxima of 15.5, 1.8, & 0.3 $\mu g/m^3$, respectively).

Chromium had no values at or below the 95th percentile and its maxima were 0.29 $\mu g/m^3$ indoors and 0.45 $\mu g/m^3$ outdoors. Outdoor manganese did have a 90th percentile (0.05 $\mu g/m^3$); its maximum outdoors was 0.21 $\mu g/m^3$; indoors the maximum was 0.12 $\mu g/m^3$.

Arsenic was detected in about 30% of the indoor and 32% of the outdoor air samples; the 75th percentiles were 0.004 $\mu g/m^3$ and 0.006 $\mu g/m^3$, respectively; the 90th percentiles were 0.008 $\mu g/m^3$ and 0.01 $\mu g/m^3$, respectively; the maxima were 0.022 and 0.026 $\mu g/m^3$, respectively. These results indicate that exposure to metals from air is very low for the studied population.

For arsenic, residence in mining towns delineated half of those in the upper 90th percentile of exposure. The other metals were also distributed geographically in a way that will contribute to knowledge of sources. None of the air values exceeded Arizona standards.

Comparisons of metals in smokers vs. non-smokers and smoking vs. non-smoking homes (18% homes with smoking) (using non-parametric comparisons, $p < .05$ for significance) showed: Smokers had higher values than non-smokers for blood Pb, Cd and Urinary Cd; homes with smokers had higher levels of indoor PM10 than homes without smoking; there were no significant differences in Cd or Pb in other media between two groups. In regard to tobacco smoke exposure in non-smokers there were detectable but not statistically significant differences in blood Pb, Cd and urinary Cd between non-smoking residents of smoking homes (n=25), or of non-smoking homes (n=101). However, for ages less than or equal to 16 years (n=33), there were detectable, and statistically significant greater concentrations of blood Pb, Cd and urinary Cd for children who reside in homes with smoking (n=10) than those who reside in households without smokers (n=23). (Rogan, Thesis, unpublished.)

Pesticides: Chlorpyrifos and diazinon indoors had a 63-65% detection rate. The distributions were at best log-normal. The 50th percentiles were 10.7 ng/m^3 and 7.3ng/m^3, respectively. The 90th percentiles were 78.8ng/m^3 and 58.3ng/m^3, respectively. The 99th percentiles were 155.1 ng/m^3 and 124.1 ng/m^3, respectively. Preliminary analysis indicates that the contribution to total exposure from indoor air exposure for chlorpyrifos is at least 25% (for an adult male). Further, the top 10% of those exposed had questionnaire responses indicating pesticide usage either at home and/or at work recently.

Discussion

The relative metal analyte contributions from different media are quite different (O'Rourke et al., 1999). Almost all fixed site air samples (indoors and out) were below the detection limit or, when detected, values were in the ng/m^3 range. Lacking compelling evidence related to particle deposition site, population susceptibility, association with a specific disease, or pharmacokinetics

of a given analyte, the importance of air concentrations to total metal concentrations leading to total exposure may be limited.

For the pesticides, the median levels found in indoor samples agreed well with other studies, although the levels corresponding to the upper 0.1-1% of the population were considerably higher than levels reported elsewhere (Gordon et al., 1999).

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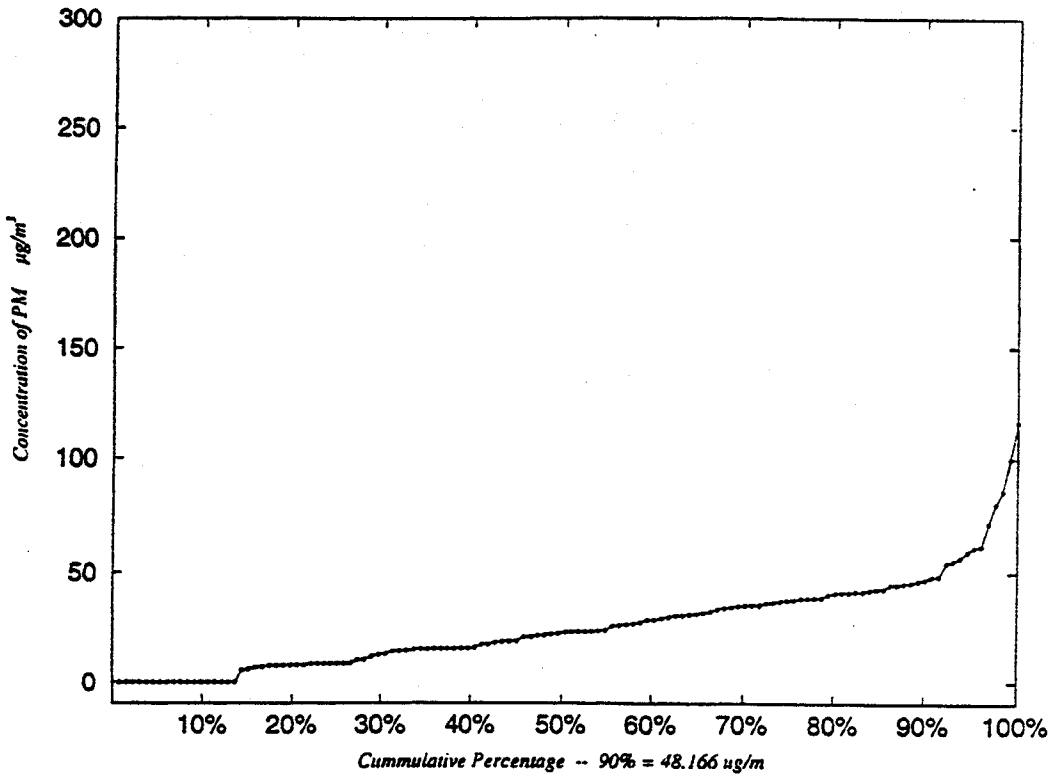

Figure 1 Cumulative Distribution of Outdoor PM10

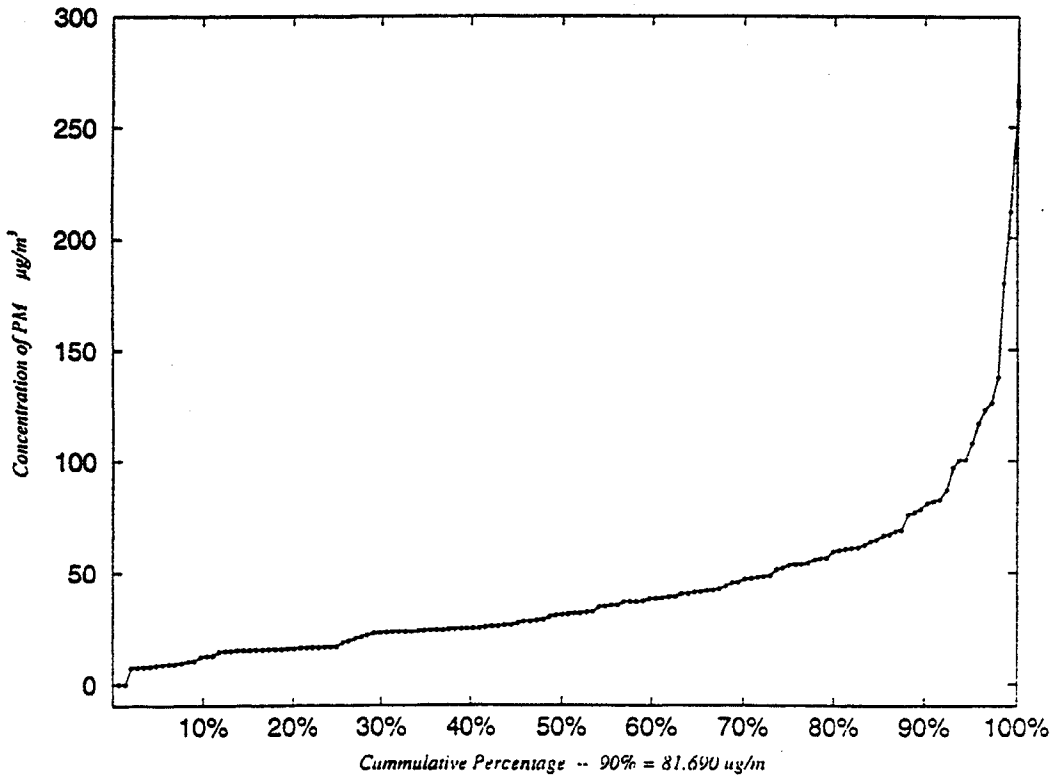

Figure 2 Cumulative Distribution of Indoor PM10

V. RELEVANT PM PROPERTIES-RELATED PAPERS (SESSION 2)

Is SO_2 a Causative Factor for the PM Associated Mortality Risks in the Netherlands?

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Abstract

Associations between serious health risks and PM have been found in numerous studies, including studies in the Netherlands (Verhoeff et al., 1996). More recent European studies have also found associations with gaseous components (Katsouyanni et al., 1997, Hoek et al., 1997), of which SO_2 is one of the gasses. A recent report in the UK (COMEAP, 1998) concludes that in ambient air SO_2 leads to an increase in total mortality of 0.6% per 10 $\mu g/m^3$.

Although these statistical associations have been found, it remains questionable as to whether or not the associations are causal. A careful analysis of a nine-year Dutch time series (Hoek et al., 1997) by successive exclusion of the highest concentrations indicates that SO_2 is probably not causally associated with the health effects, but that it is correlated. A separate analysis of the mortality over different three-year periods indicates that in the first three years SO_2 lead to a significantly lower relative risk than in the last three years, which had the lowest SO_2 concentrations. The conclusion that in the Netherlands SO_2 does not seem to be a causative factor for PM associated health effects is substantiated by further circumstantial evidence, in combination with biological arguments, indicating that a factor correlating with SO_2 (probably PM) might explain the observed associations with total mortality.