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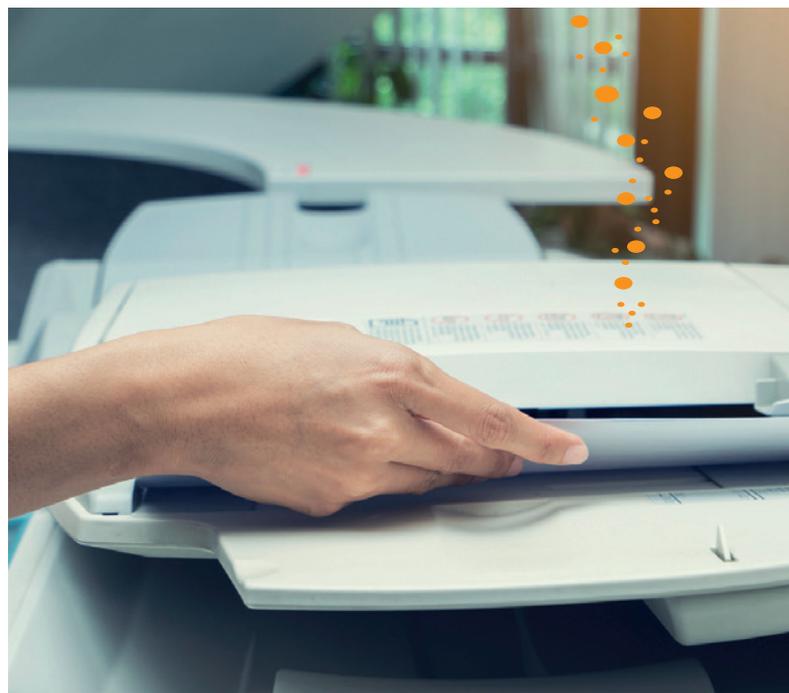
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- **assessing personal exposure**
- **verifying health and safety measures**
- **monitoring the ambient air**
- **checking the capacity of other instruments**

The significance of a measuring instrument, by the way, is not only evident in the questions it answers but also in the people who use it. On the following pages, we have collated over 110 abstracts of scientific publications for you. Here you can not only learn how versatile the testo DiSCmini is but you will also find out that our compact nanoparticle counter has already developed into one of the most important standard measuring instruments.

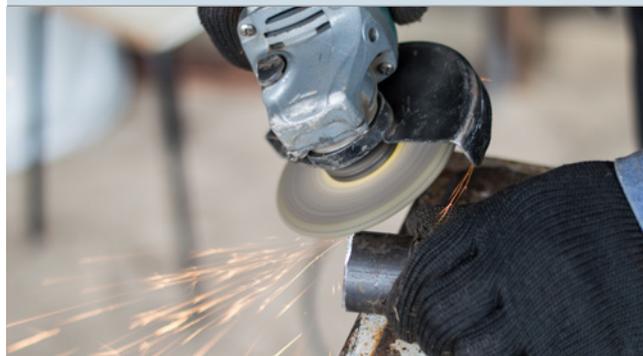
**We hope you enjoy reading!**



## 1. Personal exposure



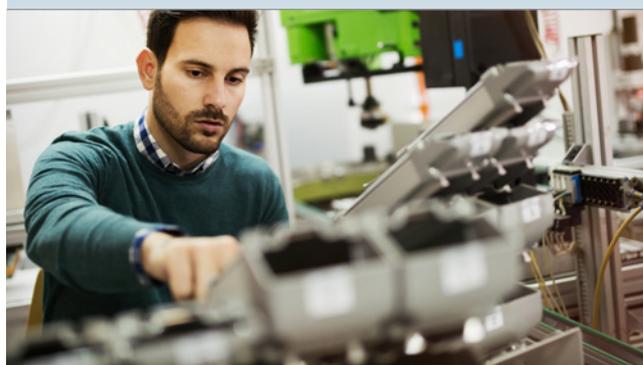
## 2. Health and safety



## 3. Monitoring of the ambient air



## 4. Instrument capacity

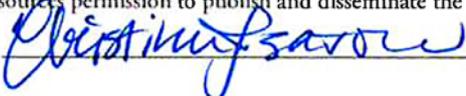


## 1. Personal Exposition

<b>Abstract 1.01</b> Aerosol characterization in real life and a methodology for human exposure studies in controlled chamber settings	<b>Page 06</b>	<b>Abstract 1.15</b> High-throughput and label-free single nanoparticle sizing based on time-resolved on-chip microscopy	<b>Page 20</b>
<b>Abstract 1.02</b> Analysis of time series of particle size distributions in nano exposure assessment	<b>Page 07</b>	<b>Abstract 1.16</b> Increase in oxidative stress levels following welding fume inhalation: a controlled human exposure study	<b>Page 21</b>
<b>Abstract 1.03</b> Assessment of personal exposure to particulate air pollution during commuting in European cities – recommendations and policy implications	<b>Page 08</b>	<b>Abstract 1.17</b> Indoor air quality in naturally ventilated Italian classrooms	<b>Page 22</b>
<b>Abstract 1.04</b> Association between traffic-related air pollution in schools and cognitive development in primary school children: A prospective cohort Study	<b>Page 09</b>	<b>Abstract 1.18</b> Metrological performances of a diffusion charger particle counter for personal monitoring	<b>Page 23</b>
<b>Abstract 1.05</b> Child exposure to indoor and outdoor air pollutants in schools in Barcelona, Spain	<b>Page 10</b>	<b>Abstract 1.19</b> Multi-metric measurement of personal exposure to ultrafine particles in selected urban microenvironments.	<b>Page 24</b>
<b>Abstract 1.06</b> Contribution of indoor-generated particles to residential exposure	<b>Page 11</b>	<b>Abstract 1.20</b> New methods for personal exposure monitoring for airborne particles	<b>Page 26</b>
<b>Abstract 1.07</b> Differences in indoor versus outdoor concentrations of ultrafine particles, PM <sub>2.5</sub> , PM <sub>absorbance</sub> and NO <sub>2</sub> in Swiss homes	<b>Page 12</b>	<b>Abstract 1.21</b> Outdoor infiltration and indoor contribution of UFP and BC, OC, secondary inorganic ions and metals in PM <sub>2.5</sub> in schools	<b>Page 27</b>
<b>Abstract 1.08</b> Effects of flame made zinc oxide particles in human lung cells - a comparison of aerosol and suspension exposures	<b>Page 13</b>	<b>Abstract 1.22</b> Outdoor ultrafine particle concentrations in front of fast food restaurants	<b>Page 28</b>
<b>Abstract 1.09</b> Effects of long-term exposure to air pollution on natural-cause mortality: an analysis of 22 European cohorts within the multicentre ESCAPE project	<b>Page 14</b>	<b>Abstract 1.23</b> Quantifying commuter exposures to volatile organic compounds	<b>Page 29</b>
<b>Abstract 1.10</b> Evaluation of decision rules in a tiered assessment of inhalation exposure to nanomaterials	<b>Page 15</b>	<b>Abstract 1.24</b> Respiratory effects of fine and ultrafine particles from indoor sources—a randomized sham-controlled exposure study of healthy volunteers	<b>Page 32</b>
<b>Abstract 1.11</b> Exposure limits for nanoparticles: report of an international workshop on nano reference values	<b>Page 16</b>	<b>Abstract 1.25</b> Surface area is the biologically most effective dose metric for acute nanoparticle toxicity in the lung	<b>Page 33</b>
<b>Abstract 1.12</b> Exposure to ultrafine particles in hospitality venues with partial smoking bans	<b>Page 17</b>	<b>Abstract 1.26</b> Titanium dioxide nanoparticles: occupational exposure assessment in the photocatalytic paving production	<b>Page 34</b>
<b>Abstract 1.13</b> Exposure to ultrafine particles and black carbon in diesel-powered commuter trains	<b>Page 18</b>	<b>Abstract 1.27</b> Ultrafine and nanoparticle formation and emission mechanisms during laser processing of ceramic materials	<b>Page 35</b>
<b>Abstract 1.14</b> Field comparison of instruments for exposure assessment of airborne ultrafine particles and particulate matter	<b>Page 19</b>	<b>Abstract 1.28</b> Validation of novel sensors to assess human exposures to airborne pollutants	<b>Page 36</b>
		<b>Abstract 1.29</b> Workplace exposure to nanoparticles	<b>Page 38</b>

Organization LUND UNIVERSITY	Document name Doctoral Thesis
Department of Design Sciences Division of Ergonomics and Aerosol Technology	Date of issue 2014-01-17
Author(s) Christina Isaxon	Sponsoring organization
Title and subtitle Aerosol characterization in real life and a methodology for human exposure studies in controlled chamber settings	
<p>Abstract</p> <p>Airborne particles are everywhere around us, and have always been. Particles generated by human activities has increased drastically since industrialization, and several epidemiological studies have shown that inhaled particles can cause adverse health effects. The concern about health effects have during the last decade shifted towards fine and ultrafine particles, not least due to the emerging field of nanotechnology. Of special interest are the particles to which we are exposed indoors – in the industrialized part of the world we spend around 90% of our time indoors (at home and at workplaces/schools). Particles generated in these environments often cause intense peaks in concentration, and are often consequences of our own activities. Especially combustion/thermal processes (such as welding, frying, burning candles etc.) cause peaks in number concentration, often more than an order of magnitude higher than ambient concentrations.</p> <p>We have conducted time-resolved particle measurements in several homes which confirm this. From these measurements, we have been able to show just how much occupants' activities affect the indoor concentration of ultrafine particles compared to outdoor concentrations. We have also estimated e.g. total integrated daily exposure. Exposure and emission measurements have also been conducted at a carbon nanotube producing facility, and a method for counting particles containing carbon nanotubes has been suggested and validated.</p> <p>Why certain particles are more dangerous than others is often investigated in animal exposure studies, where exposure levels are unrealistically high. For several reasons, the results of such studies are not simple to translate to the human system. To increase our understanding of which particle properties can cause effects in humans, a methodology for conducting human exposure studies have been developed and validated. In a controlled chamber we have exposed human test subjects to normal concentrations of common particle types; candle smoke, particles from terpene–ozone reactions and welding fume. Together with medical expertise, we have been looking for effects of these exposures. By using non-invasive tests (e.g. urine and blood samples and ECG) biochemical markers of exposure, and changes in heart rate variability (HRV) have been studied. A significant increase in the high frequency domain of the HRV during exposure for candle smoke was found.</p>	
Key words: Aerosol, human exposure study, exposure, emission, ultrafine particles, aerosol generation, aerosol characterization, candle, terpene, welding, CNT, indoor	
Classification system and/or index terms (if any)	
Supplementary bibliographical information	Language: English
ISSN and key title: 1650-9773 Publication 47	ISBN: 978-91-7473-856-8
Recipient's notes	Number of pages: 228
	Price
	Security classification

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Contents lists available at ScienceDirect

## Journal of Aerosol Science

journal homepage: [www.elsevier.com/locate/jaerosci](http://www.elsevier.com/locate/jaerosci)



# Analysis of time series of particle size distributions in nano exposure assessment



Rinke H. Klein Entink\*, Cindy Bekker, Wouter F. Fransman, Derk H. Brouwer

*Institute for Applied Scientific Research (TNO), Zeist, The Netherlands*

### ARTICLE INFO

*Article history:*

Received 22 September 2014  
Received in revised form  
18 November 2014  
Accepted 26 November 2014  
Available online 10 December 2014

*Keywords:*

Time series  
Particle size distributions  
Statistical modeling  
Nano

### ABSTRACT

Real-time exposure measurements to nano-sized particles may result in large amounts of time series data on particle size and total number concentration. Analysis of the particle size distribution have thus far been limited to either graphical analysis of the distribution over time or an evaluation of the mode over time. For large time series data, graphical analysis of distributions is complicated and an assessment of the mode ignores the important aspect of the variance in particle size. A statistical method of analysis is proposed that overcomes those problems, based on a multilevel modeling approach and assuming a lognormal model for the particle size distribution. Two empirical examples illustrate the advantages of the proposed model, showing that useful summaries and inferences can be obtained, even for large data sets. The model thus provides a tool for practitioners to deal with large amounts of particle size distribution data obtained from real-time nano measurement devices.

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## 1. Introduction

Because of the increasing number of workers involved with nanotechnology and the potential health effects of working with these nanomaterials, assessment of the exposure of workers to (manufactured) nano particles or more specifically nanoobjects and their agglomerates and aggregates (NOAA), (ISO 2012) at the workplace receives considerable attention. To locate sources of emission and to characterize different work situations in order to gain knowledge on exposure and how to reduce exposure levels, workplace aerosol measurements are performed. Because the size and associated surface area of the particles in the (workroom) air is one of the most important parameters for studying manufactured nano particles with respect to potential risk, most sampling methods for measuring nano-sized particles focus on both particle number concentration and particle size distribution (PSD) using real-time size, resolved devices, e.g. Scanning Mobility Particle Sizer (SMPS), Electrical Low Pressure Impactor (ELPI), Aerodynamic Particle Sizer (APS), etc.) rather than on the total particle number concentration in a certain size range alone (e.g. optical counters like the Condensation Particle Counter (CPC), and diffusion charging based devices like DiscMini, Nanotracer, etc.).

However, little attention has been paid on how to (statistically) analyze and report these measurement results. Both particle number concentration and PSD have been studied using graphical methods (Brouwer et al., 2004; Demou et al., 2008; Evans et al., 2010; Bekker et al., 2014). Although the authors showed that useful information could be retrieved, graphical analysis is limited to making qualitative inferences. Quantitative analyses have often been limited to averages or,

\* Correspondence to: TNO, P.O. Box 360, 3700 AJ, Zeist, The Netherlands. Tel.: +31 888 66 2614.  
E-mail address: [Rinke.kleinentink@tno.nl](mailto:Rinke.kleinentink@tno.nl) (R.H. Klein Entink).



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# Science of the Total Environment

journal homepage: [www.elsevier.com/locate/scitotenv](http://www.elsevier.com/locate/scitotenv)



## Review

# Assessment of personal exposure to particulate air pollution during commuting in European cities—Recommendations and policy implications



Angeliki Karanasiou<sup>a,\*</sup>, Mar Viana<sup>a</sup>, Xavier Querol<sup>a</sup>, Teresa Moreno<sup>a</sup>, Frank de Leeuw<sup>b</sup>

<sup>a</sup> Institute of Environmental Assessment and Water Research (IDAEA-CSIC), Barcelona, Spain

<sup>b</sup> National Institute for Public Health and the Environment (RIVM), Bilthoven, The Netherlands

## HIGHLIGHTS

- Car commuter's exposure depends on traffic intensity and emissions by nearby vehicles
- Cyclists are exposed to lower PM levels in comparison to those inside vehicles
- Renovation of public vehicles will reduce commuter's exposure

## ARTICLE INFO

### Article history:

Received 17 December 2013  
Received in revised form 28 April 2014  
Accepted 11 May 2014  
Available online 5 June 2014

Editor: P. Kassomenos

### Keywords:

Ultrafine particles  
Traffic  
Particle number concentration  
Black carbon  
Cycling  
Commuter

## ABSTRACT

Commuting is considered as one of the high-exposure periods among various daily activities, especially in high vehicle-density metropolitan areas. There is a growing awareness of the need to change our transportation habits by reducing our use of cars and shifting instead to active transport, i.e. walking or cycling. A review was undertaken using the ISI web of knowledge database with the objective to better understand personal exposure during commuting by different modes of transport, and to suggest potential strategies to minimise exposure. The air pollutants studied include particulate matter, PM black carbon, BC and particle number concentration. We focused only in European studies in order to have comparable situation in terms of vehicle fleet and policy regulations applied. Studies on personal exposure to air pollutants during car commuting are more numerous than those dealing with other types of transport, and typically conclude by emphasising that travelling by car involves exposure to relatively high particulate matter, PM exposure concentrations. Thus, compared to other transport methods, travelling by car has been shown to involve exposure both to higher PM and BC as compared with cycling. Widespread dependence on private car transport has produced a significant daily health threat to the urban commuter. However, a forward-looking, integrated transport policy, involving the phased renovation of existing public vehicles and the withdrawal of the more polluting private vehicles, combined with incentives to use public transport and the encouragement of commuter physical exercise, would reduce commuters' exposure.

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## Contents

1. Introduction . . . . .	786
2. Materials and methods . . . . .	786
2.1. Study identification and selection . . . . .	786
2.1.1. Air pollutants studied . . . . .	786
3. Results and discussion . . . . .	787
3.1. Exposure during cycling . . . . .	787
3.2. Exposure in cars . . . . .	787
3.3. Exposure in buses . . . . .	787

\* Corresponding author.

E-mail address: [angeliki.karanasiou@idaea.csic.es](mailto:angeliki.karanasiou@idaea.csic.es) (A. Karanasiou).

RESEARCH ARTICLE

# Association between Traffic-Related Air Pollution in Schools and Cognitive Development in Primary School Children: A Prospective Cohort Study

Jordi Sunyer<sup>\*1,2,3,4</sup>, Mikel Esnaola<sup>1,2,3</sup>, Mar Alvarez-Pedrerol<sup>1,2,3</sup>, Joan Forns<sup>1,2,3</sup>, Ioar Rivas<sup>1,2,3,5</sup>, Mònica López-Vicente<sup>1,2,3</sup>, Elisabet Suades-González<sup>1,2,3,6</sup>, Maria Foraster<sup>1,2,3</sup>, Raquel Garcia-Esteban<sup>1,2,3</sup>, Xavier Basagaña<sup>1,2,3</sup>, Mar Viana<sup>5</sup>, Marta Cirach<sup>1,2,3</sup>, Teresa Moreno<sup>5</sup>, Andrés Alastuey<sup>5</sup>, Núria Sebastian-Galles<sup>2</sup>, Mark Nieuwenhuijsen<sup>1,2,3</sup>, Xavier Querol<sup>5</sup>

**1** Centre for Research in Environmental Epidemiology (CREAL), Barcelona, Catalonia, Spain, **2** Pompeu Fabra University, Barcelona, Catalonia, Spain, **3** Consortium for Biomedical Research in Epidemiology and Public Health (CIBERESP), Madrid, Spain, **4** Institut Hospital del Mar d'Investigacions Mèdiques–Parc de Salut Mar, Barcelona, Catalonia, Spain, **5** Institute of Environmental Assessment and Water Research (IDAEA-CSIC), Barcelona, Catalonia, Spain, **6** Learning Disabilities Unit (UTAE), Neuropediatrics Department, Hospital Sant Joan de Déu, Universitat de Barcelona, Barcelona, Spain

\* [jsunyer@creal.cat](mailto:jsunyer@creal.cat)



 OPEN ACCESS

**Citation:** Sunyer J, Esnaola M, Alvarez-Pedrerol M, Forns J, Rivas I, López-Vicente M, et al. (2015) Association between Traffic-Related Air Pollution in Schools and Cognitive Development in Primary School Children: A Prospective Cohort Study. *PLoS Med* 12(3): e1001792. doi:10.1371/journal.pmed.1001792

**Academic Editor:** Bruce P. Lanphear, Simon Fraser University, CANADA

**Received:** September 16, 2014

**Accepted:** January 9, 2015

**Published:** March 3, 2015

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**Data Availability Statement:** Data are from the BREATHE study whose authors may be contacted at CREAL (<http://www.creal.cat/projectebreathe/>).

**Funding:** The research leading to these results has received funding from the European Research Council under the ERC Grant Agreement number 268479 – the BREATHE project. The funders had no role in study design, data collection and analysis, decision to publish, or preparation of the manuscript.

## Abstract

### Background

Air pollution is a suspected developmental neurotoxicant. Many schools are located in close proximity to busy roads, and traffic air pollution peaks when children are at school. We aimed to assess whether exposure of children in primary school to traffic-related air pollutants is associated with impaired cognitive development.

### Methods and Findings

We conducted a prospective study of children ( $n = 2,715$ , aged 7 to 10 y) from 39 schools in Barcelona (Catalonia, Spain) exposed to high and low traffic-related air pollution, paired by school socioeconomic index; children were tested four times (i.e., to assess the 12-mo developmental trajectories) via computerized tests ( $n = 10,112$ ). Chronic traffic air pollution (elemental carbon [EC], nitrogen dioxide [NO<sub>2</sub>], and ultrafine particle number [UFP; 10–700 nm]) was measured twice during 1-wk campaigns both in the courtyard (outdoor) and inside the classroom (indoor) simultaneously in each school pair. Cognitive development was assessed with the  $n$ -back and the attentional network tests, in particular, working memory (two-back detectability), superior working memory (three-back detectability), and inattentiveness (hit reaction time standard error). Linear mixed effects models were adjusted for age, sex, maternal education, socioeconomic status, and air pollution exposure at home.

Children from highly polluted schools had a smaller growth in cognitive development than children from the paired lowly polluted schools, both in crude and adjusted models



## Child exposure to indoor and outdoor air pollutants in schools in Barcelona, Spain

I. Rivas<sup>a,b,d,e,f,\*</sup>, M. Viana<sup>b</sup>, T. Moreno<sup>b</sup>, M. Pandolfi<sup>b</sup>, F. Amato<sup>b</sup>, C. Reche<sup>b</sup>, L. Bouso<sup>a,d,e</sup>, M. Àlvarez-Pedrerol<sup>a,d,e</sup>, A. Alastuey<sup>b</sup>, J. Sunyer<sup>a,c,d,e</sup>, X. Querol<sup>b</sup>

<sup>a</sup> Centre for Research in Environmental Epidemiology (CREAL), C/ Dr. Aiguader 88, 08003 Barcelona, Spain

<sup>b</sup> Institute for Environmental Assessment and Water Research (IDEA-CSIC), C/ Jordi Girona 18-26, 08034 Barcelona, Spain

<sup>c</sup> Hospital del Mar Research Institute (IMIM), C/ Dr. Aiguader 88, 08003 Barcelona, Spain

<sup>d</sup> Universitat Pompeu Fabra (UPF), C/ Dr. Aiguader 88, 08003 Barcelona, Spain

<sup>e</sup> CIBER Epidemiología y Salud Pública (CIBERESP), C/ Monforte de Lemos 3-5, 28029 Madrid, Spain

<sup>f</sup> Institut de Ciència i Tecnologia Ambientals, Universitat Autònoma de Barcelona (UAB), Edifici C Campus de la UAB, 08193 Bellaterra Cerdanyola, Spain

### ARTICLE INFO

#### Article history:

Received 13 January 2014

Accepted 11 April 2014

Available online 27 May 2014

#### Keywords:

School indoor air

PM<sub>2.5</sub>

Black carbon

Ultrafine particles

Organic carbon

Mineral matter

### ABSTRACT

Proximity to road traffic involves higher health risks because of atmospheric pollutants. In addition to outdoor air, indoor air quality contributes to overall exposure. In the framework of the BREATHE study, indoor and outdoor air pollution was assessed in 39 schools in Barcelona. The study quantifies indoor and outdoor air quality during school hours of the BREATHE schools. High levels of fine particles (PM<sub>2.5</sub>), nitrogen dioxide (NO<sub>2</sub>), equivalent black carbon (EBC), ultrafine particle (UFP) number concentration and road traffic related trace metals were detected in school playgrounds and indoor environments. PM<sub>2.5</sub> almost doubled (factor of 1.7) the usual urban background (UB) levels reported for Barcelona owing to high school-sourced PM<sub>2.5</sub> contributions: [1] an indoor-generated source characterised mainly by organic carbon (OC) from organic textile fibres, cooking and other organic emissions, and by calcium and strontium (chalk dust) and; [2] mineral elements from sand-filled playgrounds, detected both indoors and outdoors. The levels of mineral elements are unusually high in PM<sub>2.5</sub> because of the breakdown of mineral particles during playground activities. Moreover, anthropogenic PM components (such as OC and arsenic) are dry/wet deposited in this mineral matter. Therefore, PM<sub>2.5</sub> cannot be considered a good tracer of traffic emissions in schools despite being influenced by them. On the other hand, outdoor NO<sub>2</sub>, EBC, UFP, and antimony appear to be good indicators of traffic emissions. The concentrations of NO<sub>2</sub> are 1.2 times higher at schools than UB, suggesting the proximity of some schools to road traffic. Indoor levels of these traffic-sourced pollutants are very similar to those detected outdoors, indicating easy penetration of atmospheric pollutants. Spatial variation shows higher levels of EBC, NO<sub>2</sub>, UFP and, partially, PM<sub>2.5</sub> in schools in the centre than in the outskirts of Barcelona, highlighting the influence of traffic emissions. Mean child exposure to pollutants in schools in Barcelona attains intermediate levels between UB and traffic stations.

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### 1. Introduction

Some of the health effects of exposure to air pollution, such as the impact on the respiratory and cardiovascular systems, have been extensively studied. Although it is well-known that exposure to air pollutants leads to an increase in mortality and morbidity rates of the population (e.g. Baccarelli et al., 2008; Künzli et al., 2000, 2004; Pope et al., 2002;

WHO, 2005), few studies have focused on the role of air pollution on brain development. Evidence obtained from experimental studies in animals suggests that outdoor air pollution may play a major role in the inflammation of the central nervous system during sensitive periods (such as childhood) and consequently in behaviour and school performance (Block et al., 2012). A growing body of research, albeit limited, from epidemiological studies indicates that exposure to air pollution may be associated with an increased risk of neurodevelopmental disorders and cognitive impairments (Guxens and Sunyer, 2012).

Many epidemiological studies relate PM<sub>2.5</sub> (particles with and aerodynamic diameter <2.5 µm) to negative health outcomes (Dockery et al., 1993; Jerrett et al., 2005; Krewski et al., 2009; Laden et al., 2006; Lepeule et al., 2012; Pope et al., 2002). However, owing to the small size of ultrafine particles (UFP, particles <100 nm) that can translocate

*Abbreviations:* UB, urban background; UB-PR, urban background reference station of Palau Reial in Barcelona; SC, sampling campaign; UFP, ultrafine particles; LDSA, lung-deposited surface area; EC, elemental carbon; BC, black carbon; EBC, equivalent black carbon; OC, organic carbon; OM, organic matter.

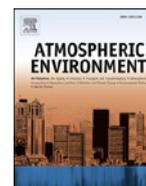
\* Corresponding author at: Centre for Research in Environmental Epidemiology (CREAL), C/Dr. Aiguader 88, 08003 Barcelona, Spain.

E-mail address: [irivas@creal.cat](mailto:irivas@creal.cat) (I. Rivas).



Contents lists available at ScienceDirect

# Atmospheric Environment

journal homepage: [www.elsevier.com/locate/atmosenv](http://www.elsevier.com/locate/atmosenv)

## Contribution of indoor-generated particles to residential exposure



C. Isaxon<sup>a,\*</sup>, A. Gudmundsson<sup>a</sup>, E.Z. Nordin<sup>a</sup>, L. Lönnblad<sup>b</sup>, A. Dahl<sup>a</sup>, G. Wieslander<sup>c</sup>,  
M. Bohgard<sup>a</sup>, A. Wierzbicka<sup>a</sup>

<sup>a</sup> Ergonomics and Aerosol Technology, Lund University, 22100 Lund, Sweden

<sup>b</sup> Astronomy and Theoretical Physics, Lund University, Sweden

<sup>c</sup> Occupational and Environmental Medicine, Uppsala University, Uppsala, Sweden

### HIGHLIGHTS

- Several high time resolution instruments were operated for seven days in 22 homes.
- Concentrations above  $10^4 \text{ cm}^{-3}$  almost only occur during active periods of occupancy.
- Known and unknown indoor activities were 86% of the total integrated daily residential exposure.
- Source strengths of specific activities ranged from  $1.6 \cdot 10^{12}$  to  $4.5 \cdot 10^{12} \text{ min}^{-1}$ .
- Correlation between UFP and mass conc of soot in total dust was on average 56%.

### ARTICLE INFO

#### Article history:

Received 4 April 2014

Received in revised form

18 July 2014

Accepted 30 July 2014

Available online 1 August 2014

#### Keywords:

Ultrafine particles

Indoor sources

Exposure

Indoor measurements

Soot

Source strength

### ABSTRACT

The majority of airborne particles in residences, when expressed as number concentrations, are generated by the residents themselves, through combustion/thermal related activities. These particles have a considerably smaller diameter than  $2.5 \mu\text{m}$  and, due to the combination of their small size, chemical composition (e.g. soot) and intermittently very high concentrations, should be regarded as having potential to cause adverse health effects.

In this study, time resolved airborne particle measurements were conducted for seven consecutive days in 22 randomly selected homes in the urban area of Lund in southern Sweden. The main purpose of the study was to analyze the influence of human activities on the concentration of particles in indoor air. Focus was on number concentrations of particles with diameters  $<300 \text{ nm}$  generated by indoor activities, and how these contribute to the integrated daily residential exposure. Correlations between these particles and soot mass concentration in total dust were also investigated.

It was found that candle burning and activities related to cooking (using a frying pan, oven, toaster, and their combinations) were the major particle sources.

The frequency of occurrence of a given concentration indoors and outdoors was compared for ultrafine particles. Indoor data was sorted into non-occupancy and occupancy time, and the occupancy time was further divided into non-activity and activity influenced time. It was found that high levels (above  $10^4 \text{ cm}^{-3}$ ) indoors mainly occur during active periods of occupancy, while the concentration during non-activity influenced time differs very little from non-occupancy time.

Total integrated daily residential exposure of ultrafine particles was calculated for 22 homes, the contribution from known activities was 66%, from unknown activities 20%, and from background/non-activity 14%.

The collected data also allowed for estimates of particle source strengths for specific activities, and for some activities it was possible to estimate correlations between the number concentration of ultrafine particles and the mass concentration of soot in total dust in 10 homes. Particle source strengths (for 7 specific activities) ranged from  $1.6 \cdot 10^{12}$  to  $4.5 \cdot 10^{12} \text{ min}^{-1}$ .

The correlation between ultrafine particles and mass concentration of soot in total dust varied between 0.37 and 0.85, with an average of 0.56 (Pearson correlation coefficient).

This study clearly shows that due to the importance of indoor sources, residential exposure to ultrafine particles cannot be characterized by ambient measurements alone.

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\* Corresponding author.

E-mail address: [christina.isaxon@design.lth.se](mailto:christina.isaxon@design.lth.se) (C. Isaxon).

## ORIGINAL ARTICLE

# Differences in indoor *versus* outdoor concentrations of ultrafine particles, PM<sub>2.5</sub>, PM<sub>absorbance</sub> and NO<sub>2</sub> in Swiss homes

Reto Meier<sup>1,2</sup>, Marloes Eeftens<sup>1,2</sup>, Harish C. Phuleria<sup>1,2,3</sup>, Alex Ineichen<sup>1,2</sup>, Elisabetta Corradi<sup>1,2</sup>, Mark Davey<sup>1,2</sup>, Martin Fierz<sup>4</sup>, Regina E. Ducret-Stich<sup>1,2</sup>, Inmaculada Aguilera<sup>1,2</sup>, Christian Schindler<sup>1,2</sup>, Thierry Rochat<sup>5</sup>, Nicole Probst-Hensch<sup>1,2</sup>, Ming-Yi Tsai<sup>1,2</sup> and Nino Künzli<sup>1,2</sup>

Indoor air quality is a growing concern as we spend the majority of time indoors and as new buildings are increasingly airtight for energy saving purposes. For a better understanding of residential indoor air pollution in Switzerland we conducted repeated 1–2-week-long indoor and outdoor measurements of particle number concentrations (PNC), particulate matter (PM), light absorbance of PM<sub>2.5</sub> (PM<sub>absorbance</sub>) and nitrogen dioxide (NO<sub>2</sub>). Residents of all homes were enrolled in the Swiss Cohort Study on Air Pollution and Lung and Heart Diseases in Adults (SAPALDIA). Indoor levels were comparable in urban areas and generally low in rural homes. Average indoor levels were 7800 particles/cm<sup>3</sup> (interquartile range = 7200); 8.7 µg/m<sup>3</sup> (6.5) PM<sub>2.5</sub> and 10.2 µg/m<sup>3</sup> (11.2) NO<sub>2</sub>. All pollutants showed large variability of indoor/outdoor ratios between sites. We observed similar diurnal patterns for indoor and outdoor PNC. Nevertheless, the correlation of average indoor and outdoor PNC between sites as well as longitudinal indoor/outdoor correlations within sites were low. Our results show that a careful evaluation of home characteristics is needed when estimating indoor exposure to pollutants with outdoor origin.

*Journal of Exposure Science and Environmental Epidemiology* advance online publication, 11 February 2015; doi:10.1038/jes.2015.3

**Keywords:** indoor air pollution; ultrafine particles; particulate matter; NO<sub>2</sub>; SAPALDIA; Switzerland

## INTRODUCTION

Epidemiological findings about health effects of ambient air pollution are usually based on the comparison of health outcomes with measured or modeled outdoor air pollution. However, outdoor air pollution may not accurately represent individual exposures as we spend a majority of our time in indoor environments.<sup>1</sup> There is a large body of literature describing indoor levels of particulate matter (PM) but little about ultrafine particles (UFP, commonly defined as particles with aerodynamic diameters below 100 nm) which are of additional health relevance.<sup>2</sup> A recent review highlighted the big variability of indoor/outdoor (I/O) ratios in various locations for all particle sizes, ranging from ratios below 0.5 up to 3 and higher.<sup>3</sup> The authors of the review explained the large variability with different infiltration factors of outdoor particles and the large influence of potential indoor emissions, most importantly smoking and cooking. Indeed, infiltration rates may change substantially in countries with cold winters where the newly constructed or retrofitted building infrastructure is increasingly airtight to save energy.<sup>4</sup> To better understand home indoor exposure to air pollution with outdoor origin of subjects enrolled in the Swiss Cohort Study on Air Pollution and Lung and Heart Diseases in Adults (SAPALDIA), we conducted parallel indoor and outdoor measurements of particles in the size range from ~ 15 to 300 nm, particulates < 2.5 µm (PM<sub>2.5</sub>)

and < 10 µm (PM<sub>10</sub>), light absorbance of PM<sub>2.5</sub> (PM<sub>absorbance</sub>) and nitrogen dioxide (NO<sub>2</sub>). It is essential for SAPALDIA to understand the extent to which outdoor levels of air pollutants remain a determinant of exposure and, therefore, of health in the indoor environment. The objectives of this paper are (1) to describe indoor and outdoor levels of the measured air pollutants with a focus on UFP within and across four SAPALDIA areas in Switzerland and (2) to investigate differences in indoor/outdoor relationships across the four study regions and seasons.

## METHODS

A total of 80 SAPALDIA homes in three urban areas (Basel, Geneva, Lugano) and one rural area (Wald) in Switzerland have been selected for I/O measurements of UFP, PM<sub>10</sub>, PM<sub>2.5</sub>, PM<sub>absorbance</sub> and NO<sub>2</sub>. Criteria for site selection were (1) geographical coverage of the cohort within each study area, and (2) ensuring the representation of determinants for air pollution, such as population density, nearby traffic intensity, altitude and proximity to industry. In all homes that agreed to participate, repeated time-matched indoor and outdoor air pollution measurements during up to three seasons were conducted in 2011 (Basel and Geneva) and 2012 (Lugano and Wald). Exact timing of the measurements is shown in Supplementary Figure S1, maps showing the location of the sites are provided elsewhere.<sup>5</sup> Whenever possible, indoor measurements were conducted in less frequented rooms to capture indoor pollutants with outdoor origin rather than the indoor “personal cloud”. Outdoor measurements were conducted in nearby

<sup>1</sup>Swiss Tropical and Public Health Institute, Basel, Switzerland; <sup>2</sup>University of Basel, Basel, Switzerland; <sup>3</sup>Centre for Environmental Science and Engineering, Indian Institute of Technology Bombay, Mumbai, India; <sup>4</sup>Institute of Aerosol and Sensor Technology, University of Applied Science Northwestern Switzerland, Windisch, Switzerland and <sup>5</sup>Division of Pulmonary Medicine, University Hospitals of Geneva, Geneva, Switzerland. Correspondence: Dr. Reto Meier, Swiss Tropical and Public Health Institute, Socinstrasse 57, PO Box, 4002 Basel, Switzerland.

Tel.: +41 61 284 87 29. Fax: +41 61 284 81 01.

E-mail: [reto.meier@unibas.ch](mailto:reto.meier@unibas.ch)

Received 21 July 2014; revised 14 November 2014; accepted 23 November 2014

RESEARCH

Open Access

# Effects of flame made zinc oxide particles in human lung cells - a comparison of aerosol and suspension exposures

David O Raemy<sup>1</sup>, Robert N Grass<sup>2</sup>, Wendelin J Stark<sup>2</sup>, Christoph M Schumacher<sup>2</sup>, Martin JD Clift<sup>1</sup>, Peter Gehr<sup>3</sup> and Barbara Rothen-Rutishauser<sup>1,4\*</sup>

## Abstract

**Background:** Predominantly, studies of nanoparticle (NPs) toxicology *in vitro* are based upon the exposure of submerged cell cultures to particle suspensions. Such an approach however, does not reflect particle inhalation. As a more realistic simulation of such a scenario, efforts were made towards direct delivery of aerosols to air-liquid-interface cultivated cell cultures by the use of aerosol exposure systems.

This study aims to provide a direct comparison of the effects of zinc oxide (ZnO) NPs when delivered as either an aerosol, or in suspension to a triple cell co-culture model of the epithelial airway barrier. To ensure dose-equivalence, ZnO-deposition was determined in each exposure scenario by atomic absorption spectroscopy. Biological endpoints being investigated after 4 or 24h incubation include cytotoxicity, total reduced glutathione, induction of antioxidative genes such as heme-oxygenase 1 (HO-1) as well as the release of the (pro)-inflammatory cytokine TNF $\alpha$ .

**Results:** Off-gases released as by-product of flame ZnO synthesis caused a significant decrease of total reduced GSH and induced further the release of the cytokine TNF $\alpha$ , demonstrating the influence of the gas phase on aerosol toxicology. No direct effects could be attributed to ZnO particles. By performing suspension exposure to avoid the factor "flame-gases", particle specific effects become apparent. Other parameters such as LDH and HO-1 were not influenced by gaseous compounds: Following aerosol exposure, LDH levels appeared elevated at both timepoints and the HO-1 transcript correlated positively with deposited ZnO-dose. Under submerged conditions, the HO-1 induction scheme deviated for 4 and 24h and increased extracellular LDH was found following 24h exposure.

**Conclusion:** In the current study, aerosol and suspension-exposure has been compared by exposing cell cultures to equivalent amounts of ZnO. Both exposure strategies differ fundamentally in their dose-response pattern. Additional differences can be found for the factor time: In the aerosol scenario, parameters tend to their maximum already after 4h of exposure, whereas under submerged conditions, effects appear most pronounced mainly after 24h. Aerosol exposure provides information about the synergistic interplay of gaseous and particulate phase of an aerosol in the context of inhalation toxicology. Exposure to suspensions represents a valuable complementary method and allows investigations on particle-associated toxicity by excluding all gas-derived effects.

**Keywords:** Zinc oxide particles, Aerosol exposure, Air liquid interface (ALI), Suspension exposure

\* Correspondence: [barbara.rothen@unifr.ch](mailto:barbara.rothen@unifr.ch)

<sup>1</sup>Adolphe Merkle Institute, Bionanomaterials, University of Fribourg, Rte de l'Ancienne Papeterie, P.O. Box 209, CH-1732, Marly, Switzerland

<sup>4</sup>Respiratory Medicine, Bern University Hospital, Inselspital, Freiburgstrasse, CH-3010, Bern, Switzerland

Full list of author information is available at the end of the article

# Effects of long-term exposure to air pollution on natural-cause mortality: an analysis of 22 European cohorts within the multicentre ESCAPE project



Rob Beelen, Ole Raaschou-Nielsen, Massimo Stafoggia, Zorana Jovanovic Andersen, Gudrun Weinmayr, Barbara Hoffmann, Kathrin Wolf, Evangelia Samoli, Paul Fischer, Mark Nieuwenhuijsen, Paolo Vineis, Wei W Xun, Klea Katsouyanni, Konstantina Dimakopoulou, Anna Oudin, Bertil Forsberg, Lars Modig, Aki S Havulinna, Timo Lanki, Anu Turunen, Bente Oftedal, Wenche Nystad, Per Nafstad, Ulf De Faire, Nancy L Pedersen, Claes-Göran Östenson, Laura Fratiglioni, Johanna Penell, Michal Korek, Göran Pershagen, Kirsten Thorup Eriksen, Kim Overvad, Thomas Ellermann, Marloes Eeftens, Petra H Peeters, Kees Meliefste, Meng Wang, Bas Bueno-de-Mesquita, Dorothea Sugiri, Ursula Krämer, Joachim Heinrich, Kees de Hoogh, Timothy Key, Annette Peters, Regina Hampel, Hans Concin, Gabriele Nagel, Alex Ineichen, Emmanuel Schaffner, Nicole Probst-Hensch, Nino Künzli, Christian Schindler, Tamara Schikowski, Martin Adam, Harish Phuleria, Alice Vilier, Françoise Clavel-Chapelon, Christophe Deledre, Sara Griani, Vittorio Krogh, Ming-Yi Tsai, Fulvio Ricceri, Carlotta Sacerdote, Claudia Galassi, Enrica Migliore, Andrea Ranzi, Giulia Cesaroni, Chiara Badaloni, Francesco Forastiere, Ibon Tamayo, Pilar Amiano, Miren Dorronsoro, Michail Katsoulis, Antonia Trichopoulos, Bert Brunekreef, Gerard Hoek

## Summary

**Background** Few studies on long-term exposure to air pollution and mortality have been reported from Europe. Within the multicentre European Study of Cohorts for Air Pollution Effects (ESCAPE), we aimed to investigate the association between natural-cause mortality and long-term exposure to several air pollutants.

**Methods** We used data from 22 European cohort studies, which created a total study population of 367 251 participants. All cohorts were general population samples, although some were restricted to one sex only. With a strictly standardised protocol, we assessed residential exposure to air pollutants as annual average concentrations of particulate matter (PM) with diameters of less than 2.5 µm (PM<sub>2.5</sub>), less than 10 µm (PM<sub>10</sub>), and between 10 µm and 2.5 µm (PM<sub>coarse</sub>), PM<sub>2.5</sub> absorbance, and annual average concentrations of nitrogen oxides (NO<sub>2</sub> and NO<sub>x</sub>), with land use regression models. We also investigated two traffic intensity variables—traffic intensity on the nearest road (vehicles per day) and total traffic load on all major roads within a 100 m buffer. We did cohort-specific statistical analyses using confounder models with increasing adjustment for confounder variables, and Cox proportional hazards models with a common protocol. We obtained pooled effect estimates through a random-effects meta-analysis.

**Findings** The total study population consisted of 367 251 participants who contributed 5 118 039 person-years at risk (average follow-up 13.9 years), of whom 29 076 died from a natural cause during follow-up. A significantly increased hazard ratio (HR) for PM<sub>2.5</sub> of 1.07 (95% CI 1.02–1.13) per 5 µg/m<sup>3</sup> was recorded. No heterogeneity was noted between individual cohort effect estimates (*I*<sup>2</sup> p value=0.95). HRs for PM<sub>2.5</sub> remained significantly raised even when we included only participants exposed to pollutant concentrations lower than the European annual mean limit value of 25 µg/m<sup>3</sup> (HR 1.06, 95% CI 1.00–1.12) or below 20 µg/m<sup>3</sup> (1.07, 1.01–1.13).

**Interpretation** Long-term exposure to fine particulate air pollution was associated with natural-cause mortality, even within concentration ranges well below the present European annual mean limit value.

**Funding** European Community's Seventh Framework Program (FP7/2007–2011).

## Introduction

Studies have shown the effects of long-term exposure to air pollution on mortality,<sup>1,2</sup> with most, especially those in the USA, reporting on the mass concentration of particulate matter (PM) smaller than 10 µm (PM<sub>10</sub>) or 2.5 µm (PM<sub>2.5</sub>) in diameter. Few European studies have investigated PM<sub>2.5</sub>, partly because of the low availability of routine monitoring data. However, some European studies have shown associations between mortality and nitrogen dioxide (NO<sub>2</sub>) or nitrogen oxides (NO<sub>x</sub>).<sup>3–8</sup>

In urban areas, NO<sub>2</sub>, NO<sub>x</sub>, and PM<sub>2.5</sub> absorbance (a marker for black carbon or soot) have larger spatial concentration contrasts than PM because they are more

closely related to motorised traffic. Interest in the health effects of coarse particles (2.5–10 µm in diameter) has also increased.<sup>9</sup> However, the comparability of previous studies is limited by the different exposure methods used.<sup>10</sup>

In the framework of the multicentre European Study of Cohorts for Air Pollution Effects (ESCAPE), we added standardised exposure assessment for PM, NO<sub>2</sub>, and NO<sub>x</sub> to health data from 22 ongoing cohort studies across Europe. The objective of ESCAPE was to investigate the association between long-term exposure to air pollution and mortality. In this Article, we report associations for natural-cause mortality. Cause-specific results will be published separately.

Published Online  
December 9, 2013  
[http://dx.doi.org/10.1016/S0140-6736\(13\)62158-3](http://dx.doi.org/10.1016/S0140-6736(13)62158-3)

See Online/Comment  
[http://dx.doi.org/10.1016/S0140-6736\(13\)62570-2](http://dx.doi.org/10.1016/S0140-6736(13)62570-2)

Institute for Risk Assessment Sciences, Utrecht University, Utrecht, Netherlands (R Beelen PhD, M Eeftens MSc, K Meliefste BSc, M Wang MSc, Prof B Brunekreef PhD, G Hoek PhD); Danish Cancer Society Research Center, Copenhagen, Denmark (O Raaschou-Nielsen PhD, Z J Andersen PhD, K T Eriksen PhD); Department of Epidemiology, Lazio Regional Health Service, Rome, Italy (M Stafoggia MSc, G Cesaroni MSc, C Badaloni MSc, F Forastiere MD); Center for Epidemiology and Screening, Department of Public Health, University of Copenhagen, Copenhagen, Denmark (Z J Andersen); Institute of Epidemiology and Medical Biometry, Ulm University, Ulm, Germany (G Weinmayr PhD, Prof G Nagel PhD); IUF – Leibniz Research Institute for Environmental Medicine, Germany and Medical Faculty, University of Düsseldorf, Düsseldorf, Germany (G Weinmayr, Prof B Hoffmann MD, D Sugiri MSc, Prof U Krämer PhD); Institute of Epidemiology II, Helmholtz Zentrum München, German Research Center for Environmental Health, Neuherberg, Germany (K Wolf PhD, Prof A Peters PhD, R Hampel PhD); Department of Hygiene, Epidemiology and Medical



# Evaluation of Decision Rules in a Tiered Assessment of Inhalation Exposure to Nanomaterials

Derk Brouwer<sup>1,2\*</sup>, Ruud Boessen<sup>1</sup>, Birgit van Duuren-Stuurman<sup>1</sup>,  
Delphine Bard<sup>3</sup>, Carsten Moehlmann<sup>4</sup>,  
Cindy Bekker<sup>1,5</sup>, Wouter Fransman<sup>1</sup> and Rinke Klein Entink<sup>1</sup>

1. TNO, Utrechtseweg 48, 3704 HE, Zeist, The Netherlands;
2. School of Public Health, Faculty of Health Sciences, University of the Witwatersrand, Education Campus, 27 St Andrews Road, 2193, Johannesburg, South Africa;
3. Health and Safety Laboratory (HSL), Harpur Hill, Buxton SK17 9JN, UK;
4. Institute for Occupational Safety and Health (IFA/DGUV), Alte Heerstrasse 111, 53757 Sankt Augustin, Germany;
5. Institute for Risk Analysis Science (IRAS), University of Utrecht, Yalelaan 2, De Uithof, 3584 CM, Utrecht, The Netherlands

\*Author to whom correspondence should be addressed. Tel: +27117172387; e-mail: [derk.brouwer@wits.ac.za](mailto:derk.brouwer@wits.ac.za)

Submitted 4 February 2016; revised 25 May 2016; revised version accepted 7 June 2016.

## ABSTRACT

Tiered or stepwise approaches to assess occupational exposure to nano-objects, and their agglomerates and aggregates have been proposed, which require decision rules (DRs) to move to a next tier, or terminate the assessment. In a desk study the performance of a number of DRs based on the evaluation of results from direct reading instruments was investigated by both statistical simulations and the application of the DRs to real workplace data sets. A statistical model that accounts for autocorrelation patterns in time-series, i.e. autoregressive integrated moving average (ARIMA), was used as 'gold' standard. The simulations showed that none of the proposed DRs covered the entire range of simulated scenarios with respect to the ARIMA model parameters, however, a combined DR showed a slightly better agreement. Application of the DRs to real workplace datasets ( $n = 117$ ) revealed sensitivity up to 0.72, whereas the lowest observed specificity was 0.95. The selection of the most appropriate DR is very much dependent on the consequences of the decision, i.e. ruling in or ruling out of scenarios for further evaluation. Since a basic assessment may also comprise of other type of measurements and information, an evaluation logic was proposed which embeds the DRs, but furthermore supports decision making in view of a tiered-approach exposure assessment.

**KEYWORDS:** decision rules; direct reading instruments; evaluation logic; exposure assessment; nanoparticle; statistical simulations; tiered approach

## INTRODUCTION

Strategies to assess exposure to nano-objects, and their agglomerates and aggregates (NOAA), (ISO, 2012)

have been proposed over the last few years. In addition to more generic approaches, as discussed by Ramachandran *et al.* (2011); Ostraat *et al.* (2013); and Brouwer

# Exposure Limits for Nanoparticles: Report of an International Workshop on Nano Reference Values

PIETER VAN BROEKHUIZEN<sup>1\*</sup>, WIM VAN VEELLEN<sup>2</sup>, WILLEM-HENK STREEKSTRA<sup>3</sup>, PAUL SCHULTE<sup>4</sup> and LUCAS REIJNDERS<sup>5</sup>

<sup>1</sup>*IVAM UvA BV, Plantage Muidergracht 14, 1018TV Amsterdam, Netherlands;* <sup>2</sup>*FNV, Amsterdam, Netherlands;* <sup>3</sup>*VNO/NCW, The Hague, Netherlands;* <sup>4</sup>*NIOSH, Cincinnati, OH 45226, USA;* <sup>5</sup>*University of Amsterdam, Institute for Biodiversity and Ecosystem Dynamics, Amsterdam, Netherlands*

Received 30 March 2012; in final form 16 April 2012

**This article summarizes the outcome of the discussions at the international workshop on nano reference values (NRVs), which was organized by the Dutch trade unions and employers' organizations and hosted by the Social Economic Council in The Hague in September 2011. It reflects the discussions of 80 international participants representing small- and medium-size enterprises (SMEs), large companies, trade unions, governmental authorities, research institutions, and non-governmental organizations (NGOs) from many European countries, USA, India, and Brazil. Issues that were discussed concerned the usefulness and acceptability of precaution-based NRVs as a substitute for health-based occupational exposure limits (OELs) and derived no-effect levels (DNELs) for manufactured nanoparticles (NPs). Topics concerned the metrics for measuring NPs, the combined exposure to manufactured nanomaterials (MNMs) and process-generated NPs, the use of the precautionary principle, the lack of information about the presence of nanomaterials, and the appropriateness of soft regulation for exposure control. The workshop concluded that the NRV, as an 8-h time-weighted average, is a comprehensible and useful instrument for risk management of professional use of MNMs with a dispersible character. The question remains whether NRVs, as advised for risk management by the Dutch employers' organization and trade unions, should be under soft regulation or that a more binding regulation is preferable.**

*Keywords:* derived no-effect levels; nano reference values; occupational exposure limits; precautionary principle; risk management

## INTRODUCTION

The increasing production and use of manufactured nanomaterials (MNMs) has given rise to initiatives of governmental authorities, industrial organizations, and civil society organizations to advocate the application of the precautionary principle for risk management (EC, 2000). The tools chosen to make this principle operational for the workplace differ in approach, but they have in common that they all aim to minimize the occupational exposure as far

as reasonably achievable. Control banding is an approach that is gaining growing acceptance among risk assessors. Several control-banding tools have been published, all making use of a two-dimensional matrix, generally combining a qualitative assessment of hazardous properties of the used nanomaterials with an estimate of the likeliness of inhalatory exposure (Paik *et al.*, 2008; Schulte *et al.*, 2008; ANSES, 2010; Höck *et al.*, 2011; Hansen *et al.*, 2011; van Duuren-Stuurman *et al.*, 2012). There are also guidances that combine control banding in a risk assessment tool (Cornelissen *et al.*, 2011). In the conventional quantitative approach to risk management of substances, health-based recommended occupational exposure limits (HBR-OELs) are accepted

\*Author to whom correspondence should be addressed.  
Tel: +31-20-525-6324; fax: +31-20-525-5850  
email: pvbroekhuizen@ivam.uva.nl

## ORIGINAL ARTICLE

# Exposure to ultrafine particles in hospitality venues with partial smoking bans

Manfred Neuberger<sup>1,2</sup>, Hanns Moshhammer<sup>1</sup> and Armin Schietz<sup>1</sup>

Fine particles in hospitality venues with insufficient smoking bans indicate health risks from passive smoking. In a random sample of Viennese inns (restaurants, cafes, bars, pubs and discotheques) effects of partial smoking bans on indoor air quality were examined by measurement of count, size and chargeable surface of ultrafine particles (UFPs) sized 10–300 nm, simultaneously with mass of particles sized 300–2500 nm (PM<sub>2.5</sub>). Air samples were taken in 134 rooms unannounced during busy hours and analyzed by a diffusion size classifier and an optical particle counter. Highest number concentrations of particles were found in smoking venues and smoking rooms (median 66,011 pt/cm<sup>3</sup>). Even non-smoking rooms adjacent to smoking rooms were highly contaminated (median 25,973 pt/cm<sup>3</sup>), compared with non-smoking venues (median 7,408 pt/cm<sup>3</sup>). The particle number concentration was significantly correlated with the fine particle mass ( $P < 0.001$ ). We conclude that the existing tobacco law in Austria is ineffective to protect customers in non-smoking rooms of hospitality premises. Health protection of non-smoking guests and employees from risky UFP concentration is insufficient, even in rooms labeled “non-smoking”. Partial smoking bans with separation of smoking rooms failed.

*Journal of Exposure Science and Environmental Epidemiology* (2013) **0**, 000–000. doi:10.1038/jes.2013.22

**Keywords:** second-hand smoke; ultrafine particles; tobacco law; smoking ban; gastronomy

## INTRODUCTION

Tobacco smoke is known to be the most important indoor source of fine and ultrafine particles (UFPs), usually captured by measuring PM<sub>2.5</sub>,<sup>1,2</sup> which is highly correlated with the nicotine concentration in the air.<sup>3,4</sup> Particles with a diameter <100 nm (commonly called “ultrafine”) are inhaled easily into the deep pulmonary tracts and partly enter the vascular system. UFPs decrease coronary flow and accelerate blood clotting and the progression of atherosclerosis by endothelial dysfunction.<sup>5</sup> The smaller the size of particles inhaled, the more severe is their effect on cardiovascular disorders.<sup>6</sup>

Outdoor PM<sub>2.5</sub> exposure in Vienna, even at relatively low levels, has been related to cardiovascular and cerebrovascular mortality on the same day and the following 14 days.<sup>7</sup> Implementation of total smoking bans lead to significant decreases of indoor particulate matter and nicotine,<sup>8–10</sup> followed by a decrease of coronary events.<sup>11</sup>

In Viennese hospitality venues, very high PM<sub>2.5</sub> concentrations had been found before.<sup>12</sup> UFPs, however, contribute little to particle mass, and air nicotine concentration correlated higher with chargeable particle surface area (dominated by ultrafines) than with PM<sub>2.5</sub>.<sup>13</sup> Recent insights into harmful effects of UFPs<sup>14</sup> and new possibilities to measure both particle number and chargeable surface area, correlated to lung-deposited surface area (LDSA),<sup>15</sup> initiated this investigation after introduction of a partial smoking ban,<sup>16</sup> which had gone into force in Austria in 2009. Since then owners of hospitality premises have to provide a non-smoking room, an adjacent smoking room had to be separated by a door until July 2010. Various exceptions weaken the already weak law: Owners of venues <50 m<sup>2</sup> do not have to

offer a non-smoking room, if they decide on their own that their establishment is a smoking venue. Furthermore, premises >50 m<sup>2</sup> and <80 m<sup>2</sup> may remain without a separated non-smoking room if the building inspection decided that for fire protection or for preservation of a historic building no separation is possible. All other venues were required to reserve the “main room” for non-smoking guests and to provide a separation to the smoking room by a door; however, no specifications on the tightness of the door and on ventilation were given.

## MATERIALS AND METHODS

### Sampling

The study was carried out between 6 November 2010 and 6 June 2011. Air samples were taken in 134 rooms of 88 hospitality premises in Vienna, which were selected among well-used inns in central districts by chance. Sixteen of those venues were cafes, 51 bars and pubs, 14 restaurants and 7 discotheques. Only 22 establishments were designated non-smoking venues. In 20 venues, smoking was permitted and 46 establishments had designated non-smoking rooms next to smoking rooms. Sampling was performed without previous notice (while having a drink) and lasted 20 min per room sampled, consecutively in central parts of non-smoking rooms and adjacent smoking rooms, and away from spot sources (smoking neighbor, open kitchen) and sinks (open doors, windows).

The air samples were taken when most guests were present (bars, pubs and discotheques in the evening or at night, restaurants at midday or in the evening and cafes in the afternoon). The apparatus was hidden in a bag, in order to avoid selection bias introduced by permission of the owners of the establishments.

All examined hospitality premises were located near the city center (post-codes 1010, 1030, 1040, 1060, 1070, 1080, 1090, 1150, 1180, 1190 and 1200).

<sup>1</sup>Institute of Environmental Health, Medical University of Vienna, Wien, Austria and <sup>2</sup>Clean Air Commission, Austrian Academy of Science, Wien, Austria. Correspondence: Professor Manfred Neuberger, Institute of Environmental Health, Medical University of Vienna, Kinderspitalgasse 15, Wien A-1090, Austria.

Tel.: +431 40160 34920; Fax: +431 40160 934936.

E-mail: [manfred.neuberger@meduniwien.ac.at](mailto:manfred.neuberger@meduniwien.ac.at)

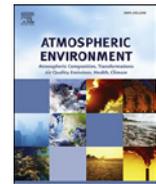
Received 21 September 2012; revised 13 January 2013; accepted 18 February 2013



Contents lists available at [ScienceDirect](#)

## Atmospheric Environment

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### Short communication

# Exposure to ultrafine particles and black carbon in diesel-powered commuter trains



Cheol-Heon Jeong\*, Alison Traub, Greg J. Evans

*Southern Ontario Centre for Atmospheric Aerosol Research, University of Toronto, Toronto, Canada*

### HIGHLIGHTS

- Ultrafine particles (UFP) and black carbon (BC) were measured in passenger trains.
- Train passengers can be exposed to elevated levels of diesel exhaust.
- UFP and BC in pull-trains were notably higher than those for other commuter modes.
- Mitigating actions for exposure in diesel-powered passenger trains are recommended.

### GRAPHICAL ABSTRACT



### ARTICLE INFO

#### Article history:

Received 23 November 2016  
Received in revised form  
4 February 2017  
Accepted 7 February 2017  
Available online 8 February 2017

#### Keywords:

Personal exposure  
Ultrafine particle  
Black carbon  
Diesel-powered commuter train  
Diesel exhaust

### ABSTRACT

Ultrafine particle (UFP), black carbon (BC) and lung deposited surface area (LDSA) concentrations measured during 43 trips on diesel-powered commuter trains revealed elevated exposures under some conditions. When the passenger coaches were pulled by a locomotive, the geometric mean concentrations of UFP, LDSA, and BC were 18, 10, and 6 times higher than the exposure levels when the locomotive pushed the coaches, respectively. In addition, UFP, LDSA, and BC concentrations in pull-trains were 5, 3, and 4 times higher than concentrations measured while walking on city sidewalks, respectively. Exposure to these pollutants was most elevated in the coach located closest to the locomotive: geometric means were  $126,000 \text{ \# cm}^{-3}$  for UFP,  $249 \text{ \mu m}^2 \text{ cm}^{-3}$  for LDSA, and  $17,800 \text{ ng m}^{-3}$  of BC; these concentrations are much higher than those previously reported for other modes of public transportation. Markedly high levels of diesel exhaust are present in passenger trains powered by diesel locomotives operated in pull-mode. Thus, it is recommended that immediate steps be taken to evaluate, and where needed, mitigate exposure in diesel-powered passenger trains, both commuter and inter-city.

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## 1. Introduction

Diesel exhaust was recently recognized as carcinogenic to humans and has been associated with a wide range of other health outcomes (IARC, 1989; Benbrahim-Tallaa et al., 2012; Straif et al., 2013). This complex mixture of particle and gas phase

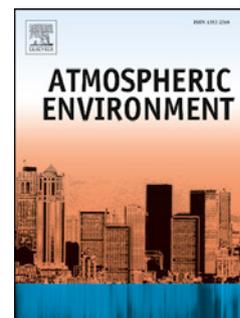
compounds contains components that can facilitate detection and assessment of associated exposures. The particle phase for example, contains elevated concentrations of ultrafine particles (UFP, < 100 nm) and black carbon (BC), both of which can be measured in high time resolution with handheld instruments. Furthermore, both these components are toxic in their own right. Some toxicological studies have suggested that UFP may be more harmful than larger particles (>100 nm) due to increased surface area for adsorption and condensation, higher deposition rates in lung alveoli, and greater ability to translocate through organs

\* Corresponding author.  
E-mail address: [ch.jeong@utoronto.ca](mailto:ch.jeong@utoronto.ca) (C.-H. Jeong).

# Accepted Manuscript

Field comparison of instruments for exposure assessment of airborne ultrafine particles and particulate matter

Andrea Spinazzè, Giacomo Fanti, Francesca Borghi, Luca Del Buono, Davide Campagnolo, Sabrina Rovelli, Andrea Cattaneo, Domenico M. Cavallo



PII: S1352-2310(17)30070-5

DOI: [10.1016/j.atmosenv.2017.01.054](https://doi.org/10.1016/j.atmosenv.2017.01.054)

Reference: AEA 15173

To appear in: *Atmospheric Environment*

Received Date: 4 November 2016

Revised Date: 26 January 2017

Accepted Date: 31 January 2017

Please cite this article as: Spinazzè, A., Fanti, G., Borghi, F., Del Buono, L., Campagnolo, D., Rovelli, S., Cattaneo, A., Cavallo, D.M., Field comparison of instruments for exposure assessment of airborne ultrafine particles and particulate matter, *Atmospheric Environment* (2017), doi: 10.1016/j.atmosenv.2017.01.054.

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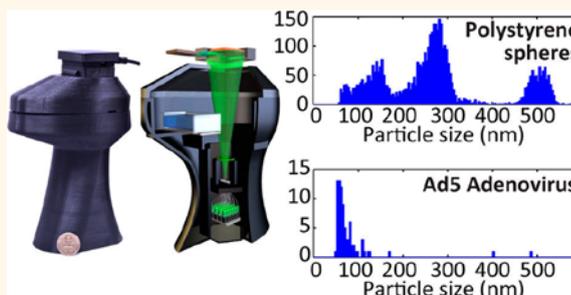
# High-Throughput and Label-Free Single Nanoparticle Sizing Based on Time-Resolved On-Chip Microscopy

Euan McLeod,<sup>\*,†,‡</sup> T. Umut Dincer,<sup>†,‡</sup> Muhammed Veli,<sup>†,‡</sup> Yavuz N. Ertas,<sup>‡</sup> Chau Nguyen,<sup>§</sup> Wei Luo,<sup>†,‡</sup> Alon Greenbaum,<sup>†,‡</sup> Alborz Feizi,<sup>‡</sup> and Aydogan Ozcan<sup>\*,†,‡,⊥,||</sup>

<sup>†</sup>Electrical Engineering Department, University of California, Los Angeles, California 90095, United States, <sup>‡</sup>Bioengineering Department, University of California, Los Angeles, California 90095, United States, <sup>§</sup>Chemistry & Biochemistry Department, University of California, Los Angeles, California 90095, United States, <sup>⊥</sup>California NanoSystems Institute, University of California, Los Angeles, California 90095, United States, and <sup>||</sup>Department of Surgery, David Geffen School of Medicine, University of California, Los Angeles, California 90095, United States

**ABSTRACT** Sizing individual nanoparticles and dispersions of nanoparticles provides invaluable information in applications such as nanomaterial synthesis, air and water quality monitoring, virology, and medical diagnostics. Several conventional nanoparticle sizing approaches exist; however, there remains a lack of high-throughput approaches that are suitable for low-resource and field settings, *i.e.*, methods that are cost-effective, portable, and can measure widely varying particle sizes and concentrations. Here we fill this gap using an unconventional approach that combines holographic on-chip microscopy with vapor-condensed nanolens self-assembly inside a cost-effective hand-held device.

By using this approach and capturing time-resolved *in situ* images of the particles, we optimize the nanolens formation process, resulting in significant signal enhancement for the label-free detection and sizing of individual deeply subwavelength particles (smaller than  $\lambda/10$ ) over a 30 mm<sup>2</sup> sample field-of-view, with an accuracy of  $\pm 11$  nm. These time-resolved measurements are significantly more reliable than a single measurement at a given time, which was previously used only for nanoparticle detection without sizing. We experimentally demonstrate the sizing of individual nanoparticles as well as viruses, monodisperse samples, and complex polydisperse mixtures, where the sample concentrations can span  $\sim 5$  orders-of-magnitude and particle sizes can range from 40 nm to millimeter-scale. We believe that this high-throughput and label-free nanoparticle sizing platform, together with its cost-effective and hand-held interface, will make highly advanced nanoscopic measurements readily accessible to researchers in developing countries and even to citizen-scientists, and might especially be valuable for environmental and biomedical applications as well as for higher education and training programs.



**KEYWORDS:** nanoparticles · particle-sizing · lensfree microscopy · field-portable

The ability to detect and size nanoparticles is extremely important in the analysis of liquid and aerosol samples for medical, biological, and environmental studies.<sup>1–8</sup> Some examples of nanoparticles that researchers have been interested in detecting and sizing include viruses,<sup>9–11</sup> exosomes,<sup>1</sup> metallic labels,<sup>12,13</sup> soot,<sup>6,14</sup> ice crystals in clouds,<sup>15</sup> and engineered nanomaterials,<sup>16</sup> among others. While there exist various nanoparticle detection and sizing methods, there is a lack of high-throughput instruments that can cover a large dynamic range of particle sizes and concentrations within a field-portable, cost-effective and rapid interface. Existing nonoptical methods,

such as transmission electron microscopy (TEM), scanning electron microscopy (SEM), and atomic force microscopy, are typically very accurate and provide a gold standard for particle sizing;<sup>1,4</sup> however they are bulky, require significant capital investment, can be slow in image acquisition, and provide extremely restricted fields of view (FOVs) that limit throughput for particle sizing. Optical techniques can be more cost-effective and rapid; however, it is in general difficult to overcome the challenge of obtaining a large enough signal-to-noise (SNR) ratio to detect and reliably size both individual nanoparticles and populations of nanoparticles.

\* Address correspondence to euanmc@ucla.edu, ozcan@ucla.edu.

Received for review January 18, 2015 and accepted February 17, 2015.

Published online February 17, 2015  
10.1021/acsnano.5b00388

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RESEARCH

Open Access



# Increase in oxidative stress levels following welding fume inhalation: a controlled human exposure study

Halshka Graczyk<sup>1</sup>, Nastassja Lewinski<sup>1,2</sup>, Jiayuan Zhao<sup>1,3</sup>, Jean-Jacques Sauvain<sup>1</sup>, Guillaume Suarez<sup>1</sup>, Pascal Wild<sup>4</sup>, Brigitta Danuser<sup>1</sup> and Michael Riediker<sup>1,5\*</sup> 

## Abstract

**Background:** Tungsten inert gas (TIG) welding represents one of the most widely used metal joining processes in industry. It has been shown to generate a large majority of particles at the nanoscale and to have low mass emission rates when compared to other types of welding. Despite evidence that TIG fume particles may produce reactive oxygen species (ROS), limited data is available for the time course changes of particle-associated oxidative stress in exposed TIG welders.

**Methods:** Twenty non-smoking male welding apprentices were exposed to TIG welding fumes for 60 min under controlled, well-ventilated settings. Exhaled breathe condensate (EBC), blood and urine were collected before exposure, immediately after exposure, 1 h and 3 h post exposure. Volunteers participated in a control day to account for oxidative stress fluctuations due to circadian rhythm. Biological liquids were assessed for total reducing capacity, hydrogen peroxide (H<sub>2</sub>O<sub>2</sub>), malondialdehyde (MDA), and 8-hydroxy-2'-deoxyguanosine (8-OHdG) concentrations at each time point. A linear mixed model was used to assess within day and between day differences.

**Results:** Significant increases in the measured biomarkers were found at 3 h post exposure. At 3 h post exposure, we found a 24 % increase in plasma-H<sub>2</sub>O<sub>2</sub> concentrations ([95%CI: 4 % to 46 %],  $p = 0.01$ ); a 91 % increase in urinary-H<sub>2</sub>O<sub>2</sub> ([2 % to 258 %],  $p = 0.04$ ); a 14 % increase in plasma-8-OHdG ([0 % to 31 %],  $p = 0.049$ ); and a 45 % increase in urinary-8-OHdG ([3 % to 105 %],  $p = 0.03$ ). Doubling particle number concentration (PNC) exposure was associated with a 22 % increase of plasma-8-OHdG at 3 h post exposure ( $p = 0.01$ ).

**Conclusion:** A 60-min exposure to TIG welding fume in a controlled, well-ventilated setting induced acute oxidative stress at 3 h post exposure in healthy, non-smoking apprentice welders not chronically exposed to welding fumes. As mass concentration of TIG welding fume particles is very low when compared to other types of welding, it is recommended that additional exposure metrics such as PNC are considered for occupational risk assessments. Our findings highlight the importance of increasing awareness of TIG welding fume toxicity, especially given the realities of welding workplaces that may lack ventilation; and beliefs among interviewed welders that TIG represents a cleaner and safer welding process.

**Keywords:** Oxidative stress, Welding fume, 8-OHdG, Hydrogen peroxide, Malondialdehyde, Apprentice welders, Tungsten Inert Gas (TIG), Occupational exposure

\* Correspondence: michael.riediker@alumni.ethz.ch

<sup>1</sup>Institute for Work and Health, University of Lausanne and Geneva, Lausanne CH-1066, Switzerland

<sup>5</sup>SAFENANO, IOM Singapore, Singapore 048622, Singapore

Full list of author information is available at the end of the article



Article

## Indoor Air Quality in Naturally Ventilated Italian Classrooms

Fernanda Carmen Fuoco <sup>1,\*</sup>, Luca Stabile <sup>1</sup>, Giorgio Buonanno <sup>1,2</sup>, Concepcion Vargas Trassiera <sup>1</sup>, Angelamaria Massimo <sup>1</sup>, Aldo Russi <sup>1</sup>,  
Mandana Mazaheri <sup>2</sup>, Lidia Morawska <sup>2</sup> and Alexandro Andrade <sup>3</sup>

<sup>1</sup> Department of Civil and Mechanical Engineering, University of Cassino and Southern Lazio, Cassino (FR) 03043, Italy; E-Mails: [l.stabile@unicas.it](mailto:l.stabile@unicas.it) (L.S.); [buonanno@unicas.it](mailto:buonanno@unicas.it) (G.B.); [c.vargas@unicas.it](mailto:c.vargas@unicas.it) (C.V.T.); [a.massimo@unicas.it](mailto:a.massimo@unicas.it) (A.M.); [a.russi@unicas.it](mailto:a.russi@unicas.it) (A.R.)

<sup>2</sup> International Laboratory for Air Quality and Health, Queensland University of Technology, Brisbane (QLD) 4001, Australia; E-Mails: [m.mazaheri@qut.edu.au](mailto:m.mazaheri@qut.edu.au) (M.M.); [l.morawska@qut.edu.au](mailto:l.morawska@qut.edu.au) (L.M.);

<sup>3</sup> Center of Health Sciences and Sport, Santa Catarina State University, Florianopolis 88080-350, Brazil; E-Mail: [alexandro.andrade@udesc.br](mailto:alexandro.andrade@udesc.br) (A.A.)

\* Author to whom correspondence should be addressed; E-Mail: [fc.fuoco@unicas.it](mailto:fc.fuoco@unicas.it) (F.C.F.); Tel.: +39-776-299-3618; Fax: +39-776-299-4002.

Academic Editor: Pasquale Avino

Received: 22 September 2015 / Accepted: 27 October 2015 / Published:

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**Abstract:** Characterization of indoor air quality in school classrooms is crucial to children's health and performance. The present study was undertaken to characterize the indoor air quality in six naturally ventilated classrooms of three schools in Cassino (Italy). Indoor particle number, mass, black carbon, CO<sub>2</sub> and radon concentrations, as well as outdoor particle number were measured within school hours during the winter and spring season. The study found the concentrations of indoor particle number were influenced by the concentrations in the outdoors; highest BC values were detected in classrooms during peak traffic time. The effect of different seasons' airing mode on the indoor air quality was also detected. The ratio between indoor and outdoor particles was of  $0.85 \pm 0.10$  in winter, under airing conditions of short opening window periods, and  $1.00 \pm 0.15$  in spring when the windows were opened for longer periods. This was associated to a higher degree of penetration of outdoor particles due to longer period of window opening. Lower CO<sub>2</sub> levels were found in classrooms in spring (908 ppm) than in winter (2206 ppm). Additionally, a



## Metrological Performances of a Diffusion Charger Particle Counter for Personal Monitoring

Giorgio Buonanno<sup>1,2\*</sup>, Rohan E. Jayaratne<sup>2</sup>, Lidia Morawska<sup>2</sup>, Luca Stabile<sup>1</sup>

<sup>1</sup> Department of Civil and Mechanical Engineering, University of Cassino and Southern Lazio, via Di Biasio 43, 03043 Cassino, Italy

<sup>2</sup> International Laboratory for Air Quality and Health, Queensland University of Technology, GPO Box 2434, Brisbane, Australia

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### ABSTRACT

Airborne particles have been shown to be associated with a wide range of adverse health effects, and have thus attracted an increasing amount of attention by medical researchers. However, accurate evaluations of the related exposure-dose-response relationships are highly dependent on the ability to track people's actual exposure to airborne particles. This is quite a complex task, particularly in relation to submicrometer and ultrafine particles, which can vary quite significantly in terms of particle surface area and number concentration. It is thus necessary to develop suitable monitors that can be worn in order to measure personal exposure to these particles.

This paper presents an evaluation of the metrological performance of six diffusion charger sensors, namely NanoTracer (Philips Aerasure) monitors, when measuring particle number and surface area concentrations, as well as particle number distribution mean, when compared to reference instruments. Tests in the laboratory (by generating monodisperse and polydisperse aerosols) and in the field (using natural ambient particles) were designed to evaluate the responses of these devices under both steady-state and dynamics conditions.

The results show that the NanoTracers performed well when measuring steady state aerosols, although they strongly underestimated the actual concentrations during dynamic response testing. The field experiments also showed that, when the majority of the particles were smaller than 20 nm, which occurs during particle formation events in the atmosphere, the NanoTracers underestimated the number concentration quite significantly. Overall, even though NanoTracers can be used for personal monitoring of exposure to ultrafine particles, they have some limitations which need to be considered in order to obtain meaningful results.

**Keywords:** Ultrafine particles; Alveolar deposited surface area concentration; Personal monitoring; Exposure-risk assessment.

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### INTRODUCTION

In recent years, a number of studies have focused on aerosol monitoring in order to estimate human exposure to particle concentrations. This increase in technical and scientific attention was motivated by medical studies relating high particle concentration exposure to adverse health effects (Kreyling *et al.*, 2006; Pope and Dockery, 2006; Schmid *et al.*, 2009). However, the view within the medical community is not unanimous when it comes to determining which aerosol physical properties are of most significance in relation to these health effects. Scientific interest has recently shifted from mass concentration (PM) (Loomis, 2000; Pope, 2000) to surface area and number concentration (Giechaskiel

*et al.*, 2009; Franck *et al.*, 2011; Cauda *et al.*, 2012), with a focus on smaller particles, such as ultrafine particles (UFPs with a diameter smaller than 100 nm), due to their ability to be deposited in lower regions of the respiratory tract, thus leading to a range of adverse health effects (ICRP, 1994; Wang, 2005; Hofmann, 2011).

#### **Exposure Assessment: State-of-the-Art**

Assessing the exposure of urban populations to aerosol particles can be carried out according to five different spatial scales: i) "city scale", the broadest and most common scale used to characterize air quality across several city blocks using remote measurements; ii) "outdoor scale", which is representative of particle exposure outside a building/s of interest; iii) "indoor scale", which is measured within buildings and reflects indoor-based exposure; iv) "individual scale", where the sampling location is within 3 meters of the person, and v) "personal scale", using portable instruments as personal monitors, with a distance of < 30 cm between

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\* Corresponding author.

E-mail address: [buonanno@unicas.it](mailto:buonanno@unicas.it)

**\*Highlights (for review)**

**Multi-metric measurement of personal exposure to ultrafine particles in selected urban microenvironments.**

Andrea Spinazzè<sup>(a)</sup>, Andrea Cattaneo<sup>(a)</sup>, Damiano R. Scocca<sup>(a)</sup>, Matteo Bonzini<sup>(b)</sup>, Domenico M. Cavallo<sup>(a)</sup>

<sup>(a)</sup> Department of Science and High Technology, University of Insubria, Via Valleggio 11, 22100 Como, Italy

<sup>(b)</sup> Department of Clinical and Experimental Medicine, University of Insubria, Via Guicciardini 9, 21100 Varese, Italy

**Highlights**

- Ultrafine particles (UFP) personal exposure were measured in urban environments.
- UFP were characterized by number, mass concentration, mean diameter and surface-area.
- Appreciable differences among microenvironments and monitoring periods were observed.
- Concentration patterns were related to typical sources of urban pollutants (traffic).
- Temporal and microenvironmental patterns were determinants of UFP exposure.

1    **Abstract**

2        At the beginning of the study, our hypothesis was that visiting certain microenvironments (MEs)  
3    is one of the most important determinants of personal exposure to ultrafine particles (UFP) and that  
4    moving between microenvironments significantly differentiates exposure. The overall aim of this  
5    study is to perform relevant exposure measurements to extend our knowledge on environmental  
6    exposure to UFP in urban environments. The UFP concentrations in different urban MEs were  
7    measured by personal monitoring in repeated sampling campaigns along a fixed route. The  
8    measurement runs were performed on one-week periods and at different times of day (AM: 08.00 -  
9    10.30; PM: 16.00 - 18.30) and repeated in different periods of the year (winter, spring, summer, and  
10   autumn) for a total of 56 runs (> 110 hours). Measurements included on-line monitoring of the UFP  
11   particle number concentration (PNC), mean diameter (mean-d) and lung-deposited surface-area  
12   (LDSA). Additionally, the PNC, particle mass concentration (PMC) profiles for quasi-ultrafine  
13   particles (QUFP; PM<sub>0.25</sub>) were estimated. A significant seasonal difference in the PNC and PMC,  
14   mean diameter and surface area was observed as well as between different times of the day and  
15   days of the week. In addition, differences in the UFP concentrations were also found in each ME,  
16   and there were specific mean-diameter and surface area concentrations. In general, the mean  
17   particle diameters showed an inverse relationship with the PNC, while the LDSA had the opposite  
18   behaviour. Appreciable differences among all MEs and monitoring periods were observed; the  
19   concentration patterns and variations seemed related to the typical sources of urban pollutants  
20   (traffic), proximity to sources and time of day. The highest exposures were observed for walking or  
21   biking along high-trafficked routes and while using public buses. The UFP exposure levels in  
22   modern cars, equipped with high-efficiency filters and in air recirculation mode, were significantly  
23   lower.

24    **Keywords**

25    Air pollution; Ultrafine particles; Personal Exposure; Particle size; Surface Area; Commuting



# HHS Public Access

Author manuscript

*Curr Environ Health Rep.* Author manuscript; available in PMC 2016 March 25.

Published in final edited form as:

*Curr Environ Health Rep.* 2015 December ; 2(4): 399–411. doi:10.1007/s40572-015-0070-z.

## New Methods for Personal Exposure Monitoring for Airborne Particles

Kirsten A. Koehler<sup>1,\*</sup> and Thomas Peters<sup>2</sup>

Kirsten A. Koehler: [Kirsten.koehler@jhu.edu](mailto:Kirsten.koehler@jhu.edu); Thomas Peters: [thomas-m-peters@uiowa.edu](mailto:thomas-m-peters@uiowa.edu)

1

2

### Abstract

Airborne particles have been associated with a range of adverse cardiopulmonary outcomes, which has driven its monitoring at stationary, central sites throughout the world. Individual exposures, however, can differ substantially from concentrations measured at central sites due to spatial variability across a region and sources unique to the individual, such as cooking or cleaning in homes, traffic emissions during commutes, and widely varying sources encountered at work. Personal monitoring with small, battery-powered instruments enables the measurement of an individual's exposure as they go about their daily activities. Personal monitoring can substantially reduce exposure misclassification and improve the power to detect relationships between particulate pollution and adverse health outcomes. By partitioning exposures to known locations and sources, it may be possible to account for variable toxicity of different sources. This review outlines recent advances in the field of personal exposure assessment for particulate pollution. Advances in battery technology have improved the feasibility of 24-hour monitoring, providing the ability to more completely attribute exposures to microenvironment (e.g., work, home, commute). New metrics to evaluate the relationship between particulate matter and health are also being considered, including particle number concentration, particle composition measures, and particle oxidative load. Such metrics provide opportunities to develop more precise associations between airborne particles and health and may provide opportunities for more effective regulations.

### Keywords

exposure; particulate matter; personal monitoring; sensor technology

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\*Corresponding author.

#### Conflict of Interest

Kirsten A. Koehler declares that she has no conflict of interest.

Thomas Peters has a patent US20130220034 A1 with royalties paid to University of Iowa.

#### Compliance with Ethics Guidelines

#### Human and Animal Rights and Informed Consent

This article does not contain any studies with human or animal subjects performed by any of the authors.



## Outdoor infiltration and indoor contribution of UFP and BC, OC, secondary inorganic ions and metals in PM<sub>2.5</sub> in schools



I. Rivas<sup>a, b, d, e, f, \*</sup>, M. Viana<sup>a</sup>, T. Moreno<sup>a</sup>, L. Bouso<sup>b, d, e</sup>, M. Pandolfi<sup>a</sup>, M. Alvarez-Pedrerol<sup>b, d, e</sup>, J. Forn<sup>b, d, e, g</sup>, A. Alastuey<sup>a</sup>, J. Sunyer<sup>b, c, d, e</sup>, X. Querol<sup>a</sup>

<sup>a</sup> Institute for Environmental Assessment and Water Research (IDEA-CSIC), C/ Jordi Girona 18-26, 08034 Barcelona, Spain

<sup>b</sup> Centre for Research in Environmental Epidemiology (CREAL), C/ Dr. Aiguader 88, 08003 Barcelona, Spain

<sup>c</sup> Hospital del Mar Research Institute (IMIM), C/ Dr. Aiguader 88, 08003 Barcelona, Spain

<sup>d</sup> Universitat Pompeu Fabra (UPF), C/ Dr. Aiguader 88, 08003 Barcelona, Spain

<sup>e</sup> CIBER Epidemiología y Salud Pública (CIBERESP), C/ Monforte de Lemos 3-5, 28029 Madrid, Spain

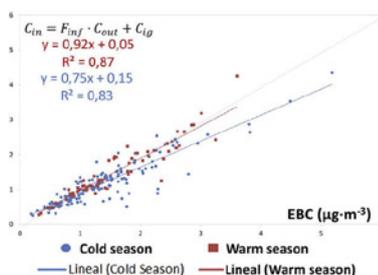
<sup>f</sup> Institut de Ciència i Tecnologia Ambientals, Universitat Autònoma de Barcelona (UAB), Edifici C Campus UAB, 08193 Bellaterra Cerdanyola, Spain

<sup>g</sup> Department of Genes and Environment, Division of Epidemiology, Norwegian Institute of Public Health, Oslo, Norway

### HIGHLIGHTS

- Infiltration of outdoor pollutants into indoor air at schools is assessed.
- Many pollutants have a high infiltration, with maximum reached by EBC and Cd.
- Building age & type of window do not determine infiltration levels.
- Type of window and sandy playground determine indoor mineral levels.

### GRAPHICAL ABSTRACT



### ARTICLE INFO

#### Article history:

Received 24 July 2014

Received in revised form

20 January 2015

Accepted 22 January 2015

Available online 23 January 2015

#### Keywords:

Particulate matter

Black carbon

Ultrafine particles

Road traffic

Indoor air quality

### ABSTRACT

Infiltration of outdoor-sourced particles into indoor environments in 39 schools in Barcelona was assessed during school hours. Tracers of road traffic emissions (NO<sub>2</sub>, Equivalent Black Carbon (EBC), Ultrafine Particles (UFP), Sb), secondary inorganic aerosols (SO<sub>4</sub><sup>2-</sup>, NO<sub>3</sub>, NH<sub>4</sub><sup>+</sup>) and a number of PM<sub>2.5</sub> trace elements showed median indoor/outdoor (I/O) ratios ≤ 1, indicating that outdoor sources importantly contributed to indoor concentrations. Conversely, OC and mineral components had I/O ratios > 1. Different infiltration factors were found for traffic and secondary components (0.31–0.75 and 0.50–0.92, cold and warm season respectively), with maxima corresponding to EBC and Cd. Higher concentrations of indoor-generated particles were observed when closed windows hindered dispersion (cold season). Building age was not a major determinant of indoor levels. Neither were the window's material, except for NO<sub>2</sub> (with an increase of 8 μg m<sup>-3</sup> for wood framed windows) and the mineral components (also dependent on the presence of sand in a distance <20 m) that reach the indoor environment via soil adhering to footwear with their dispersion being more barred by Aluminium/PVC framed windows than the wooden ones. Enlarged indoor concentrations of some trace elements suggest the presence of indoor sources that should be further investigated in order to achieve a healthier school indoor environment.

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\* Corresponding author. Institute for Environmental Assessment and Water Research (IDEA-CSIC), C/ Jordi Girona 18-26, 08034 Barcelona, Spain.  
E-mail address: [irivas@creal.cat](mailto:irivas@creal.cat) (I. Rivas).

## ORIGINAL ARTICLE

# Outdoor ultrafine particle concentrations in front of fast food restaurants

Cristina Vert<sup>1</sup>, Kees Meliefste<sup>1</sup> and Gerard Hoek<sup>1</sup>

Ultrafine particles (UFPs) have been associated with negative effects on human health. Emissions from motor vehicles are the principal source of UFPs in urban air. A study in Vancouver suggested that UFP concentrations were related to density of fast food restaurants near the monitoring sites. A previous monitoring campaign could not separate the contribution of restaurants from road traffic. The main goal of this study has been the quantification of fast food restaurants' contribution to outdoor UFP concentrations. A portable particle number counter (DiscMini) has been used to carry out mobile monitoring in a largely pedestrianized area in the city center of Utrecht. A fixed route passing 17 fast food restaurants was followed on 8 days. UFP concentrations in front of the restaurants were 1.61 times higher than in a nearby square without any local sources used as control area and 1.22 times higher compared with all measurements conducted in between the restaurants. Adjustment for other sources such as passing mopeds, smokers or candles did not explain the increase. In conclusion, fast food restaurants result in significant increases in outdoor UFP concentrations in front of the restaurant.

*Journal of Exposure Science and Environmental Epidemiology* (2016) **26**, 35–41; doi:10.1038/jes.2015.64; published online 4 November 2015

**Keywords:** ultrafine particles; outdoor air; fast food restaurants

## INTRODUCTION

Ultrafine particles (UFPs) defined as particles < 100 nm have been shown to be harmful for human health.<sup>1,2</sup> Because of their small size, UFPs can penetrate deep into the lungs and may enter the blood vessels. Sources of UFPs in outdoor air include combustion processes in especially motorized traffic, industry and residential heating and secondary formation from gaseous precursors.<sup>1–4</sup> A variety of sources of UFPs in indoor air has been identified, including cooking, smoking and electric appliances. Some studies have suggested that high UFP concentrations occur inside restaurants, especially barbecue restaurants<sup>5</sup> and fast food restaurants<sup>6</sup>. Cooking styles influence the concentration of particles emitted in the air, for example, frying (particularly deep frying) produces high particle number emissions. Although studies have reported high UFP or fine particles inside of bars, cafes and restaurants,<sup>5–9</sup> there is limited evidence of the effect that ventilation of indoor air from hospitality venues has on outdoor air quality. A land use regression model from Vancouver, Canada reported that the density of fast food restaurants in 100- or 200-m buffers was one of the predictors of spatial variation of UFPs.<sup>10</sup> A targeted added monitoring campaign in Vancouver could not disentangle the impact of restaurants from high road traffic intensity.<sup>10</sup> Because of the smoking ban in restaurants in many countries, including the Netherlands, smokers nowadays often smoke in front of the restaurants and bars, further complicating monitoring campaigns to assess impacts of (fast food) restaurants on outdoor air quality.

The main objective of this study was to determine the influence of fast food restaurants on outdoor UFP concentrations near the

restaurants. The study was performed in a low traffic area in the city center of Utrecht, the Netherlands to limit the effect of other UFP sources. We evaluated the impact of outdoor smoking and other sources on the relationship between proximity to restaurants and outdoor UFP concentration.

## METHODS

### Study Design

We designed a route in a largely pedestrianized area in the city center of Utrecht (328,577 inhabitants in 2014) (Figure 1) to measure if restaurants increase UFP concentrations. The route is largely free of motorized traffic. Most of the route consists of narrow streets. We selected 17 restaurants distributed over the route. We used mobile monitoring while walking using the DISCmini in a specially designed backpack to measure 1-s particle number concentrations. The technician stopped for 1–5 min in front of each restaurant and manually recorded the time she was in front of each restaurant. We further recorded the presence of other sources, including smokers, outdoor candle burning and passing motor vehicles, mopeds and (diesel powered) street washing machines with a 1-min resolution. UFP concentrations measured in front of the restaurants were compared with concentrations in between the restaurants. Because of the high density of restaurants along the route, this comparison may underestimate the impact of restaurants as the concentrations not immediately in front of the restaurants may also be affected by restaurant emissions. We therefore also included a “blank area” in the route, which was a small square without any traffic, restaurants and bars (Figure 1). Measurements were taken for 1–3 min in the blank area every monitoring session.

<sup>1</sup>Institute for Risk Assessment Sciences (IRAS), Division of Environmental Epidemiology, Utrecht University, Utrecht, The Netherlands. Correspondence: Dr Gerard Hoek, Institute for Risk Assessment Sciences (IRAS), Division of Environmental Epidemiology, Utrecht University, P.O. Box 80178, Utrecht 3508, The Netherlands. Tel.: +31 30 253 94 98. Fax: +31 30 253 94 99.

E-mail: g.hoek@uu.nl

Received 16 April 2015; revised 10 September 2015; accepted 16 September 2015; published online 4 November 2015

THESIS

QUANTIFYING COMMUTER EXPOSURES TO VOLATILE ORGANIC COMPOUNDS

Submitted by

Ashleigh Kayne

Department of Environmental and Radiological Health Sciences

In partial fulfillment of the requirements

For the Degree of Master of Science

Colorado State University

Fort Collins, Colorado

Spring 2014

Master's Committee:

Advisor: John Volckens

Jennifer Peel

Jeff Collett

## ABSTRACT

## QUANTIFYING COMMUTER EXPOSURES TO VOLATILE ORGANIC COMPOUNDS

Motor-vehicles can be a predominant source of air pollution in cities. Traffic-related air pollution is often unavoidable for people who live in populous areas. Commuters may have high exposures to traffic-related air pollution as they are close to vehicle tailpipes. Volatile organic compounds (VOCs) are one class of air pollutants of concern because exposure to VOCs carries risk for adverse health effects. Specific VOCs of interest for this work include benzene, toluene, ethylbenzene, and xylenes (BTEX), which are often found in gasoline and combustion products. Although methods exist to measure time-integrated personal exposures to BTEX, there are few practical methods to measure a commuter's time-resolved BTEX exposure which could identify peak exposures that could be concealed with a time-integrated measurement.

This study evaluated the ability of a photoionization detector (PID) to measure commuters' exposure to BTEX using Tenax TA samples as a reference and quantified the difference in BTEX exposure between cyclists and drivers with windows open and closed. To determine the suitability of two measurement methods (PID and Tenax TA) for use in this study, the precision, linearity, and limits of detection (LODs) for both the PID and Tenax TA measurement methods were determined in the laboratory with standard BTEX calibration gases. Volunteers commuted from their homes to their work places by cycling or driving while wearing a personal exposure backpack containing a collocated PID and Tenax TA sampler. Volunteers completed a survey and indicated if the windows in their vehicle were open or closed. Comparing pairs of exposure data from the Tenax TA and PID sampling methods determined the suitability of the PID to measure the BTEX exposures of commuters. The difference between BTEX exposures of cyclists and drivers with windows open and closed in Fort Collins was determined.

Both the PID and Tenax TA measurement methods were precise and linear when evaluated in the laboratory using standard BTEX gases. The LODs for the Tenax TA sampling tubes (determined with a

sample volume of 1,000 standard cubic centimeters which is close to the approximate commuter sample volumes collected) were orders of magnitude lower (0.04 to 0.7 parts per billion (ppb) for individual compounds of BTEX) compared to the PIDs' LODs (9.3 to 15 ppb of a BTEX mixture), which makes the Tenax TA sampling method more suitable to measure BTEX concentrations in the sub-parts per billion (ppb) range. PID and Tenax TA data for commuter exposures were inversely related. The concentrations of VOCs measured by the PID were substantially higher than BTEX concentrations measured by collocated Tenax TA samplers. The inverse trend and the large difference in magnitude between PID responses and Tenax TA BTEX measurements indicates the two methods may have been measuring different air pollutants that are negatively correlated. Drivers in Fort Collins, Colorado with closed windows experienced greater time-weighted average BTEX exposures than cyclists ( $p$ : 0.04). Commuter BTEX exposures measured in Fort Collins were lower than commuter exposures measured in prior studies that occurred in larger cities (Boston and Copenhagen). Although route and intake may affect a commuter's BTEX dose, these variables are outside of the scope of this study. Within the limitations of this study (including: small sample size, small representative area of Fort Collins, and respiration rates not taken into account), it appears health risks associated with traffic-induced BTEX exposures may be reduced by commuting via cycling instead of driving with windows closed and living in a less populous area that has less vehicle traffic.

Although the PID did not reliably measure low-level commuter BTEX exposures, the Tenax TA sampling method did. The PID measured BTEX concentrations reliably in a controlled environment, at high concentrations (300-800 ppb), and in the absence of other air pollutants. In environments where there could be multiple chemicals present that may produce a PID signal (such as nitrogen dioxide), Tenax TA samplers may be a better choice for measuring BTEX. Tenax TA measurements were the only suitable method within this study to measure commuter's BTEX exposure in Fort Collins, Colorado.

Article

## Respiratory Effects of Fine and Ultrafine Particles from Indoor Sources—A Randomized Sham-Controlled Exposure Study of Healthy Volunteers

Vanessa J. Soppa <sup>1,\*</sup>, Roel P. F. Schins <sup>1</sup>, Frauke Hennig <sup>1</sup>, Bryan Hellack <sup>2</sup>, Ulrich Quass <sup>2</sup>, Heinz Kaminski <sup>2</sup>, Thomas A. J. Kuhlbusch <sup>2,3</sup>, Barbara Hoffmann <sup>1,4</sup> and Gudrun Weinmayr <sup>1</sup>

<sup>1</sup> IUF-Leibniz Research Institute for Environmental Medicine, Auf'm Hennekamp 50, 40225 Düsseldorf, Germany; E-Mails: roel.schins@uni-duesseldorf.de (R.P.F.S.); frauke.hennig@IUF-Duesseldorf.de (F.H.); barbara.hoffmann@IUF-Duesseldorf.de (B.H.); gudrun.weinmayr@IUF-Duesseldorf.de (G.W.)

<sup>2</sup> Air Quality and Sustainable Nanotechnology Unit, Institut für Energie- und Umwelttechnik (IUTA) e.V., Bliersheimer Straße 58–60, 47229 Duisburg, Germany; E-Mails: hellack@iuta.de (B.H.); quass@iuta.de (U.Q.); kaminski@iuta.de (H.K.); tky@iuta.de (T.A.J.K.)

<sup>3</sup> Center for Nanointegration (CENIDE), University of Duisburg-Essen, Carl-Benz-Straße 199, 47057 Duisburg, Germany

<sup>4</sup> Medical Faculty, Heinrich-Heine-University of Düsseldorf, Universitätsstraße 1, 40225 Düsseldorf, Germany

\* Author to whom correspondence should be addressed; E-Mail: [vanessa.soppa@IUF-Duesseldorf.de](mailto:vanessa.soppa@IUF-Duesseldorf.de); Tel.: +49-211-3389-282; Fax: +49-21-3389-283.

Received: 28 March 2014; in revised form: 18 June 2014 / Accepted: 23 June 2014 /

Published: 4 July 2014

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**Abstract:** Particulate air pollution is linked to impaired respiratory health. We analyzed particle emissions from common indoor sources (candles burning (CB), toasting bread (TB), frying sausages (FS)) and lung function in 55 healthy volunteers (mean age 33.0 years) in a randomized cross-over controlled exposure study. Lung-deposited particle surface area concentration (PSC), size-specific particle number concentration (PNC) up to 10 µm, and particle mass concentration (PMC) of PM<sub>1</sub>, PM<sub>2.5</sub> and PM<sub>10</sub> were determined during exposure (2 h). FEV<sub>1</sub>, FVC and MEF<sub>25%–75%</sub> was measured before, 4 h and 24 h after exposure. Wilcoxon-rank sum tests (comparing exposure scenarios) and mixed linear regression using particle concentrations and adjusting for personal characteristics.



Contents lists available at ScienceDirect

## Journal of Aerosol Science

journal homepage: [www.elsevier.com/locate/jaerosci](http://www.elsevier.com/locate/jaerosci)



# Surface area is the biologically most effective dose metric for acute nanoparticle toxicity in the lung



Otmar Schmid<sup>a,b,\*</sup>, Tobias Stoeger<sup>a,b</sup>

<sup>a</sup> Comprehensive Pneumology Center, Member of the German Center for Lung Research, Max-Lebsche-Platz 31, 81377 Munich, Germany

<sup>b</sup> Institute of Lung Biology and Disease, Helmholtz Zentrum München, 85764 Neuherberg, Germany

### ARTICLE INFO

Available online 26 April 2016

#### Keywords:

Nanoparticle toxicity  
Lung Inflammation  
Dose–response  
Surface area  
Dose metric  
In vivo animal model

### ABSTRACT

In this study we provide guidance on the biologically most relevant dose metric for pulmonary toxicity of biopersistent, spherical nanoparticles (NPs). A retrospective analysis of nine *in vivo* studies on particle-induced, acute pulmonary toxicity in animal models (mouse, rat) was performed encompassing five different types of nanomaterials (polystyrene, titanium dioxide, carbonaceous materials, transition metal oxides (Co, Ni, Zn) and hydrothermally synthesized  $\alpha$ -quartz) with a wide range of primary particle diameters (9–535 nm) and mass-specific BET surface areas (6–800 m<sup>2</sup>/g). The acute influx of polymorphonuclear neutrophils (PMNs) into the lungs after intratracheal instillation of NPs was chosen as a toxicological endpoint for acute lung inflammation. The allometrically scaled toxicological data were investigated with respect to various dose metrics, namely (primary) particle number, joint length, BET and geometric surface area, volume and mass.

Surface area is identified as the biologically most relevant dose metric for spherical NPs explaining about 80% of the observed variability in acute pulmonary toxicity ( $R^2=0.77$ ). None of the other dose metrics explains more than 50% of the observed variability in pulmonary inflammation. Moreover, using surface area as the dose metric allows identification of material-based toxicity classes independent of particle size. Typical materials without intrinsic toxicity – here referred to as low-solubility, low-toxicity (LSLT) materials – show low surface-specific toxicity with an EC<sub>50</sub> dose of 175 m<sup>2</sup>/g-lung (geometric mean;  $\sigma_g=2.2$ ), where EC<sub>50</sub> represents the dose inducing 50% of the maximum effect (here 30% PMN). In contrast, transition metal oxides (here Co, Ni, Zn) – materials known for their intrinsic toxicity – display a 12-fold enhanced surface-specific toxicity compared to LSLT particles (EC<sub>50</sub>=15 m<sup>2</sup>/g-lung).

This analysis implies that surface-related modes of action are driving acute pulmonary toxicity for the types of NPs investigated here. The relevance of other dose metrics such as number and volume is acknowledged in the context of different modes of action, namely shape-induced toxicity (fiber paradigm) and extremely high particle lung burden (overload conditions), respectively. So which dose metric should be monitored by aerosol scientists involved in health related aerosol exposure measurements? The short answer is – all of them (except length), but there is a strong preference towards surface area.

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\* Corresponding author at: Institute of Lung Biology and Disease, Helmholtz Zentrum München, 85764 Neuherberg, Germany. Tel.: +49 89 3187 2557.  
E-mail address: [otmar.schmid@helmholtz-muenchen.de](mailto:otmar.schmid@helmholtz-muenchen.de) (O. Schmid).

<http://dx.doi.org/10.1016/j.jaerosci.2015.12.006>

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RESEARCH PAPER

## Titanium dioxide nanoparticles: occupational exposure assessment in the photocatalytic paving production

Andrea Spinazzè · Andrea Cattaneo · Marina Limonta ·  
Valentina Bollati · Pier Alberto Bertazzi · Domenico M. Cavallo

Received: 14 March 2016 / Accepted: 25 May 2016  
© Springer Science+Business Media Dordrecht 2016

**Abstract** Limited data are available regarding occupational exposure assessment to nano-sized titanium dioxide (nano-TiO<sub>2</sub>). The objective of this study is to assess the occupational exposure of workers engaged in the application of nano-TiO<sub>2</sub> onto concrete building materials, by means of a multi-metric approach (mean diameter, number, mass and surface area concentrations). The measurement design consists of the combined use of (i) direct-reading instruments to evaluate the total particle number concentrations relative to the background concentration and the mean size-dependent characteristics of particles (mean diameter and surface area concentration) and to estimate the 8-h

time-weighted average (8-h TWA) exposure to nano-TiO<sub>2</sub> for workers involved in different working tasks; and (ii) filter-based air sampling, used for the determination of size-resolved particle mass concentrations. A further estimation was performed to obtain the mean 8-h TWA exposure values expressed as mass concentrations ( $\mu\text{g nano-TiO}_2/\text{m}^3$ ). The multi-metric characterization of occupational exposure to nano-TiO<sub>2</sub> was significantly different both for different work environments and for each work task. Generally, workers were exposed to engineered nanoparticles (ENPs; <100 nm) mean levels lower than the recommended reference values and proposed occupational exposure limits (40,000 particle/cm<sup>3</sup>; 300  $\mu\text{g}/\text{m}^3$ ) and relevant exposures to peak concentration were not likely to be expected. The estimated 8-h TWA exposure showed differences between the unexposed and exposed subjects. For these last, further differences were defined between operators involved in different work tasks. This study provides information on nano-TiO<sub>2</sub> number and mass concentration, size distribution, particles diameter and surface area concentrations, which were used to obtain work shift-averaged exposures.

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A. Spinazzè (✉) · A. Cattaneo · M. Limonta ·  
D. M. Cavallo  
Dipartimento di Scienza e Alta Tecnologia, Università  
degli studi dell'Insubria, Via Valleggio 11, 22100 Como,  
Italy  
e-mail: andrea.spinazze@uninsubria.it

V. Bollati · P. A. Bertazzi  
EPIGET-Epidemiology, Epigenetics and Toxicology Lab,  
Dipartimento di Scienze Cliniche e di Comunità,  
Università degli Studi di Milano, Via San Barnaba 8,  
Milan, Italy

V. Bollati · P. A. Bertazzi  
Unità di Epidemiologia, Fondazione Cà Granda, IRCCS  
Ospedale Maggiore Policlinico, Milan, Italy

**Keywords** Occupational exposure · Exposure assessment · Titanium dioxide · Engineered nanoparticles · Engineered nanomaterial · Occupational health



Contents lists available at ScienceDirect

## Journal of Aerosol Science

journal homepage: [www.elsevier.com/locate/jaerosci](http://www.elsevier.com/locate/jaerosci)

# Ultrafine and nanoparticle formation and emission mechanisms during laser processing of ceramic materials



A.S. Fonseca<sup>a,b,\*</sup>, M. Viana<sup>a</sup>, X. Querol<sup>a</sup>, N. Moreno<sup>a</sup>, I. de Francisco<sup>c</sup>, C. Estepa<sup>c</sup>, G.F. de la Fuente<sup>c</sup>

<sup>a</sup> Institute of Environmental Assessment and Water Research (IDÆA-CSIC), C/Jordi Girona 18, 08034 Barcelona, Spain

<sup>b</sup> Universidad de Barcelona, Facultad de Química, Martí i Franquès 1-11, 08028 Barcelona, Spain

<sup>c</sup> Instituto de Ciencia de Materiales de Aragón (ICMA – Universidad de Zaragoza), María de Luna 3, E-50018 Zaragoza, Spain

## ARTICLE INFO

### Article history:

Received 25 February 2015

Received in revised form

25 May 2015

Accepted 27 May 2015

Available online 6 June 2015

### Keywords:

Tile sintering

Furnace

New particle formation

LDSA

Particle transport

Indoor air

## ABSTRACT

The use of laser technology in the ceramic industry is undergoing an increasing trend, as it improves surface properties. The present work aimed to assess ultrafine and nanoparticle emissions from two different types of laser treatments (tile sintering and ablation) applied to two types of tiles. New particle formation mechanisms were identified, as well as primary nanoparticle emissions, with concentrations reaching up to  $6.7 \times 10^6$  particles  $\text{cm}^{-3}$  and a mean diameter of 18 nm. Nanoparticle emission patterns were strongly dependent on temperature and raw tile chemical composition. Nucleation events were detected during the thermal treatment independently of the laser application. TEM images evidenced spherical ultrafine particles, originating from the tile melting processes. When transported across the indoor environment, particles increased in size (up to 38 nm) with concentrations remaining high ( $2.3 \times 10^6$  particles  $\text{cm}^{-3}$ ). Concentrations of metals such as Zn, Pb, Cu, Cr, As and Tl were found in particles  $< 250$  nm.

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## 1. Introduction

Laser irradiation of ceramic material is a novel technique with numerous advantages regarding the sintering process such as speed, temperature and enhanced durability and surface properties of structural materials (Schmatjko, Endres, Schmidt, & Banz, 1988; Toenshoff & Gedrat, 1991; Jarvis, Nastasi, Hubbard, & Hirvonen, 1993; de Francisco et al., 2011; Lahoz, de la Fuente, Pedra, & Carda, 2011). The use of high powered CO<sub>2</sub> lasers for industrial ceramic materials processing was studied in the framework of LIFE projects and is currently being assessed for two different industrial processes: (i) tile sintering in a high-temperature furnace and, (ii) ablation of ceramic materials. A recently developed “in-situ” melting method (tile sintering) makes use of a CO<sub>2</sub> laser scanner combined with simultaneous external heating of the substrate (in a conventional furnace) and uniform movement (Estepa & de la Fuente, 2006; de Francisco et al., 2011). This innovative technology allows to obtain coatings of practically any oxide material on an alumina substrate (Estepa & de la Fuente, 2006; de Francisco et al., 2011). In addition, this novel tool can also make use of CO<sub>2</sub> lasers in pulsed mode (induced laser ablation) to perform engravings on the surface of ceramics (Lahoz et al., 2011).

\* Corresponding author at: Institute of Environmental Assessment and Water Research (IDÆA-CSIC), C/Jordi Girona 18, 08034 Barcelona, Spain. Tel.: +34 934006100; fax: +34 932045904.

E-mail address: [ana.godinho@idaea.csic.es](mailto:ana.godinho@idaea.csic.es) (A.S. Fonseca).

<http://dx.doi.org/10.1016/j.jaerosci.2015.05.013>

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## VALIDATION OF NOVEL SENSORS TO ASSESS HUMAN EXPOSURES TO AIRBORNE POLLUTANTS



**Juana Maria Delgado-Saborit<sup>(1)</sup>, Adobi Okam, Maryam Shehab<sup>(1)</sup>**

**ADVISORY COMMITTEE: Roy M Harrison<sup>(1)</sup>, Jon G Ayres<sup>(2)</sup>, Ross Anderson<sup>(3)</sup> and Ben Armstrong<sup>(4)</sup>**

**(1) Division of Environmental Health & Risk Management, School of Geography, Earth & Environmental Sciences; College of Life and Environmental Sciences. University of Birmingham, Edgbaston, Birmingham B15 2TT, United Kingdom**

**(2) Institute of Occupational and Environmental Medicine, School of Health and Population Sciences; College of Medical and Dental Sciences. University of Birmingham, Edgbaston, Birmingham, B15 2TT, United Kingdom**

**(3) MRC Centre, Environmental Research Group, King's College London, Franklin-Wilkins Building; 150 Stamford Street, London, SE1 9NH, United Kingdom**

**(4) Public and Environmental Health Research Unit, London School of Hygiene and Tropical Medicine, Keppel Street, London WC1E 7HT, United Kingdom**

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### BACKGROUND

- Epidemiologic research traditionally uses data collected in central site monitors as the primary data source.
  - Poor **correlation between central site and personal exposure** results in biased estimates of the health effect.
- **High temporal resolution sensors with built-in accelerometers** are now available.
  - Such coupling of **temporal resolution and spatial information** on personal activities could be a potential tool to apportion sources affecting lung doses.
  - Useful in determining the **impact of several activities** have on exposure and in elucidating the level of spatiotemporal correlation of pollutants leading to confounding effects.
- Most studies measuring personal exposures have been limited to single pollutants, and few have attempted measuring **ultrafine particles (UFP)** at personal level.
- To date, there has been no **systematic comparison of concurrently measured concentrations and estimated doses with short time resolution to multi-pollutants** at the personal level.

### SPECIFIC GOALS OF RESEARCH

To **validate** a series of portable battery operated personal sensors against reference methods to establish the fundamental performance characteristics that will enable their use to assess doses and personal exposures.

1. To **measure the levels of a mixture of pollutants** (UFP, PM<sub>2.5</sub>, BC and NO<sub>2</sub>) in different environments relevant to doses, such as at the personal level, indoors at home and outdoors at a central site.
2. To **estimate lung doses** to each air pollutant (UFP, PM<sub>2.5</sub>, BC and NO<sub>2</sub>)
3. To **compare estimates of lung deposition dose** (as number, surface area and mass) derived from highly size-resolved particle concentration data with those estimated from poorly size resolved mass and number data (UFP and PM<sub>2.5</sub>).
4. To **identify which activities**, and microenvironments **contribute most** to doses and personal exposures.
5. To **compare the contributions to lung doses from different sources** such as gas-appliances emissions and traffic.
6. To characterise the **profile of the pollutant mixture** associated with key activities and microenvironments in Objective 4.
7. To assess the **effect** of location of homes with reference to **traffic**; the use of **gas cookers** on the degree of association between different pollutants at the dose level, and the degree of correlation between UFP and NO<sub>2</sub> in lung dose estimates.
8. To characterize the **degree of misclassification** of using central site monitors, home and personal exposure as a surrogate of lung dose in epidemiological studies.

### ON-LINE VALIDATION

- All the sensors were collocated alongside the reference methods described in table 1 at four validation monitoring sites, including suburban, urban, rural sites
- The monitors run for 14 days at each of the four ambient sites during the cold (October-March) and the warm seasons (April-September) collecting 112 24-h integrated samples and 32,256 5-min samples.
- Concentrations of concurrent gases (e.g. O<sub>3</sub>, NO, NO<sub>x</sub>, CO) are available and possible interferences with other gases as well as will temperature and humidity will be assessed.

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### AIMS OF RESEARCH

- To estimate **inhaled doses** to a **mixture of air pollutants** (including different particle metrics) namely UFP, PM<sub>2.5</sub>, BC and NO<sub>2</sub>, by coupling personal measurement with accelerometer readings and
- To compare doses with a range of alternative **surrogate exposure** metrics like personal exposures, indoors-at-home and central site levels,
- To assess the **degree of misclassification** associated with using **surrogate measures**,
- To **identify key activities** and sources contributing to the dose burden of these pollutants.

### DESCRIPTION OF SENSOR S

- A combination of sensors and monitors will be used to characterise exposures at the personal level, indoors at home and at the central site (Table 1).
- Suggested Data Quality Objectives at 5-min and 24-h time-scales are 15% for accuracy and 20% for precision.

Pollutant	Personal Exposure	Indoors Home	Central Site
PM 2.5	RTI MicroPEM	RTI MicroPEM	TEOM-FDMS
UFP (0.3µm)	Discmini UFP sensor	Discmini UFP sensor	TSI 3022A
NO <sub>2</sub>	Aeroqual 500 Sensor	Aeroqual 500 Sensor	API M300E NO/NO <sub>2</sub> /Nox
Black Carbon	MicroAeth AE-51	MicroAeth AE-51	Aethalometer AE-22



FIG 4. DISCMINI UFP, BC MICROAETH, PM<sub>2.5</sub> MICROPEM, NO<sub>2</sub> AEROQUAL SENSORS



FIG 1. VALIDATION SET-UP HARWELL & LONDON

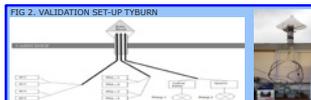


FIG 2. VALIDATION SET-UP TYBURN

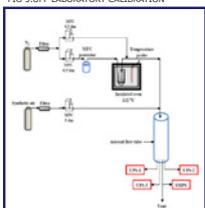


FIG3. VALIDATION SET-UP IN KITCHEN

**LABORATORY VALIDATION**

The **DISCmini UFP sensors** was validated in the laboratory by comparing the UFP concentrations and average diameter measured by the DISCmini sensor with those measured by a SMPS (TSI 3080) with a DMA (TSI 3081) connected to a CPC (TSI 3022A) after being challenged with Bis-(2-ethylhexyl)sebacate (BES, CAS 122-62-3) particles generated in the lab. (Fig 6)

FIG 5. UFP LABORATORY CALIBRATION



The laboratory validation of the **Aeroqual NO<sub>2</sub> sensor** consist of comparing the sensor readings using known NO<sub>2</sub> concentrations generated in a calibration system, spanning the range of 0 to 500 ppb. (Fig 5)

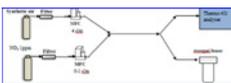


FIG 6. NO2 LABORATORY CALIBRATION

**NO2 SENSOR VALIDATION RESULTS**

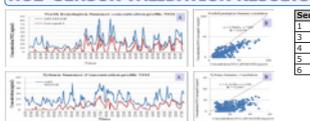


FIG 7. NO2 ON-LINE VALIDATION - A) temporal series; B) linear fit Aeroqual vs chemiluminescence analyser. Top presents North Kensington data. Bottom presents Tyburn data

TABLE 4. Laboratory Validation

Sensor	Regression coefficients	R2
1	1.1616 x + 79.244	0.9986
3	1.2055 x - 13.302	0.9983
4	1.1899 x + 57.147	0.9998
5	1.2025 x + 71.398	0.9990
6	1.1515 x - 52.916	0.9969
7	1.2025 x + 71.398	0.9990

Sensors exposed to high NO<sub>2</sub> concentrations present good R2, but overestimate concentrations  
 Sensors not exposed to high NO<sub>2</sub> concentrations do not perform well

**PRELIMINARY EXPOSURE RESULTS**



Preliminary analysis of BC exposure data shows that personal exposures are higher than home concentrations by a factor of 2.  
 Commuting and cooking are identified as activities relevant to exposures.

FIG 9. Human Exposure to PM<sub>2.5</sub> - Preliminary results

FIG 10. Human Exposure to PM<sub>2.5</sub> - Preliminary results

**OFF-LINE VALIDATION**

The **microaethalometer BC sensor** was validated by comparing the integrated mass of BC measured by the microaethalometer with:  
 1- the elemental carbon concentrations determined by chemical analysis using a Sunset OC/EC analyser of a quartz filter sample collected on a separate gravimetric sampling train.  
 2- the reflectance of the Teflon and paper filters using a smoke stain reflectometer (SSR) EEL Model 43D Reflectometer Digital with the integrated BC concentrations provided by the microaethalometer.  
 The **PM<sub>2.5</sub> MicroPEM sensor** has been validated against:  
 • the sensor's own downstream filter continuously sampling for 7 days  
 • a second Teflon filter collected on a separate sampling train consisting of a PM<sub>2.5</sub> cyclone/filter holder/pump.

**UFP VALIDATION RESULTS**

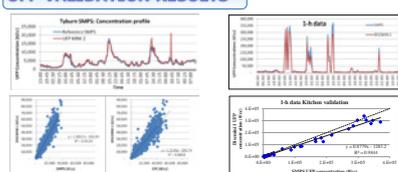


FIG 11. UFP AMBIENT ON-LINE VALIDATION - A) Example of SMPS temporal series -Tyburn Summer; B) linear fit CPC vs UFP sensor - ALL SITES; C) linear fit SMPS vs UFP sensor ALL SITES

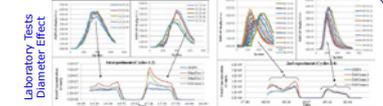


FIG 13. LABORATORY VALIDATION

TABLE 5. UFP DISCmini SENSOR SUMMARY RESULTS

Test	Min - Max conc (#/cc)	Average Dia (nm)	Time scale	Regression coefficients	R2	Bias (%)
Lab Cycles 1-3	1.10 <sup>0</sup> - 2.0.10 <sup>1</sup>	400 - 500	3 min	1.1908 x + 10913	0.87	23
Lab Cycles 4-10	1.10 <sup>0</sup> - 1.0.10 <sup>1</sup>	250	3 min	1.024 x - 359	0.91	-15
Ambient air	2.10 <sup>0</sup> - 4.0.10 <sup>1</sup>	30 - 50	60 min	1.8923 x - 359	0.91	-10
Kitchen	1.10 <sup>0</sup> - 1.0.10 <sup>1</sup>	18	5 min	0.8418 x + 353.9	0.96	-29
Kitchen	1.10 <sup>0</sup> - 4.0.10 <sup>1</sup>	18	60 min	0.8779 x - 1363	0.98	-14

**PM2.5 VALIDATION RESULTS**

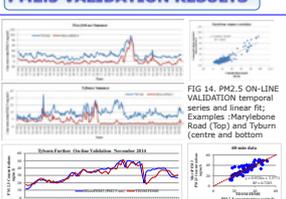


FIG 14. PM2.5 ON-LINE VALIDATION temporal series and linear fit: Examples -Marylebone Road (Top) and Tyburn (centre and bottom)

❑ Fails in the QA/QC protocol lead to:  
 ❑ Background measurements in negative values  
 ❑ Sudden drop of the sensor voltage and background conc.  
 ❑ Correction of the raw data was applied:  
 ❑ correction of negative values  
 ❑ correction of sensor voltage drop  
 ❑ correction of readings against inside filter if ratio of sensor/gravimetry was in the range 0.7-1.3

TABLE 6. AURN sites validation (TEOM- FDMS)

MicroPEM	Raw / Refined	Regression Coefficients	R2
1	Raw	0.3902 x - 2.7354	0.4443
	Refined	0.3854 x + 2.5594	0.4257
2	Raw	0.5511 x + 2.7401	0.6127
	Refined	0.6391 x + 0.7543	0.4481
3	Raw	0.7855 x - 0.6663	0.6181
	Refined	0.0057 x + 11.754	0.000
4	Raw	0.6433 x - 2.8545	0.6511
	Refined		

TABLE 7. Kitchen validation (GRIMM)

MicroPEM	Time resolution	Regression Coefficients	R2
1	60 min	0.9685 x - 1.568	0.904
2	60 min	0.8628 x - 0.8141	0.896
3	60 min	0.9149 x - 0.6619	0.913
4	60 min	0.9388 x - 4.8918	0.739

**BC VALIDATION RESULTS**



FIG 15. BLACK CARBON ON-LINE VALIDATION - A) temporal series; B) linear fit microaethalometer AE-51 vs Aethalometer AE-22

TABLE 8. BC VALIDATION SENSOR

Microaeth	Time scale	AURN outdoors Regression coefficients	R2	Kitchen (Indoors) Regression coefficients	R2
1	60 min	0.2997 x + 45.65	0.8665	0.0721 x + 60.909	0.7501
2	60 min	0.7672 x + 168.81	0.9060	0.7664 x + 76.519	0.7175
3	60 min	0.9311 x + 5.66	0.9202	0.844 x + 80.685	0.7687
4	60 min	0.737 x + 99.55	0.8163	0.9681 x + 69.463	0.6659

FIG 16. OFF-LINE VALIDATION. Correlation between reflectance in a paper filter (left) and Teflon filter (right)

**SUMMARY AND CONCLUSION**

The results shows that the UFP and BC sensors measures concentrations consistently similar to those measured by the reference analysers.  
 The PM<sub>2.5</sub> sensor underestimates the concentrations and needs further post-processing and QAQC measures.  
 The NO<sub>2</sub> sensor shows poor correlation with the chemiluminescence analyser and could not be validate.

## Literature Review - Workplace exposure to nanoparticles

### Workplace exposure to nanoparticles

#### **Authors:**

Simon Kaluza, Judith kleine Balderhaar, Bruno Orthen, Bundesanstalt für Arbeitsschutz und Arbeitsmedizin (BAuA, project leader), Germany

Bertrand Honnert, Institut National de Recherche et de Sécurité pour la prévention des accidents du travail et des maladies professionnelles (INRS), France

Elzbieta Jankowska, Piotr Pietrowski, Centralny Instytut Ochrony Pracy - Państwowy Instytut Badawczy (CIOP-PIB), Poland

Maria Gracia Rosell, Celia Tanarro, José Tejedor, Agurtzane Zugasti, Instituto Nacional de Seguridad e Higiene en el Trabajo (INSHT), Spain

#### **Edited by:**

Joanna Kosk-Bienko, European Agency for Safety and Health at Work (EU-OSHA), Spain

This report was commissioned by the European Agency for Safety and Health at Work. Its contents, including any opinions and/or conclusions expressed, are those of the author(s) alone and do not necessarily reflect the views of EU-OSHA.

## Literature Review - Workplace exposure to nanoparticles

### 1 Executive summary

The European Agency for Safety and Health at Work has published a series of expert forecasts providing an overview of the potential emerging risks in the world of work (physical, biological, psychosocial and chemical risks). Among the top ten emerging risks, three have in common their physico-chemical state as insoluble particles or fibres: nanoparticles and ultrafine particles, diesel exhaust, and man-made mineral fibres. The experts agreed that nanoparticles and ultrafine particles pose the strongest emerging risk.

Nanomaterials possess various new properties and their industrial use creates new opportunities, but they also present new risks and uncertainties. Growing production and use of nanomaterials result in an increasing number of workers and consumers exposed to nanomaterials. This leads to a greater need for information on possible health and environmental effects of nanomaterials. This report focuses on the possible adverse health effects of workplace exposure to engineered nanomaterials and possible subsequent activities taken to manage the risk. Nanomaterials originating from natural sources as well as non-intended nanoscale by-products, such as diesel engine exhaust and welding fumes, are not included in this review. In order to provide a broad overview, information from different sources such as scientific literature, policy documents, legislation and work programs were collected. Documents from the EU were given priority, although national and international activities have also been described. Studies published up to November 2008 have been considered in the report.

When particle size is decreased to the nanoscale range, physical and chemical properties often change with consequent new product opportunities. Thus a considerable future expansion of the nano-market is expected. Nevertheless it should be remembered that nanomaterials are not fully new: some established chemicals like amorphous silica or carbon black show a nanostructure. The knowledge about the occupational exposure to new nanomaterials is very limited. In addition, the measurement techniques to determine exposure are not fully developed. Various physical and chemical parameters have to be considered.

Different methods to investigate possible health effects of nanomaterials, such as in vivo- and in vitro-methods and methods to determine physico-chemical properties, are currently under discussion. The standardised in vivo-studies represent at present the best standard to detect toxicity evoked by nanomaterials. Effects like inflammation, fibrosis and tumours were induced by several granular nanomaterials in the lungs after respiratory exposure. Currently the mechanism of tumour formation is not fully understood and scientific uncertainties remain. Thus, the evaluation of toxicity is not only influenced by results from toxicity studies but also by the policy decision to what extent the precautionary principle is applied in case of scientific uncertainties. Skin exposure is not yet investigated in detail. Generally, in case of insoluble substances skin exposure is not as relevant as respiratory exposure.

The current principles of risk assessment seem to be in general appropriate; however, the validation of in vitro methods and the development of a testing strategy remain future tasks. Classification and labelling as well as occupational exposure limits, which are derived from toxicological data, are appropriate instruments for management of risks resulting from exposure to nanomaterials, but critically depend on the availability of studies on toxicity.

Several handling guidelines describing possible risk management activities and best practice were published. These are mainly based on technical feasibility and some of them recommend, based on the precautionary principle, to minimise exposure as far as possible. The protective measures that are typically used to protect against insoluble materials, like dusts, are often recommended also for nanomaterials. Because of the particular smallness of nanomaterials, especially the filter materials/media used in general ventilation systems, personal respiratory protective devices and the materials of gloves have to be examined. Preliminary studies indicate a protective effect, but further research is needed. In relation to filtering half masks, the lack of tightness (inadequate sealing) between face and the mask seems to be the most important risk factor. Control banding methods are used to assess occupational exposure in the case of non-existent occupational exposure limits or exposure measurements. First initiatives to adapt this method to nanomaterials have been developed, but need further elaboration. An important instrument of risk management providing information about hazards and appropriate control measures is the Material Safety Data Sheet. To what extent this instrument considers nanospecific properties sufficiently is currently under discussion.

### Literature Review - Workplace exposure to nanoparticles

Several statutory instruments are in place to ensure an appropriate level of protection of workers. The general framework is provided by the regulation on occupational safety and health of workers (EU Directive 89/391/EEC) and specifically for chemical safety - the directive on the protection of the health and safety of workers from the risks related to chemical agents at work (Directive 98/24/EC). Substance-specific regulation is intended by the biocide Directive (Directive 98/8/EC) and the regulation No 1907/2006 (REACH – Registration, Evaluation, Authorisation and Restriction of Chemicals). Currently it is discussed how to consider appropriately the broad variety of nanomaterials in these regulations.

The Community strategy on health and safety at work for the period of 2007 – 2012 includes nanotechnology as an important topic to be worked on in the context of the identification of new, emerging risks. Furthermore a communication from the European Commission 'Towards a European Strategy for Nanotechnology' was published. The European Commission developed an "Action Plan" to implement a safe, integrated and responsible approach for nanosciences and nanotechnologies. To ensure a safe and ethical development and use of nanotechnologies, the European Commission issued a Code of Conduct. There are many ongoing initiatives/activities aiming at the development of a safe, sustainable, responsible research and development of this new technology. Large scale research and standardisation programmes have been started and partly finalised to establish standards, close data gaps and reduce uncertainties. European and global collaboration is recognized as an important aspect in achieving these goals. Activities have been initiated by organisations such as the International Organization for Standardization (ISO) and the Organization for Economic Co-operation and Development (OECD) to support a globally harmonised development. Collaboration between EU and US is also being developed to investigate the regulatory challenges posed by nanotechnologies and to assess the effectiveness of existing approaches on both sides of the Atlantic. The project takes a comparative perspective and contributes to the early identification of regulatory methodologies and best practices that promote regulatory convergence between the EU and US.

As the conclusion of this review of the most recent publications, the following topics are identified as priorities for future actions and activities:

- identification of nanomaterials and description of exposure
- measurement of exposures to nanomaterials and efficacy of protective measures
- risk assessment of nanomaterials in line with the current statutory framework
- in vivo studies for assessment of the health effects of nanomaterials
- validation of the in vitro methods and methods of physico-chemical properties as methods to determine health effects
- training of workers and practical handling guidelines for activities involving nanomaterials in the workplace.

<b>Abstract 2.01</b>	<b>Seite 43</b>	<b>Abstract 2.14</b>	<b>Seite 58</b>
Airborne manufactured nano-objects released from commercially available spray products: Temporal and spatial influences		Handbook of nanosafety. Measurement, exposure and toxicology	
<b>Abstract 2.02</b>	<b>Seite 44</b>	<b>Abstract 2.15</b>	<b>Seite 60</b>
Assessment of nanoparticle exposure in nanosilica handling process: including characteristics of nanoparticles leaking from a vacuum cleaner		Increase in oxidative stress levels following welding fume inhalation: a controlled human exposure study	
<b>Abstract 2.03</b>	<b>Seite 45</b>	<b>Abstract 2.16</b>	<b>Seite 61</b>
Characterization and control of occupational exposure to nanoparticles and ultrafine particles		Indoor air quality in naturally ventilated Italian classrooms	
<b>Abstract 2.04</b>	<b>Seite 47</b>	<b>Abstract 2.17</b>	<b>Seite 62</b>
Characterization of exposure to carbon nanotubes in an industrial Setting		Lung-deposited surface area concentration measurements in selected occupational and non-occupational environments	
<b>Abstract 2.05</b>	<b>Seite 48</b>	<b>Abstract 2.18</b>	<b>Seite 63</b>
Characterization of Tungsten Inert Gas (TIG) welding fume generated by apprentice welders		Measurements of nanoscale TiO <sub>2</sub> and Al <sub>2</sub> O <sub>3</sub> in industrial workplace environments – methodology and results	
<b>Abstract 2.06</b>	<b>Seite 49</b>	<b>Abstract 2.19</b>	<b>Seite 64</b>
Comparison of nanoparticle exposures between fumed and sol-gel nano-silica manufacturing facilities		Measuring nanomaterial release from carbon nanotube composites: review of the state of the science	
<b>Abstract 2.07</b>	<b>Seite 50</b>	<b>Abstract 2.20</b>	<b>Seite 65</b>
Concerns related to safety management of engineered nanomaterials in research environment		Multi-walled carbon nanotubes in polymer matrices phase 2.5 report—comparison of existing studies of release measurement for MWCNT-polymer composites	
<b>Abstract 2.08</b>	<b>Seite 51</b>	<b>Abstract 2.21</b>	<b>Seite 67</b>
Consolidated framework for EHS of manufactured nanomaterials		Nanoparticle exposure at nanotechnology workplaces: A review	
<b>Abstract 2.09</b>	<b>Seite 53</b>	<b>Abstract 2.22</b>	<b>Seite 68</b>
Effect of natural ventilation and manual airing on indoor air quality in naturally ventilated Italian classrooms		Nanoparticle release from dental composites	
<b>Abstract 2.10</b>	<b>Seite 54</b>	<b>Abstract 2.23</b>	<b>Seite 69</b>
Engineered nanomaterials exposure in the production of graphene		Nano-Scaled Particles and Fibres Occupational Exposure Assessment: An Integrated Approach from Air Sampling to Skin and Surface Contamination	
<b>Abstract 2.11</b>	<b>Seite 55</b>	<b>Abstract 2.24</b>	<b>Seite 70</b>
Evaluation of a diffusion charger for measuring aerosols in a workplace		Potential release scenarios for carbon nanotubes used in composites	
<b>Abstract 2.12</b>	<b>Seite 56</b>	<b>Abstract 2.25</b>	<b>Seite 71</b>
Exposure to engineered nanoparticles: Model and measurements for accident situations in laboratories		Process-generated nanoparticles from ceramic tile sintering: Emissions, exposure and environmental release	
<b>Abstract 2.13</b>	<b>Seite 57</b>	<b>Abstract 2.26</b>	<b>Seite 72</b>
First order risk assessment for nanoparticle inhalation exposure during injection molding of polypropylene composites and production of tungsten-carbide-cobalt fine powder based upon pulmonary inflammation and surface area dose		Production of nanoscaled silicon particles at a pilot plant	
		<b>Abstract 2.27</b>	<b>Seite 75</b>
		Range-Finding risk assessment of inhalation exposure to Nanodiamonds in a Laboratory Environment	

## 2. 2. Health and safety

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**Abstract 2.28** **Page 76**  
Real-time single airborne nanoparticle detection with nanomechanical resonant filter-fiber

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**Abstract 2.29** **Page 77**  
Release of nanomaterials from ink and toner cartridges for printers

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**Abstract 2.30** **Page 80**  
Safe handling of nano materials and other advanced materials at workplaces

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**Abstract 2.31** **Page 84**  
Safety management of nanomaterials

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**Abstract 2.32** **Page 85**  
Sensitive photonic system to measure oxidative potential of airborne nanoparticles and ROS levels in exhaled air

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**Abstract 2.33** **Page 86**  
Spread of nano-objects in the air as a result of switching-on a microwave

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**Abstract 2.34** **Page 87**  
Tiered Approach to an exposure measurement and assessment of nanoscale aerosols released from engineered nanomaterials in workplace operations

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**Abstract 2.35** **Page 90**  
Ultrafine and nanoparticle formation and emission mechanisms during laser processing of ceramic materials

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**Abstract 2.36** **Page 91**  
Workplace exposure to nanoparticles and the application of provisional nanoreference values in times of uncertain risks

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**Abstract 2.37** **Page 92**  
Workplace exposure to titanium dioxide nanopowder released from a bag filter system



## ORIGINAL ARTICLE

# Airborne manufactured nano-objects released from commercially available spray products: temporal and spatial influences

Cindy Bekker<sup>1</sup>, Derk H. Brouwer<sup>1</sup>, Birgit van Duuren-Stuurman<sup>1</sup>, Ilse L. Tuinman<sup>2</sup>, Peter Tromp<sup>3</sup> and Wouter Fransman<sup>1</sup>

This paper reports a study of the dispersion of manufactured nano-objects (MNOs) through the air, both in time and space, during the use of two commercially available nano-spray products and comparable products without MNOs. The main objective was to identify whether personal exposure can occur at a greater distance than the immediate proximity of the source (> 1 m from the source), that is, in the “far field” (bystanders), or at a period after the emission occurred (re-entry). The spray experiments were conducted in an experimental room with well-controlled environmental and ventilation conditions (19.5 m<sup>3</sup>). The concentration of MNOs was investigated by measuring real-time size distribution, number, and active surface area concentration. For off-line analysis of the particles in the air, samples for scanning/transmission electron microscopy and elemental analysis were collected. The release of MNOs was measured at ~30 and 290 cm from the source (“near field” and “far field”, respectively). For all four spray products, the maximum number and surface area concentrations in the “near field” exceeded the maximum concentrations reached in the “far field”. At 2 min after the emission occurred, the concentration in both the “near field” and “far field” reached a comparable steady-state level above background level. These steady-state concentrations remained elevated above background concentration throughout the entire measurement period (12 min). The results of the real-time measurement devices mainly reflect the liquid aerosols emitted by the spray process itself rather than only the MNO, which hampers the interpretation of the results. However, the combination of the off-line analysis and the results of the real-time devices indicates that after the use of nano-spray products, personal exposure to MNOs can occur not only in the near field, but also at a greater distance than the immediate proximity of the source and at a period after emission occurred.

*Journal of Exposure Science and Environmental Epidemiology* (2014) **24**, 74–81; doi:10.1038/jes.2013.36; published online 17 July 2013

**Keywords:** inhalation exposure; personal exposure; exposure modeling

## INTRODUCTION

The increasing production and application of manufactured nano-objects (MNOs) have become a potential source for human exposure. Consequently, this raises concerns and questions about the possible effects of MNOs on human health, based on the fact that as objects reach the nanoscale size, the properties of the materials change and they become dependent on their size, shape, and composition.<sup>1</sup> Although the health effects of MNOs are unknown, numerous studies indicate that inhaled nano-objects can reach various organs, including the brain, and cause adverse effects to the cells.<sup>2–6</sup> Therefore, it is important to monitor and manage the exposure to MNOs.

The conceptual model for assessment of inhalation exposure to MNOs described by Schneider et al.<sup>7</sup> identifies four so-called “source domains” in the life cycle of MNOs, that is: (1) synthesis, (2) handling of nano-powder, (3) dispersion of ready-to-use nanoproducts (e.g., spraying), and (4) fracturing and abrasion of end products. Of these, spraying is an important scenario within the third source domain as it is a common and major source of exposure.

At the time of writing, there were only six publications in which inhalation exposure to (or emission of) nano-objects during the use of spray products had been investigated. These studies monitored the presence of MNOs in the near field,<sup>8,9</sup> breathing zone,<sup>10,11</sup> or exhaust air of a small experimental chamber.<sup>12,13</sup>

Hence, these studies primarily focused on the emission potential of sprays in close proximity to the source (< 1 m from the source). In order to identify whether personal exposure can occur at a greater distance than the immediate proximity of the source (to reflect potential bystanders exposure) or at a period after the emission occurred (to reflect potential exposure after re-entering the room), it is important to study the dispersion of the MNOs through the air in both time and space. The conceptual model for inhalation exposure described by Schneider et al.<sup>7</sup> identifies the so-called “transmission compartments”, including the near-field compartment, which can be defined as a volume of air within 1 m in any direction of the person’s head, and the far-field compartment, which represents the remainder of the chamber. The results of the present study will give more insight into this spatial effect on the concentration of MNOs in the near and far field including the time necessary to bridge this distance.

To our knowledge, this is the first published study focusing on the influence of both spatial and temporal variations on the concentration of airborne MNOs released from commercially available spray products. To do so, the aerosol concentration was measured at two different distances from the source (near and far field) for a period of 12 min in a controlled environment using various real-time monitoring instruments to measure number concentration, size distribution, and active surface area concentration. In addition, air samples were analyzed by

<sup>1</sup>TNO Quality of Life, Risk Analysis for Products In Development, P.O. Box 360, Zeist, The Netherlands; <sup>2</sup>TNO Quality of Life, CBRN Protection, P.O. Box 45, Rijswijk, The Netherlands and <sup>3</sup>TNO Quality of Life, Applied Environmental Chemistry, P.O. Box 80015, Utrecht, The Netherlands. Correspondence: Cindy Bekker, TNO Quality of Life, Risk Analysis for Products in Development, P.O. Box 360, Zeist, 3704 HE, The Netherlands. Tel.: +31 0 888663658.

E-mail: [cindy.bekker@tno.nl](mailto:cindy.bekker@tno.nl)

Received 11 December 2012; accepted 25 April 2013; published online 17 July 2013

# Assessment of Nanoparticle Exposure in Nanosilica Handling Process: Including Characteristics of Nanoparticles Leaking from a Vacuum Cleaner

Boowook KIM<sup>1</sup>, Hyunwook KIM<sup>2\*</sup> and Il Je YU<sup>3</sup>

<sup>1</sup>Occupational Lung Disease Institute, Korea Workers' Compensation and Welfare Service, Republic of Korea

<sup>2</sup>Department of Preventive Medicine, Catholic University of Korea, Republic of Korea

<sup>3</sup>Toxicological Research Center, Hoseo University, Republic of Korea

*Received April 28, 2013 and accepted November 26, 2013*

*Published online in J-STAGE December 21, 2013*

**Abstract:** Nanosilica is one of the most widely used nanomaterials across the world. However, their assessment data on the occupational exposure to nanoparticles is insufficient. The present study performed an exposure monitoring in workplace environments where synthetic powders are prepared using fumed nanosilica. Furthermore, after it was observed during exposure monitoring that nanoparticles were emitted through leakage in a vacuum cleaner (even with a HEPA-filter installed in it), the properties of the leaked nanoparticles were also investigated. Workers were exposed to high-concentration nanosilica emitted into the air while pouring it into a container or transferring the container. The use of a vacuum cleaner with a leak (caused by an inadequate sealing) was found to be the origin of nanosilica dispersion in the indoor air. While the particle size of the nanosilica that emitted into the air (during the handling of nanosilica by a worker) was mostly over 100 nm or several microns ( $\mu\text{m}$ ) due to the coagulation of particles, the size of nanosilica that leaked out of vacuum cleaner was almost similar to the primary size (mode diameter 11.5 nm). Analysis of area samples resulted in 20% (60% in terms of peak concentration) less than the analysis of the personals sample.

**Key words:** Exposure assessment, Nanomaterials, Silica nanoparticle, Aerosol characteristic, Vacuum cleaner leakage

## Introduction

Nanosilica is one of the most widely used nanomaterials across the world. In South Korea, 34,136 tons of 93 types of nanomaterials are manufactured or imported annually, and silica occupies the second place with 9,408 tons<sup>1</sup>.

Silica exists in two phases: crystalline, and amorphous. Crystalline silica is especially notorious for inducing lung

cancer and is categorized into Group 1 by International Agency for Research on Cancer. Nanosilica is mainly produced through pyrolysis or polymerization processes in the amorphous phase. The adverse health effect of amorphous nanosilica has not been clearly demonstrated to date, nor has any occupational exposure limit (OEL) been attributed to it yet<sup>2</sup>.

Besides toxicity evaluation, exposure monitoring plays a very important role in risk assessment for nanosilica. Therefore, it is necessary to establish a scale to systematically quantify the measurement results of exposure monitoring in various environments<sup>3</sup>.

\*To whom correspondence should be addressed.

E-mail: hwkim@catholic.ac.kr

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Chemical Substances and Biological Agents

# Studies and Research Projects

■ REPORT R-777

## Characterization and Control of Occupational Exposure to Nanoparticles and Ultrafine Particles

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*Maximilien Debia, Charles Beaudry, Scott Weichenthal,  
Robert Tardif, André Dufresne*

*Université de Montréal*



This publication is available free of charge on the Web site.

This study was funded in the framework of an agreement between the IRSST and NanoQuébec.

The conclusions and recommendations are those of the authors.

This publication has been translated; only the original version (R-746) is authoritative.

## ABSTRACT

Many workers are exposed to a range of particles present on a nanometric scale. In occupational hygiene, it is common to differentiate manufactured nanoparticles (NP) from ultrafine particles (UFP) coming from natural, human or industrial sources. Given that major deficiencies exist in the usual risk assessment approaches for these particles, the objective of this research was to assess occupational UFP and NP exposures. The secondary objective was comprehensive testing of the assessment capabilities regarding occupational NP and UFP exposures in an industrial and laboratory context. Two main types of assessment were performed during this research. The first concerns the assessment of the fine and ultrafine particle concentrations with a particle counter (P-Trak, model 8525), and the second pertains to the assessment of fine and ultrafine particle size distribution with an electrical low pressure impactor (ELPI). The measurements were taken in two welding schools, an aluminium smelter, the research centre of a thermoplastics processing company, and three university laboratories producing and/or using nanoparticles.

The results revealed that aluminium smelter workers, people who perform welding tasks, and workers in the thermoplastic processing industry are exposed to UFPs. However, the assessments performed under this study do not reveal high NP concentrations in research laboratories. Only NP production by milling generated detectable NP concentrations. NP handling in glove boxes of two other laboratories seems to prevent worker exposure adequately.

There is currently no consensus concerning UFP and NP exposure evaluation measures. However, our findings suggest that the P-Trak is suitable for occupational assessment of UFP concentrations, whereas several uncertainties remain to assess NP exposure, particularly in their agglomerated form. In view of this research, it appears that a characterization and control study of occupational NP and UFP exposure should include assessment of the mass and particle number concentrations, measurement of granulometric distribution and electron microscopic characterization of nanoscale particles.



# Characterization of Exposure to Carbon Nanotubes in an Industrial Setting

Ana Sofia Fonseca<sup>1,2\*</sup>, Anna-Kaisa Viitanen<sup>3</sup>, Antti J. Koivisto<sup>3,4</sup>,  
Anneli Kangas<sup>3</sup>, Marika Huhtiniemi<sup>3</sup>, Tareq Hussein<sup>5,6</sup>, Esa Vanhala<sup>3</sup>  
Mar Viana<sup>1</sup>, Xavier Querol<sup>1</sup> and Kaarle Hämeri<sup>5</sup>

1. Institute of Environmental Assessment and Water Research (IDAEA-CSIC), C/ Jordi Girona 18, 08034 Barcelona, Spain

2. Faculty of Chemistry, Department of Analytical Chemistry, University of Barcelona, Martí i Franquès, 1–11, 08028 Barcelona, Spain

3. Finnish Institute of Occupational Health, Nanosafety Research Centre, Topeliuksenkatu 41 a A, FI-00250 Helsinki, Finland

4. National Research Centre for the Working Environment, Lersø Parkallé 105, Copenhagen DK-2100, Denmark

5. Department of Physics, University of Helsinki, PO Box 64, FI-00014 Helsinki, Finland

6. Faculty of Science, Department of Physics, University of Jordan, Amman, JO-11942, Jordan

\*Author to whom correspondence should be addressed. Tel: +34-934006100; fax: +34-93-2045904; e-mail: [ana.godinho@idaea.csic.es](mailto:ana.godinho@idaea.csic.es)

Submitted 24 March 2014; revised 24 September 2014; revised version accepted 26 October 2014.

## ABSTRACT

While production and use of carbon nanotubes (CNTs) is increasing, workers exposure to CNTs is expected to increase as well, with inhalation being potentially the main pathway for uptake. However, there have been few studies reporting results about workers' personal exposure to CNTs. In this study, worker exposure to single-walled CNTs (SWCNTs) during the production of conductive films in a modern up-scaling factory was assessed. Particulate matter concentrations (2.5–10 µm) and concentrations of CO and CO<sub>2</sub> were monitored by using real-time instruments. Workers' exposure levels to SWCNTs were qualitatively estimated by analyzing particle samples by transmission electron microscopy (TEM). TEM samples identified high aspect ratio (length/width > 500) SWCNTs in workplace air. SWCNT concentrations estimated from micrographs varied during normal operation, reactor use without local exhaust ventilation (LEV), and cleaning between  $1.7 \times 10^{-3}$ , 5.6 and  $6.0 \times 10^{-3}$  SWCNT cm<sup>-3</sup>, respectively. However, during cleaning it was unclear whether the SWCNTs originated from the cleaning itself or from other reactor openings. We were unable to quantify the SWCNT emissions with online particle instrumentation due to the SWCNT low concentrations compared to background particle concentrations, which were on average  $2.6 \pm 1.1 \times 10^3$  cm<sup>-3</sup>. However, CO concentrations were verified as a good indicator of fugitive emissions of SWCNTs. During normal operation, exposure levels were well below proposed limit values ( $1.0 \times 10^{-2}$  fibers cm<sup>-3</sup> and 1 µg m<sup>-3</sup>) when LEV was used. Based on the results in this study, the analysis of TEM grids seems to be the only direct method to detect SWCNTs in workplace air.

**KEYWORDS:** fibers; industry; nanoparticle; nanotube; occupational exposure limits; SWCNT; workplace exposure



# Characterization of Tungsten Inert Gas (TIG) Welding Fume Generated by Apprentice Welders

Halshka Graczyk<sup>1+</sup>, Nastassja Lewinski<sup>1,2+</sup>, Jiayuan Zhao<sup>1</sup>,  
Nicolas Concha-Lozano<sup>1</sup> and Michael Riediker<sup>1,3\*</sup>

1. Institute for Work and Health, University of Lausanne and Geneva, 1066 Epalinges-Lausanne, Switzerland;

2. Department of Chemical and Life Science Engineering, Virginia Commonwealth University, Richmond, VA 23284, USA;

3. SAFENANO, IOM Singapore, Singapore 048622

\*Author to whom correspondence should be addressed. Tel: +41-(0)21-314-7453; fax: +41-(0)21-314-7430; e-mail:

[michael.riediker@alumni.ethz.ch](mailto:michael.riediker@alumni.ethz.ch)

†These authors contributed equally to this work.

Submitted 28 April 2015; revised 26 August 2015; revised version accepted 14 September 2015.

## ABSTRACT

Tungsten inert gas welding (TIG) represents one of the most widely used metal joining processes in industry. Its propensity to generate a greater portion of welding fume particles at the nanoscale poses a potential occupational health hazard for workers. However, current literature lacks comprehensive characterization of TIG welding fume particles. Even less is known about welding fumes generated by welding apprentices with little experience in welding. We characterized TIG welding fume generated by apprentice welders ( $N = 20$ ) in a ventilated exposure cabin. Exposure assessment was conducted for each apprentice welder at the breathing zone (BZ) inside of the welding helmet and at a near-field (NF) location, 60 cm away from the welding task. We characterized particulate matter ( $PM_{2.5}$ ), particle number concentration and particle size, particle morphology, chemical composition, reactive oxygen species (ROS) production potential, and gaseous components. The mean particle number concentration at the BZ was  $1.69E+06$  particles  $cm^{-3}$ , with a mean geometric mean diameter of 45 nm. On average across all subjects, 92% of the particle counts at the BZ were below 100 nm. We observed elevated concentrations of tungsten, which was most likely due to electrode consumption. Mean ROS production potential of TIG welding fumes at the BZ exceeded average concentrations previously found in traffic-polluted air. Furthermore, ROS production potential was significantly higher for apprentices that burned their metal during their welding task. We recommend that future exposure assessments take into consideration welding performance as a potential exposure modifier for apprentice welders or welders with minimal training.

**KEYWORDS:** gas metal arc welding (GTAW); nanoparticles; occupational exposure,  $PM_{2.5}$ ; tungsten inert gas (TIG); welding fumes; workplace air

## INTRODUCTION

Worldwide, ~2 million employees work full-time in welding processes, in addition to numerous other workers who perform welding tasks as part of their

occupation (Cena *et al.*, 2014). Workers that participate in welding tasks are exposed to a complex and heterogeneous mixture of welding fumes that consist of metals, metal oxides, gases, and vapours (Lehnert

# Comparison of Nanoparticle Exposures Between Fumed and Sol-gel Nano-silica Manufacturing Facilities

Sewan OH<sup>1,3</sup>, Boowook KIM<sup>2</sup> and Hyunwook KIM<sup>3\*</sup>

<sup>1</sup>Ministry of Employment and Labor, Republic of Korea

<sup>2</sup>Occupational Lung Disease Institute, Korea Workers' Compensation and Welfare Service, Republic of Korea

<sup>3</sup>Department of Preventive Medicine, College of Medicine, The Catholic University of Korea, Republic of Korea

*Received June 10, 2013 and accepted January 23, 2014*

*Published online in J-STAGE February 28, 2014*

**Abstract:** Silica nanoparticles (SNPs) are widely used all around the world and it is necessary to evaluate appropriate risk management measures. An initial step in this process is to assess worker exposures in their current situation. The objective of this study was to compare concentrations and morphologic characteristics of fumed (FS) and sol-gel silica nanoparticles (SS) in two manufacturing facilities. The number concentration (NC) and particle size were measured by a real-time instrument. Airborne nanoparticles were subsequently analyzed using a TEM/EDS. SNPs were discharged into the air only during the packing process, which was the last manufacturing step in both the manufacturing facilities studied. In the FS packing process, the geometric mean (GM) NC in the personal samples was 57,000 particles/cm<sup>3</sup>. The geometric mean diameter (GMD) measured by the SMPS was 64 nm. Due to the high-temperature formation process, the particles exhibited a sintering coagulation. In the SS packing process that includes a manual jet mill operation, the GM NC was calculated to be 72,000 particles/cm<sup>3</sup> with an assumption of 1,000,000 particles/cm<sup>3</sup> when the upper limit is exceeded (5% of total measure). The particles from SS process had a spherical-shaped morphology with GMD measured by SMPS of 94 nm.

**Key words:** Workplace, Exposure assessment, Nanoparticle, Fumed silica, Sol-gel silica

## Introduction

Silica nanoparticles (SNPs) are one of the most abundantly produced nanomaterials in the world. A total of 34,136 tons of nanomaterials in 93 varieties are produced or imported every year in Korea. Among them, silica accounts for the second largest amount, 9,408 tons, after calcium carbonate<sup>1</sup>.

Silica is classified into crystalline and amorphous

phases. Crystalline silica, which induces silicosis, is known to be a lung-cancer-causing substance classified by the International Agency for Research on Cancer (IARC) as a Group 1 carcinogen, whereas amorphous silica in IARC Group 3 is not categorized as a human carcinogen<sup>2</sup>. The health hazards associated with SNPs that are typically produced by pyrolysis or polymerization in the amorphous phase have not been clarified yet, and workplace standards have not been established. Differences in toxicity were established amongst different amorphous SNPs by a recent comparative study. The study also suggested that the toxicity of fumed silica nanoparticles (FS) prepared by a pyrolysis method was relatively higher compared to that

\*To whom correspondence should be addressed.

E-mail: hwkim@catholic.ac.kr

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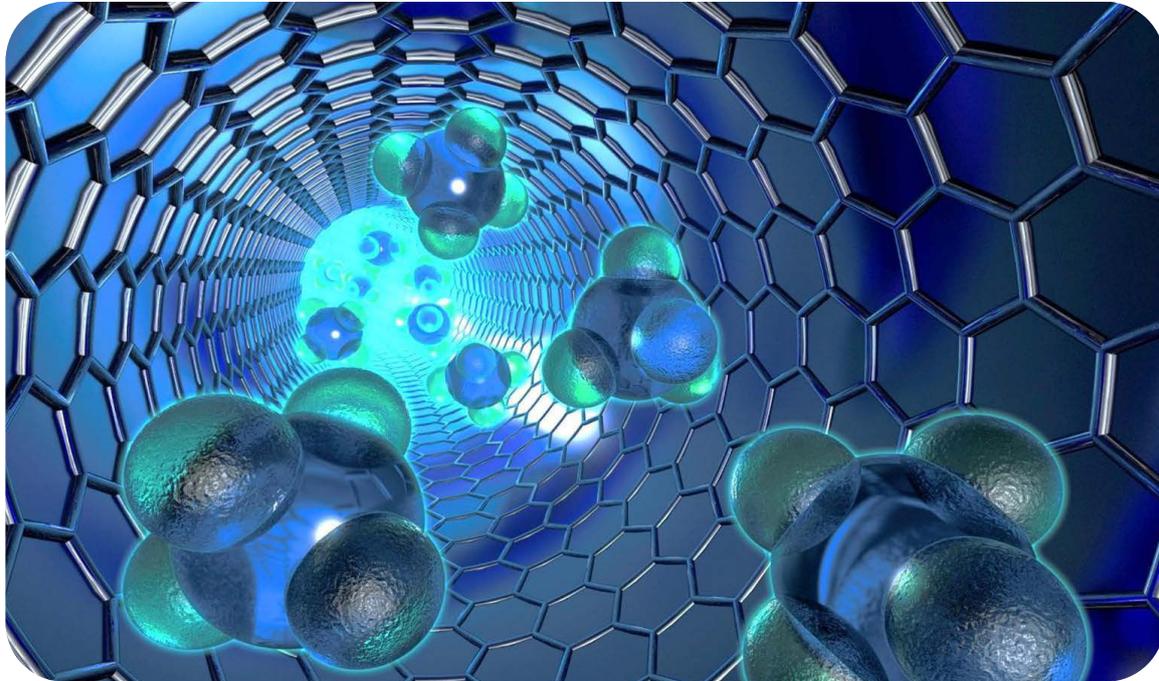
## Concerns related to Safety Management of Engineered Nanomaterials in research environment

**A Groso, Th Meyer**

Occupational Safety and Health, School of Basic Sciences, Ecole Polytechnique  
Fédérale de Lausanne, 1015 Lausanne, Switzerland

Contact e-mail: [thierry.meyer@epfl.ch](mailto:thierry.meyer@epfl.ch)

**Abstract.** Since the rise of occupational safety and health research on nanomaterials a lot of progress has been made in generating health effects and exposure data. However, when detailed quantitative risk analysis is in question, more research is needed, especially quantitative measures of workers exposure and standards to categorize toxicity/hazardousness data. In the absence of dose-response relationships and quantitative exposure measurements, control banding (CB) has been widely adopted by OHS community as a pragmatic tool in implementing a risk management strategy based on a precautionary approach. Being in charge of health and safety in a Swiss university, where nanomaterials are largely used and produced, we are also faced with the challenge related to nanomaterials' occupational safety. In this work, we discuss the field application of an in-house risk management methodology similar to CB as well as some other methodologies. The challenges and issues related to the process will be discussed. Since exact data on nanomaterials hazardousness are missing for most of the situations, we deduce that the outcome of the analysis for a particular process is essentially the same with a simple methodology that determines only exposure potential and the one taking into account the hazardousness of ENPs. It is evident that when reliable data on hazardousness factors (as surface chemistry, solubility, carcinogenicity, toxicity etc.) will be available, more differentiation will be possible in determining the risk for different materials. On the protective measures side, all CB methodologies are inclined to overprotection side, only that some of them suggest comprehensive protective/preventive measures and others remain with basic advices. The implementation and control of protective measures in research environment will also be discussed.



# Consolidated Framework for EHS of Manufactured Nanomaterials

30.04.2015

Authors:

Karl Höhener / Dr. Jürgen Höck  
TEMAS AG

Elaborated in the frame of:  
**ERA-NET SIINN**, Safe Implementation of Innovative Nanoscience and Nanotechnology

Final Report of Deliverable no. D2.6, under the European Commission's 7th Framework Programme  
Grant Agreement Number 265799



## Foreword

The European ERA-NET "Safe Implementation of Innovative Nanoscience and Nanotechnology" (SIINN) has as its primary aim the promotion of the rapid transfer of the results of nanoscience and nanotechnology research into industrial applications by helping to create reliable conditions.

One of the highest priorities of SIINN is to focus on developing a consolidated framework for environmental and health safety (EHS) for addressing nano-related risks and the management of these risks for humans and the environment.

This framework addresses:

- European and national policy-makers
- European and national stakeholders and decision-makers
- industry, industry unions, and industrial associations and interest groups
- researchers working in the field
- relevant European Technology Platforms and clusters
- the European Commission
- international organisations such as the OECD, ISO, CEN, etc.
- specialists for workers safety, human health and the environment
- non-governmental organisations
- insurance companies, risk assessment and validation organizations

The purpose of the consolidated framework document is to present to the target groups - in a condensed and accessible form - a gateway to basic information and definitions for nano-materials, the identification of: best practices, synergy potentials and the elaboration of recommendations for future collaborations on the strategic and operational level addressing MNM EHS. This includes precautionary measures, pre-normative work, steps towards regulations as well as common actions and projects.

This document is intended as a summary that functions as an introduction to and overview of the selected topics. However, it has been designed to be open for necessary changes, additions and updates. It is not intended to be comprehensive and final. As a living document it has thus undergone several consultation and consolidation rounds among a broad range of key stakeholders in the field. Consequently, the information depicted in the respective chapters of the document is only a snapshot in time.

The SIINN ERA-NET is funded under the ERA-NET scheme of the Seventh Framework Programme of the European Commission, Research Directorate General, Grant Agreement No. 265799.

[www.siinn.eu](http://www.siinn.eu)

Dr. Show-Ling Lee-Müller

Coordinator of ERA-NET SIINN  
Projekträger Jülich – PtJ  
Forschungszentrum Jülich



Contents lists available at ScienceDirect

## Building and Environment

journal homepage: [www.elsevier.com/locate/buildenv](http://www.elsevier.com/locate/buildenv)



# Effect of natural ventilation and manual airing on indoor air quality in naturally ventilated Italian classrooms



Luca Stabile<sup>a,\*</sup>, Marco Dell'Isola<sup>a</sup>, Andrea Frattolillo<sup>b</sup>, Angelamaria Massimo<sup>a</sup>, Aldo Russi<sup>a</sup>

<sup>a</sup> Department of Civil and Mechanical Engineering, University of Cassino and Southern Lazio, Cassino, FR, Italy

<sup>b</sup> Department of Civil and Environmental Engineering and Architecture, University of Cagliari Cagliari, Italy

### ARTICLE INFO

#### Article history:

Received 12 October 2015

Received in revised form

23 December 2015

Accepted 9 January 2016

Available online 12 January 2016

#### Keywords:

Schools

Exposure

Particles

Radon

Airing

Blower-door test

CO<sub>2</sub>

### ABSTRACT

The present work aimed to evaluate the effect of the ventilation on indoor air quality in Italian classrooms. To this end, schools located in the Central Italy were considered in the survey. The results of two experimental analyses are presented: a) data on classrooms' permeability and resultant air exchange rate, b) trends of indoor air quality parameters during heating and non-heating seasons to assess the possible effect of the manual airing technique.

Pressurization tests were performed in 16 classrooms to evaluate their air infiltration due to envelope's leakages. The indoor air quality was investigated in 6 classrooms through CO<sub>2</sub>, particle number concentration and radon concentration measurements which were also related to the manual airing performed by window opening.

Results of the pressurization tests revealed that, even in classrooms characterized by a poor maintenance state, the permeability of the envelopes was too low to guarantee acceptable air exchange rates. The analysis of the classrooms' air quality showed that during the fall and winter seasons the airing was ineffective, while it positively affected the indoor air quality during the spring season when strong reductions in CO<sub>2</sub> and radon concentrations were recorded. The effect of the manual airing on the infiltration of outdoor generated pollutants was also assessed. As an example, a greater airing effect resulted in a higher penetration of sub-micrometric particles from outdoor: in fact, particle penetration factors of 0.83 and 1 were measured in fall/winter and spring seasons, respectively.

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## 1. Introduction

Guaranteeing a proper indoor air quality (IAQ) in classrooms represents a strategic approach to improve children's wellness and health [1,2]. In fact, children spend a significant amount of time in schools (almost 7000 h of instruction in classroom between the ages of 7 and 14 for children living in Organization for Economic Cooperation and Development countries [3]) but, in the past, no particular attention was paid to the healthiness of such microenvironments [4]. Generally, people residing in indoor microenvironments can be exposed to long-lasting high concentration levels of several pollutants both produced indoors and penetrated from outdoors [5–8]. Indeed, schools' buildings may reduce the

exposure to outdoor pollutants thanks to their low gas and particle infiltration efficiencies [9–11] but, consequently, they do not allow a proper exfiltration of indoor-generated pollutants [12,13]. This explains the high indoor-emitted pollutant concentrations (e.g. radon, particles emitted by indoor sources, volatile organic compounds and formaldehyde from furniture) measured in classrooms elsewhere in the world [1,14–20]. The exposure in school environments may be critical for children who represent a susceptible population in terms of health effects because of their higher inhalation rates resulting in larger specific doses than adults since their organs and tissues are growing [21,22]. Besides the exposure to pollutants, high CO<sub>2</sub> concentration level in classrooms may also result in significant adverse impact on students' health and performance, such as lower attention and vigilance [23,24]. Therefore, even if the indoor exposure in classrooms should be tackled firstly reducing the emission sources (e.g. using low polluting materials [25]), guaranteeing adequate ventilation rates could represent a

\* Corresponding author. Department of Civil and Mechanical Engineering, University of Cassino and Southern Lazio, Via Di Biasio 43, 03043 Cassino, FR, Italy.  
E-mail address: [l.stabile@unicas.it](mailto:l.stabile@unicas.it) (L. Stabile).



## Engineered nanomaterials exposure in the production of graphene

Andrea Spinazzè<sup>a</sup>, Andrea Cattaneo<sup>a</sup>, Davide Campagnolo<sup>b</sup>, Valentina Bollati<sup>c,d</sup>, Pier Alberto Bertazzi<sup>c,d</sup>, and Domenico M. Cavallo<sup>a</sup>

<sup>a</sup>Dipartimento di Scienza e Alta Tecnologia, Università degli studi dell'Insubria, Como, Italy; <sup>b</sup>Dipartimento di Scienze Biomediche e Cliniche 'Luigi Sacco', Università degli Studi di Milano, Milano, Italy; <sup>c</sup>Dipartimento di Scienze Cliniche e di Comunità, Università degli Studi di Milano, Milano, Italy; <sup>d</sup>Unità di Epidemiologia, Fondazione Cà Granda, IRCCS Ospedale Maggiore Policlinico, Milano, Italy

### ABSTRACT

The objective of this study was to obtain the multi-metric occupational exposure assessment to graphene family nanomaterials (GFNs) particles of workers engaged in the large-scale production of graphene. The study design consisted of the combination of (i) direct-reading instruments, used to evaluate the total particle number concentrations relative to the background concentration (time series with spatial approach) and the mean size-dependent characteristics of particles (mean diameter and surface-area concentration) and (ii) filter-based air sampling for the determination of size-resolved particle mass concentrations. The data obtained from direct reading measurement were then used to estimate the 8-h time weighted average (8-h TWA) exposure to GFNs particles for workers involved in different working tasks. Workers were generally exposed to 8-h TWA GFNs particle levels lower than the proposed reference value (40,000 particle/cm<sup>3</sup>). Furthermore, despite high short-term exposure conditions were present during specific operations of the production process, the possibility of significant exposure peaks is not likely to be expected. The estimated 8-h TWA concentration showed differences between the unexposed (<100 particle/cm<sup>3</sup>; <0.05 µg/m<sup>3</sup>) and exposed subjects (mean concentration ranging from 909 to 6438 particle/cm<sup>3</sup> and from 0.38 to 3.86 µg/m<sup>3</sup>). The research outcomes can be of particular interest because the exposure of workers in real working conditions was assessed with a multi-metric approach; in this regard, the study suggests that workers who are directly involved in some specific working task (material sampling for quality control) have higher potential for occupational exposure than operators who are in charge of routine production work.

### ARTICLE HISTORY

Received 16 February 2016  
Accepted 20 May 2016

### EDITOR

Tiina Reponen

## Introduction

### Background

The graphene family of nanomaterials (GFNs) has been recently introduced into many fields of science and technology (Jang and Zhamu 2008; Rafiee et al. 2009). Given the potential occupational and public exposure to graphene due to its versatile applications, scientists are directing more attention toward investigating the safety aspects of these nanomaterials (Hu and Zhou 2013). What is emerging from the available results is a variety of effects that are strictly related to the nature of the graphene used: the size, layer number, chemical groups, and surface of graphene may have a strong impact on the biological and toxicological responses (Hu and Zhou 2013). Nevertheless, to date, no occupational or environmental exposure limits for GFNs have been set by any regulatory agency (Lo et al. 2011), and limited data are

available regarding occupational exposure assessment in the GFNs production industry. In summary, further research is still required in this emerging field to draw conclusions regarding the potential hazards and risk characterization by way of the link between these exposure assessments (Allen et al. 2010; Guo et al. 2010; De et al. 2011; Bianco et al. 2013).

The preliminary hypothesis of this study was that the production process may cause occupational exposure arising from the emission and dispersion of GFNs particles, mainly in the form of airborne nanoparticles ("NPs," i.e., particle with diameter <100 nm). The main objective of the study is to assess the occupational exposures to GFNs of workers engaged in the large-scale production of graphene. The exposure assessment was performed via environmental monitoring and aimed at the multi-metric characterization (i.e., particle number, mass and surface-area concentrations, particle mean

**CONTACT** Andrea Spinazzè ✉ [andrea.spinazze@uninsubria.it](mailto:andrea.spinazze@uninsubria.it) Dipartimento di Scienza e Alta Tecnologia, Università degli Studi dell'Insubria, Via Valleggio 11, 22100 Como (CO), Italy.

Supplemental data for this article can be accessed on the [publisher's website](#).

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# Evaluation of a Diffusion Charger for Measuring Aerosols in a Workplace

Donna J. H. Vosburgh<sup>1\*</sup>, Bon Ki Ku<sup>2</sup> and Thomas M. Peters<sup>3</sup>

1. Department of Occupational and Environmental Safety and Health, University of Wisconsin-Whitewater, 800 West Main Street, Whitewater, WI 53190, USA

2. Division of Applied Research and Technology, National Institute for Occupational Safety and Health, 4676 Columbia Parkway, MS-R5, Cincinnati, OH 45226, USA

3. Department of Occupational and Environmental Health, The University of Iowa, S331 CPHB, 105 River Street, Iowa City, IA 52242, USA

\*Author to whom correspondence should be addressed. Tel: 1-262-472-1252; fax: 1-262-472-1091; e-mail: [vosburgd@uww.edu](mailto:vosburgd@uww.edu)

Submitted 16 August 2013; revised 21 November 2013; revised version accepted 12 December 2013.

## ABSTRACT

The model DC2000CE diffusion charger from EcoChem Analytics (League City, TX, USA) has the potential to be of considerable use to measure airborne surface area concentrations of nanoparticles in the workplace. The detection efficiency of the DC2000CE to reference instruments was determined with monodispersed spherical particles from 54 to 565.7 nm. Surface area concentrations measured by a DC2000CE were then compared to measured and detection efficiency adjusted reference surface area concentrations for polydispersed aerosols (propylene torch exhaust, incense, diesel exhaust, and Arizona road dust) over a range of particle sizes that may be encountered in a workplace. The ratio of surface area concentrations measured by the DC2000CE to that measured with the reference instruments for unimodal and multimodal aerosols ranged from 0.02 to 0.52. The ratios for detection efficiency adjusted unimodal and multimodal surface area concentrations were closer to unity (0.93–1.19) for aerosols where the majority of the surface area was within the size range of particles used to create the correction. A detection efficiency that includes the entire size range of the DC2000CE is needed before a calibration correction for the DC2000CE can be created. For diesel exhaust, the DC2000CE retained a linear response compared to reference instruments up to 2500 mm<sup>2</sup> m<sup>-3</sup>, which was greater than the maximum range stated by the manufacturer (1000 mm<sup>2</sup> m<sup>-3</sup>). Physical limitations with regard to DC2000CE orientation, movement, and vibration were identified. Vibrating the DC2000CE while measuring aerosol concentrations may cause an increase of ~35 mm<sup>2</sup> m<sup>-3</sup>, whereas moving the DC2000CE may cause concentrations to be inflated by as much as 400 mm<sup>2</sup> m<sup>-3</sup>. Depending on the concentration of the aerosol of interest being measured, moving or vibrating a DC2000CE while measuring the aerosol should be avoided.

**KEYWORDS:** diffusion charger; nanoparticles; surface area monitor

## INTRODUCTION

Nanoparticles are defined as particles with one or more dimensions <100 nm (ASTM International, 2006), and they occur in many workplaces. Regardless of age

or breathing pattern, diffusion causes nanoparticles to have high rates of deposition throughout the respiratory system (Daigle *et al.*, 2003; Kim and Jaques, 2005). Toxicological studies have found that some



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## Science of the Total Environment

journal homepage: [www.elsevier.com/locate/scitotenv](http://www.elsevier.com/locate/scitotenv)



# Exposure to engineered nanoparticles: Model and measurements for accident situations in laboratories

Tobias Walser <sup>a,\*</sup>, Stefanie Hellweg <sup>a</sup>, Ronnie Juraske <sup>a</sup>, Norman A. Luechinger <sup>b</sup>, Jing Wang <sup>a,c</sup>, Martin Fierz <sup>d</sup>

<sup>a</sup> Institute for Environmental Engineering, ETH Zurich, 8093, Zurich, Switzerland

<sup>b</sup> Nanograde LLC, 8093, Zurich, Switzerland

<sup>c</sup> Empa, Analytical Chemistry, 8600, Dübendorf, Switzerland

<sup>d</sup> Institute for Aerosol and Sensor Technology, University of Applied Sciences Northwestern Switzerland, 5210, Windisch, Switzerland

### ARTICLE INFO

#### Article history:

Received 22 November 2011

Received in revised form 16 January 2012

Accepted 16 January 2012

Available online 10 February 2012

#### Keywords:

Workplace exposure

Engineered nanoparticles

Emission scenarios

One-box model

### ABSTRACT

In the life cycle of engineered nanoparticles (ENP), their manufacturing requires particular attention because of unwanted potential ENP emissions to workplaces. We simulated three scenarios of equipment failure during gas phase production of nanoparticles in a laboratory. The emission plume of nanoparticles was tracked with high spatial and temporal resolution by 10 measurement devices. While under normal production conditions, no elevated ENP concentrations were observed, worst case scenarios led to homogeneous indoor ENP concentrations of up to  $10^6 \text{ cm}^{-3}$  in a  $300 \text{ m}^3$  production room after only 60 s. The fast dispersal in the room was followed by an exponential decrease in number concentration after the emission event. Under conditions like those observed – rapid dispersal and good mixing – a single measurement device alone can provide valuable information for an ENP exposure assessment. A one-box model adequately reflected measured number concentrations ( $r^2 > 0.99$ ). The ENP emission rates to the workplace were estimated between  $2.5 \cdot 10^{11}$  and  $6 \cdot 10^{12} \text{ s}^{-1}$  for the three emission scenarios. The worst case emission rate at the production zone was also estimated at  $2 \cdot 10^{13} \text{ s}^{-1}$  with a stoichiometric calculation based on the precursor input, density and particle size. ENP intake fractions were  $3.8\text{--}5.1 \cdot 10^{-4}$  inhaled ENP per produced ENP in the investigated setting. These could only be substantially lowered by leaving the production room within a few minutes after the emission event.

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## 1. Introduction

Engineered nanoparticles (ENP) are increasingly produced and used in various consumer and industrial products. While enhanced functionality is achieved due to nanospecific properties, ENP can be released into the environment over the entire life cycle of nano-enabled products with possibly harmful consequences. Important entrance points to the outdoor environment include waste water streams and landfills, mainly in the use and disposal phase with potential impacts on aquatic and soil organisms (Som et al., 2010). From a human health perspective, indoor workplaces require particular attention because of the possibility of inhaling ENP during production (Oberdörster et al., 1995; Kreyling et al., 2006). Population intake fractions of chemical compounds are commonly several orders of magnitude higher for indoor releases than for outdoor releases (Nazaroff, 2008; Hellweg et al., 2009), which might also be true for ENP indoor emissions (Humbert et al., 2011). However, only few studies regarding workplace air monitoring of nanoparticle production are

available (for a review, see e.g. (Brouwer, 2010; Kuhlbusch et al., 2011)) and these are often focused on carbon compounds produced with laboratory equipment (Maynard et al., 2004), or on investigating further processing steps, such as bag filling and packaging (Kuhlbusch et al., 2004).

While under normal circumstances ENP emissions to the workplace have been shown to be very limited, bagging, packaging, or cleaning of process equipment can increase ENP indoor concentrations (Kuhlbusch et al., 2011; Wang et al., 2011). Worst case scenarios, such as accidental ENP emissions to the workplace could lead to further unwanted ENP exposure situations which are yet to be investigated (Kuhlbusch et al., 2011). Whereas wet ENP production processes such as colloidal or liquid phase methods hardly ever lead to exposure, dry production processes have an inherently higher ENP emission potential (Kuhlbusch et al., 2011). Noticeably, the growing industrial production of nanooxides is mainly done with gas phase techniques (Hendren et al., 2011). For instance, flame spray pyrolysis is applied on an industrial scale with a worldwide nanoparticle output in the range of > 1000 tons annually (Tsuzuki, 2009; Hendren et al., 2011). Even though these mature production systems are designed to guarantee a high safety level, nanoparticle emissions can occur if production or protection equipment fails. Such an

\* Corresponding author.

E-mail address: [tobias.walser@ifu.baug.ethz.ch](mailto:tobias.walser@ifu.baug.ethz.ch) (T. Walser).



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journal homepage: [www.journals.elsevier.com/nanoimpact](http://www.journals.elsevier.com/nanoimpact)

Research paper

# First order risk assessment for nanoparticle inhalation exposure during injection molding of polypropylene composites and production of tungsten-carbide-cobalt fine powder based upon pulmonary inflammation and surface area dose



Antti Joonas Koivisto<sup>a,\*</sup>, Kirsten Inga Kling<sup>a</sup>, Marcus Levin<sup>a</sup>, Wouter Fransman<sup>b</sup>, Ilse Gosens<sup>c</sup>, Flemming Ralph Cassee<sup>c,d</sup>, Keld Alstrup Jensen<sup>a</sup>

<sup>a</sup> National Research Centre for the Working Environment, Lersø Parkallé 105, Copenhagen DK-2100, Denmark

<sup>b</sup> TNO, PO Box 360, 3700AJ Zeist, The Netherlands

<sup>c</sup> National Institute for Public Health and the Environment (RIVM), Bilthoven, The Netherlands

<sup>d</sup> Environmental Epidemiology, Institute of Risk Assessment Sciences, Utrecht University, TD Utrecht, The Netherlands

## ARTICLE INFO

## Article history:

Received 30 August 2016

Received in revised form 18 October 2016

Accepted 16 November 2016

Available online 19 November 2016

## Keywords:

Nanomaterial

Inhalation exposure

First order risk assessment

Lung inflammation

Polymorphonuclear neutrophils

## ABSTRACT

Inhalation exposure to low toxicity and biodegradable particles has shown to induce polymorphonuclear neutrophilia (PMN) in the lungs, which is a strong indicator for lung inflammation. Recently, Schmid and Stoeger (2016; <http://dx.doi.org/10.1016/j.jaerosci.2015.12.006>) reviewed mice and rat intratracheal instillation studies and assessed the relation between particles dry powder BET surface area dose and PMN influx for granular biodegradable particles (GBPs) and transition metal oxides. In this study, we measured workers alveolar lung deposited surface area (LDSA) concentrations ( $\mu\text{m}^2 \text{cm}^{-3}$ ) during injection molding of polypropylene (PP) car bumpers and production of tungsten-carbide-cobalt (WCCo) fine grade powder using diffusion chargers. First order risk assessment was performed by comparing the doses calculated from measured LDSA concentrations during an 8-h work day with the  $\text{NOEL}_{1/100}$ , the one hundredth of no observed effect level, assigned for GBPs ( $0.11 \text{ cm}^2 \text{ g}^{-1}$ ) and transition metal oxide particles ( $9 \times 10^{-3} \text{ cm}^2 \text{ g}^{-1}$ ). During the injection molding of PP car bumpers, LDSA concentrations varied from 23 to  $39.8 \mu\text{m}^2 \text{ cm}^{-3}$ . During 8-h exposure PP, particle doses were at a maximum of  $1.4 \times 10^{-3} \text{ cm}^2 \text{ g}^{-1}$ , which was a factor 100 lower compared to the  $\text{NOEL}_{1/100}$  assigned for GBPs. In the WCCo fine powder production plant, the LDSA concentrations were below  $18.7 \mu\text{m}^2 \text{ cm}^{-3}$ , which corresponds to the 8-h dose of  $2.7 \times 10^{-3} \text{ cm}^2 \text{ g}^{-1}$ . This is 3 times lower than the  $\text{NOEL}_{1/100}$  assigned for transition metal oxide particles. The LDSA concentrations were generally low compared to urban background levels of  $44.2 \mu\text{m}^2 \text{ cm}^{-3}$  in European cities.

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## 1. Introduction

In an occupational environment, particle concentrations in air can be highly elevated compared to the background due to high energy processes and use of chemicals that lead to particle formation (Hämeri et al., 2009). Process generated particles and increasing use of engineered nanomaterials (Vance et al., 2015) present new challenges to understand exposure, hazard and risk management in occupational environments (Hämeri et al., 2009; Pietroiusti and Magrini, 2014; Bekker et al., 2015).

Currently, only few occupational exposure limit values exist for particulate matter (PM) and are usually given in inhalable ( $\text{PM}_{10}$ ;  $D_p \leq 10 \mu\text{m}$ ) or respirable ( $\text{PM}_{4.0}$ ;  $D_p \leq 4.0 \mu\text{m}$ ) mass concentration (Cherrie et al., 2013; Kuempel et al., 2014). However, many studies have shown that  $\text{PM}_{10}$  or  $\text{PM}_{4.0}$  mass concentration is only a rough

indicator for a biologically effective dose of the complex mixture of airborne particles (Oberdörster, 2000; Maynard and Kuempel, 2005; Borm et al., 2007; Wittmaack, 2007; Gebel, 2012; Simkó et al., 2014; Schmid and Stoeger, 2016; Braakhuis et al., 2016). There is a need to develop risk assessment techniques where PM exposure and dose assessment is closely related to the biological response (Pietroiusti and Magrini, 2014).

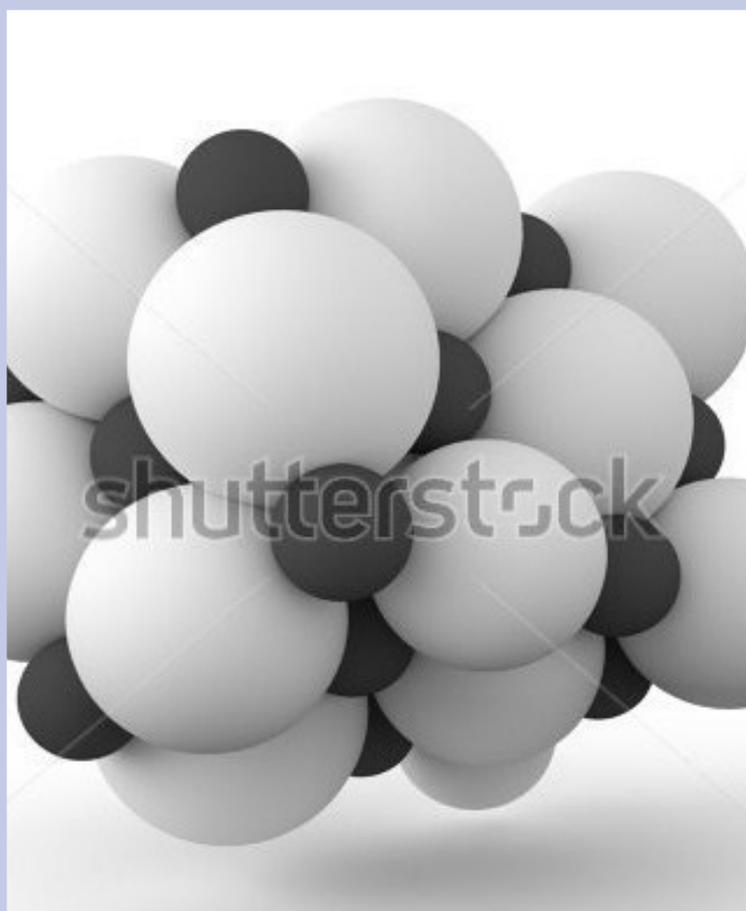
For regulatory purposes and efficient hazard assessment, nanomaterials can be grouped according to their intrinsic physical properties and biological interactions (Arts et al., 2014, 2015, 2016; Braakhuis et al., 2016; Dekkers et al., 2016; Godwin et al., 2015). Granular biodegradable particles (GBPs) are the largest material group considering their material production volumes and use (Piccinno et al., 2012). GBPs are classified as low toxicity particles (Moreno-Horn and Gebel, 2014; Arts et al., 2016) although all GBPs may cause inflammation depending on the deposited dose. Ongoing inflammatory processes may cause secondary mutagenicity that may finally lead to lung cancer

\* Corresponding author.

E-mail address: [jok@nrcwe.dk](mailto:jok@nrcwe.dk) (A.J. Koivisto).

# HANDBOOK OF NANOSAFETY

MEASUREMENT, EXPOSURE AND TOXICOLOGY



Ulla Vogel, Kai Savolainen, Qinglan Wu,  
Martie van Tongeren, Derk Brouwer, Markus Berges



# Handbook of nanosafety. Measurement, exposure and toxicology

## Content

Foreword .....	3
1. General introduction.....	7
2. Nanotechnology and exposure scenarios .....	29
3. Nanomaterials and human health .....	81
4. From source to dose: Emission, Transport, Aerosoldynamics and Dose assessment for WP aerosol exposure .....	191
5. Monitoring and sampling strategy for (manufactured) Nano objects agglomerates and aggregates (NOAA); potential added value of the NANODEVICE project .....	254
6. Quality control of measurement devices - What can be done to guarantee high quality measurements? .....	308
7. Examples and case studies .....	331
8. Risk assessment and risk management.....	410
9. Future outlook of engineered nanomaterials and nanotechnologies..	483

RESEARCH

Open Access



# Increase in oxidative stress levels following welding fume inhalation: a controlled human exposure study

Halshka Graczyk<sup>1</sup>, Nastassja Lewinski<sup>1,2</sup>, Jiayuan Zhao<sup>1,3</sup>, Jean-Jacques Sauvain<sup>1</sup>, Guillaume Suarez<sup>1</sup>, Pascal Wild<sup>4</sup>, Brigitta Danuser<sup>1</sup> and Michael Riediker<sup>1,5\*</sup> 

## Abstract

**Background:** Tungsten inert gas (TIG) welding represents one of the most widely used metal joining processes in industry. It has been shown to generate a large majority of particles at the nanoscale and to have low mass emission rates when compared to other types of welding. Despite evidence that TIG fume particles may produce reactive oxygen species (ROS), limited data is available for the time course changes of particle-associated oxidative stress in exposed TIG welders.

**Methods:** Twenty non-smoking male welding apprentices were exposed to TIG welding fumes for 60 min under controlled, well-ventilated settings. Exhaled breathe condensate (EBC), blood and urine were collected before exposure, immediately after exposure, 1 h and 3 h post exposure. Volunteers participated in a control day to account for oxidative stress fluctuations due to circadian rhythm. Biological liquids were assessed for total reducing capacity, hydrogen peroxide (H<sub>2</sub>O<sub>2</sub>), malondialdehyde (MDA), and 8-hydroxy-2'-deoxyguanosine (8-OHdG) concentrations at each time point. A linear mixed model was used to assess within day and between day differences.

**Results:** Significant increases in the measured biomarkers were found at 3 h post exposure. At 3 h post exposure, we found a 24 % increase in plasma-H<sub>2</sub>O<sub>2</sub> concentrations ([95%CI: 4 % to 46 %],  $p = 0.01$ ); a 91 % increase in urinary-H<sub>2</sub>O<sub>2</sub> ([2 % to 258 %],  $p = 0.04$ ); a 14 % increase in plasma-8-OHdG ([0 % to 31 %],  $p = 0.049$ ); and a 45 % increase in urinary-8-OHdG ([3 % to 105 %],  $p = 0.03$ ). Doubling particle number concentration (PNC) exposure was associated with a 22 % increase of plasma-8-OHdG at 3 h post exposure ( $p = 0.01$ ).

**Conclusion:** A 60-min exposure to TIG welding fume in a controlled, well-ventilated setting induced acute oxidative stress at 3 h post exposure in healthy, non-smoking apprentice welders not chronically exposed to welding fumes. As mass concentration of TIG welding fume particles is very low when compared to other types of welding, it is recommended that additional exposure metrics such as PNC are considered for occupational risk assessments. Our findings highlight the importance of increasing awareness of TIG welding fume toxicity, especially given the realities of welding workplaces that may lack ventilation; and beliefs among interviewed welders that TIG represents a cleaner and safer welding process.

**Keywords:** Oxidative stress, Welding fume, 8-OHdG, Hydrogen peroxide, Malondialdehyde, Apprentice welders, Tungsten Inert Gas (TIG), Occupational exposure

\* Correspondence: michael.riediker@alumni.ethz.ch

<sup>1</sup>Institute for Work and Health, University of Lausanne and Geneva, Lausanne CH-1066, Switzerland

<sup>2</sup>SAFENANO, IOM Singapore, Singapore 048622, Singapore

Full list of author information is available at the end of the article



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Article

## Indoor Air Quality in Naturally Ventilated Italian Classrooms

Fernanda Carmen Fuoco <sup>1,\*</sup>, Luca Stabile <sup>1</sup>, Giorgio Buonanno <sup>1,2</sup>, Concepcion Vargas Trassiera <sup>1</sup>, Angelamaria Massimo <sup>1</sup>, Aldo Russi <sup>1</sup>, Mandana Mazaheri <sup>2</sup>, Lidia Morawska <sup>2</sup> and Alexandro Andrade <sup>3</sup>

<sup>1</sup> Department of Civil and Mechanical Engineering, University of Cassino and Southern Lazio, Cassino (FR) 03043, Italy; E-Mails: l.stabile@unicas.it (L.S.); buonanno@unicas.it (G.B.); c.vargas@unicas.it (C.V.T.); a.massimo@unicas.it (A.M.); a.russi@unicas.it (A.R.)

<sup>2</sup> International Laboratory for Air Quality and Health, Queensland University of Technology, Brisbane (QLD) 4001, Australia; E-Mails: m.mazaheri@qut.edu.au (M.M.); l.morawska@qut.edu.au (L.M.);

<sup>3</sup> Center of Health Sciences and Sport, Santa Catarina State University, Florianopolis 88080-350, Brazil; E-Mail: alexandro.andrade@udesc.br

\* Author to whom correspondence should be addressed; E-Mail: fc.fuoco@unicas.it; Tel.: +39-776-299-3618; Fax: +39-776-299-4002.

Academic Editor: Pasquale Avino

Received: 22 September 2015 / Accepted: 27 October 2015 / Published: 2 November 2015

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**Abstract:** Characterization of indoor air quality in school classrooms is crucial to children's health and performance. The present study was undertaken to characterize the indoor air quality in six naturally ventilated classrooms of three schools in Cassino (Italy). Indoor particle number, mass, black carbon, CO<sub>2</sub> and radon concentrations, as well as outdoor particle number were measured within school hours during the winter and spring season. The study found the concentrations of indoor particle number were influenced by the concentrations in the outdoors; highest BC values were detected in classrooms during peak traffic time. The effect of different seasons' airing mode on the indoor air quality was also detected. The ratio between indoor and outdoor particles was of  $0.85 \pm 0.10$  in winter, under airing conditions of short opening window periods, and  $1.00 \pm 0.15$  in spring when the windows were opened for longer periods. This was associated to a higher degree of penetration of outdoor particles due to longer period of window opening. Lower CO<sub>2</sub> levels were found in classrooms in spring (908 ppm) than in winter (2206 ppm). Additionally, a greater reduction in radon concentrations was found in spring. In addition, high PM<sub>10</sub> levels were found in classrooms during break time due to re-suspension of coarse particles.



Contents lists available at ScienceDirect

## Journal of Aerosol Science

journal homepage: [www.elsevier.com/locate/jaerosci](http://www.elsevier.com/locate/jaerosci)



# Lung-deposited surface area concentration measurements in selected occupational and non-occupational environments



Otmar Geiss\*, Ivana Bianchi, Josefa Barrero-Moreno

European Commission, Joint Research Centre, Institute for Health and Consumer Protection, Via E. Fermi, 2749, 21027 Ispra, VA, Italy

### ARTICLE INFO

#### Article history:

Received 1 December 2015  
Received in revised form  
16 February 2016  
Accepted 27 February 2016  
Available online 10 March 2016

#### Keywords:

Lung-deposited surface area  
Diffusion chargers  
Occupational environments  
Chamber studies  
LDSA

### ABSTRACT

Previous experimental and epidemiologic studies suggested that exposure to ultrafine particles (UFP) may result in adverse health effects. Metrics such as the number-concentration and especially the surface-area or lung-deposited surface area (LDSA) appear to be appropriate metrics of dose for predicting pulmonary inflammation of insoluble and poorly soluble ultrafine particles. Currently not much data including LDSA concentrations is available. The aim of this study was therefore to measure LDSA concentrations in a variety of occupational and non-occupational environments as well as in chamber tests. To this end, novel handheld online-monitors were deployed and evaluated for their suitability to be used in a variety of micro-environments and under different conditions. Chamber emissions tests included incense and candle burning, 3D printing and cigarette/e-cigarette smoking. The LDSA concentration was measured in occupational environments such as a canteen kitchen, a welding workshop and in a car. Measurements were also conducted in a private house with a wood-burning stove and with ongoing parallel cooking activities. Depending on the type of micro-environment, the ongoing activities or the material investigated in the chamber-tests, large differences were observed in terms of measured LDSA concentrations, some exceeding up to 1000 times that of the baseline concentration detected before activities initiated. In some of the investigated environments LDSA concentrations were measured for the first time. The data might therefore serve as reference for future studies. The handheld instrument used to measure this data worked well both for stationary measurements as well as for personal monitoring and proved to be an alternative to bulkier benchtop instruments.

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## 1. Introduction

Experimental and epidemiologic studies conducted in the past indicated that exposure to ultrafine particles (UFP) may result in adverse health effects (Hoek et al., 2010; Mills et al., 2009; R uckerl, Schneider, Breitner, Cyrys, & Peters, 2011). Currently there is however no common agreement on an appropriate metric of exposure for ultrafine particles.

Exposure to coarse airborne particles has typically been assessed by measuring the mass-concentration. For ultrafine particles however, other metrics such as the number-concentration and especially the surface-area seem to be more appropriate metrics of dose for predicting pulmonary inflammation caused by insoluble and poorly soluble particles (Aitken, Chaudhry, Boxall, & Hull, 2006; Oberdorster, Oberdorster, & Oberdorster, 2005; Sager & Castranova, 2009; Waters et al.,

\* Corresponding author. Tel.: +39 0332 786323; fax: +39 0332 786012.  
E-mail address: [otmar.geiss@ec.europa.eu](mailto:otmar.geiss@ec.europa.eu) (O. Geiss).



## Measurements of Nanoscale TiO<sub>2</sub> and Al<sub>2</sub>O<sub>3</sub> in Industrial Workplace Environments – Methodology and Results

Heinz Kaminski\*, Mathias Beyer, Heinz Fissan, Christof Asbach, Thomas A.J. Kuhlbusch

*Institute of Energy and Environmental Technology (IUTA e.V.), Bliersheimer Str. 58–60, 47229 Duisburg, Germany*

### ABSTRACT

The possible release of engineered nanomaterials was investigated based on a previously developed but now refined methodology. Data from altogether eight industrial work areas in production plants of nanostructured TiO<sub>2</sub> and Al<sub>2</sub>O<sub>3</sub> particles were obtained and used to test the methodology and to derive a first assessment of possible exposure of workers. Particle size distributions were determined in work area environments with concurrent measurements at a comparison site. Data from the comparison site were used to estimate the particle background level in the work area and distinguish it from potentially released nanomaterial. The analysis is based on the comparison of time resolved data from the work area and the comparison site as well as data determined during periods with and without work activities in the work area. The data analysis method introduced delivers size-resolved information on the potential nanoparticle exposure of workers.

A significant release of particles in the size range 100–562 nm was observed in the work area of bagging aluminum oxide and is stemming from damaging or overfilling of bags, and the necessary activities during the cleaning of the work area. The maximum particle diameter of these particles was around 340 nm. At all other investigated locations no significant releases of particles in the size range 100–562 nm were determined. Also, no significant release of particles < 100 nm was observed in all work areas.

The average PM<sub>10</sub> exposure during the work activities varied from 48 to 1,330 µg/m<sup>3</sup> in the different work areas. The maximum concentrations of aluminum were 118 µg/m<sup>3</sup> and 58 µg/m<sup>3</sup> for PM<sub>10</sub> and PM<sub>1</sub>, respectively, during the bagging of Al<sub>2</sub>O<sub>3</sub> in small bags. In comparison, the maximum concentrations of titanium were 550 µg/m<sup>3</sup> and 434 µg/m<sup>3</sup> for PM<sub>10</sub> and PM<sub>1</sub>, respectively, during the bagging of TiO<sub>2</sub> and indicate a significant release of coarser particles.

**Keywords:** Nanoparticles; Exposure; TiO<sub>2</sub>; Al<sub>2</sub>O<sub>3</sub>; Measurement strategy; Data analysis.

### INTRODUCTION

The production and use of functional nanomaterials with new chemical and/or physical properties is one of the key technologies of the 21<sup>st</sup> century. Nanoparticles (particle with at least one dimension smaller than 100 nm, (EU, 2011) with novel properties are used in a wide range of applications. For example, the use of nanoparticles during the material production may influence material properties (surface properties, catalytic activity, etc.; Roco, 2005). Besides the unique properties of nanomaterials resulting in special applications, possible negative health effects are under discussion (Maynard *et al.*, 2006; Handy and Shaw, 2007). A possible risk from these materials for human beings or the environment may only arise if exposure exists to a potentially hazardous material (Krug and Klug, 2008).

There are various scenarios for human exposure to nanoparticles, but exposure scenarios during particle manufacturing and handling processes are among the most important as the concentrations may potentially be the highest. The measurement strategy and investigations on possible release of nanoparticles during production and handling of TiO<sub>2</sub> (mean primary particle size 21 nm) and Al<sub>2</sub>O<sub>3</sub> (mean primary particle size 13 nm) presented here were developed to assess possible exposure to airborne nanoparticles and hence allow for a first risk estimate within the production areas. The received data are discussed in the section *Discussion and Conclusions* together with comparisons of literature data which are provided in a review of existing studies.

### MEASUREMENT STRATEGY

Several assessment strategies have been developed for the determination of exposure to engineered nanoparticles at workplaces (e.g., Methner *et al.*, 2009; Brouwer *et al.*, 2012; Ramachandran *et al.*, 2012; Witschger *et al.*, 2012; nanoGEM, 2013). Two questions of priority are related to

\* Corresponding author.  
Tel.: +49-(0)2065-418 105; Fax: +49-(0)2065-418 211  
E-mail address: kaminski@iuta.de

## Measuring Nanomaterial Release from Carbon Nanotube Composites: Review of the State of the Science

Stacey Harper,<sup>1</sup> Wendel Wohlleben,<sup>2</sup> Maria Doa,<sup>3</sup> Bernd Nowack,<sup>4</sup> Shaun Clancy,<sup>5</sup> Richard Canady,<sup>6\*</sup> and Andrew Maynard<sup>7</sup>

<sup>1</sup> Environmental and Molecular Toxicology / Chemical, Biological and Environmental Engineering, Oregon State University, Corvallis, OR 97331

<sup>2</sup> BASF SE, Material Physics, 67056 Ludwigshafen, Germany

<sup>3</sup> US Environmental Protection Agency, Washington, DC 20460

<sup>4</sup> EMPA-Swiss Federal Laboratories for Material Science and Technology, Technology and Society Laboratory, CH-9014 St. Gallen, Switzerland

<sup>5</sup> Evonik Corporation, Parsippany, NJ 07054

<sup>6</sup> Center for Risk Science Innovation and Application, ILSI Research Foundation, Washington, DC 20005

<sup>7</sup> University of Michigan Risk Science Center, Ann Arbor, MI 48109

Email: [rcanady@ilsil.org](mailto:rcanady@ilsil.org)

**Abstract.** Hazard studies of “as-produced” nanomaterials are increasingly available, yet a critical gap exists in exposure science that may impede safe development of nanomaterials. The gap is that we do not understand what is actually released because nanomaterials can change when released in ways that are not understood. We also generally do not have methods capable of quantitatively measuring what is released to support dose assessment. This review presents a case study of multi-walled carbon nanotubes (MWCNTs) for the measurement challenge to bridge this gap. As the use and value of MWCNTs increases, methods to measure what is released in ways relevant to risk evaluation are critically needed if products containing these materials are to be economically, environmentally, and socially sustainable. This review draws on the input of over 50 experts engaged in a program of workshops and technical report writing to address the release of MWCNTs from nanocomposite materials across their life cycle. The expert analyses reveals that new and sophisticated methods are required to measure and assess MWCNT exposures for realistic exposure scenarios. Furthermore, method requirements vary with the materials and conditions of release across life cycle stages of products. While review shows that the likelihood of significant release of MWCNTs appears to be low for many stages of composite life cycle, measurement methods are needed so that exposures from MWCNT-composites are understood and managed. In addition, there is an immediate need to refocus attention from study of “as-produced” nanomaterials to coordinated research on actual release scenarios.





Consumer Products Monograph Series

# Multi-Walled Carbon Nanotubes in Polymer Matrices

Phase 2.5 Report—Comparison of Existing  
Studies of Release Measurement for  
MWCNT-Polymer Composites



A Publication of the Center for Risk Science Innovation and Application  
of the ILSI Research Foundation



# Comparison of Existing Studies of Release Measurement for MWCNT-Polymer Composites

## Phase 2.5 Report

### Authors

*Richard Canady,<sup>1</sup> Thomas Kuhlbusch,<sup>2</sup> Mareile Renker,<sup>2</sup> Elyse Lee,<sup>1</sup> and Lyubov Tsytsikova<sup>1</sup>*

<sup>1</sup>Center for Risk Science Innovation and Application, ILSI Research Foundation, Washington, DC, USA

<sup>2</sup>Air Quality & Sustainable Nanotechnology, IUTA e.V., Bliersheimer Strasse 60, 47229 Duisburg, Germany

### Acknowledgment

Experts were convened and concepts developed for this paper by the NanoRelease Consumer Products Steering Committee (<http://www.ilsil.org/ResearchFoundation/Pages/NanoRelease1.aspx>), who also reviewed and provided comments addressed in the final document. NanoRelease is funded by the US Environmental Protection Agency, the American Chemistry Council Nanotechnology Panel, Environment Canada, Health Canada, the American Cleaning Institute, the Society of Organic Chemical Manufacturers and Affiliates, the Adhesives and Sealant Council, the Personal Care Products Council, and the ILSI Research Foundation. More than 60 experts listed on the NanoRelease web site from government, academia, industry, and civil society organizations have also contributed time and expertise in support of the project. We especially thank Christina West for editorial assistance in completing this manuscript. The authors are aware of no conflicts of interest in the development of this review.



## REVIEW

## Open Access

# Nanoparticle exposure at nanotechnology workplaces: A review

Thomas AJ Kuhlbusch<sup>1,3\*</sup>, Christof Asbach<sup>1</sup>, Heinz Fissan<sup>1,3</sup>, Daniel Göhler<sup>2</sup> and Michael Stintz<sup>2</sup>

## Abstract

Risk, associated with nanomaterial use, is determined by exposure and hazard potential of these materials. Both topics cannot be evaluated absolutely independently. Realistic dose concentrations should be tested based on stringent exposure assessments for the corresponding nanomaterial taking into account also the environmental and product matrix. This review focuses on current available information from peer reviewed publications related to airborne nanomaterial exposure. Two approaches to derive realistic exposure values are differentiated and independently presented; those based on workplace measurements and the others based on simulations in laboratories. An assessment of the current available workplace measurement data using a matrix, which is related to nanomaterials and work processes, shows, that data are available on the likelihood of release and possible exposure. Laboratory studies are seen as an important complementary source of information on particle release processes and hence for possible exposure. In both cases, whether workplace measurements or laboratories studies, the issue of background particles is a major problem. From this review, major areas for future activities and focal points are identified.

**Keywords:** Nanoobjects, nanomaterial, airborne, release, exposure, workplace, handling, processing

## 1. Introduction

Research and product developments in the area of nanotechnology have steadily increased especially due to new, beneficial properties of nanomaterials. Nanotechnology as a cross-cutting technology, nowadays used in electrical devices, in construction and composite materials, as catalysts and as antibacterial coatings, is more and more present in workplaces as well as consumer products. This steady increase is accompanied with larger production, handling and processing facilities for nanostructured materials and higher tonnage of nanomaterials.

New nanomaterials, an inherent part of nanotechnological developments, allow on the one hand new products and solutions to e.g. societal problems related to natural resources, drinking water, energy generation and storage, but also raise concerns due to their new specific properties. The major concern is, that the new properties and the high mobility of some nanomaterials may lead to health or environmental effects. This concern

has been identified early and was taken seriously by public bodies and the industry. First specific research investigations in toxicology related to particles at the nanoscale were already conducted in the late 1980's [1]. During the last two decades the amount of toxicological research on nanomaterials has increased from less than 10 publications before 1998 to more than 200 in 2010 (ISI Web of Knowledge, 02/2011). A risk, however, may only arise if both a hazard potential of the nanomaterial and exposure exist. Therefore first studies of workplace related exposure were initiated by the International Carbon Black Association (ICBA) in 1998 [2,3]. In parallel Maynard et al. [4] conducted first studies related to nanomaterial exposure of carbon nanotubes (CNT). The number of workplace studies and published results has increased significantly since then and a first ISO-guide-line on inhalation exposure characterization and assessment has been set-up [5].

Different approaches can be pursued to derive exposure relevant information in workplaces: (a) Studies based on real workplaces and (b) process based studies in simulated workplaces and of simulated work processes. The major advantage of the prior approach is

\* Correspondence: [tky@iuta.de](mailto:tky@iuta.de)

<sup>1</sup>Air Quality & Sustainable Nanotechnology, Institute of Energy and Environmental Technology e.V. (IUTA), D-47229 Duisburg, Germany  
Full list of author information is available at the end of the article



Contents lists available at ScienceDirect

Acta Biomaterialia

journal homepage: [www.elsevier.com/locate/actabiomat](http://www.elsevier.com/locate/actabiomat)



## Nanoparticle release from dental composites

K.L. Van Landuyt<sup>a,\*</sup>, B. Hellack<sup>b</sup>, B. Van Meerbeek<sup>a</sup>, M. Peumans<sup>a</sup>, P. Hoet<sup>c</sup>, M. Wiemann<sup>d</sup>, T.A.J. Kuhlbusch<sup>b</sup>, C. Asbach<sup>b</sup>

<sup>a</sup> KU Leuven BIOMAT, Department of Oral Health Sciences, University of Leuven & Dentistry, University Hospitals Leuven, Kapucijnenvoer 7, 3000 Leuven, Belgium

<sup>b</sup> Institute of Energy and Environmental Technology (IUTA) e.V., Bliersheimer Straße 60, 47229 Duisburg, Germany

<sup>c</sup> Research Unit Experimental Toxicology, Center for Environmental and Health Research, Department of Public Health and Primary Care, University of Leuven, Herestraat 49, 3001 Leuven, Belgium

<sup>d</sup> IBE R&D gGmbH, Institute for Lung Health, Mendelstraße 11, 48149 Münster, Germany

### ARTICLE INFO

#### Article history:

Received 22 May 2013

Received in revised form 20 September 2013

Accepted 30 September 2013

Available online 10 October 2013

#### Keywords:

Dental composite

Nanoparticle

Biocompatibility

Filler

Dust

### ABSTRACT

Dental composites typically contain high amounts (up to 60 vol.%) of nanosized filler particles. There is a current concern that dental personnel (and patients) may inhale nanosized dust particles (<100 nm) during abrasive procedures to shape, finish or remove restorations but, so far, whether airborne nanoparticles are released has never been investigated. In this study, composite dust was analyzed in real work conditions. Exposure measurements of dust in a dental clinic revealed high peak concentrations of nanoparticles in the breathing zone of both dentist and patient, especially during aesthetic treatments or treatments of worn teeth with composite build-ups. Further laboratory assessment confirmed that all tested composites released very high concentrations of airborne particles in the nanorange ( $>10^6 \text{ cm}^{-3}$ ). The median diameter of airborne composite dust varied between 38 and 70 nm. Electron microscopic and energy dispersive X-ray analysis confirmed that the airborne particles originated from the composite, and revealed that the dust particles consisted of filler particles or resin or both. Though composite dust exhibited no significant oxidative reactivity, more toxicological research is needed. To conclude, on manipulation with the bur, dental composites release high concentrations of nanoparticles that may enter deeply into the lungs.

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### 1. Introduction

Modern dental composites (“tooth-colored filling material”) for tooth restoration are made of a polymer filled with inorganic filler particles. In order to prevent excessive shrinkage, dental composites are highly filled with filler content, usually between 50 and 70 vol.%. A plethora of different types and sizes of filler particles can be found in contemporary dental composites. In the past, composites used to contain quartz fillers [1,2], but as quartz is radio-lucent, composites today usually contain radio-opaque glass filler particles containing elements with high atomic masses, such as barium, strontium, zirconium or ytterbium. These amorphous glass particles are usually larger than 0.4–1  $\mu\text{m}$  but, to optimize filler packing, nanosized filler particles (<100 nm; e.g., pyrogenic silica) are added to fill the spaces between these large particles. The latest innovations in filler technology have made it possible to add even larger amounts of nanosized particles without overly increasing the viscosity of the unpolymerized composite, and one manufacturer even succeeded in fabricating a composite containing only nanosized particles (Filtek Supreme XTE, 3M ESPE) [3]. Only the

latest generation of composites are called nanohybrid and nanocomposites, but actually, all dental composites on the market today contain considerable amounts of nanosized filler particles [4].

Dental composites are nowadays routinely used to restore decayed and traumatized teeth, and they will be increasingly used now that the World Health Organization has started promulgating phasing down the use of amalgam [5]. Moreover, unlike amalgam, composites can be glued to the tooth surface, which gives way to many more indications for the use of composites. Composites are, for example, frequently used for cosmetic treatments, such as closing unaesthetic diastemas between teeth, veneering discolored teeth and correcting the position and shape of teeth [6]. Moreover, thanks to the good mechanical properties of composites and the latest improvements in adhesive technology, composites are also increasingly used to rehabilitate severely worn dentition [7]. Composites are then used to replace the tooth tissue lost to erosion or abrasion, which represents a less expensive and less invasive alternative to treatment with full-mouth, fixed ceramic restorations.

Normal use of composites encompasses the application of a non-polymerized composite paste, followed by polymerization by blue light, and finishing and shaping by bur or polishing disks in situ. Some researchers have expressed concern that there may

\* Corresponding author. Tel.: +32 16 332745; fax: +32 16 332752.

E-mail address: [kirsten.vanlanduyt@med.kuleuven.be](mailto:kirsten.vanlanduyt@med.kuleuven.be) (K.L. Van Landuyt).



Review

# Nano-Scaled Particles and Fibres Occupational Exposure Assessment: An Integrated Approach from Air Sampling to Skin and Surface Contamination

Andrea Prodi , Francesca Larese Filon

University of Trieste, Clinical Unit of Occupational Medicine, via della Pietà 19, 34129 Trieste.

 Corresponding author. E-mail: [andrea.prodi@phd.units.it](mailto:andrea.prodi@phd.units.it)

**Received:** May 16, 2016; **Accepted:** Jun. 15, 2016; **Published:** Jun. 27, 2016

**Citation:** Andrea Prodi, Francesca Larese Filon, Nano-Scaled Particles and Fibres Occupational Exposure Assessment: An Integrated Approach from Air Sampling to Skin and Surface Contamination. *Nano Biomed. Eng.*, 2016, 8(2): 91-104.

**DOI:** 10.5101/nbe.v8i2.p91-104.

## Abstract

Workers may be exposed to nanoparticles (NPs) by inhalation, cutaneous contact and gastroenteric pathways, but today there is no standardized method for either assessing or monitoring the occupational exposure. Moreover, there is no all-in-one assessment strategy, so it is preferable to consider different perspectives. Every assessment should be preceded by a preliminary analysis of the workplace in order to gather useful data on the potential exposure sources, which will help in outlining the assessment strategy. The purpose of air monitoring should be to characterize NP emissions and assess, as a minimum, the mass, particle number concentration, granulometric distribution, specific surface and chemical composition. There are several techniques which may assess these characteristics: the most used in real occupational contexts are mobility particle sizers, particle counters (optical, condensation, etc.), surface area monitors, while personal samplers are promising tools which still have been used almost only in research or controlled contexts. Skin and surfaces may be sampled according to the nature of substances and the circumstances of exposure. Sampling methods can be divided in three main categories: interception (e.g. carbon tabs), removal (e.g. adhesive tape stripping, wiping), in situ methods (e.g. UV fluorescence). Chemical analysis methods (e.g. spectroscopy) and electron microscopy techniques may enhance available data. Considering the available information, we suggest a stepwise approach for risk assessment composed of three steps, starting from a quick and relatively cheap screening method to assess exposure, followed by 2 gradually more accurate but costly approaches to perform whether a significant exposure is detected.

**Keywords:** Nanoparticles; Nanomaterials; Risk assessment; Air sampling; Contamination; Skin; Surfaces; Workplace; Occupational health

## Introduction

Nanoparticles (NPs) production and use is increasing worldwide due to novel interesting applications in electronics, medicine, cosmetics, textiles, semiconductors, varnishes, surface treatments,

etc. Many benefits are expected from their use but potential toxic effects related to NPs exposures have been highlighted [1-4]. Due to their small size NPs are able to enter into our body. Through inhalation route they can damage the lung, some of them can translocate to the bloodstream reaching other organs



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# Environment International

journal homepage: [www.elsevier.com/locate/envint](http://www.elsevier.com/locate/envint)



## Review

### Potential release scenarios for carbon nanotubes used in composites



Bernd Nowack <sup>a,\*</sup>, Raymond M. David <sup>b</sup>, Heinz Fissan <sup>c</sup>, Howard Morris <sup>d</sup>,  
Jo Anne Shatkin <sup>e</sup>, Michael Stintz <sup>f</sup>, Richard Zepp <sup>g</sup>, Derk Brouwer <sup>h</sup>

<sup>a</sup> Empa – Swiss Federal Laboratories for Materials Science and Technology, Technology and Society Laboratory, CH-9014 St Gallen, Switzerland

<sup>b</sup> BASF Corporation, Florham Park, NJ, USA

<sup>c</sup> Institute of Energy and Environmental Technology (IUTA e. V.), Center for Nanointegration Duisburg-Essen (CENIDE), Duisburg, Germany

<sup>d</sup> Safe Work Australia – 220 Northbourne Avenue, Braddon, ACT 2612, Australia

<sup>e</sup> CLF Ventures, Inc., 62 Summer Street, Boston, MA, USA

<sup>f</sup> Technische Universität Dresden, Institute of Process Engineering and Environmental Technology, Research Group Mechanical Process Engineering, 01069 Dresden, Germany

<sup>g</sup> US Environmental Protection Agency, National Exposure Research Laboratory, Ecosystem Research Division, Athens, GA 30605-2700, USA

<sup>h</sup> TNO, Research Group Quality & Safety, Zeist, Netherlands

#### ARTICLE INFO

##### Article history:

Received 12 December 2012

Accepted 16 April 2013

Available online 23 May 2013

##### Keywords:

Carbon nanotubes

Exposure

Release

Scenarios

#### ABSTRACT

The expected widespread use of carbon nanotube (CNT)–composites in consumer products calls for an assessment of the possible release and exposure to workers, consumers and the environment. Release of CNTs may occur at all steps in the life cycle of products, but to date only limited information is available about release of CNTs from actual products and articles. As a starting point for exposure assessment, exploring sources and pathways of release helps to identify relevant applications and situations where the environment and especially humans may encounter releases of CNTs. It is the aim of this review to identify various potential release scenarios for CNTs used in polymers and identify the greatest likelihood of release at the various stages throughout the life-cycle of the product. The available information on release of CNTs from products and articles is reviewed in a first part. In a second part nine relevant release scenarios are described in detail: injection molding, manufacturing, sports equipment, electronics, windmill blades, fuel system components, tires, textiles, incineration, and landfills. Release from products can potentially occur by two pathways; (a) where free CNTs are released directly, or more frequently (b) where the initial release is a particle with CNTs embedded in the matrix, potentially followed by the subsequent release of CNTs from the matrix.

The potential for release during manufacturing exists for all scenarios, however, this is also the situation when exposure can be best controlled. For most of the other life cycle stages and their corresponding release scenarios, potential release of CNTs can be considered to be low, but it cannot be excluded totally. Direct release to the environment is also considered to be very low for most scenarios except for the use of CNTs in tires where significant abrasion during use and release into the environment would occur. Also the possible future use of CNTs in textiles could result in consumer exposure. A possibility for significant release also exists during recycling operations when the polymers containing CNTs are handled together with other polymers and mainly occupational users would be exposed.

It can be concluded that in general, significant release of CNTs from products and articles is unlikely except in manufacturing and subsequent processing, tires, recycling, and potentially in textiles. However except for high energy machining processes, most likely the resulting exposure for these scenarios will be low and to a non-pristine form of CNTs. Actual exposure studies, which quantify the amount of material released should be conducted to provide further evidence for this conclusion.

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#### Contents

1. Introduction . . . . .	2
2. Release scenarios of nanomaterials in general . . . . .	3

\* Corresponding author.

E-mail address: [nowack@empa.ch](mailto:nowack@empa.ch) (B. Nowack).



Contents lists available at ScienceDirect

# Science of the Total Environment

journal homepage: [www.elsevier.com/locate/scitotenv](http://www.elsevier.com/locate/scitotenv)



## Process-generated nanoparticles from ceramic tile sintering: Emissions, exposure and environmental release



A.S. Fonseca<sup>a,b,\*</sup>, A. Maragkidou<sup>c</sup>, M. Viana<sup>a</sup>, X. Querol<sup>a</sup>, K. Hämeri<sup>c</sup>, I. de Francisco<sup>d</sup>, C. Estepa<sup>d</sup>, C. Borrell<sup>d</sup>, V. Lennikov<sup>d</sup>, G.F. de la Fuente<sup>d</sup>

<sup>a</sup> Institute of Environmental Assessment and Water Research (IDEA-CSIC), C/ Jordi Girona 18, 08034 Barcelona, Spain

<sup>b</sup> Universidad de Barcelona, Facultad de Química, Martí i Franquès 1-11, 08028 Barcelona, Spain

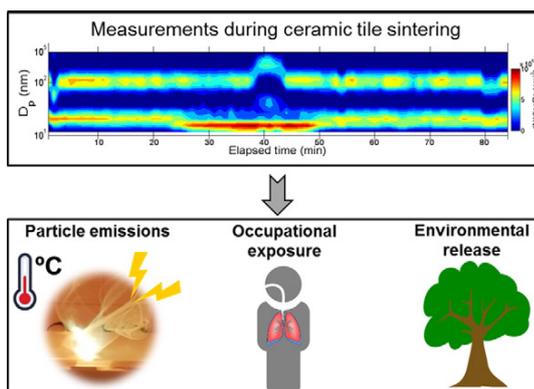
<sup>c</sup> University of Helsinki, Department of Physics, Division of Atmospheric Sciences, P.O. Box 48, (Erik Palmenin aukio 1, Dynamicum), FI-00014, Finland

<sup>d</sup> Instituto de Ciencia de Materiales de Aragón (ICMA - Universidad de Zaragoza), María de Luna 3, E-50018 Zaragoza, Spain

### HIGHLIGHTS

- Particle emissions and impact on worker exposure and the environment were assessed
- Nucleation processes were detected during thermal treatment
- Nanoparticles were emitted into workplace on a statistically significant level
- Workers exposure concentrations would exceed the recommended exposure limits
- A potential risk of nanoparticle release to the outdoor air was identified

### GRAPHICAL ABSTRACT



### ARTICLE INFO

#### Article history:

Received 3 December 2015

Received in revised form 15 January 2016

Accepted 18 January 2016

Available online 2 February 2016

#### Keywords:

Occupational exposure

Industrial laser furnace

New particle formation

Particle transport

Indoor air

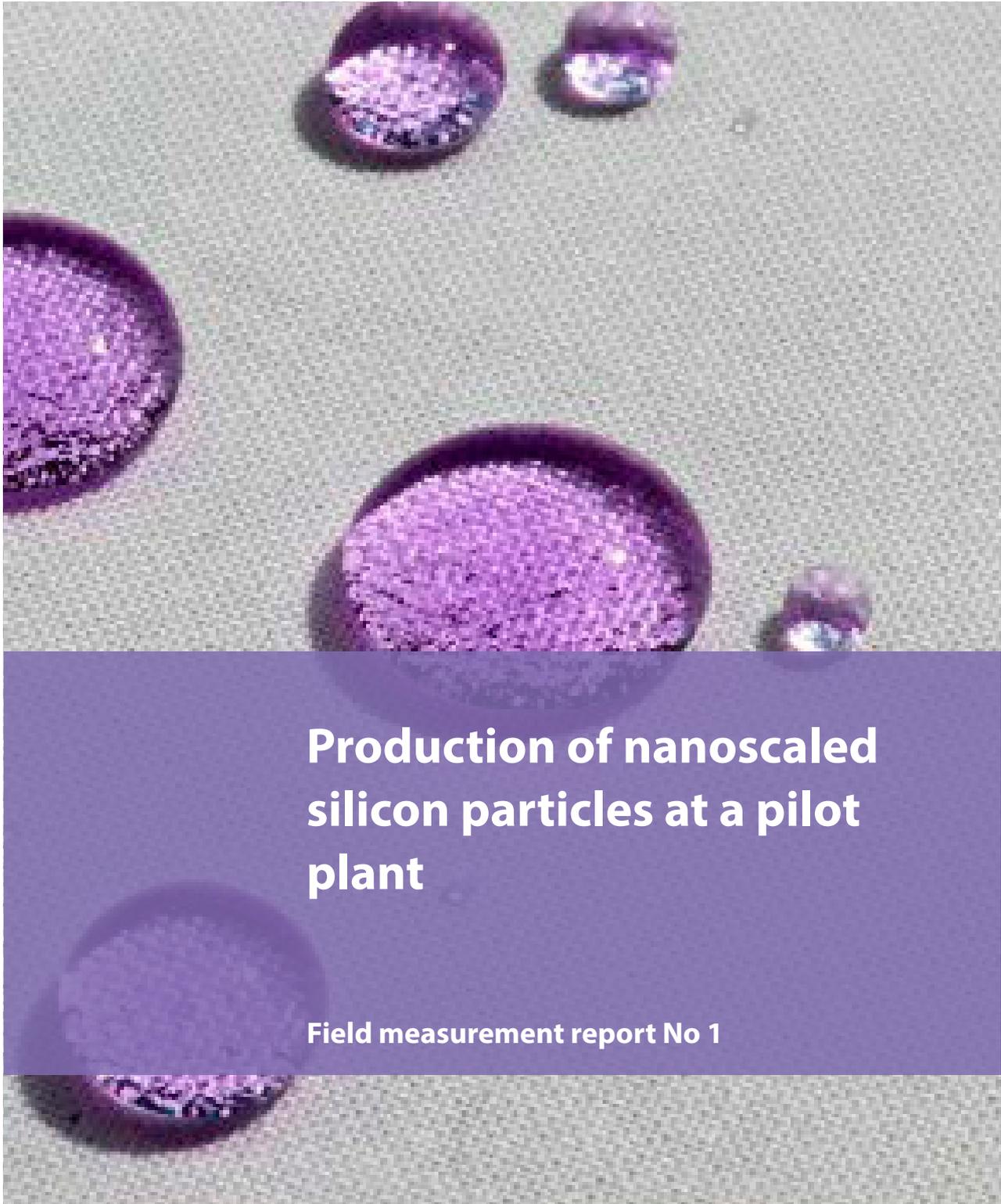
Ultrafine particles

### ABSTRACT

The ceramic industry is an industrial sector in need of significant process changes, which may benefit from innovative technologies such as laser sintering of ceramic tiles. Such innovations result in a considerable research gap within exposure assessment studies for process-generated ultrafine and nanoparticles. This study addresses this issue aiming to characterise particle formation, release mechanisms and their impact on personal exposure during a tile sintering activity in an industrial-scale pilot plant, as a follow-up of a previous study in a laboratory-scale plant. In addition, possible particle transformations in the exhaust system, the potential for particle release to the outdoor environment, and the effectiveness of the filtration system were also assessed. For this purpose, a tiered measurement strategy was conducted.

The main findings evidence that nanoparticle emission patterns were strongly linked to temperature and tile chemical composition, and mainly independent of the laser treatment. Also, new particle formation (from gaseous precursors) events were detected, with nanoparticles < 30 nm in diameter being formed during the thermal treatment. In addition, ultrafine and nano-sized airborne particles were generated and emitted into workplace air during sintering process on a statistically significant level. These results evidence the risk of occupational exposure to ultrafine and nanoparticles during tile sintering activity since workers would be exposed to

\* Corresponding author at: C/ Jordi Girona 18, 08034 Barcelona, Spain.  
E-mail address: [ana.godinho@idaea.csic.es](mailto:ana.godinho@idaea.csic.es) (A.S. Fonseca).



# Production of nanoscaled silicon particles at a pilot plant

Field measurement report No 1

Production of nanoscaled silicon particles at a pilot plant



**Imprint**

This report is a final product of the project NanoValid - project F2268 - and was generated under the lead responsibility of Miriam Baron (Federal Institute for Occupational Safety and Health).

The research leading to these results has received funding from the European Union Seventh Framework Programme (FP7/2007-2013) under grant agreement n° 263147 (NanoValid – Development of reference methods for hazard identification, risk assessment and LCA of engineered nanomaterials).

The responsibility for the contents of this publication lies with the authors.

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**Project monitoring:**

Miriam Baron  
Federal Institute for Occupational Safety and Health (BAuA)

**Main authors:**

Miriam Baron, Nico Dziurawitz, Sabine Plitzko (BAuA)

**With contributions from:**

Rolf Packroff, Aart Rouw, Torsten Wolf (BAuA)

Heather McShane, William Hendershot  
McGill University

Marcus Hank, Lothar Keck  
Grimm Aerosol Technik GmbH & Co. KG

**Figures:**

Christof Asbach, Tim Hülser  
Institute of Energy and Environmental Technology e.V.

Nanofibre testcenter Berlin (BAuA)

**Project support:**

Elke Kahler-Jenett, Katharina Niesmann (BAuA)

**Design:**

Carolin Schneider, eckedesign Berlin

**Editing:**

Johanna Ebbeskotte, Markus Flender (BAuA)

**Publisher:**

Federal Institute for Occupational Safety and Health (BAuA)  
Friedrich-Henkel-Weg 1-25, 44149 Dortmund, Germany  
Nöldnerstr. 40-42, 10317 Berlin, Germany  
Telephone +49 231 9071-0  
**www.baua.de**

**NanoValid:**

Project Coordinator: Rudolf Reuther, Nordmiljö AB  
rudolf.reuther@enas-online.com  
Telephone +46 563 92253 (Sweden) or +49 170 7011534 (Germany)  
**www.nanovalid.eu**

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First published: July 2015

## 2 Summary

Within NanoValid, the BAuA laboratory for nanomaterials assessed and evaluated inhalative exposure to nanomaterials at different workplaces. The aim of these field studies was to check if the installed protective measures were effective and if a risk of the workers was sufficiently reduced. In all studies, the risk assessment combined measurements and a non-measurement approach in terms of an additional inspection of the specific workplace situation. The present report refers to a pilot plant, where nanoscaled silicon particles were produced in a closed system and subsequently bagged. The occupational safety and health situation was evaluated both by measurements and by an additional inspection of the specific workplace situation and during activities with nanomaterials.

This report presents:

- an activity-based risk assessment (non-exposure measurement method)
- a detailed measurement report, including morphological analysis of particles
- a conclusion combining the findings of both approaches
- a trial for intentional release (simulation of a leakage)

The activity-based risk assessment describes the general production process and then specifically addresses the activities synthesis, bagging and cleaning. The measurement report focuses on particle number concentrations, particle size distribution and particle samples for morphological characterisation.

On all measurement days, no release of product particles was observed during production, bagging and cleaning. However, since the enclosure of the nanosilicon production site was maintained under reduced pressure, air from the large surrounding hall entered the site. Therefore, the nanoparticle background was rather high.

Post-process analysis of contact samples revealed nanoscaled Si particles, which were probably released during nanosilicon production and bagging, but gave no significant signal in the measurements.

To study the effect of accidental release of silicon particles through a leakage in a closed production system, an additional aerosol generator was used. This way, the distribution of polystyrene particles (PSL) and NaCl could be studied by spiking the atmosphere with intentionally released nanoparticles. During this simulated leakage, a significant increase of NaCl particles above the background concentration was observed.

The exposure data showed that the installed occupational safety and health measures were suitable to handle the expected low level of nanoscaled emissions. Some general improvements were recommended concerning organisational protection measures.

Article

## Range-Finding Risk Assessment of Inhalation Exposure to Nanodiamonds in a Laboratory Environment

Antti J. Koivisto <sup>1,\*</sup>, Jaana E. Palomäki <sup>1</sup>, Anna-Kaisa Viitanen <sup>1</sup>, Kirsi M. Siivola <sup>1</sup>,  
Ismo K. Koponen <sup>2</sup>, Mingzhou Yu <sup>3</sup>, Tomi S. Kanerva <sup>1</sup>, Hannu Norppa <sup>1</sup>, Harri T. Alenius <sup>1</sup>,  
Tareq Hussein <sup>4,5</sup>, Kai M. Savolainen <sup>1</sup> and Kaarle J. Hämeri <sup>5</sup>

<sup>1</sup> Nanosafety Research Centre, Finnish Institute of Occupational Health, Topeliuksenkatu 41 a A, FI-00250 Helsinki, Finland; E-Mails: jaana.palomaki@tukes.fi (J.E.P.); anna-kaisa.viitanen@ttl.fi (A.-K.V.); kirsi.siivola@ttl.fi (K.M.S.); tomi.kanerva@ttl.fi (T.S.K.); hannu.norppa@ttl.fi (H.N.); harri.alenius@ttl.fi (H.T.A.); kai.savolainen@ttl.fi (K.M.S.)

<sup>2</sup> National Research Centre for the Working Environment, Lersø Parkallé 105, Copenhagen DK-2100, Denmark; E-Mail: ikk@arbejdsmiljoforskning.dk

<sup>3</sup> Institute of Earth Environment, Chinese Academy of Sciences, Fenghui Road, Xi'an 710075, China; E-Mail: yumingzhou1738@yahoo.com

<sup>4</sup> Department of Physics, Faculty of Science, The University of Jordan, Amman JO-11942, Jordan

<sup>5</sup> Department of Physics, University of Helsinki, Gustaf Hällströmin Katu 2, P.O. Box 64, Helsinki FI-00014, Finland; E-Mails: tareq.hussein@helsinki.fi (T.H.); kaarle.hameri@helsinki.fi (K.J.H.)

\* Author to whom correspondence should be addressed; E-Mail: joonas.koivisto@ttl.fi;  
Tel.: +358-407-222-029.

Received: 13 March 2014; in revised form: 4 May 2014 / Accepted: 8 May 2014 /

Published: 16 May 2014

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**Abstract:** This study considers fundamental methods in occupational risk assessment of exposure to airborne engineered nanomaterials. We discuss characterization of particle emissions, exposure assessment, hazard assessment with *in vitro* studies, and risk range characterization using calculated inhaled doses and dose-response translated to humans from *in vitro* studies. Here, the methods were utilized to assess workers' risk range of inhalation exposure to nanodiamonds (NDs) during handling and sieving of ND powder. NDs were agglomerated to over 500 nm particles, and mean exposure levels of different work tasks varied from 0.24 to 4.96  $\mu\text{g}\cdot\text{m}^{-3}$  (0.08 to 0.74  $\text{cm}^{-3}$ ). *In vitro*-experiments suggested that ND exposure may cause a risk for activation of inflammatory cascade. However, risk range characterization based on *in vitro* dose-response was not performed



# Real-time single airborne nanoparticle detection with nanomechanical resonant filter-fiber

Silvan Schmid, Maksymilian Kurek, Jens Q. Adolphsen & Anja Boisen

Department of Micro- and Nanotechnology, Technical University of Denmark, DTU Nanotech, Building 345 East, DK-2800 Kongens Lyngby, Denmark.

SUBJECT AREAS:  
CHARACTERIZATION  
AND ANALYTICAL  
TECHNIQUES  
NANOSENSORS  
NEMS  
NANOPARTICLES

Received  
20 November 2012

Accepted  
31 January 2013

Published  
15 February 2013

Correspondence and  
requests for materials  
should be addressed to  
S.S. (silvan.schmid@  
nanotech.dtu.dk)

Nanomechanical resonators have an unprecedented mass sensitivity sufficient to detect single molecules, viruses or nanoparticles. The challenge with nanomechanical mass sensors is the direction of nano-sized samples onto the resonator. In this work we present an efficient inertial sampling technique and gravimetric detection of airborne nanoparticles with a nanomechanical resonant filter-fiber. By increasing the nanoparticle momentum the dominant collection mechanism changes from diffusion to more efficient inertial impaction. In doing so we reach a single filter-fiber collection efficiency of  $65 \pm 31\%$  for 28 nm silica nanoparticles. Finally, we show the detection of single 100 nm silver nanoparticles. The presented method is suitable for environmental or security applications where low-cost and portable monitors are demanded. It also constitutes a unique technique for the fundamental study of single filter-fiber behavior. We present the direct measurement of diffusive nanoparticle collection on a single filter-fiber qualitatively confirming Langmuir's model from 1942.

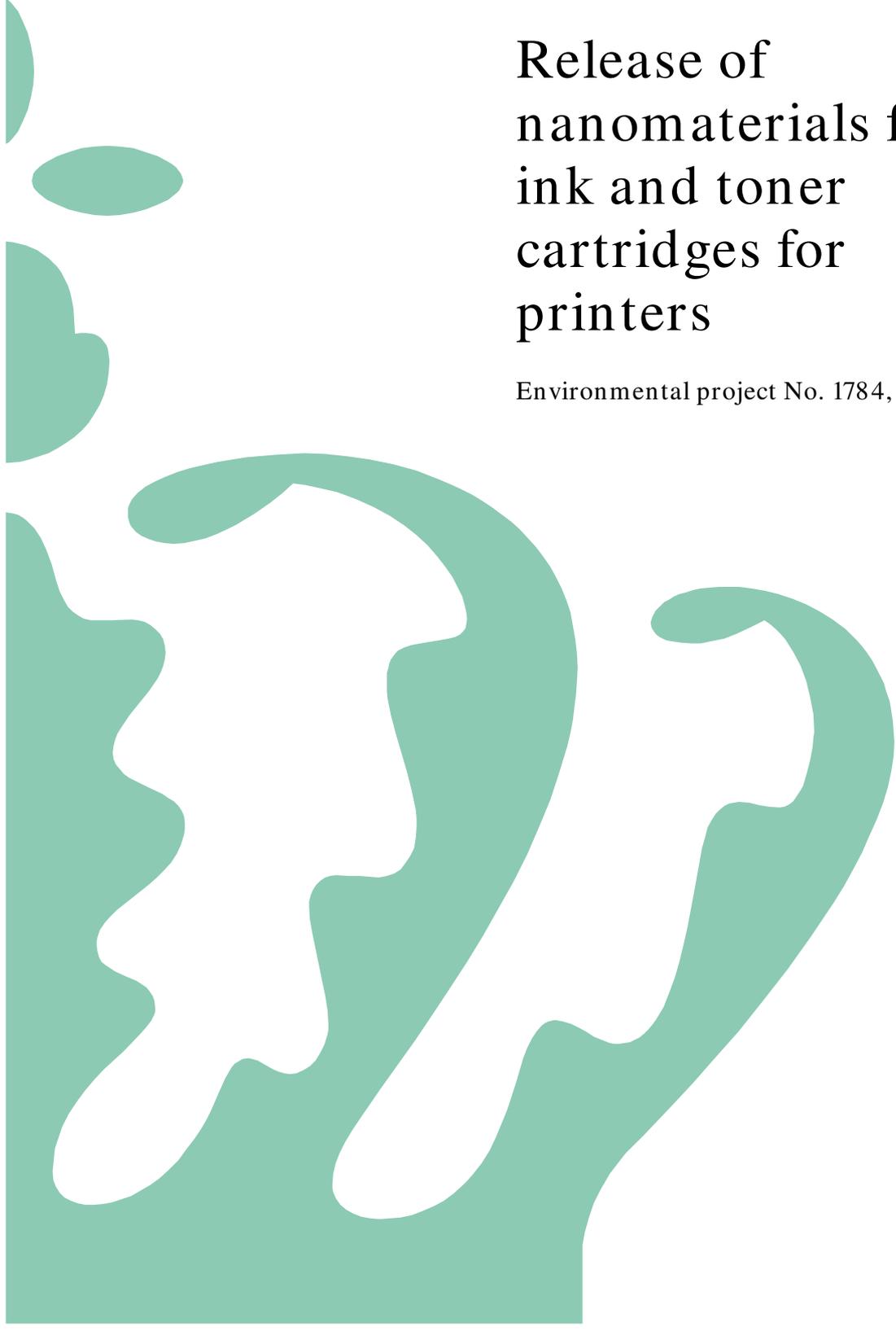
The industrial use of engineered nanoparticles has increased dramatically in recent years, raising the risk of human exposure to nanomaterials. The uptake of airborne nanoparticles by inhalation is a major exposure scenario<sup>1,2</sup>. Engineered airborne nanoparticles can cause severe harm such as pulmonary inflammation, asthma, chronic obstructive pulmonary disease, and lung cancer when inhaled<sup>3,4</sup>. From the respiratory tract they can translocate to secondary organs such as the lymphatic or blood circulation<sup>5</sup>. Low-cost, portable personal airborne nanoparticle monitors have been demanded for years by authorities and the nanoparticle producing industry<sup>6</sup>.

Nanomechanical resonators have been used to detect single biomolecules<sup>7</sup>, viruses<sup>8,9</sup>, and nanoparticles<sup>10-12</sup>. The mass sensitivity of a mechanical resonator is a function of its resonance frequency and inverse of its mass. This has led to the realization of nanomechanical resonators with a mass resolution down to the yoctogram ( $10^{-24}$  g) range<sup>13</sup>. The superiority of nanomechanical mass sensors is restricted to point mass measurements compared to distributed mass sensing where the added mass is homogeneously covering an entire surface<sup>14</sup>. Thus, the main application-field of nanomechanical mass sensors lies in the detection of single sample entities, e.g. in nanomechanical mass spectrometry<sup>7</sup>. In order to achieve the high mass resolution, nanomechanical resonators are often kept in ultrahigh vacuum and/or cryogenic temperatures<sup>7,10,13,15,16</sup>. This is impractical in case a small and portable sensor is required. It has been shown that nanomechanical resonators driven at room temperature and ambient pressure have a mass resolution in the attogram ( $10^{-18}$  g) range<sup>17</sup>. This is sufficient to detect single airborne viruses or nanoparticles.

The challenge with all nanomechanical mass sensors is the small probability that a sample entity will spontaneously hit the small resonator surface. In high vacuum, absorption events in minute cycles have been recorded<sup>7</sup>. In air, the generally poor sampling efficiency has been improved by dielectrophoretic attraction<sup>11</sup> or by partial vacuum<sup>12</sup>. Nevertheless, sampling times of several minutes to hours are typically required in order to collect a small number of particles.

Here, we show that it is possible to efficiently collect and detect single airborne nanoparticles on a nanomechanical resonator in real-time. Nanomechanical resonators have shown the required sensitivity to detect the mass of single nanoparticles in air. But a suitable method to collect airborne nano-samples on a nanomechanical resonator with a high collection efficiency has been missing. In our sampling approach we utilize a method well known from air filtration in which the nanomechanical resonator acts as a single filter-fiber. The aerosol containing the nanoparticles is streaming through the sensor chip passing the doubly-clamped resonator, see Fig. 1a. We

Ministry of Environment and Food  
The Danish Environmental Protection Agency



# Release of nanomaterials from ink and toner cartridges for printers

Environmental project No. 1784, 2015

**Title:**

Release of nanomaterials from ink and toner cartridges for printers

**Editing:**

Kathe Tønning  
Christian Holst Fischer  
Manja Annette Behrens  
Thomas Nørregaard Jensen  
Morten Køcks  
Peter Bøgh Pedersen

**Published by:**

The Danish Environmental Protection Agency  
Strandgade 29  
1401 Copenhagen K  
Denmark  
[www.mst.dk/english](http://www.mst.dk/english)

**Year:**

2015

**ISBN nr.**

978-87-93352-65-0

**Disclaimer:**

When the occasion arises, the Danish Environmental Protection Agency will publish reports and papers concerning research and development projects within the environmental sector, financed by study grants provided by the Danish Environmental Protection Agency. It should be noted that such publications do not necessarily reflect the position or opinion of the Danish Environmental Protection Agency.

However, publication does indicate that, in the opinion of the Danish Environmental Protection Agency, the content represents an important contribution to the debate surrounding Danish environmental policy.

Sources must be acknowledged.

# Conclusion and summary

This project has aimed at investigating toner and ink cartridges for printers on the Danish market in order to determine whether this group of products must be reported to the Danish nanoproduct register.

The project has been divided into three phases. These are briefly summarized in the following.

## **Categorisation based on type and selection of printer cartridges**

Initially, printer cartridges on the Danish market were divided into two main types classified as ink and toner. These two types are used in inkjet and laser printers, respectively.

Based on this categorisation, 12 cartridges were selected in collaboration with the Danish Environmental Protection Agency for further analysis. The analyses were performed in order to ascertain the potential content of nanoparticles in the products. Six toner cartridges and six ink cartridges were selected. The six toner cartridges included both original (black and colour) and refillable/refilled cartridges (black) for five different laser printers, and the six ink cartridges included original and refillable/refilled cartridges for five different inkjet printers.

## **Analysis of particle sizes in printer cartridges**

The analysis has had two purposes; to investigate if a specific product contains nanomaterials and to determine whether these are released during reasonably foreseeable use.

Using dynamic light scattering the content of nanomaterial in solution was determined. Nanoparticles were found in four out of the six types of toner and it cannot be excluded that nanoparticles are also present in the remaining two toner powders. The analysis of the ink products showed that all original inks contained nanoparticles. It cannot be excluded that the unoriginal inks also contain nanoparticles, as the analyses could not be conducted due to insufficient particle concentration relative to the transmission of the sample.

## **Release during printing and other relevant use of the printer cartridges**

Release of nanomaterials from printer cartridges (both laser cartridges and inkjet cartridges) was investigated during the printing process and during the process of cartridge replacement. During the printing operation, no particle concentration higher than the background level was detected. This level was measured immediately before initiating the printing process. Thus, no release of nanomaterial was observed during the printing process. However, some scientific publications exist that demonstrate release of nanoparticles from laser printers during the printing process.

One of the printer cartridges chosen for testing is a refillable toner cartridge, which is to be refilled with toner powder by the consumer. Thus, reasonably foreseeable use of this product includes the refilling process, and therefore measurements were made on the release of nanomaterials during the refilling process. The measurements showed that the particle concentration (nanoparticles) was much higher than the background level and it can thus be concluded that nanomaterials are released during reasonably foreseeable use.



**Safe handling of  
nanomaterials and  
other advanced materials  
at workplaces**

# Table of Contents

<b>1</b>	<b>Abbreviations and acronyms</b>	<b>4</b>
<b>2</b>	<b>Summary</b>	<b>5</b>
<b>3</b>	<b>Introduction</b>	<b>6</b>
<b>4</b>	<b>Routes of exposure</b>	<b>9</b>
<b>5</b>	<b>Decision criteria to derive occupational safety</b>	<b>11</b>
5.1	<b>Decision criterion 1:</b> Physical condition of the nanomaterial	13
5.2	<b>Decision criterion 2:</b> Solubility of the nanomaterial	14
5.3	<b>Decision criterion 3:</b> Fibre morphology	15
5.4	<b>Decision criterion 4:</b> Toxicity of the nanoscale substance (substance toxicity additionally to toxic properties of dusts)	16
5.5	Handling nanomaterials in laboratories	17
5.6	Specific information in the material safety data sheet	18
<b>6</b>	<b>Protection measures for handling of nanoparticles bound in a matrix</b>	<b>21</b>
6.1	Substitution	21
6.2	Technical protection measures	21
6.3	Occupational safety measures	21
6.4	Effectiveness check	22
<b>7</b>	<b>Protection measures for handling of nanoparticles dissolved in liquids</b>	<b>23</b>
7.1	Substitution	23
7.2	Technical protection measures	24
7.3	Organisational protection measures	24
7.4	Personal protection measures	24
7.5	Effectiveness check	25
<b>8</b>	<b>General protection measures for handling soluble powders</b>	<b>27</b>
8.1	Substitution	27
8.2	Technical protection measures	27
8.3	Organisational protection measures	28
8.4	Personal protection measures	29
8.5	Effectiveness check	29



<b>9</b>	<b>Protection measures for dry, dusty and insoluble nanomaterials</b>	<b>31</b>
9.1	Substitution	31
9.2	Technical protection measures	31
9.3	Organisational protection measures	32
9.4	Personal protection measures	33
9.5	Explosion protection	33
9.6	Effectiveness check	34
9.7	Placing on the market	35
<b>10</b>	<b>Additional protection measures for nanofibres</b>	<b>36</b>
10.1	Substitution	36
10.2	Technical protection measures	36
10.3	Organisational protection measures	36
10.4	Personal protection measures	37
10.5	Effectiveness check	37
<b>11</b>	<b>Instruction course, occupational health and toxicological advice</b>	<b>39</b>
11.1	Instruction course	39
11.2	Occupational health and toxicological advice	40
11.3	Health surveillance	41
<b>12</b>	<b>Storage of nanomaterials</b>	<b>43</b>
<b>13</b>	<b>Disposal Procedures</b>	<b>45</b>
13.1	Waste disposal	45
<b>14</b>	<b>Sample letter for questions addressed at a manufacturer</b>	<b>46</b>
<b>15</b>	<b>Conclusions</b>	<b>47</b>
<b>16</b>	<b>References</b>	<b>49</b>
	<b>Imprint</b>	<b>52</b>

## 2 Summary

A rising number of companies, especially small and medium enterprises (SME), are active in the field of nanotechnology. For safe development of this industry, forethought of occupational safety and health considerations is important. This guideline on good working practice with nanomaterials addresses research institutions as well as SME industries. **Four decision criteria** are presented that support the reader in deriving the appropriate occupational safety measures in a comprehensible way. These occupational safety measures are tailored to the defined groups of nanomaterials and follow the precautionary approach. They comply with the priority list of the STOP principle: substitution, technical measures, organisational measures and personal protection measures.

❖ **Four decision criteria can be implemented in risk assessment to find appropriate risk reduction strategies.**





20<sup>th</sup> International Congress of Chemical and Process Engineering CHISA 2012  
25 – 29 August 2012, Prague, Czech Republic

## Safety management of nanomaterials

A. Groso<sup>a</sup>, A. Magrez<sup>b</sup>, Th. Meyer<sup>a</sup> a\*

<sup>a</sup>SB-SST, EPFL, Station 6, 1015 Lausanne, Switzerland

<sup>b</sup>ICMP-LPMC, EPFL, Station 3, 1015 Lausanne, Switzerland

---

### Abstract

In this work, we present a practical and engineering risk management procedure for a university-wide safety and health management of nanomaterials, developed as a multi-stakeholder effort (government, accident insurance, researchers and experts for occupational safety and health). It provides the identification and evaluation of potential hazards and establishes effective control mechanisms to ensure protection of the employee and the environment. The process, similar to control banding approach, starts using a schematic decision tree that allows classifying the nano laboratory into three hazard classes (from Nano 3 - highest hazard to Nano1 - lowest hazard). The first differentiation in the decision tree for hazard class determination regards the environment, whether the process is carried out in a closed (complete process confinement) or open system. In case the process is not fully enclosed (glove box or completely sealed environment), different types of activities with nanomaterials are discussed (activity with nanofibers, powders, suspensions and activity with nanoobjects in solid matrix). For each determined hazard level we then propose a list of required risk mitigation measures (technical, organizational, personal, reception and storage, shipping and handling, medical survey and cleaning facilities). The target 'users' of this safety and health methodology are researchers and safety officers in the first place. They can rapidly access the precautionary hazard class of their activities and the corresponding adequate protective and preventive measures.

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*Keywords:* Nanomaterial; risk; safety management; research

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\* Corresponding author. Tel.: +41 21 693 3614 ; fax: +41 21 693 3190.  
E-mail address: [thierry.meyer@epfl.ch](mailto:thierry.meyer@epfl.ch).



EUROSENSORS 2015

## Sensitive photonic system to measure oxidative potential of airborne nanoparticles and ROS levels in exhaled air

A. Laulagnet<sup>a</sup>, J.J. Sauvain<sup>a</sup>, N. Concha-Lozano<sup>a</sup>, M. Riediker<sup>b</sup>, G. Suárez<sup>a\*</sup>

<sup>a</sup>*Institute for Work and Health, route de la Corniche 2, CH-1066 Epalinges-Lausanne, Switzerland*

<sup>b</sup>*SAFENANO-IOM Singapore, Singapore*

### Abstract

A photonic system has been developed that enables sensitive quantitative determination of reactive oxygen species (ROS) – mainly hydrogen peroxide (H<sub>2</sub>O<sub>2</sub>) – in aerosol samples such as airborne nanoparticles and exhaled air from patients. The detection principle relies on the amplification of the absorbance under multiple scattering conditions due to optical path lengthening [1,2]. In this study, the presence of cellulose membrane that acts as random medium into the glass optical cell considerably improved the sensitivity of the detection based on colorimetric FOX assay (FeII / orange xylenol). Despite the loss of assay volume (cellulose occupies 75% of cell volume) the limit of detection is enhanced by one order of magnitude reaching the value of 9 nM (H<sub>2</sub>O<sub>2</sub> equivalents). Spectral analysis is performed automatically with a periodicity of 5 to 15 s, giving rise to real-time ROS measurements. Moreover, the elution of air sample into the collection chamber via a micro-diffuser (impinger) enables quantitative determination of ROS contained in or generated from airborne samples. As proof-of-concept the photonic ROS detection system was used in the determination of both ROS generated from traffic pollution and ROS contained in the exhaled breath as lung inflammation biomarkers.

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Peer-review under responsibility of the organizing committee of EUROSENSORS 2015

**Keywords:** Oxidative potential; nanoparticle; oxidative stress; ROS; chemical sensor; photonic device; real-time detection

### 1. Introduction

Of the unintentional routes of human exposure to particulates, chemicals or mineral fibers, inhalation is considered the most significant. The lungs are an efficient entry portal for a variety of gaseous and aerosol-

\* Corresponding author. Tel.: 41-21-314-5897; fax: +41-21-314-7420.  
E-mail address: [guillaume.suarez@chuv.ch](mailto:guillaume.suarez@chuv.ch)

Elżbieta Jankowska

## ROZPRZESTRZENIANIE SIĘ W POWIETRZU NANOBIĘKTÓW WYTWARZANYCH W WYNIKU WŁĄCZENIA KUCHENKI MIKROFALOWEJ

SPREAD OF NANO-OBJECTS IN THE AIR  
AS A RESULT OF SWITCHING-ON A MICROWAVE

Centralny Instytut Ochrony Pracy – Państwowy Instytut Badawczy / Central Institute for Labour Protection –  
National Research Institute, Warszawa, Poland  
Zakład Zagrożeń Chemicznych, Pyłowych i Biologicznych / Department of Chemical, Aerosol and Biological Hazards

### STRESZCZENIE

**Wstęp:** W wyniku włączenia w pomieszczeniu kuchenki mikrofalowej w powietrzu są wytwarzane cząstki o nanowymiarach. Wytwarzane cząstki mogą się rozprzestrzeniać w powietrzu w pomieszczeniu. **Materiał i metody:** Badanie rozprzestrzeniania się cząstek w powietrzu w pomieszczeniu przeprowadzono przez określanie stężeń liczbowych i powierzchniowych oraz średnich wymiarów cząstek. Użyto do tego urządzeń DiscMini umiejscowionych w 6 punktach pomiarowych, pozwalających śledzić zmiany parametrów cząstek przede wszystkim w pobliżu źródła ich wytwarzania i w obszarze działania wentylacji miejscowej (dygestorium), a także w innych punktach, np. w pobliżu okna lub w środku pomieszczenia. **Wyniki:** Kiedy dygestorium było wyłączone, tzn. w pomieszczeniu występowała wentylacja zrównoważona, włączenie kuchenki spowodowało 9,42–14,14-krotny wzrost stężeń liczbowych cząstek o nanowymiarach w odniesieniu do tła i 3,51–4,81-krotny wzrost stężeń powierzchniowych. Kiedy dygestorium było włączone, tzn. w pomieszczeniu występowało podciśnienie, włączenie kuchenki spowodowało 3,20–4,43-krotny wzrost stężeń liczbowych cząstek o nanowymiarach w odniesieniu do tła i 1,61–1,89-krotny wzrost stężeń powierzchniowych cząstek. **Wnioski:** Z analizy danych wynika, że włączenie kuchenki mikrofalowej na 5 min skutkuje wytwarzaniem nanoobjektów po ok. 3 min od włączenia kuchenki, z maksymalnymi wartościami stężeń do 12 min od włączenia kuchenki, we wszystkich 6 punktach pomiarowych zlokalizowanych w badanym pomieszczeniu. Dotyczy to obydwu sytuacji, tzn. włączonego i wyłączzonego dygestorium. Med. Pr. 2016;67(3):353–363

**Słowa kluczowe:** nanoobjekty, rozprzestrzenianie się cząstek, kuchenka mikrofalowa, narażenie, stężenie liczbowe i powierzchniowe, średni wymiar cząstek

### ABSTRACT

**Background:** Switching-on a microwave results in the creation of nano-sized particles, which can spread through the air of a given premise, e.g., room. **Material and Methods:** The study was carried out to determine the number and surface concentrations as well as the mean particles size using a DiscMini measurement device distributed in 6 measuring points to track changes of particle parameters, primarily at the source of particle creation and in the area of local ventilation (fume cupboard), and also in other places, e.g., near the window or in the middle of the room. **Results:** Where the fume cupboard was switched-off, i.e., normal pressure ventilation in the room, switching-on the microwave caused a 9.42–14.14-fold increase in the number concentration of nano-sized particles relative to the background and a 3.51–4.81-fold increase in the surface concentration. Where the fume cupboard was switched-on, i.e., negative pressure ventilation in the room switching-on the microwave caused a 3.20–4.43-fold increase in the number concentration of nano-size particles relative to the background and a 1.61–1.89-fold increase in the surface concentration. **Conclusions:** The analysis of the data shows that switching-on a microwave for 5 min results in the creation of nano-objects already after about 3 min with the maximum concentration values after 12 min since switching-on the microwave in all 6 measurement points distributed in the test room. This applies to both situations, i.e., when the fume cupboard was switched-off or switched-on. Med Pr 2016;67(3):353–363

**Key words:** nano-objects, spread of the particles, microwave, exposure, number and surface concentrations, mean particle size

Autorka do korespondencji / Corresponding author: Elżbieta Jankowska, Centralny Instytut Ochrony Pracy – Państwowy Instytut Badawczy, Zakład Zagrożeń Chemicznych, Pyłowych i Biologicznych, ul. Czerniakowska 16, 00-701 Warszawa, e-mail: eljan@ciop.pl  
Nadesłano: 1 lipca 2015, zatwierdzono: 20 grudnia 2015

Finansowanie / Funding: praca wykonana w ramach projektu II.P.02 „Badanie procesu rozprzestrzeniania się nanoobjektów w powietrzu pomieszczeń pracy” realizowanego w Centralnym Instytucie Ochrony Pracy – Państwowym Instytucie Badawczym w ramach programu wieloletniego pn. „Poprawa bezpieczeństwa i warunków pracy” III etap, czas realizacji: lata 2014–2016. Kierownik projektu: dr inż. Elżbieta Jankowska.

# Tiered Approach to an Exposure Measurement and Assessment of Nanoscale Aerosols Released from Engineered Nanomaterials in Workplace Operations





# 1 Executive Summary

Engineered nanomaterials (ENMs) are often fascinating, new materials with significantly improved or completely novel properties [BIAC]. Some other ENMs are materials, which have been marketed for decades, e.g., carbon black, synthetic amorphous silica, pigments, etc. are or may also be affected by the nanotechnology debate. They are being handled in the workplaces both in research and in production. The Chemical Industry in Germany has subscribed to the Responsible Care Global Charter and is therefore committed to a safe, responsible and sustainable development of this highly promising technology. This includes appropriate organizational measures as well as the implementation of a high level of industrial hygiene standards. Amongst others, it has led to the development of the Guidelines on the Responsible Use of Nanomaterials in the Workplace, jointly issued by BAuA and VCI in 2007 [BAuA, VCI], [Heinemann]. The German Social Accident Insurance (DGUV) has also committed itself to support the responsible use of nanomaterials [IFA 1]

Industrial hygienists are interested in the measurement and management of the exposure to the inhalable and respirable dust fraction, including the nanoscale fraction [Dust Fraction], [DIN EN 1]. The tiered approach and thus the present document focuses on a size range from 1 nm to 100 nm and is designed to support assessment of health risks from solid, particulate substances released as nanoscale aerosol from ENMs in routine workplace operations. Therefore, aerosols containing nano-objects and their nanoscale aggregates and agglomerates are targeted by this approach. Efficient, reliable, but also pragmatic exposure assessment is a crucial element and the starting point for the effective management of risks potentially posed by hazardous chemicals in the workplace.

Therefore, the Institute of Energy and Environmental Technology e.V. (IUTA), the Federal Institute for Occupational Safety and Health (BAuA), the German Social Accident Insurance Institution for the Raw Materials and Chemical Industry (BG RCI), the Institute for Occupational Safety and Health of the DGUV (IFA), the Technical University Dresden (TUD) and the German Chemical Industry Association (VCI) established a working group to address and discuss the challenges of exposure measurement and assessment<sup>2</sup> of nanoscale aerosols released from ENMs in the workplace.<sup>3</sup> The working group aimed at a harmonized approach towards such exposure measurement. The outcome was designed to be pragmatic and widely usable, rather than to form the basis for further scientific and research oriented studies. A tiered approach is the result, which can be widely used by small and medium size enterprises as well as large chemical companies with global business operations.

THE MAIN FINDINGS OF THE WORKING GROUP CAN BE SUMMARIZED AS FOLLOWS:

- Safe work places where ENMs are produced or processed can be achieved, using existing technology, and which conforms with best industrial hygiene practi-

ces. Existing substance-specific, binding, health based OELs must be complied with and are not subject of or overridden by the current approach.

- Exposure measurement of nanoscale aerosols released from ENMs in the work-place is possible and exposure assessment methodologies exist. However, methodologies are not yet standardized and more difficult to apply as in routine operations, e.g. gravimetric dust measurements according to DIN EN 481.

- Equipment required for measurement of exposure to nanoscale aerosols released from ENMs is sophisticated and the results produced, e.g., total particle number concentration, have no direct correlation to the chemical identity. Calibration of equipment is still a challenge and validation using round robin testing, which is typically correlated with SMPS results, is difficult as no commonly accepted reference method is available.

- At the moment, for a practitioner, a tiered approach to exposure assessment appears to be the most appropriate strategy. This approach is split into 3 tiers. In the first step (Tier 1) information is gathered according to established industrial hygiene practices. In the next tier (Tier 2) a basic exposure assessment using a limited set of easy-to-use equipment is conducted, where as in the highest tier 6 (Tier 3) the latest state-of-the-art measurement technology is employed to assess the potential for workplace exposure to nanoscale aerosols released from ENMs if required.

- Existing legally binding OELs, e.g. synthetic amorphous silica [TRGS 900: EC No. 231-545-4], carbon black [ACGIH], etc., have to be complied with. Where no such substance-specific, binding, health-based OEL values for ENMs exist, the tiered approach is using 3 criteria for the assessment of the data:

- 1) Interference value exceeded for nanoscale aerosols released from ENMs.

- 2) Significant increase over aerosol background level in the workplace air.

- 3) Chemical identity of the nano-objects and their nanoscale aggregates and agglomerates detected in the aerosol.

- The application of the decision logic leads in total to 7 different cases (Case A – G), which may guide the risk management decisions of the practitioner.

- This step-by-step approach may need to be revisited as soon as new scientific findings are available (especially on binding, health-based occupational exposure limit values). The presented exposure assessment strategy of nanoscale aerosols released from ENMs in the workplace may serve as a starting point for further standardization.

<sup>2</sup> Exposure measurement and assessment are an integral element in the overall risk assessment in the workplace.

<sup>3</sup> The presented approach considers permanently situated workplaces, e.g., in a production facility. Varying assignments, e.g., as typical in the construction industry are less in its focus.



## 2 Drivers and Specific Challenges

ENMs are being handled more and more in workplaces, both in research and in production, as a wide range of different ENMs are used to develop and produce new structures, materials and devices.

Currently only a few substance-specific, health-based exposure limits for ENMs in workplace operations have been proposed [NIOSH 1], [Pauluhn 1 and 2], [Schulte]. Even though OECD test protocols are applicable for ENMs [OECD 1], uncertainties concerning the hazards and risks potentially posed by ENMs exist. Exposure assessment and control become thus even more important. Therefore, an urgent need exists for reliable exposure measurement and assessment of aerosols containing ENMs in workplace operations.

As long as the field of toxicology of ENMs is evolving and no substance-specific, binding, health-based OELs have been established and validated, control of exposure in the workplace has to adequately protect the workforce.

Efforts have been undertaken thus far by various organizations and initiatives<sup>4</sup>, to tackle the issue of workplace air emissions and exposure measurement by monitoring potentially affected workplaces and starting to harmonize the required protocols.

The focus of these initiatives was either tailored to a project [NANOCARE] or more research oriented [TNO], whereas a pragmatic approach, which could be easily applied by and thus widely applicable to the practitioner in the field, was missing and therefore is in the focus of this joint initiative to present a tiered approach.

Internationally active organizations and companies, who are involved in the development of innovative materials including ENMs with novel and superior properties, develop, produce and use materials containing ENMs worldwide. The current approach is an example for an initiative of the Institute of Energy and Environmental Technology e.V. (IUTA), the Federal Institute for Occupational Safety and Health (BAuA), the German Social Accident Insurance Institution for the Raw Materials and Chemical Industry (BG RCI), the Institute for Occupational Safety and Health of the DGUV (IFA), the Technical University Dresden (TUD) and the German Chemical Industry Association (VCI) aiming to produce coherent industrial hygiene including an exposure assessment strategy and methodologies to enable effective and efficient decisions for the management of risks during the production and handling of ENMs. The presented approach, which could be used for routine exposure measurement and assessment in the field, may also be beneficial for small and medium enterprises (SMEs), for downstream users in non-chemical industries and consultants for occupational safety, which may be less experienced in exposure assessment of nanoscale aerosols released from ENMs in workplace operations.

A tiered approach to the exposure assessment of nanoscale aerosols released from ENMs in workplace operations is deemed most effective. Its main advantage is the most efficient use of limited, qualified resources to ensure a high level of protection of the workforce.

<sup>4</sup> e.g., the German BMBF project NANOCARE [NANOCARE], the EU project NANOSH [NANOSH], OECD [OECD 2], NIOSH [Methner] as well as TNO, PEROSH and IFA [TNO]



Contents lists available at ScienceDirect

## Journal of Aerosol Science

journal homepage: [www.elsevier.com/locate/jaerosci](http://www.elsevier.com/locate/jaerosci)

# Ultrafine and nanoparticle formation and emission mechanisms during laser processing of ceramic materials

A.S. Fonseca<sup>a,b,\*</sup>, M. Viana<sup>a</sup>, X. Querol<sup>a</sup>, N. Moreno<sup>a</sup>, I. de Francisco<sup>c</sup>, C. Estepa<sup>c</sup>, G.F. de la Fuente<sup>c</sup>

<sup>a</sup> Institute of Environmental Assessment and Water Research (IDÆA-CSIC), C/Jordi Girona 18, 08034 Barcelona, Spain

<sup>b</sup> Universidad de Barcelona, Facultad de Química, Martí i Franquès 1-11, 08028 Barcelona, Spain

<sup>c</sup> Instituto de Ciencia de Materiales de Aragón (ICMA – Universidad de Zaragoza), María de Luna 3, E-50018 Zaragoza, Spain

## ARTICLE INFO

## Article history:

Received 25 February 2015

Received in revised form

25 May 2015

Accepted 27 May 2015

Available online 6 June 2015

## Keywords:

Tile sintering

Furnace

New particle formation

LDSA

Particle transport

Indoor air

## ABSTRACT

The use of laser technology in the ceramic industry is undergoing an increasing trend, as it improves surface properties. The present work aimed to assess ultrafine and nanoparticle emissions from two different types of laser treatments (tile sintering and ablation) applied to two types of tiles. New particle formation mechanisms were identified, as well as primary nanoparticle emissions, with concentrations reaching up to  $6.7 \times 10^6$  particles  $\text{cm}^{-3}$  and a mean diameter of 18 nm. Nanoparticle emission patterns were strongly dependent on temperature and raw tile chemical composition. Nucleation events were detected during the thermal treatment independently of the laser application. TEM images evidenced spherical ultrafine particles, originating from the tile melting processes. When transported across the indoor environment, particles increased in size (up to 38 nm) with concentrations remaining high ( $2.3 \times 10^6$  particles  $\text{cm}^{-3}$ ). Concentrations of metals such as Zn, Pb, Cu, Cr, As and Tl were found in particles  $< 250$  nm.

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## 1. Introduction

Laser irradiation of ceramic material is a novel technique with numerous advantages regarding the sintering process such as speed, temperature and enhanced durability and surface properties of structural materials (Schmatjko, Endres, Schmidt, & Banz, 1988; Toenshoff & Gedrat, 1991; Jarvis, Nastasi, Hubbard, & Hirvonen, 1993; de Francisco et al., 2011; Lahoz, de la Fuente, Pedra, & Carda, 2011). The use of high powered CO<sub>2</sub> lasers for industrial ceramic materials processing was studied in the framework of LIFE projects and is currently being assessed for two different industrial processes: (i) tile sintering in a high-temperature furnace and, (ii) ablation of ceramic materials. A recently developed “in-situ” melting method (tile sintering) makes use of a CO<sub>2</sub> laser scanner combined with simultaneous external heating of the substrate (in a conventional furnace) and uniform movement (Estepa & de la Fuente, 2006; de Francisco et al., 2011). This innovative technology allows to obtain coatings of practically any oxide material on an alumina substrate (Estepa & de la Fuente, 2006; de Francisco et al., 2011). In addition, this novel tool can also make use of CO<sub>2</sub> lasers in pulsed mode (induced laser ablation) to perform engravings on the surface of ceramics (Lahoz et al., 2011).

\* Corresponding author at: Institute of Environmental Assessment and Water Research (IDÆA-CSIC), C/Jordi Girona 18, 08034 Barcelona, Spain. Tel.: +34 934006100; fax: +34 932045904.

E-mail address: [ana.godinho@idaea.csic.es](mailto:ana.godinho@idaea.csic.es) (A.S. Fonseca).

<http://dx.doi.org/10.1016/j.jaerosci.2015.05.013>

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# Workplace exposure to nanoparticles and the application of provisional nanoreference values in times of uncertain risks

Pieter van Broekhuizen · Fleur van Broekhuizen · Ralf Cornelissen · Lucas Reijnders

Received: 17 July 2011 / Accepted: 6 February 2012  
© Springer Science+Business Media B.V. 2012

**Abstract** Nano reference values (NRVs) for occupational use of nanomaterials were tested as provisional substitute for Occupational Exposure Limits (OELs). NRVs can be used as provisional limit values until Health-Based OELs or derived no-effect levels (DNEL) become available. NRVs were defined for 8 h periods (time weighted average) and for short-term exposure periods (15 min-time weighted average). To assess the usefulness of these NRVs, airborne number concentrations of nanoparticles (NPs) in the workplace environment were measured during paint manufacturing, electroplating, light equipment manufacturing, non-reflective glass production, production of pigment concentrates and car refinishing. Activities monitored were handling of solid engineered NPs (ENP), abrasion, spraying and heating during occupational use of nanomaterials (containing ENPs) and machining nanosurfaces. The measured concentrations are often presumed to contain ENPs as well as process-generated NPs (PGNP). The PGNP are found to be a significant source for potential exposure and cannot be ignored in risk assessment. Levels of NPs identified in

workplace air were up to several millions of nanoparticles/cm<sup>3</sup>. Conventional components in paint manufacturing like CaCO<sub>3</sub> and talc may contain a substantial amount of nanosized particulates giving rise to airborne nanoparticle concentrations. It is argued that risk assessments carried out for e.g. paint manufacturing processes using conventional non-nano components should take into account potential nanoparticle emissions as well. The concentrations measured were compared with particle-based NRVs and with mass-based values that have also been proposed for workers protection. It is concluded that NRVs can be used for risk management for handling or processing of nanomaterials at workplaces provided that the scope of NRVs is not limited to ENPs only, but extended to the exposure to process-generated NPs as well.

**Keywords** Nanomaterial · Nanoparticle · Risk management · Occupational Exposure Limit · Nano reference value · Health effects · Exposure measurement

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P. van Broekhuizen (✉) · F. van Broekhuizen · R. Cornelissen  
IVAM UvA BV, Plantage Muidergracht 14,  
1018TV Amsterdam, The Netherlands  
e-mail: pvbroekhuizen@ivam.uva.nl

L. Reijnders  
Institute for Biodiversity and Ecosystem Dynamics,  
University of Amsterdam, Amsterdam, The Netherlands

## Introduction

Working with nanomaterials may result in exposure of workers to nanoparticles (NPs) and the possibility that adverse health effects develop (Borm et al. 2006; Yokel and MacPhail 2011). A recent proposal of the

## Research Article

# Workplace Exposure to Titanium Dioxide Nanopowder Released from a Bag Filter System

Jun Ho Ji,<sup>1,2</sup> Jong Bum Kim,<sup>3,4</sup> Gwangjae Lee,<sup>1</sup> Jung-Hun Noh,<sup>5</sup>  
Se-Jin Yook,<sup>5</sup> So-Hye Cho,<sup>6</sup> and Gwi-Nam Bae<sup>3,4,7</sup>

<sup>1</sup>EcoPictures Co. Ltd., Seoul 137-865, Republic of Korea

<sup>2</sup>Research & Business Foundation, Sungkyunkwan University, Suwon 440-746, Republic of Korea

<sup>3</sup>Center for Environment, Health, and Welfare Research, Korea Institute of Science and Technology, Seoul 136-791, Republic of Korea

<sup>4</sup>Green School, Korea University, Seoul 136-713, Republic of Korea

<sup>5</sup>School of Mechanical Engineering, Hanyang University, Seoul 133-791, Republic of Korea

<sup>6</sup>Center for Materials Architecture, Korea Institute of Science and Technology, Seoul 136-791, Republic of Korea

<sup>7</sup>University of Science and Technology, Daejeon 305-303, Republic of Korea

Correspondence should be addressed to Gwi-Nam Bae; gnbae@kist.re.kr

Received 17 December 2014; Revised 12 March 2015; Accepted 12 March 2015

Academic Editor: Vladimir Murashov

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Many researchers who use laboratory-scale synthesis systems to manufacture nanomaterials could be easily exposed to airborne nanomaterials during the research and development stage. This study used various real-time aerosol detectors to investigate the presence of nanoaerosols in a laboratory used to manufacture titanium dioxide (TiO<sub>2</sub>). The TiO<sub>2</sub> nanopowders were produced via flame synthesis and collected by a bag filter system for subsequent harvesting. Highly concentrated nanopowders were released from the outlet of the bag filter system into the laboratory. The fractional particle collection efficiency of the bag filter system was only 20% at particle diameter of 100 nm, which is much lower than the performance of a high-efficiency particulate air (HEPA) filter. Furthermore, the laboratory hood system was inadequate to fully exhaust the air discharged from the bag filter system. Unbalanced air flow rates between bag filter and laboratory hood systems could result in high exposure to nanopowder in laboratory settings. Finally, we simulated behavior of nanopowders released in the laboratory using computational fluid dynamics (CFD).

## 1. Introduction

It is estimated that millions of new workers and researchers will be exposed to engineered nanomaterials (ENMs) in occupational environments [1]. Various nanoaerosol sources in ENM manufacturing workplaces show complex relations to ENM exposure assessment. While identifying the sources, it becomes necessary to distinguish between ENMs and incidental nanoaerosols [2].

Many recent studies have investigated ENM exposure. Airborne multiwalled carbon nanotubes (MWCNTs) released within a research facility were measured via personal and area air sampling and by real-time aerosol monitoring [3–7]. Lee et al. [8] monitored potential exposure to nanoaerosols

at workplaces where titanium dioxide (TiO<sub>2</sub>) and silver (Ag) nanoparticles were manufactured. A series of studies [9–12] attempted to differentiate task- or process-related ENMs from background or incidental nanoaerosols in workplaces.

However, a more urgent problem exists at the research and development stage in laboratories. Many researchers or students who manufacture ENMs using laboratory-scale synthesis systems could be easily exposed to airborne ENMs. Current knowledge indicates that a well-designed exhaust hood system with a high-efficiency particulate air (HEPA) filter can effectively remove ENMs. However, malfunction or failure of this system is not easily detected by regular activity, since ENMs may not be visible with the naked eye even when released at high concentrations. This occurs

### 3. Monitoring of the ambient air

<b>Abstract 3.01</b> A micro aerosol sensor for the measurement of airborne ultrafine particles	<b>Page 94</b>	<b>Abstract 3.14</b> Sensing the air we breathe - the OpenSense Zurich dataset	<b>Page 111</b>
<b>Abstract 3.02</b> BAERLIN2014 – the influence of land surface types on and the horizontal heterogeneity of air pollutant levels in Berlin	<b>Page 95</b>	<b>Abstract 3.15</b> Short-term associations between traffic-related noise, particle number and traffic flow in three European cities	<b>Page 112</b>
<b>Abstract 3.03</b> Deriving high-resolution urban air pollution maps using mobile sensor nodes	<b>Page 96</b>	<b>Abstract 3.16</b> Spatio-temporal variation of urban ultrafine particle number concentrations	<b>Page 113</b>
<b>Abstract 3.04</b> Development and validation of a UAV based system for air pollution measurements	<b>Page 97</b>	<b>Abstract 3.17</b> Study of personal exposure to nanoparticles considering meteorological variables in 4 streets with different types of vehicles in Bogotá	<b>Page 114</b>
<b>Abstract 3.05</b> The effects of the built environment, traffic patterns, and micrometeorology on street level ultrafine particle concentrations at a block scale: Results from multiple urban sites	<b>Page 98</b>	<b>Abstract 3.18</b> The association between greenness and traffic-related air pollution at schools	<b>Page 115</b>
<b>Abstract 3.06</b> Emission rates of particle number, mass and black carbon by the Los Angeles International Airport (LAX) and its impact on air...	<b>Page 99</b>	<b>Abstract 3.19</b> The exposome in practice: Design of the EXPOsOMICS project	<b>Page 116</b>
<b>Abstract 3.07</b> Emissions from an international airport increase particle number concentrations 4-fold at 10 km downwind	<b>Page 100</b>	<b>Abstract 3.20</b> The Fort Collins Commuter Study: Impact of route type and transport mode on personal exposure to multiple air pollutants	<b>Page 117</b>
<b>Abstract 3.08</b> Enabling Large-Scale Urban Air Quality Monitoring with Mobile Sensor Nodes	<b>Page 101</b>	<b>Abstract 3.21</b> Total and size-resolved particle number and black carbon concentrations in urban areas near Schiphol airport (the Netherlands)	<b>Page 118</b>
<b>Abstract 3.09</b> International airport impacts to air quality: size and related properties of large increases in ultrafine particle number concentrations	<b>Page 103</b>	<b>Abstract 3.22</b> Ultrafine particle metrics and research considerations: review of the 2015 UFP workshop	<b>Page 119</b>
<b>Abstract 3.10</b> Intra-urban variation of ultrafine particles as evaluated by process related land use and pollutant driven regression modelling	<b>Page 104</b>	<b>Abstract 3.23</b> Ultrafine particles at airports	<b>Page 120</b>
<b>Abstract 3.11</b> Lung deposited surface area size distributions of particulate matter in different urban areas	<b>Page 105</b>	<b>Abstract 3.24</b> Ultrafine particles over Germany an aerial survey	<b>Page 124</b>
<b>Abstract 3.12</b> Pushing the spatio-temporal resolution limit of urban air pollution maps	<b>Page 106</b>	<b>Abstract 3.25</b> Understanding the health effects of ambient ultrafine particles	<b>Page 125</b>
<b>Abstract 3.13</b> Remote sensing of sulphur and particle emission from ships	<b>Page 107</b>	<b>Abstract 3.26</b> Vertical profiles and chemical properties of aerosol particles upon Ny-Ålesund (Svalbard Islands)	<b>Page 129</b>

Article

# A Micro Aerosol Sensor for the Measurement of Airborne Ultrafine Particles

Chao Zhang <sup>1</sup>, Rong Zhu <sup>1,\*</sup> and Wenming Yang <sup>2</sup>

<sup>1</sup> State Key Laboratory of Precision Measurement Technology and Instrument, Department of Precision Instrument, Tsinghua University, Beijing 100084, China; zhangchao14@mails.tsinghua.edu.cn

<sup>2</sup> School of Mechanical Engineering, University of Science and Technology Beijing, Beijing 100083, China; wmyang@ustb.edu.cn

\* Correspondence: zr\_gloria@mail.tsinghua.edu.cn; Tel.: +86-10-6278-8935

Academic Editor: W. Rudolf Seitz

Received: 18 December 2015; Accepted: 16 March 2016; Published: 18 March 2016

**Abstract:** Particle number concentration and particle size are the two key parameters used to characterize exposure to airborne nanoparticles or ultrafine particles that have attracted the most attention. This paper proposes a simple micro aerosol sensor for detecting the number concentration and particle size of ultrafine particles with diameters from 50 to 253 nm based on electrical diffusion charging. The sensor is composed of a micro channel and a couple of planar electrodes printed on two circuit boards assembled in parallel, which thus integrate charging, precipitating and measurement elements into one chip, the overall size of which is  $98 \times 38 \times 25 \text{ mm}^3$ . The experiment results demonstrate that the sensor is useful for measuring monodisperse aerosol particles with number concentrations from 300 to  $2.5 \times 10^4 / \text{cm}^3$  and particle sizes from 50 to 253 nm. The aerosol sensor has a simple structure and small size, which is favorable for use in handheld devices.

**Keywords:** ultrafine particles; number concentration; particle size; micro aerosol sensor

## 1. Introduction

Airborne nanoparticles or ultrafine particles [1,2] distributed in the atmospheric, indoor and industrial environments seriously threaten human health [3,4]. The number concentration and particle size are the two key parameters used to describe exposure to airborne nanoparticles or ultrafine particles. The toxicology research results show that aerosol particles can deposit in different parts of the human respiratory organs [4–7] according to the sizes of the particles. The particles with sizes of less than  $10 \mu\text{m}$  can enter the nasal cavity, those smaller than  $7 \mu\text{m}$  can enter the throat, and if less than  $2.5 \mu\text{m}$ , they enter the lungs. Nanoparticles or ultrafine particles can enter into the human lungs and alveolar area, and further enter into the human blood circulation system [8,9].

Measurements of the size and concentration of aerosol particles mainly involve two kinds of methods based on optical and electrical mechanisms [1]. Optical measurements require a sensor or a particle detector in the detection zone; three of the most widely used sensors are the optical particle counter (OPC) [10], the laser particle counter (LPC) [11], and the condensation particle counter (CPC) [12]. However particle size detection by light scattering loses sensitivity when the size is less than the wavelength of the light or laser used, so OPCs or LPCs can only detect particle sizes larger than  $0.1 \mu\text{m}$  [1]. CPCs can detect particles with sizes less than  $0.1 \mu\text{m}$ , but to date the limitations of their compactness, portability and cost do not allow their application for personal monitoring. The particles with sizes ranging from 1 nm to 300 nm can be detected by electrical measurement. Electrical measurements can be classified into two groups, according to their specific measurement principle. One, exemplified by the Scanning Electrical Mobility Spectrometer (SEMS) [13] or Differential Mobility Analyzer (DMA) [14] techniques, is based on the fact that the electric mobility of charged particles is

Atmos. Chem. Phys., 16, 7785–7811, 2016  
[www.atmos-chem-phys.net/16/7785/2016/](http://www.atmos-chem-phys.net/16/7785/2016/)  
doi:10.5194/acp-16-7785-2016  
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## BAERLIN2014 – the influence of land surface types on and the horizontal heterogeneity of air pollutant levels in Berlin

Boris Bonn<sup>1,a</sup>, Erika von Schneidemesser<sup>1</sup>, Dorota Andrich<sup>1,b</sup>, Jörn Quedenau<sup>1</sup>, Holger Gerwig<sup>2</sup>, Anja Lüdecke<sup>2</sup>, Jürgen Kura<sup>2</sup>, Axel Pietsch<sup>2</sup>, Christian Ehlers<sup>3</sup>, Dieter Klemp<sup>3</sup>, Claudia Kofahl<sup>3</sup>, Rainer Nothard<sup>4</sup>, Andreas Kerschbaumer<sup>4</sup>, Wolfgang Junkermann<sup>5</sup>, Rüdiger Grote<sup>5</sup>, Tobias Pohl<sup>6</sup>, Konradin Weber<sup>6</sup>, Birgit Lode<sup>1</sup>, Philipp Schönberger<sup>1</sup>, Galina Churkina<sup>1</sup>, Tim M. Butler<sup>1</sup>, and Mark G. Lawrence<sup>1</sup>

<sup>1</sup>Institute for Advanced Sustainability Studies (IASS), 14467 Potsdam, Germany

<sup>2</sup>Division Environmental Health and Protection of Ecosystems, German Environment Agency, 06844 Dessau-Roßlau, Germany

<sup>3</sup>IEK-8, Research Centre Jülich, 52425 Jülich, Germany

<sup>4</sup>Senate Department for Urban Development and the Environment, 10179 Berlin, Germany

<sup>5</sup>Karlsruhe Institute of Technology, Institute of Meteorology and Climate Research, Atmospheric Environmental Research (IMK-IFU), Campus Alpin, 82467 Garmisch-Partenkirchen, Germany

<sup>6</sup>Environmental Measurement Techniques, University of Applied Sciences, 40474 Düsseldorf, Germany

<sup>a</sup>now at: Institute for Forest Sciences, Albert-Ludwig University, 79110 Freiburg, Germany

<sup>b</sup>now at: Andritz AG, Graz, Austria

Correspondence to: Erika von Schneidemesser (evs@iass-potsdam.de)

Received: 20 January 2016 – Published in Atmos. Chem. Phys. Discuss.: 25 February 2016

Revised: 19 May 2016 – Accepted: 6 June 2016 – Published: 24 June 2016

**Abstract.** Urban air quality and human health are among the key aspects of future urban planning. In order to address pollutants such as ozone and particulate matter, efforts need to be made to quantify and reduce their concentrations. One important aspect in understanding urban air quality is the influence of urban vegetation which may act as both emitter and sink for trace gases and aerosol particles. In this context, the “Berlin Air quality and Ecosystem Research: Local and long-range Impact of anthropogenic and Natural hydrocarbons 2014” (BAERLIN2014) campaign was conducted between 2 June and 29 August in the metropolitan area of Berlin and Brandenburg, Germany. The predominant goals of the campaign were (1) the characterization of urban gaseous and particulate pollution and its attribution to anthropogenic and natural sources in the region of interest, especially considering the connection between biogenic volatile organic compounds and particulates and ozone; (2) the quantification of the impact of urban vegetation on organic trace gas levels and the presence of oxidants such as ozone; and (3) to explain the local heterogeneity of pollutants by defining the distribution of sources and sinks relevant for the interpreta-

tion of model simulations. In order to do so, the campaign included stationary measurements at urban background station and mobile observations carried out from bicycle, van and airborne platforms. This paper provides an overview of the mobile measurements (Mobile BAERLIN2014) and general conclusions drawn from the analysis. Bicycle measurements showed micro-scale variations of temperature and particulate matter, displaying a substantial reduction of mean temperatures and particulate levels in the proximity of vegetated areas compared to typical urban residential area (background) measurements. Van measurements extended the area covered by bicycle observations and included continuous measurements of O<sub>3</sub>, NO<sub>x</sub>, CO, CO<sub>2</sub> and point-wise measurement of volatile organic compounds (VOCs) at representative sites for traffic- and vegetation-affected sites. The quantification displayed notable horizontal heterogeneity of the short-lived gases and particle number concentrations. For example, baseline concentrations of the traffic-related chemical species CO and NO varied on average by up to  $\pm 22.2$  and  $\pm 63.5$  %, respectively, on the scale of 100 m around any measurement location. Airborne observations revealed the dominant source

# Deriving High-Resolution Urban Air Pollution Maps Using Mobile Sensor Nodes

David Hasenfratz<sup>a,\*</sup>, Olga Saukh<sup>a</sup>, Christoph Walser<sup>a</sup>, Christoph Hueglin<sup>b</sup>, Martin Fierz<sup>c</sup>,  
Tabita Arn<sup>a</sup>, Jan Beutel<sup>a</sup>, Lothar Thiele<sup>a</sup>

<sup>a</sup>Computer Engineering and Networks Laboratory, ETH Zurich, Switzerland

<sup>b</sup>Laboratory for Air Pollution and Environmental Technology, EMPA, Switzerland

<sup>c</sup>Institute for Aerosol and Sensor Technology, FHNW, Switzerland

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## Abstract

Up-to-date information on urban air pollution is of great importance, *e.g.*, for environmental protection agencies to assess air quality and provide advice to the general public in a timely manner. In particular, ultrafine particles (UFPs) are widely spread in urban environments and may have a severe impact on human health. However, the lack of knowledge about the spatio-temporal distribution of UFPs hampers profound evaluation of these effects. In this paper, we analyze one of the largest spatially resolved UFP data set publicly available today containing over 50 million measurements. We collected the measurements throughout more than two years using mobile sensor nodes installed on top of public transport vehicles in the city of Zurich, Switzerland. Based on these data, we develop land-use regression models to create pollution maps with a high spatial resolution of  $100\text{ m} \times 100\text{ m}$ . We compare the accuracy of the derived models across various time scales and observe a rapid drop in accuracy for maps with sub-weekly temporal resolution. To address this problem, we propose a novel modeling approach that incorporates past measurements annotated with metadata into the modeling process. In this way, we achieve a 26 % reduction in the root-mean-square error—a standard metric to evaluate the accuracy of air quality models—of pollution maps with semi-daily temporal resolution. We believe that our findings can help epidemiologists to better understand the adverse health effects related to UFPs and serve as a stepping stone towards detailed real-time pollution assessment.

**Keywords:** Mobile sensor network, Air pollution, Land-use regression, High-resolution pollution maps, Ultrafine particles, Health-optimal routing

Article

# Development and Validation of a UAV Based System for Air Pollution Measurements

Tommaso Francesco Villa <sup>1</sup>, Farhad Salimi <sup>2</sup>, Kye Morton <sup>3</sup>, Lidia Morawska <sup>1,\*</sup> and Felipe Gonzalez <sup>3</sup>

<sup>1</sup> International Laboratory for Air Quality and Health (ILAQH), Queensland University of Technology (QUT), 2 George St, Brisbane QLD 4000, Australia; [tf.villa@hdr.qut.edu.au](mailto:tf.villa@hdr.qut.edu.au)

<sup>2</sup> Menzies Institute for Medical Research, University of Tasmania, Hobart, Tasmania 7000, Australia; [farhad.salimi@utas.edu.au](mailto:farhad.salimi@utas.edu.au)

<sup>3</sup> Australian Research Centre for Aerospace Automation (ARCAA), Queensland University of Technology (QUT), 2 George St, Brisbane QLD 4000, Australia; [kye.morton@hdr.qut.edu.au](mailto:kye.morton@hdr.qut.edu.au) (K.M.); [felipe.gonzalez@qut.edu.au](mailto:felipe.gonzalez@qut.edu.au) (F.G.)

\* Correspondence: [l.morawska@qut.edu.au](mailto:l.morawska@qut.edu.au); Tel.: +61-7-3138-2616

Academic Editor: Hans Tømmervik

Received: 23 November 2016; Accepted: 19 December 2016; Published: 21 December 2016

**Abstract:** Air quality data collection near pollution sources is difficult, particularly when sites are complex, have physical barriers, or are themselves moving. Small Unmanned Aerial Vehicles (UAVs) offer new approaches to air pollution and atmospheric studies. However, there are a number of critical design decisions which need to be made to enable representative data collection, in particular the location of the air sampler or air sensor intake. The aim of this research was to establish the best mounting point for four gas sensors and a Particle Number Concentration (PNC) monitor, onboard a hexacopter, so to develop a UAV system capable of measuring point source emissions. The research included two different tests: (1) evaluate the air flow behavior of a hexacopter, its downwash and upwash effect, by measuring air speed along three axes to determine the location where the sensors should be mounted; (2) evaluate the use of gas sensors for CO<sub>2</sub>, CO, NO<sub>2</sub> and NO, and the PNC monitor (DISCmini) to assess the efficiency and performance of the UAV based system by measuring emissions from a diesel engine. The air speed behavior map produced by test 1 shows the best mounting point for the sensors to be alongside the UAV. This position is less affected by the propeller downwash effect. Test 2 results demonstrated that the UAV propellers cause a dispersion effect shown by the decrease of gas and PN concentration measured in real time. A Linear Regression model was used to estimate how the sensor position, relative to the UAV center, affects pollutant concentration measurements when the propellers are turned on. This research establishes guidelines on how to develop a UAV system to measure point source emissions. Such research should be undertaken before any UAV system is developed for real world data collection.

**Keywords:** UAV remote gas sensing; downwash effect; air quality; hexacopter; optical sensor; air pollution; particle number concentration monitor

## 1. Introduction

Unmanned Aerial Vehicles (UAVs), carrying onboard sensors, can be used to directly measure shipping emissions, emissions from industrial stacks or ground vehicles when it is too difficult or dangerous to use both manned aircrafts [1] and ground level stations [2]. However, accurate sampling of small plumes emitted by combustion sources such as trucks, petrol locomotives, ships and dredgers, industrial and even domestic chimneys demands appropriate location of the air sensor intakes onboard the UAV. Therefore, the use of UAVs for air pollution measurement, particularly at slow speeds or stationary flights, can only be effective if the location point of the air sensor intake is optimized, such



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## The effects of the built environment, traffic patterns, and micrometeorology on street level ultrafine particle concentrations at a block scale: Results from multiple urban sites

Wonsik Choi<sup>a,b,\*</sup>, Dilara Ranasinghe<sup>a</sup>, Karen Bunavage<sup>a</sup>, J.R. DeShazo<sup>c</sup>, Lisa Wu<sup>c</sup>, Rodrigo Seguel<sup>a,d</sup>, Arthur M. Winer<sup>e</sup>, Suzanne E. Paulson<sup>a,b</sup>

<sup>a</sup> University of California, Los Angeles, Department of Atmospheric and Oceanic Sciences, 405 Hilgard Ave., Los Angeles, CA 90095, USA

<sup>b</sup> University of California, Los Angeles, Institute of the Environment and Sustainability, La Kretz Hall, Suite 300, Los Angeles, CA 90095, USA

<sup>c</sup> University of California, Los Angeles, Luskin Center for Innovation, Luskin School of Public Affairs, 3250 Public Affairs Bldg., Los Angeles, CA 90095, USA

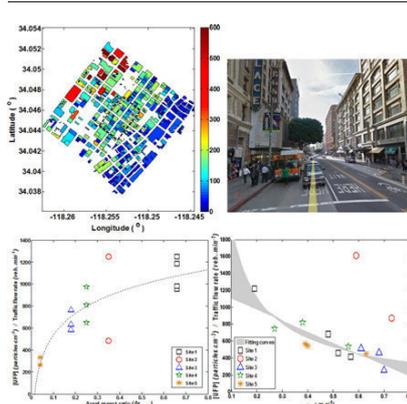
<sup>d</sup> Center for Environmental Sciences, Faculty of Sciences, University of Chile, Las Palmeras 3425 Ñuñoa, Santiago, Chile

<sup>e</sup> University of California, Los Angeles, Fielding School of Public Health, Environmental Health Sciences Department, 650 Charles Young Dr., Los Angeles, CA 90095, USA

### HIGHLIGHTS

- This study quantitatively examined built-environment effects on near-road UFP level.
- Block-scaled UFP conc. strongly depend on built environment and surface turbulence.
- Areal aspect ratio was a major contributor to UFP variations in the morning.
- Surface turbulence was a major contributor to UFP variations in the afternoon.
- Heterogeneous building morphology helps reduce UFP levels in the afternoon.

### GRAPHICAL ABSTRACT



### ARTICLE INFO

#### Article history:

Received 2 December 2015  
Received in revised form 4 February 2016  
Accepted 12 February 2016  
Available online 22 March 2016

Editor: D. Barcelo

#### Keywords:

Ultrafine particles  
Built-environment  
Aspect ratio

### ABSTRACT

This study attempts to explain explicitly the direct and quantitative effects of complicated urban built-environment on near-road dispersion and levels of vehicular emissions at the scale of several city blocks, based on ultrafine particle concentrations ([UFP]). On short timescales, ultrafine particles are an excellent proxy for other roadway emissions. Five measurement sites in the greater Los Angeles with different built environments but similar mesoscale meteorology were explored. After controlling for traffic, for most sampling days and sites, morning [UFP] were higher than those in the afternoon due to limited dispersion capacity combined with a relatively stable surface layer. [UFP] at the intersection corners were also higher than those over the sampling sites, implying that accelerating vehicles around the intersections contributed to [UFP] elevation. In the calm morning, the areal aspect ratio ( $Ar_{area}$ ), developed in this study for real urban configurations, showed a strong relationship with block-scale [UFP].  $Ar_{area}$  includes the building area-weighted building height, the amount of open space, and the building footprint. In the afternoon, however, when wind speeds were generally

\* Corresponding author at: Pukyong National University, Geo-Science Institute, 45 Yongso-ro, Nam-gu, Busan, Republic of Korea.  
E-mail address: wschoi@atmos.ucla.edu (W. Choi).



Contents lists available at ScienceDirect

## Atmospheric Environment

journal homepage: [www.elsevier.com/locate/atmosenv](http://www.elsevier.com/locate/atmosenv)



# Emission rates of particle number, mass and black carbon by the Los Angeles International Airport (LAX) and its impact on air quality in Los Angeles



Farimah Shirmohammadi, Mohammad H. Sowlat, Sina Hasheminassab, Arian Saffari, George Ban-Weiss, Constantinos Sioutas\*

University of Southern California, Department of Civil and Environmental Engineering, Los Angeles, CA, USA

### HIGHLIGHTS

- LAX airport as a major source of pollution comparing to adjacent freeway emissions.
- Particle number emission factors for takeoffs and landings were comparable.
- Nearly 4-fold reduction in PN emission factors for takeoffs during the past decade.
- Distinctly smaller particle mean diameter downwind of the airport than freeways.

### ARTICLE INFO

#### Article history:

Received 14 September 2016  
Received in revised form  
29 November 2016  
Accepted 2 December 2016  
Available online 3 December 2016

#### Keywords:

Aircraft emissions  
Vehicular emissions  
Ultrafine particles  
Emission factor  
LAX airport

### ABSTRACT

This study describes a series of air monitoring measurements of particle number (PN), black carbon (BC) and  $PM_{2.5}$  mass concentrations in the vicinity of the Los Angeles International Airport (LAX) (roughly 150 m downwind of the LAX's south runways) as well as on-road measurements of the aforementioned pollutants using a mobile platform on three major freeways (i.e., I-110, I-105, and I-405) during May–July 2016. All measurements were performed in the “impact zone” of LAX with the predominant westerly winds from coast to inland. The overall impact of aircraft emissions from the LAX airport and its facilities in comparison to vehicular emissions from freeways on air quality was evaluated on a local scale (i.e. areas in the vicinity of the airport). PN concentration was, on average,  $4.1 \pm 1.2$  times greater at the LAX site than on the studied freeways. Particle number emission factors for takeoffs and landings were comparable, with average values of  $8.69 \times 10^{15}$  particles/kg fuel and  $8.16 \times 10^{15}$  particles/kg fuel, respectively, and indicated a nearly 4-fold statistically significant reduction in PN emission factors for takeoffs during the past decade. BC emission factors were  $0.12 \pm 0.02$  and  $0.11 \pm 0.01$  g/kg fuel during takeoffs and landings, respectively. Additionally, the mean  $PM_{2.5}$  emission factor values for takeoffs and landings were also comparable, with values of  $0.38 \pm 0.04$  and  $0.40 \pm 0.05$  g/kg fuel, respectively. Within the impact zone of the airport, an area of roughly  $100 \text{ km}^2$  downwind of the LAX, measurements indicated that the LAX daily contributions to PN, BC, and  $PM_{2.5}$  were approximately 11, 2.5, and 1.4 times greater than those from the three surrounding freeways. These results underscore the significance of the LAX airport as a major source of pollution within its zone of impact comparing to freeway emissions.

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## 1. Introduction

Exposure to airborne particulate matter (PM) in urban areas has been a major concern for public health. Among the various

combustion sources of PM in urban areas, considerable attention has been paid to airport-related emissions, as accurate assessment of these emissions and how they compare to other predominant PM sources such as traffic emissions is essential in understanding the impact of airports on air quality, climate and human health. A recent assessment of aviation's contribution to overall ambient  $PM_{2.5}$  in the United States using the Community Multiscale Air Quality (CMAQ) model showed that the contribution of emissions

\* Corresponding author.

E-mail address: [sioutas@usc.edu](mailto:sioutas@usc.edu) (C. Sioutas).



## Emissions from an International Airport Increase Particle Number Concentrations 4-fold at 10 km Downwind

Neelakshi Hudda,<sup>†</sup> Tim Gould,<sup>‡</sup> Kris Hartin,<sup>§</sup> Timothy V. Larson,<sup>‡</sup> and Scott A. Fruin<sup>\*,†,||</sup>

<sup>†</sup>Keck School of Medicine, Department of Preventive Medicine, University of Southern California, Los Angeles, California 90089, United States

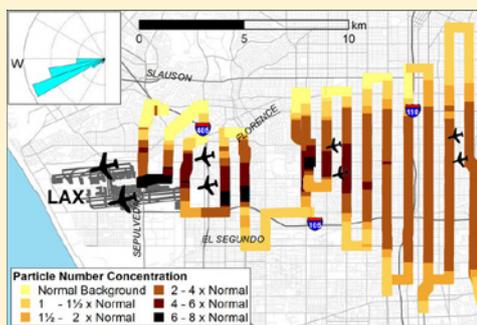
<sup>‡</sup>Department of Civil and Environmental Engineering, University of Washington, Seattle, Washington 98195, United States

<sup>§</sup>Department of Environmental and Occupational Health Sciences, University of Washington, Seattle, Washington 98195, United States

### Supporting Information

**ABSTRACT:** We measured the spatial pattern of particle number (PN) concentrations downwind from the Los Angeles International Airport (LAX) with an instrumented vehicle that enabled us to cover larger areas than allowed by traditional stationary measurements. LAX emissions adversely impacted air quality much farther than reported in previous airport studies. We measured at least a 2-fold increase in PN concentrations over unimpacted baseline PN concentrations during most hours of the day in an area of about 60 km<sup>2</sup> that extended to 16 km (10 miles) downwind and a 4- to 5-fold increase to 8–10 km (5–6 miles) downwind. Locations of maximum PN concentrations were aligned to eastern, downwind jet trajectories during prevailing westerly winds and to 8 km downwind concentrations exceeded 75 000 particles/cm<sup>3</sup>, more than the average freeway PN concentration in Los Angeles.

During infrequent northerly winds, the impact area remained large but shifted to south of the airport. The freeway length that would cause an impact equivalent to that measured in this study (i.e., PN concentration increases weighted by the area impacted) was estimated to be 280–790 km. The total freeway length in Los Angeles is 1500 km. These results suggest that airport emissions are a major source of PN in Los Angeles that are of the same general magnitude as the entire urban freeway network. They also indicate that the air quality impact areas of major airports may have been seriously underestimated.



### INTRODUCTION

Previous studies that directly measured the impact of aviation activity on air quality have mostly conducted measurements in close proximity of airports. Few studies have reported significant air quality impacts extending beyond a kilometer.<sup>1–4</sup> Carslaw et al. 2006<sup>1</sup> analyzed differences in pollutant concentrations by wind speed and direction along with differences in aircraft and ground traffic activity at Heathrow Airport in London. They found airport contributions of up to 15% of total oxides of nitrogen (NO<sub>x</sub>) at a site 1.5 km downwind of the nearest runway. At Hong Kong International Airport, Yu et al. 2004<sup>2</sup> used nonparametric regression analysis on pollutant concentrations by wind speed and direction. They calculated that aircraft nearly doubled sulfur dioxide concentrations 3 km away and also increased concentrations of carbon monoxide and respirable suspended particles under similar wind speeds and directions. Fanning et al. 2007<sup>3</sup> measured particle numbers concentrations in the 10–100 nm range and found significant increases above background at 1.9, 2.7, and 3.3 km downwind of the Los Angeles International Airport (LAX) blast fence. Although measurements were stationary and not concurrent, they also noted that takeoffs produced high concentrations and downwind gradients within 600 m of the

blast fence. Dodson et al. 2009<sup>4</sup> found that aircraft activity at a regional airport in Warwick, RI contributed 24–28% of the total black carbon (BC) measured at five sites 0.16–3.7 km from the airport.

Several other airport and aviation emissions studies focused on quantifying the air quality impacts from jet takeoffs<sup>5,6</sup> and measured air pollutant concentrations very close to runways. Of particular relevance to this study, Hsu et al. 2013<sup>7</sup> linked flight activity at LAX with 1 min average PN concentrations. Their models suggested that aircraft produced a median PN concentration of nearly 150 000 particles/cm<sup>3</sup> at the end of the departure runway. PN concentrations decreased rapidly with distance to 19 000 particles/cm<sup>3</sup> at a location 250 m downwind and to 17 000 particles/cm<sup>3</sup> at a location 500 m further downwind. The rapid drop-off in concentration, however, may have reflected an increasing offset from the centerline of impacts with greater downwind measurement distance. Similar magnitude PN concentrations and correlations

Received: January 22, 2014

Revised: May 12, 2014

Accepted: May 14, 2014

Published: May 29, 2014

DISS. ETH NO. 22481

# Enabling Large-Scale Urban Air Quality Monitoring with Mobile Sensor Nodes

A thesis submitted to attain the degree of

DOCTOR OF SCIENCES of ETH ZURICH  
(Dr. sc. ETH Zurich)

presented by  
DAVID HASENFRATZ  
M.Sc. ETH Zurich

born on 26.11.1984  
citizen of Switzerland, Hungary

accepted on the recommendation of  
Prof. Dr. Lothar Thiele, examiner  
Prof. Dr. Koen Langendoen, co-examiner

2015

# Abstract

Urban air pollution is a major concern in many cities worldwide. Atmospheric pollutants are responsible for health problems ranging from asthma to cancer. Air pollution also causes environmental damages.

Monitoring airborne pollutants is of utmost importance to reliably assess the impact of air pollution on the human health, enable urban planners to craft and accurately evaluate new policies, and increase public awareness. Nowadays, air pollution is monitored by networks of highly accurate but fixed measurement stations. Hence, the gathered data has a low spatial resolution and can not be used to assess the spatial variability of pollutants in detail. As a result, little is known about the spatial distribution of air pollutants in urban environments.

In this thesis, we tackle this challenge and derive fine-grained intraurban pollution maps valuable for a range of applications. We use compact low-cost sensors installed on top of public transport vehicles to obtain a high spatial measurement resolution within a large urban area. We develop algorithms that allow us to accurately monitor the phenomena of interest despite using noisy, low-cost sensors. Finally, we use the measurements to derive air pollution maps with a high spatial and temporal resolution. The main contributions of this thesis are:

- We build a mobile air quality monitoring network by equipping public transport vehicles with low-cost air quality sensor nodes collecting spatially resolved measurements. It is the first mobile air pollution monitoring network operating for over three years by now.
- We are the first to study multi-hop calibration of mobile sensor networks, with respect to a reference signal, in detail. We develop a new calibration algorithm to accurately calibrate networks of low-cost sensors by highly reducing error propagation in the network. Further, we assess the quality of the measurements by integrating generic models for the phenomena monitored and the sensors used.
- We describe a new modeling approach and use the measurements collected with our mobile network to derive accurate urban pollution maps with an unprecedented spatial and temporal resolution. The maps open up many new application opportunities. For example, we introduce a novel route planning service, which helps urban dwellers to reduce their exposure to airborne pollutants.

SUPPORTING INFORMATION

# International airport impacts to air quality: size and related properties of large increases in ultrafine particle number concentrations

N. Hudda<sup>1</sup> and S.A. Fruin<sup>1\*†</sup>

<sup>1</sup>Keck School of Medicine, Environmental Health Division, University of Southern California, Los Angeles, CA 90033, United States

Corresponding Author

\*Telephone: 323-442-2870. Fax: 323-442-3272. E-mail: [fruin@usc.edu](mailto:fruin@usc.edu).

Present Address

†S. A. Fruin: Department of Preventive Medicine, Environmental Health Sciences, University of Southern California, 2001 North Soto Street, Los Angeles, CA 90089-9013, United States

Number of Pages: 10

Number of Figures: 8

Number of Tables: 2



## Intra-urban variation of ultrafine particles as evaluated by process related land use and pollutant driven regression modelling

Yahya Ghassoun<sup>a,\*</sup>, Matthias Ruths<sup>b</sup>, Marc-Oliver Löwner<sup>c</sup>, Stephan Weber<sup>b</sup>

<sup>a</sup> Institute of Geodesy and Photogrammetry, Technische Universität Braunschweig, Pockelsstraße 3, 38106 Braunschweig, Germany

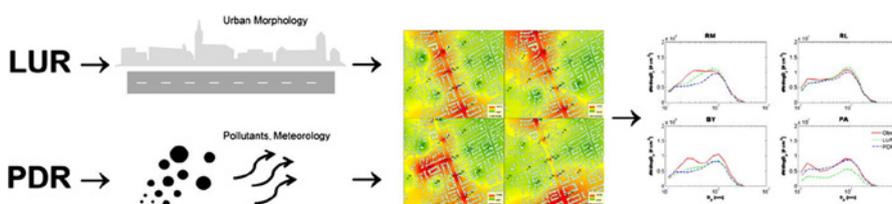
<sup>b</sup> Climatology and Environmental Meteorology, Institute of Geoecology, Technische Universität Braunschweig, Langer Kamp 19c, 38106 Braunschweig, Germany

<sup>c</sup> Institute of Geodesy and Geoinformation Science, Technische Universität Berlin, Strasse des 17. Juni 135, 10623 Berlin, Germany

### HIGHLIGHTS

- Two regression type models for urban ultrafine particle concentrations are compared.
- Land use regression model is driven by urban morphological parameters exclusively.
- Other regression type model uses pollutant and meteorological input parameters.
- Both models resolve spatial differences of ultrafine particle number concentrations.
- Both models adequately predict particle number size distributions <100 nm.

### GRAPHICAL ABSTRACT



### ARTICLE INFO

#### Article history:

Received 19 February 2015  
Received in revised form 8 July 2015  
Accepted 9 July 2015  
Available online xxxx

Editor: D. Barcelo

#### Keywords:

UFP  
Aerosol  
Geographic information system  
Urban morphology  
Microenvironment  
Multiple regression

### ABSTRACT

The microscale intra-urban variation of ultrafine particle concentrations (UFP, diameter  $D_p < 100$  nm) and particle number size distributions was studied by two statistical regression approaches. The models were applied to a 1 km<sup>2</sup> study area in Braunschweig, Germany. A land use regression model (LUR) using different urban morphology parameters as input is compared to a multiple regression type model driven by pollutant and meteorological parameters (PDR). While the LUR model was trained with UFP concentration the PDR model was trained with measured particle number size distribution data. The UFP concentration was then calculated from the modelled size distributions. Both statistical approaches include explanatory variables that try to address the 'process chain' of particle emission, dilution and deposition.

LUR explained 74% and 85% of the variance of UFP for the full data set with a root mean square error (RMSE) of 668 cm<sup>-3</sup> and 1639 cm<sup>-3</sup> in summer and winter, respectively. PDR explained 56% and 74% of the variance with RMSE of 4066 cm<sup>-3</sup> and 6030 cm<sup>-3</sup> in summer and winter, respectively. Both models are capable to depict the spatial variation of UFP across the study area and in different outdoor microenvironments. The deviation from measured UFP concentrations is smaller in the LUR model than in PDR.

The PDR model is well suited to predict urban particle number size distributions from the explanatory variables (total particle number concentration, black carbon and wind speed). The urban morphology parameters in the LUR model are able to resolve size dependent concentration variations but not as adequately as PDR.

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### 1. Introduction

Particulate air pollution in urban areas is associated with significant impacts on human health (e.g. Brook et al., 2010; Heal et al., 2012;

\* Corresponding author.

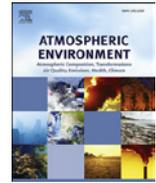
E-mail addresses: [y.ghassoun@tu-bs.de](mailto:y.ghassoun@tu-bs.de) (Y. Ghassoun), [m.ruths@tu-bs.de](mailto:m.ruths@tu-bs.de) (M. Ruths), [m-o.loewner@tu-berlin.de](mailto:m-o.loewner@tu-berlin.de) (M.-O. Löwner), [s.weber@tu-bs.de](mailto:s.weber@tu-bs.de) (S. Weber).



Contents lists available at ScienceDirect

## Atmospheric Environment

journal homepage: [www.elsevier.com/locate/atmosenv](http://www.elsevier.com/locate/atmosenv)



# Lung deposited surface area size distributions of particulate matter in different urban areas

Heino Kuuluvainen<sup>a,\*</sup>, Topi Rönkkö<sup>a</sup>, Anssi Järvinen<sup>a</sup>, Sampo Saari<sup>a</sup>, Panu Karjalainen<sup>a</sup>, Tero Lähde<sup>b</sup>, Liisa Pirjola<sup>b</sup>, Jarkko V. Niemi<sup>c</sup>, Risto Hillamo<sup>d</sup>, Jorma Keskinen<sup>a</sup>

<sup>a</sup> Department of Physics, Tampere University of Technology, Tampere, Finland

<sup>b</sup> Department of Technology, Metropolia University of Applied Sciences, Helsinki, Finland

<sup>c</sup> Helsinki Region Environmental Services Authority HSY, Helsinki, Finland

<sup>d</sup> Finnish Meteorological Institute, Helsinki, Finland

### HIGHLIGHTS

- Lung deposited surface area (LDSA) size distributions measured in a metropolitan area.
- An electrical low pressure impactor (ELPI) calibrated to measure the LDSA.
- The LDSA was influenced by traffic more than the mass of fine particles (PM<sub>2.5</sub>).
- Both the nucleation and soot mode found to have a contribution to the LDSA.
- Size distribution data is important for the use of epidemiological studies.

### ARTICLE INFO

#### Article history:

Received 19 November 2015

Received in revised form

14 April 2016

Accepted 15 April 2016

Available online 16 April 2016

#### Keywords:

Particulate matter

Lung deposited surface area

Size distribution

Urban environment

Health risk

Electrical low pressure impactor

### ABSTRACT

Lung deposited surface area (LDSA) concentration is considered as a relevant metric for the negative health effects of aerosol particles. We report for the first time the size distributions of the LDSA measured in urban air. The measurements were carried out in the metropolitan area of Helsinki, including mobile laboratory and stationary measurements in different outdoor environments, such as traffic sites, a park area, the city center and residential areas. The main instrument in this study was an electrical low pressure impactor (ELPI), which was calibrated in the field to measure the LDSA concentration. The calibration factor was determined to be  $60 \mu\text{m}^2/(\text{cm}^3 \text{ pA})$ . In the experiments, the LDSA size distributions were found to form two modes at the traffic sites and in the city center. Both of these traffic related particle modes, the nucleation mode and the soot mode, had a clear contribution to the total LDSA concentration. The average total concentrations varied from 12 to  $94 \mu\text{m}^2/\text{cm}^3$ , measured in the park area and at the traffic site next to a major road, respectively. The LDSA concentration was found to correlate with the mass of fine particles (PM<sub>2.5</sub>), but the relation of these two metrics varied between different environments, emphasizing the influence of traffic on the LDSA. The results of this study provide valuable information on the total concentrations and size distributions of the LDSA for epidemiological studies. The size distributions are especially important in estimating the contribution of outdoor concentrations on the concentrations inside buildings and vehicles through size-dependent penetration factors.

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## 1. Introduction

Particulate matter in urban air is a significant risk to human health. Over the past few decades, this has been taken into account

in the legislation controlling the urban air quality and emission sources. Still, the particulate matter is estimated to cause worldwide about 2.1 million deaths per year (Silva et al., 2013) and contribute to the incidence of various cardiopulmonary diseases and lung cancer (Pope III et al., 2002; Hoek et al., 2002). The first epidemiological evidence of the inverse health effects of urban aerosols was based on particle mass concentration measurements

\* Corresponding author.

E-mail address: [heino.kuuluvainen@tut.fi](mailto:heino.kuuluvainen@tut.fi) (H. Kuuluvainen).

# Pushing the Spatio-Temporal Resolution Limit of Urban Air Pollution Maps

David Hasenfratz, Olga Saukh, Christoph Walser, Christoph Hueglin\*, Martin Fierz†, and Lothar Thiele  
Computer Engineering and Networks Laboratory, ETH Zurich, Switzerland  
\*Laboratory for Air Pollution and Environmental Technology, EMPA, Switzerland  
†Institute for Aerosol and Sensor Technology, University of Applied Sciences Northwestern Switzerland  
{hasenfratz, saukh, walser, thiele}@tik.ee.ethz.ch christoph.hueglin@empa.ch martin.fierz@fhnw.ch

**Abstract**—Up-to-date information on urban air pollution is of great importance for health protection agencies to assess air quality and provide advice to the general public in a timely manner. In particular, ultrafine particles (UFPs) are widely spread in urban environments and may have a severe impact on human health. However, the lack of knowledge about the spatio-temporal distribution of UFPs hampers profound evaluation of these effects. In this paper, we analyze one of the largest spatially resolved UFP data set publicly available today containing over 25 million measurements. We collected the measurements throughout more than a year using mobile sensor nodes installed on top of public transport vehicles in the city of Zurich, Switzerland. Based on these data, we develop land-use regression models to create pollution maps with a high spatial resolution of  $100\text{ m} \times 100\text{ m}$ . We compare the accuracy of the derived models across various time scales and observe a rapid drop in accuracy for maps with sub-weekly temporal resolution. To address this problem, we propose a novel modeling approach that incorporates past measurements annotated with metadata into the modeling process. In this way, we achieve a 26% reduction in the root-mean-square error—a standard metric to evaluate the accuracy of air quality models—of pollution maps with semi-daily temporal resolution. We believe that our findings can help epidemiologists to better understand the adverse health effects related to UFPs and serve as a stepping stone towards detailed real-time pollution assessment.

## I. INTRODUCTION

Air pollution is a major concern in many cities worldwide. Atmospheric pollutants considerably affect human health; they are responsible for a variety of respiratory and cardiovascular illnesses and are known to cause cancer if humans are exposed to them for extended periods of time [1]. Additionally, air pollution is responsible for environmental problems, such as eutrophication and acidification of ecosystems.

Most countries have mass emission limits for particulate matter  $\text{PM}_{10}$  and  $\text{PM}_{2.5}$  (*i.e.*, particles with a diameter of less than  $10\text{ }\mu\text{m}$  and  $2.5\text{ }\mu\text{m}$ , respectively), but have no restrictions on ultrafine particles (UFPs). UFPs are particles with a diameter of less than  $100\text{ nm}$ . In ambient air, UFPs are mainly man-made as byproducts of specific high temperature processes, such as combustion reactions in car engines. The adverse health effects of UFPs are most probably underestimated when they are traditionally monitored by mass as part of  $\text{PM}_{10}$  and  $\text{PM}_{2.5}$  [2]. This is because UFPs make a dominant contribution to the total number of urban particle concentrations, but their contribution to the total particle mass is small [3]. Therefore, UFPs were not considered particularly hazardous in the past. There are strong indications, however, that adverse health

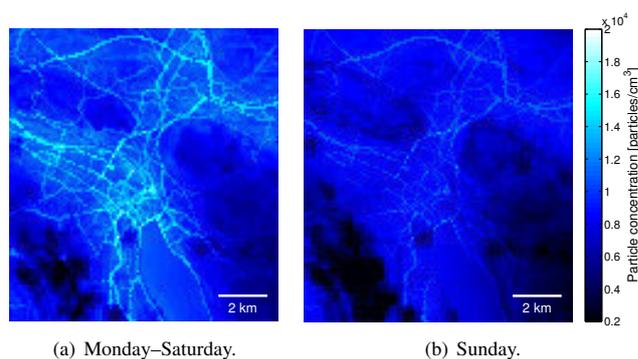


Figure 1. Novel ultrafine particle concentration maps for Zurich (Switzerland). The particle concentrations are higher during the week (Monday–Saturday) than on weekends (Sunday) due to higher traffic volumes.

effects are more related to particle concentration rather than to particle mass [2]. To better understand the adverse health effects of UFPs, it is essential to have spatially resolved UFP concentration measurements at hand [4].

Nowadays, air pollution is monitored by networks of static measurement stations operated by official authorities. These stations are highly reliable and able to accurately measure a wide range of air pollutants. However, their high acquisition and maintenance costs severely limit the number of installations. As a result, very little is known about the spatial distribution of air pollutants in urban environments and there is a lack of accurate intraurban air pollution maps. However, for air pollutants with high spatial variability, such as UFPs, the public availability of reliable pollution maps is essential. They raise the citizens' awareness about air pollution and empower environmental scientists to craft and evaluate new policies.

**Contributions and road-map.** To tackle the challenges above, we propose to use a mobile measurement system. Node mobility trades off temporal resolution against spatial resolution, enabling a high spatial resolution across large areas without the need for thousands of fixed sensors. However, due to the lower temporal resolution of any covered location, it is a formidable challenge to derive pollution maps with a high temporal resolution at daily or hourly time scales. In this paper, we demonstrate that a mobile measurement system can effectively be used to derive accurate UFP pollution maps with high spatio-temporal resolution.



**Ministry of Environment  
and Food of Denmark**  
Environmental  
Protection Agency

# Remote sensing of sulphur and particle emission from ships

Environmental project No. 1835, 2016



**Title:**

Remote sensing of sulphur and particle emission from ships

**Authors:**

Morten Køcks, Danish Technological Institute  
Sabine Lindholst, Danish Technological Institute  
Jens Ravnsbæk, Danish Technological Institute

**Published by:**

The Danish Environmental Protection Agency  
Strandgade 29  
DK-1401 Copenhagen K  
[www.mst.dk](http://www.mst.dk)

**Photography:**

Danish Technological Institute

**Illustration:**

Danish Technological Institute

**Year:**

2016

**ISBN no.**

978-87-93435-40-7

**Disclaimer:**

The Danish Environmental Protection Agency publishes reports and papers about research and development projects within the environmental sector, financed by the Agency. The contents of this publication do not necessarily represent the official views of the Danish Environmental Protection Agency. By publishing this report, the Danish Environmental Protection Agency expresses that the content represents an important contribution to the related discourse on Danish environmental policy.

Sources must be acknowledged.

# Summary and conclusion

In 2015, the maximum allowed sulphur content in fuel was reduced from 1% sulphur to 0.1% sulphur in Emission Control Areas (ECAs), referring to the International Maritime Organization (IMO).<sup>1</sup> Therefore, shipowners must either use low sulphur fuel or implement an emission abatement method, i.e. a scrubber system, which removes the sulphur oxides from the vessel exhaust gas. Either approach will result in a significant extra cost for the shipowners and opens up for possible violation. In order to create a level-playing-field for the shipowners and a credible risk of being observed when violating regulations, the ships have to be monitored. That calls for a simple and robust control method.

The overall project objective was to develop method(s) for fast determination of the sulphur content in fuel. The prime focus in the project was to estimate the sulphur content through plume measurements (remote sensing) when ships pass the eastern part of the Great Belt Bridge (Storebælt) (proof of concept). In parallel, two other potential fast methods that aim at fast analysis of the sulphur content directly in fuel were investigated, as they could be a supplement to remote sensing. During the project, the project objective was modified to aim at cost-effective monitoring technology for indicative classification due to awareness of similar international activities and already developed - but expensive - solutions.

In work package (WP) 1, the objective was to investigate and develop suitable methods for monitoring particulate matter (PM), SO<sub>2</sub> and CO<sub>2</sub> in vessel exhaust plumes from a distance of several hundred metres. In addition, initial CO<sub>2</sub> background measurements at the Great Belt Bridge were covered in order to determine whether background fluctuations were pronounced (due to, e.g., road traffic). In WP 2, the objective was to test the selected sensors and developed method at measurement locations at the Great Belt Bridge (proof of concept). The potential of the different possible measurement locations on the bridge, defined in WP 1, are to be investigated with respect to remote sensing of sulphur content in fuel. That will take place during different measurement campaigns aiming at a final measurement campaign of several weeks, and all of the campaigns will focus on cost-effective monitoring technology. The objective of WP 3 was to investigate the potential for developing a fast method for direct analysis of sulphur content in fuel within minutes. Such a method could allow the relevant authorities to check the sulphur content in fuel when the ships are at berth or at sea. That could be a strong supplement/alternative to the remote sensing approach. Finally, WP 4 will concentrate on the dissemination of project results. Due to the new regulations implemented in 2010 and 2015, the surveillance of sulphur pollution has been a burning topic in this decade. Because of the topicality, the dissemination of project results received its own work package.

Based on a comprehensive literature study, market survey and validation experiments in the lab, a basic sensor technology as well as a preliminary measurement location on the Great Belt Bridge were accomplished in WP 1, with the aim to implement cost-effective monitoring. Preliminary measurements from both Aarhus harbour and similar locations gave the project team strong confidence in the measurements from the Great Belt Bridge, due to unmistakable and significant CO<sub>2</sub> signals from a number of ships, when cost-effective CO<sub>2</sub> sensors were used. Based on the results, it was decided to continue measuring on the Great Belt Bridge and to carry out preliminary measure-

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<sup>1</sup> [http://www.imo.org/en/OurWork/Environment/PollutionPrevention/AirPollution/Pages/Sulphur-oxides-\(SOx\)---Regulation-14.aspx](http://www.imo.org/en/OurWork/Environment/PollutionPrevention/AirPollution/Pages/Sulphur-oxides-(SOx)---Regulation-14.aspx)

ments from one of the pylon platforms on the bridge. There were many similarities between that location and other measurement positions used until that point in the project, but there were also similarities between what is being carried out at the port entrance of, e.g., Gothenburg. Preliminary CO<sub>2</sub> background measurements from the pylon platform did not show significantly higher background fluctuations than the ones observed at, e.g., Aarhus harbour and similar locations.

In WP 2, the sensors were brought to the Great Belt Bridge. It appeared that a number of locations at the Great Belt Bridge have potential with respect to remote sensing of sulphur content in fuel, based on cost-effective monitoring technology. These locations include measurements from the pylon platform but also from below the bridge. However, a number of improvements must be made on the sensor solution before such a solution can be commercialised. They depend on the permitted measurement uncertainty, and on whether an indicative classification of ships will be acceptable. They must be followed up by further inspection by the authorities, either when the ship is in port or at sea.

A final 2-week measurement campaign was carried out after a number of smaller, dedicated measurement campaigns at different strategic locations at the Great Belt Bridge using different sensor set-ups. In this context, it was very difficult to achieve a satisfactory high gas concentration for the chosen CO<sub>2</sub> sensor. That is to some extent surprising, as:

- 1) initial harbour measurements (WP 1) gave promising results from rather similar measuring conditions.
- 2) initial modelling suggests relatively high gas concentrations at some of the measurement locations. A possible explanation for this discrepancy could be that the ships in the Great Belt sail faster than at the other measurement locations, and therefore the plume is present for a shorter time span.

Preliminary calculations of sulphur fuel content, based on our measurements from the Great Belt, suggest that the present method can be used for a very rough estimate of sulphur content in fuel. This conclusion is based on measurements from both the pylon platform (measurement campaign during 1% sulphur conditions) and from a location right below the bridge at the lantern defining the outer boundary of the northbound lane (campaign during 0.1% sulphur conditions). However, it should be emphasized that the present method has a considerable uncertainty that is associated with the measurement, which is difficult to define at the moment. Currently, it is not advised to use the present method for routine monitoring. That is why a lot of work still exists in the attempt to make cost-effective monitoring best practice.

To achieve a reliable monitoring platform based on cost-effective sensor technology, further and more detailed modelling of exhaust gas plumes will be necessary in order to locate and define optimum measurement conditions. The initial modelling that was carried out suggests that it should be possible to locate higher gas concentrations at the Great Belt Bridge. In addition, it might be necessary with an improved sensor signal-to-noise ratio, if significantly higher gas concentrations are not located, together with an innovative concept regarding the measurement probe.

In this context, it should also be noted that Chalmers, Sweden, will be using their state-of-the-art sensor technology to carry out parallel measurements from the pylon platform during the period 2015-2016 (Danish EPA tender). To the best of our knowledge, they have so far obtained reliable measurement results. This is of course very satisfactory from an overall monitoring point of view, but in the long run it is not expected that this technology has the optimum potential to be broadened, due to the significant cost of such a monitoring platform.

## Sensing the Air We Breathe – the OpenSense Zurich Dataset

Jason Jingshi Li<sup>1</sup>, Boi Faltings<sup>1</sup>, Olga Saukh<sup>2</sup>, David Hasenfratz<sup>2</sup>, and Jan Beutel<sup>2</sup>

<sup>1</sup>Artificial Intelligence Laboratory, EPF Lausanne, Switzerland

<sup>2</sup>Computer Engineering and Networks Laboratory, ETH Zurich, Switzerland

{jason.li, boi.faltings} @epfl.ch, {saukh, hasenfratz, beutel} @tik.ee.ethz.ch

### Abstract

Monitoring and managing urban air pollution is a significant challenge for the sustainability of our environment. We quickly survey the air pollution modeling problem, introduce a new dataset of mobile air quality measurements in Zurich, and discuss the challenges of making sense of these data.

### Introduction

Urban outdoor air pollution currently accounts for up to 1.3 million deaths per year (World-Health-Organization 2011), and monitoring and managing urban air pollution is a significant challenge for the sustainability. In this paper, we introduce a new and growing dataset of mobile air quality measurements for the city of Zurich from the OpenSense project. We begin with a quick survey of background knowledge on urban air pollution and existing modeling literature. Then, we describe the data collection process and the engineering challenges of delivering high-quality measurements using inexpensive, small, and mobile sensors. In the end, we summarize the general problem of interpreting the collected data and describe three reasoning approaches and detail how they relate to each other.

### Background

Urban air pollution are mostly the results of human economic activity involving the burning of fossil fuels. Various primary pollutants are emitted from their respective point, line, and area sources, such as single chimneys, roads, or construction zones. They are carried away by horizontal wind, diffused by eddies in the air, and may undergo chemical reactions to produce secondary pollutants in the atmosphere. Some of the pollutants get deposited into ground level, which in turn may affect plant growths, human and animal health (see Fig. 1).

A traditional finite-volume physical model attempts to reconstruct these processes by first estimating the possible emissions, and then using it with various meteorological parameters to serve as inputs to a series of physical equations that model the transport, diffusion, and chemistry of air pollution. The typical purpose of such a modeling exercise is to understand the natural processes in order to find

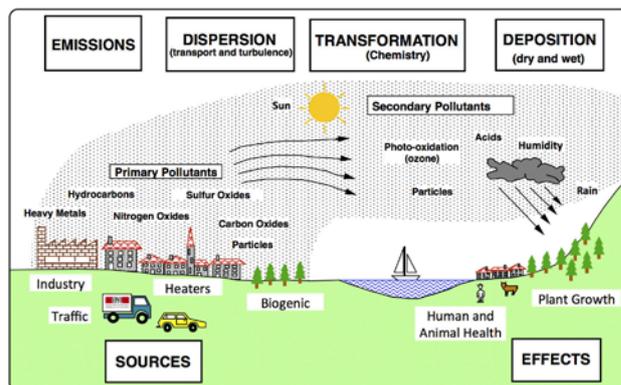


Figure 1: Air pollution processes and their effects. Courtesy of Prof. Alain Clappier, Uni. Strasbourg.

an effective and efficient strategy that is an optimal trade-off between environmental impacts and economic productivity (Godish 2003). Currently there is a myriad of physical models that are actively deployed and used by regulatory authorities and universities such as CMAQ (Byun and Schere 2006), CAMx (CAMx 2011), CHIMERE (Bessagnet et al. 2008), and ADMS (Colville et al. 2002).

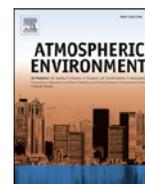
By contrast, a statistical model constructs an estimation based on measurements. In the literature, datasets are consisted of simultaneous repeated measurements from a handful of stations. Various techniques have been used for spatial interpolation, such as Gaussian Process regression, also known as Kriging (Carroll et al. 1997). Land-use information may also be used as additional inputs to the model (Larson, Henderson, and Brauer 2009; Liu et al. 2008). Recently, Bayesian melding was introduced as a way to integrate physical and statistical models (Liu, Le, and Zidek 2011).

The main modeling challenge is to accurately capture the processes and correlations at different scales in an open system, and correctly interpret the measurements and the subsequent model output. Oreske et al. in (1994) argued that under an open system any confirmation of a model from agreements between observations and predictions can only be partial, and thus models can only be evaluated in relative terms. Nevertheless, a good model can be interpreted as heuristic for real processes. Due to the growing number of



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## Atmospheric Environment

journal homepage: [www.elsevier.com/locate/atmosenv](http://www.elsevier.com/locate/atmosenv)

## Short-term associations between traffic-related noise, particle number and traffic flow in three European cities



X. Morelli <sup>a, b</sup>, M. Foraster <sup>c, d, e</sup>, I. Aguilera <sup>f, g</sup>, X. Basagana <sup>c, d, e</sup>, E. Corradi <sup>f, g</sup>, A. Deltell <sup>h</sup>, R. Ducret-Stich <sup>f, g</sup>, H. Phuleria <sup>f, g</sup>, M.S. Ragettli <sup>f, g</sup>, M. Rivera <sup>i</sup>, A. Thomasson <sup>j</sup>, N. Künzli <sup>f, g</sup>, R. Slama <sup>a, b, \*</sup>

<sup>a</sup> Inserm, U823, Institut Albert Bonniot, Team of Environmental Epidemiology Applied to Reproduction and Respiratory Health, F-38000 Grenoble, France

<sup>b</sup> Univ. Grenoble Alpes, IAB, F-38000 Grenoble, France

<sup>c</sup> Centre for Research in Environmental Epidemiology (CREAL), Barcelona, Spain

<sup>d</sup> Universitat Pompeu Fabra (UPF), Barcelona, Spain

<sup>e</sup> CIBER Epidemiología y Salud Pública (CIBERESP), Spain

<sup>f</sup> Swiss Tropical and Public Health Institute, Basel, Switzerland

<sup>g</sup> University of Basel, Basel, Switzerland

<sup>h</sup> GREFEMA (Grup de Recerca en Enginyeria de Fluids, Energia i Medi Ambient), University of Girona, Girona, Spain

<sup>i</sup> University of Montreal Hospital Research Center (CRCHUM), Montréal, Canada

<sup>j</sup> Air Rhône-Alpes, Grenoble, France

### H I G H L I G H T S

- 20-min measurements of air pollution, noise and road traffic were taken at 141 sites.
- Traffic noise levels and traffic counts were far more constant over time than ultrafine particles number concentrations.
- Simultaneous measurements of traffic count and noise were moderately to well correlated.
- Simultaneous measurements of ultrafine particles and noise were poorly correlated.
- This should allow future studies to disentangle the short-term effects of ultrafine particles and noise.

### A R T I C L E I N F O

#### Article history:

Received 28 April 2014

Received in revised form

2 December 2014

Accepted 4 December 2014

Available online 5 December 2014

#### Keywords:

Air pollution

Spatiotemporal variation

Traffic

Traffic noise

Ultrafine particles

### A B S T R A C T

Outdoor noise and particulate matter concentration share common sources, including road traffic in urban areas, raising the potential for mutual confounding in epidemiological studies of their health effects. While some studies evaluated their long-term correlation, little is known about their short-term correlation. Our aim was to study the correlation of short-term noise, ultrafine (<0.1 μm) particulate matter number concentration (UFP), and traffic flow in urban areas. A secondary aim was to document the temporal variability of these short-term measurements. We simultaneously measured traffic noise levels, UFP concentrations as well as motor vehicles' flows for 20 min in 141 locations, on one to three occasions, in three middle size European cities (Basel, Girona, Grenoble). The reproducibility of the short-term noise measurements and traffic counts over time was high, as reported by the intraclass correlation coefficient (ICC), which quantified the agreement between repeated measurements (ICC = 0.86–0.97, according to city, for noise and ICC = 0.93–0.94 for traffic counts); this was not the case for UFP number concentrations (ICC = –0.11 to 0.14). The Pearson correlations of simultaneous 20-min measurements of UFP number concentrations and noise levels were in the 0.43–0.55 range, depending on the city; correlations between noise levels and vehicle counts varied from 0.54 to 0.72; and correlations between UFP concentrations and vehicle counts were lower ( $r = 0.15–0.37$  depending on the city). Measurements during as little time as 20 min of outdoor noise and traffic, but not of UFP, were strongly reproducible

\* Corresponding author. Institut Albert Bonniot, Inserm-Univ J. Fourier (U823)

Research Center, BP 170, 38042 Grenoble Cedex 9, France.

E-mail address: [remy.slama@ujf-grenoble.fr](mailto:remy.slama@ujf-grenoble.fr) (R. Slama).



Contents lists available at ScienceDirect

## Atmospheric Environment

journal homepage: [www.elsevier.com/locate/atmosenv](http://www.elsevier.com/locate/atmosenv)

## Spatio-temporal variation of urban ultrafine particle number concentrations



Martina S. Ragetti<sup>a, b, 1</sup>, Regina E. Ducret-Stich<sup>a, b, 1</sup>, Maria Foraster<sup>c, d, e</sup>, Xavier Morelli<sup>f</sup>, Inmaculada Aguilera<sup>a, b</sup>, Xavier Basagaña<sup>c, d, e</sup>, Elisabetta Corradi<sup>b</sup>, Alex Ineichen<sup>a, b</sup>, Ming-Yi Tsai<sup>a, b</sup>, Nicole Probst-Hensch<sup>a, b</sup>, Marcela Rivera<sup>g</sup>, Rémy Slama<sup>f</sup>, Nino Künzli<sup>a, b, \*</sup>, Harish C. Phuleria<sup>h, 1</sup>

<sup>a</sup> Swiss Tropical and Public Health Institute, Basel, Switzerland<sup>b</sup> University of Basel, Switzerland<sup>c</sup> Centre for Research in Environmental Epidemiology (CREAL), Barcelona, Spain<sup>d</sup> Universitat Pompeu Fabra (UPF), Barcelona, Spain<sup>e</sup> CIBER Epidemiología y Salud Pública (CIBERESP), Barcelona, Spain<sup>f</sup> Inserm and University J. Fourier Grenoble, Team of Environmental Epidemiology Applied to Reproduction and Respiratory Health, Grenoble, France<sup>g</sup> Centre de Recherche du Centre Hospitalier de l'Université de Montréal (CRCHUM), Montreal, Canada<sup>h</sup> Centre for Environmental Science and Engineering, Indian Institute of Technology Bombay, Mumbai, India

## HIGHLIGHTS

- Spatial variation of short-term (20-min) UFP concentration was assessed in Basel.
- Hybrid models were built to predict UFP levels on sidewalks.
- The main predictor (explained  $\leq 50\%$ ) was the suburban background UFP level.
- Best models included both GIS variables and field observations ( $R^2 = 0.7$ ).
- Concurrent UFP on the sidewalks and nearby residences correlated well ( $R^2 = 0.8$ ).

## ARTICLE INFO

## Article history:

Received 27 February 2014

Received in revised form

27 July 2014

Accepted 29 July 2014

Available online 30 July 2014

## Keywords:

Nanoparticles

Exposure assessment

Traffic

Monitoring

Short-term exposure

Switzerland

## ABSTRACT

Methods are needed to characterize short-term exposure to ultrafine particle number concentrations (UFP) for epidemiological studies on the health effects of traffic-related UFP. Our aims were to assess season-specific spatial variation of short-term (20-min) UFP within the city of Basel, Switzerland, and to develop hybrid models for predicting short-term median and mean UFP levels on sidewalks. We collected measurements of UFP for periods of 20 min (MiniDiSC particle counter) and determined traffic volume along sidewalks at 60 locations across the city, during non-rush hours in three seasons. For each monitoring location, detailed spatial characteristics were locally recorded and potential predictor variables were derived from geographic information systems (GIS). We built multivariate regression models to predict local UFP, using concurrent UFP levels measured at a suburban background station, and combinations of meteorological, temporal, GIS and observed site characteristic variables. For a subset of sites, we assessed the relationship between UFP measured on the sidewalk and at the nearby residence (i.e., home outdoor exposure on e.g. balconies). The average median 20-min UFP levels at street and urban background sites were  $14,700 \pm 9100$  particles  $\text{cm}^{-3}$  and  $9900 \pm 8600$  particles  $\text{cm}^{-3}$ , respectively, with the highest levels occurring in winter and the lowest in summer. The most important predictor for all models was the suburban background UFP concentration, explaining 50% and 38% of the variability of the median and mean, respectively. While the models with GIS-derived variables ( $R^2 = 0.61$ ) or observed site characteristics ( $R^2 = 0.63$ ) predicted median UFP levels equally well, mean UFP predictions using only site characteristic variables ( $R^2 = 0.62$ ) showed a better fit than models using only GIS variables ( $R^2 = 0.55$ ). The best model performance was obtained by using a combination of GIS-derived variables and locally observed site characteristics (median:  $R^2 = 0.66$ ; mean:  $R^2 = 0.65$ ). The 20-min UFP

\* Corresponding author. Swiss Tropical and Public Health Institute, P.O. Box, 4002, Basel, Switzerland.

E-mail address: [Nino.Kuenzli@unibas.ch](mailto:Nino.Kuenzli@unibas.ch) (N. Künzli).<sup>1</sup> Equal contribution.

# Study of Personal Exposure to Nanoparticles Considering Meteorological Variables in 4 Streets with Different Types of Vehicles in Bogotá

Lorena Bonilla Patiño, Jaime Rueda Gómez, Augusto Molano Rojas, Ivan Robayo Molina  
**Secretaría Distrital de Ambiente – Universidad Distrital Francisco José de Caldas**

[lorenabonilla.1995@gmail.com](mailto:lorenabonilla.1995@gmail.com), [jaime.rueda@ambientebogota.gov.co](mailto:jaime.rueda@ambientebogota.gov.co), [ifrobayom@unal.edu.co](mailto:ifrobayom@unal.edu.co), [augustomolano14@gmail.com](mailto:augustomolano14@gmail.com)

## Introduction

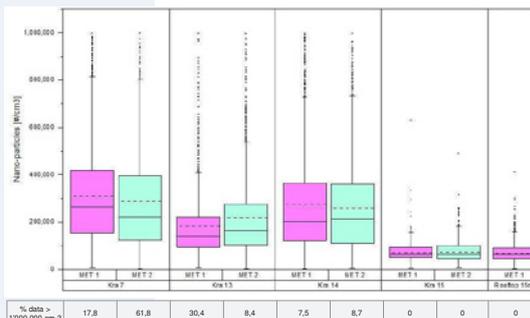
In Bogotá has been estimated that the public transport contribute nearly with 40% of total PM emissions. In order to reduce those concentration levels, a Diesel Particle Filter Program is been developed.

Therefore, since 2015 the District Secretariat of environment has started the measurements of personal exposure to Nanoparticles,

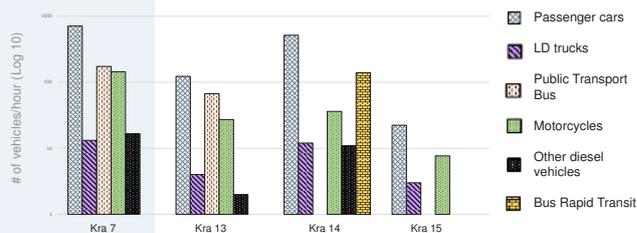
The study compares the particle number concentration PNC in four streets, also the behavior of the mean concentration on the week-days of PNC in relation to PM<sub>2.5</sub> (Height: 14m) measured by the air quality monitoring stations, and the variation associated to the Meteorological variables, mainly wind speed and direction.

## Results

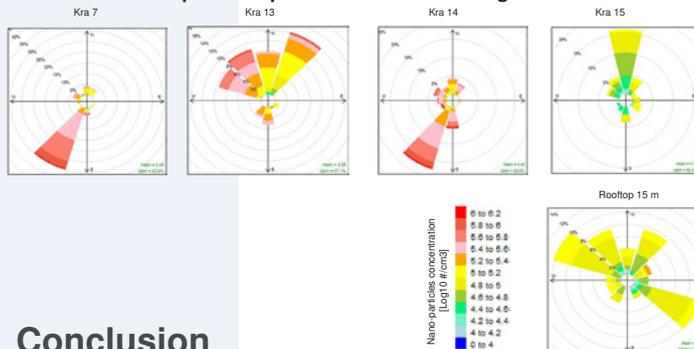
### I.- Nano-particles concentration according to methodology and road.



### II. Number of vehicles per hour



### III. Nano-particles pollutant rose according to road corridor



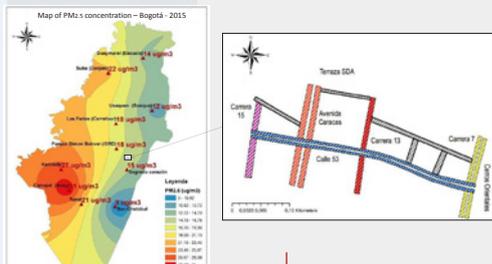
## Conclusion

- The results show that high nanoparticles concentrations are associated with high number of diesel engines present on the fleet of public transport. it means also more dispersion on the data.
- A correlation between number of Nanoparticles and PM<sub>2.5</sub> was calculated with R=0.52. However, the weekly behavior from nanoparticles and PM<sub>2.5</sub> reported by the network of air quality monitoring stations, is not the same. It shows, an influence of the proximity to the source in the nanoparticles counting.
- The obtained results indicate there is not any strong correlation between the meteorological monitored variables and the nano-particle concentration

## Methodology

### Considerations:

- The zone where the study was developed has same PM<sub>2.5</sub> concentration.
- Measurement in the rush hour (7:00 am 9:00 am) The typologies of the vehicles transiting in the 4 streets are different.



Diffusion Size Classifier  
DiSCmini - Testo.

Portable Weather  
Station Davis

MET1: Measurement at  
one side of the road

MET 2: Measurement at  
each side of the road.



R Studio for data statistical analysis

## Acknowledgements

- Jose Alejandro Murad Pedraza - Associated professor - Universidad Distrital Francisco Jose de Caldas.
- Rodrigo Alberto Manrique Forero - Former subdirector of Air, Auditory and Visual Quality group - District Secretariat of Environment.
- Hugo Enrique Sáenz Pulido - Coordinator of PDDAB group - District Secretariat of Environment.





Contents lists available at ScienceDirect

## Science of the Total Environment

journal homepage: [www.elsevier.com/locate/scitotenv](http://www.elsevier.com/locate/scitotenv)



### The association between greenness and traffic-related air pollution at schools



Payam Dadvand<sup>a,b,c,\*</sup>, Ioar Rivas<sup>a,b,c,d</sup>, Xavier Basagaña<sup>a,b,c</sup>, Mar Alvarez-Pedrerol<sup>a,b,c</sup>, Jason Su<sup>e</sup>,  
Montserrat De Castro Pascual<sup>a,b,c</sup>, Fulvio Amato<sup>d</sup>, Michael Jerret<sup>e</sup>, Xavier Querol<sup>d</sup>,  
Jordi Sunyer<sup>a,b,c</sup>, Mark J. Nieuwenhuijsen<sup>a,b,c</sup>

<sup>a</sup> Centre for Research in Environmental Epidemiology (CREAL), C/Dr. Aiguader 88, 08003 Barcelona, Spain

<sup>b</sup> CIBER Epidemiología y Salud Pública (CIBERESP), C/Monforte de Lemos 3-5, 28029 Madrid, Spain

<sup>c</sup> Universitat Pompeu Fabra (UPF), Plaça de la Mercè, 08002 Barcelona, Spain

<sup>d</sup> Institute of Environmental Assessment and Water Research (IDAEA), Spanish National Research Council (CSIC), C/Jordi Girona 18-26, 08034 Barcelona, Spain

<sup>e</sup> Environmental Health Sciences, School of Public Health, University of California, Berkeley, 50 University Hall, Berkeley, CA, 94720-7360, USA

#### HIGHLIGHTS

- Reduced indoor and outdoor air pollution associated with greenness within schools.
- Reduced indoor and outdoor air pollution associated with greenness around schools.
- Reduction in indoor air pollution was mediated by reduction in outdoor levels.

#### ARTICLE INFO

##### Article history:

Received 27 October 2014  
Received in revised form 13 March 2015  
Accepted 23 March 2015  
Available online 7 April 2015

Editor: Lidia Morawska

##### Keywords:

Air pollution  
Green space  
Child health  
NDVI  
School  
Vegetation

#### ABSTRACT

Greenness has been reported to improve mental and physical health. Reduction in exposure to air pollution has been suggested to underlie the health benefits of greenness; however, the available evidence on the mitigating effect of greenness on air pollution remains limited and inconsistent. We investigated the association between greenness within and surrounding school boundaries and monitored indoor and outdoor levels of traffic-related air pollutants (TRAPs) including NO<sub>2</sub>, ultrafine particles, black carbon, and traffic-related PM<sub>2.5</sub> at 39 schools across Barcelona, Spain, in 2012. TRAP levels at schools were measured twice during two one-week campaigns separated by 6 months. Greenness within and surrounding school boundaries was measured as the average of satellite-derived normalized difference vegetation index (NDVI) within boundaries of school and a 50 m buffer around the school, respectively. Mixed effects models were used to quantify the associations between school greenness and TRAP levels, adjusted for relevant covariates. Higher greenness within and surrounding school boundaries was consistently associated with lower indoor and outdoor TRAP levels. Reduction in indoor TRAP levels was partly mediated by the reduction in outdoor TRAP levels. We also observed some suggestions for stronger associations between school surrounding greenness and outdoor TRAP levels for schools with higher number of trees around them. Our observed reduction of TRAP levels at schools associated with school greenness can be of public importance, considering the burden of health effects of exposure to TRAPs in schoolchildren.

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#### 1. Introduction

Contact with greenness has been shown to improve perceived and objective physical and mental health (Bowler et al., 2010; Lee and Maheswaran, 2011). Although the underlying mechanisms of health benefits of greenness are not well understood, reduction in exposure to air pollution has been suggested as one explanation (Bowler et al., 2010). The available evidence, however, on the mitigating effect of greenness on air pollution with regard to human exposure remains limited and inconsistent (Dadvand et al., 2012a, Hagler et al., 2012).

*Abbreviations:* BC, black carbon; BREATHE, BRain dEvelopment and Air polluTion ultra-fine particles in scHool children; CI, confidence intervals; IQR, interquartile range; NDVI, normalized difference vegetation index; LDSA, lung-deposited surface area; LUR, land use regression; PM<sub>2.5</sub>, particulate matter with aerodynamic diameter ≤2.5 μm; RC, regression coefficient; TRAP, traffic-related air pollutant; UFP, ultrafine particles; VOC, volatile organic compound.

\* Corresponding author at: CREAL, Doctor Aiguader, 88, 08003 Barcelona, Spain.

E-mail address: [pdadvand@creal.cat](mailto:pdadvand@creal.cat) (P. Dadvand).



Contents lists available at ScienceDirect

## International Journal of Hygiene and Environmental Health

journal homepage: [www.elsevier.com/locate/ijheh](http://www.elsevier.com/locate/ijheh)



### The exposome in practice: Design of the EXPOSOMICS project



P. Vineis<sup>a,\*</sup>, M. Chadeau-Hyam<sup>a</sup>, H. Gmuender<sup>b</sup>, J. Gulliver<sup>a</sup>, Z. Herceg<sup>c</sup>, J. Kleinjans<sup>d</sup>, M. Kogevinas<sup>e</sup>, S. Kyrtopoulos<sup>f</sup>, M. Nieuwenhuijsen<sup>e</sup>, D.H. Phillips<sup>g</sup>, N. Probst-Hensch<sup>h</sup>, A. Scalbert<sup>c</sup>, R. Vermeulen<sup>i</sup>, C.P. Wild<sup>c</sup>, The EXPOSOMICS Consortium<sup>1</sup>

<sup>a</sup> MRC-PHE Centre for Environment and Health, School of Public Health, Imperial College London, UK

<sup>b</sup> Genedata AG, Basel, Switzerland

<sup>c</sup> International Agency for Research on Cancer (IARC), Lyon, France

<sup>d</sup> Maastricht University, Department of Health Risk Analysis and Toxicology, Maastricht, Netherlands

<sup>e</sup> Barcelona Institute for Global Health (ISGlobal), Barcelona, Spain

<sup>f</sup> National Hellenic Research Foundation, Institute of Biology, Medicinal Chemistry and Biotechnology, Division of Organic and Medicinal Chemistry, Athens, Greece

<sup>g</sup> King's College London, Analytical and Environmental Sciences Division, MRC-PHE Centre for Environment and Health, London, UK

<sup>h</sup> Swiss Tropical School of Public Health, Department of Epidemiology and Public Health, Basel, Switzerland and University of Basel, Basel, Switzerland

<sup>i</sup> Utrecht University, Institute for Risk Assessment Sciences, Environmental Epidemiology Division, Utrecht, Netherlands

#### ARTICLE INFO

##### Article history:

Received 5 July 2016

Received in revised form 12 August 2016

Accepted 16 August 2016

#### ABSTRACT

EXPOSOMICS is a European Union funded project that aims to develop a novel approach to the assessment of exposure to high priority environmental pollutants, by characterizing the external and the internal components of the exposome. It focuses on air and water contaminants during critical periods of life. To this end, the project centres on 1) exposure assessment at the personal and population levels within existing European short and long-term population studies, exploiting available tools and methods which have been developed for personal exposure monitoring (PEM); and 2) multiple “omic” technologies for the analysis of biological samples (internal markers of external exposures). The search for the relationships between external exposures and global profiles of molecular features in the same individuals constitutes a novel advancement towards the development of “next generation exposure assessment” for environmental chemicals and their mixtures. The linkage with disease risks opens the way to what are defined here as ‘exposome-wide association studies’ (EWAS).

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**Abbreviations:** PEM, personal exposure monitoring; GIS, geographic information system; EWAS, exposome-wide association studies; STS, experimental short-term studies; MCO, mother-child cohorts; ALTS, adult long-term studies; LUR, land-use regression; DBP, disinfection by-products; OP, oxidative potential; UFP, ultrafine particles; PM, particulate matter.

\* Corresponding author at: MRC-PHE Centre for Environment and Health, School of Public Health, Imperial College London, Norfolk Place, W2 1PG, London UK.

E-mail address: [p.vineis@imperial.ac.uk](mailto:p.vineis@imperial.ac.uk) (P. Vineis).

<sup>1</sup> The EXPOSOMICS Consortium includes (in alphabetic order): Andre F.S. Amaral, Toby Athersuch, Sabrina Bertinetti, Marc Chadeau-Hyam, Leda Chatzi, Theo De Kok, Michaela Dijmarescu, Almudena Espin Perez, Mario Fernandez, Claudia Galassi, Akram Ghantous, Hans Gmuender, John Gulliver, John Henderson, Zdenko Herceg, Gerard Hoek, Medea Imboden, Pooja Jain, Debbie Jarvis, Frank Kelly, Pekka Keski-Rahkonen, Jos Kleinjans, Manolis Kogevinas, Julian Krauskopf, Soterios Kyrtopoulos, David Morley, Nahid Mostafavi Montazeri, Alessio Naccarati, Tim Nawrot, Mark Nieuwenhuijsen, Georgiadis Panos, David Phillips, Michelle Plusquin, George Preston, Nicole Probst-Hensch, Andrea Ranzi, Stephen Rappaport, Laia Font Ribeira, Lorenzo Richiardi, Susan M. Ring, Oliver Robinson, Alberto Rodriguez, Augustin Scalbert, Terrence Simmons, Martyn T. Smith, Jordi Sunyer, Sonia Tarallo, Veronique Terrasse, Ming Tsai, Erik van Nunen, Karin van Veldhoven, Roel C.H. Vermeulen, Cristina M. Villanueva, Paolo Vineis, Jelle Vlaanderen, Martine Vrijheid, Christopher P. Wild, Timo Wittenberger.

<http://dx.doi.org/10.1016/j.ijheh.2016.08.001>

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ORIGINAL ARTICLE

# The Fort Collins Commuter Study: Impact of route type and transport mode on personal exposure to multiple air pollutants

Nicholas Good<sup>1,2</sup>, Anna Mölter<sup>2</sup>, Charis Ackerson<sup>2</sup>, Annette Bachand<sup>2</sup>, Taylor Carpenter<sup>2</sup>, Maggie L. Clark<sup>2</sup>, Kristen M. Fedak<sup>2</sup>, Ashleigh Kayne<sup>2</sup>, Kirsten Koehler<sup>3</sup>, Brianna Moore<sup>2</sup>, Christian L'Orange<sup>1,2</sup>, Casey Quinn<sup>2</sup>, Viney Ugave<sup>1</sup>, Amy L. Stuart<sup>4</sup>, Jennifer L. Peel<sup>2</sup> and John Volckens<sup>1,2</sup>

Traffic-related air pollution is associated with increased mortality and morbidity, yet few studies have examined strategies to reduce individual exposure while commuting. The present study aimed to quantify how choice of mode and route type affects personal exposure to air pollutants during commuting. We analyzed within-person difference in exposures to multiple air pollutants (black carbon (BC), carbon monoxide (CO), ultrafine particle number concentration (PNC), and fine particulate matter (PM<sub>2.5</sub>)) during commutes between the home and workplace for 45 participants. Participants completed 8 days of commuting by car and bicycle on direct and alternative (reduced traffic) routes. Mean within-person exposures to BC, PM<sub>2.5</sub>, and PNC were higher when commuting by cycling than when driving, but mean CO exposure was lower when cycling. Exposures to CO and BC were reduced when commuting along alternative routes. When cumulative exposure was considered, the benefits from cycling were attenuated, in the case of CO, or exacerbated, in the case of particulate exposures, owing to the increased duration of the commute. Although choice of route can reduce mean exposure, the effect of route length and duration often offsets these reductions when cumulative exposure is considered. Furthermore, increased ventilation rate when cycling may result in a more harmful dose than inhalation at a lower ventilation rate.

*Journal of Exposure Science and Environmental Epidemiology* (2016) **26**, 397–404; doi:10.1038/jes.2015.68; published online 28 October 2015

**Keywords:** air pollution; carbon monoxide; commute; particle number; particulate matter; traffic

## INTRODUCTION

Air pollution is a leading cause of disease and premature death in many countries.<sup>1</sup> Despite recent reduction in air pollution levels in the developed countries,<sup>2,3</sup> evidence suggests that no safe threshold of exposure exists.<sup>4</sup> Transport is a major source of air pollution,<sup>5</sup> and living in proximity to major roads has been associated with increased risk of exposure and adverse health.<sup>5</sup> Commuters appear to be at particular risk because of their daily exposure to traffic-related air pollution.<sup>5</sup> Data from the 2009 American Community Survey suggests that a typical commuter in the United States would spend 1.2 years of their working lifetime commuting.<sup>6</sup>

Commuting by car is one of the most popular transport modes in the United States and Europe and is increasing elsewhere.<sup>5</sup> Commuting by bicycle is an option available to many people and is increasingly encouraged as a healthy and low-emission alternative to driving.<sup>7</sup> However, studies have suggested that cyclists may experience increased air pollution exposure and, because of their higher minute ventilation, substantially higher intake compared with drivers (see, e.g., Hatzopoulou *et al.*<sup>8</sup>). Evidence on air pollution exposures and related health effects specifically for cyclists, however, is limited, and introduces uncertainty into calculations for

estimating the net health cost–benefit of switching from driving to cycling.<sup>9</sup>

The major strategies to reduce the adverse health effects of air pollution have evolved around minimizing emissions. An alternative (non-emissions reductions driven) approach is to reduce exposure by providing and facilitating behavioral choices that will result in lower exposures. By understanding the relationship between the choices commuters make and their exposure, it may be possible to reduce exposure by informing behavior and adapting urban infrastructure. A number of studies<sup>10–14</sup> have investigated pollution levels on different routes, suggesting that routes can be chosen to reduce exposure. However, studies of actual commuters making realistic choices regarding route and mode are limited, and no studies have incorporated both cycling and driving in a non-prescribed (uncontrolled) setting. This study employed a crossover design on a panel of commuters living and working within Fort Collins, Colorado, United States, to assess the impact of switching transport mode from car to bicycle and of switching from direct routes to alternative (lower trafficked) routes on exposure to traffic-related air pollutants. The city of Fort Collins offered an ideal study domain to achieve these objectives; over 500 km of on-road cycling lanes and multi-use paths<sup>15</sup> exist within the 78 km<sup>2</sup> city limits.

<sup>1</sup>Department of Mechanical Engineering, Colorado State University, Fort Collins, Colorado, USA; <sup>2</sup>Department of Environmental and Radiological Health Sciences, Colorado State University, Fort Collins, Colorado, USA; <sup>3</sup>Department of Environmental Health Sciences, Johns Hopkins University, Baltimore, MD, USA and <sup>4</sup>Departments of Environmental and Occupational Health, and Civil and Environmental Engineering, University of South Florida, Tampa, Florida, USA. Correspondence: Dr. John Volckens, Department of Mechanical Engineering, Colorado State University, Fort Collins, CO 80523-1301, USA.

Tel.: +970 491 6341. Fax: +970 491 3827.

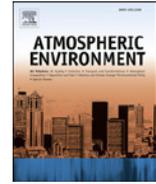
E-mail: john.volckens@colostate.edu

Received 25 June 2015; revised 15 September 2015; accepted 17 September 2015; published online 28 October 2015



Contents lists available at ScienceDirect

## Atmospheric Environment

journal homepage: [www.elsevier.com/locate/atmosenv](http://www.elsevier.com/locate/atmosenv)

# Total and size-resolved particle number and black carbon concentrations in urban areas near Schiphol airport (the Netherlands)

M.P. Keuken<sup>a,\*</sup>, M. Moerman<sup>a</sup>, P. Zandveld<sup>a</sup>, J.S. Henzing<sup>a</sup>, G. Hoek<sup>b</sup><sup>a</sup> TNO, Netherlands Organisation for Applied Research, Utrecht, The Netherlands<sup>b</sup> Institute for Risk Assessment Sciences (IRAS), University of Utrecht, The Netherlands

## HIGHLIGHTS

- Ultrafine particles are a factor 3 elevated 7 km downwind Schiphol airport.
- The size-distribution of these particles is dominated by particles of 10–20 nm.
- 45,000/60,000 addresses exposed to 5–10,000 (annual)/10–20,000 (hourly) #/cm<sup>3</sup>.

## ARTICLE INFO

## Article history:

Received 4 September 2014

Received in revised form

5 January 2015

Accepted 5 January 2015

Available online 6 January 2015

## Keywords:

Airport emissions

Ultrafine particles

Black carbon

Dispersion modelling

## ABSTRACT

The presence of black carbon, and size-resolved and total particle number concentrations (PNC) were investigated in the vicinity of Schiphol airport in the Netherlands, the fourth busiest airport in Europe. Continuous measurements were conducted between March and May 2014 at Adamse Bos, located 7 km from Schiphol, and in 2012 at Cabauw, a regional background site 40 km south of Schiphol. No significantly elevated black carbon levels were found near Schiphol. However, PNC increased during periods in which the wind direction was from Schiphol: at Cabauw by 20% and at Adamse Bos by a factor of three, from 14,100 (other wind directions) to 42,000 # cm<sup>-3</sup> between 06.00 and 23.00. The size distribution of Schiphol-related PNC was dominated by ultrafine particles, ranging from 10 to 20 nm. Four relevant particle number (PN) emission sources at Schiphol were identified as being responsible for the elevated PNC levels at Adamse Bos: take-off and climb-out on the Kaagbaan and Aalsmeerbaan runways, planes waiting at the gates, and landing on the Buitenveldertbaan runway. PN emissions from road traffic at and near the airport were less important than air traffic. The exposure to Schiphol-related PNC in urban areas northeast of Schiphol in Amsterdam and Amstelveen was estimated for 2012 using a Gaussian Plume model. The results showed that a considerable number of the 555,000 addresses in the modelling domain were exposed to elevated PNC. For example: 45,000 addresses suffered *long-term* exposure to an additional annual background PNC of 5–10,000 # cm<sup>-3</sup> originating from Schiphol and 60,000 addresses suffered *short-term* exposure (14% of the time) of additional 10–15,000 # cm<sup>-3</sup> originating from Schiphol. Further research on emission sources and the dispersion of PN is recommended and may support future studies on eventual health effects.

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## 1. Introduction

Many epidemiological studies have established associations between exposure to the mass of ambient particulate matter (PM) and adverse health effects. Various physical and chemical fractions in PM have been proposed as the cause of these acute and chronic

effects (Cassée et al., 2013). One of the suspect fractions concerns the large number of submicron particles because the latter may contain potential toxic species and can penetrate deep into the respiratory system (Loane et al., 2013; Oberdörster et al., 2005). The number of submicron particles is dominated by ultrafine particles, which are smaller than 100 nm (Sioutas et al., 2005). Submicron particles in ambient air originate in primary emissions from combustion processes and the secondary formation of sulphates, nitrates and organic PM from gas-to-particle conversion in ambient air (Chow and Watson, 2007). During initial cooling and further

\* Corresponding author.

E-mail address: [menno.keuken@tno.nl](mailto:menno.keuken@tno.nl) (M.P. Keuken).



Conference Report

# Ultrafine Particle Metrics and Research Considerations: Review of the 2015 UFP Workshop

Richard W. Baldauf <sup>1,2,\*</sup>, Robert B. Devlin <sup>1</sup>, Peter Gehr <sup>3</sup>, Robert Giannelli <sup>2</sup>, Beth Hassett-Sipple <sup>1</sup>, Heejung Jung <sup>4</sup>, Giorgio Martini <sup>5</sup>, Joseph McDonald <sup>1,2</sup>, Jason D. Sacks <sup>1</sup> and Katherine Walker <sup>6</sup>

- <sup>1</sup> Office of Research and Development, US Environmental Protection Agency, Research Triangle Park, NC 27711, USA; devlin.robert@epa.gov (R.B.D.); hassett-sipple.beth@epa.gov (B.H.-S.); mcdonald.joseph@epa.gov (J.M.); sacks.jason@epa.gov (J.D.S.)
- <sup>2</sup> Office of Transportation and Air Quality, US Environmental Protection Agency, Ann Arbor, MI 48105, USA; giannelli.bob@epa.gov
- <sup>3</sup> Institute of Anatomy, University of Bern, 3000 Bern, Switzerland; gehr@ana.unibe.ch
- <sup>4</sup> Department of Mechanical Engineering, University of California, Riverside, CA 92521, USA; heejung@engr.ucr.edu
- <sup>5</sup> European Commission-Joint Research Centre, Ispra 21027, Italy; giorgio.martini@jrc.ec.europa.eu
- <sup>6</sup> Health Effects Institute, Boston, MA 02110, USA; KWalker@healtheffects.org
- \* Correspondence: baldauf.richard@epa.gov

Academic Editor: Doug Brugge

Received: 31 August 2016; Accepted: 13 October 2016; Published: 28 October 2016

## 1. Preface

In February 2015, the United States Environmental Protection Agency (EPA) sponsored a workshop in Research Triangle Park, NC, USA to review the current state of the science on emissions, air quality impacts, and health effects associated with exposures to ultrafine particles [1]. The workshop provided scientific presentations on the sources and trends of ultrafine particles (UFP) emissions and air quality concentrations, evidence of health effects associated with UFP exposure, metrics and indicators of UFP emissions, UFP measurement methods, control strategies, and policy considerations. This workshop brought together experts from around the world to share information and discuss future next steps on UFP research and policy. The following sections provide a summary of the presentations and discussions during this workshop, specifically highlighting the observations offered by individual speakers, summaries of the panel discussions, and potential opportunities to continue dialogue and enhance coordination and collaboration across multiple scientific disciplines.

## 2. Recent Reviews of the Scientific Evidence on UFPs

The workshop began with a summary of two recent reviews of the scientific literature on UFPs, one by the EPA as part of its 2009 particulate matter (PM) Integrated Science Assessment (ISA) [2] and the other by the Health Effects Institute (HEI) [3]. These reviews set the stage on how the weight of evidence is assessed during the National Ambient Air Quality Standard (NAAQS) review process in the United States of America (USA) by the EPA and the gaps identified in these reviews for the UFP literature that needed consideration in future research.

Jason Sacks of the EPA presented the overall conclusions of the 2009 EPA ISA, which formed the scientific foundation for the most recent review of the USA PM NAAQS that was completed in December 2012 [4]. As part of that review, the EPA assembled the available scientific evidence for UFPs and other PM size fractions to make causality determinations that reflect the overall weight of evidence for specific exposure durations (i.e., either short- or long-term exposure) and health or welfare effects (See Text Box 1 for the five-level hierarchy of causality determinations). The EPA's approach to making causality determinations, which is supported by an independent panel of subject



## Ultrafine Particles at Airports

Discussion and assessment of ultrafine particles (UFP) in aviation and at airports in 2012

The data in this publication is a result of a coordinated effort by the airports represented in the Environmental Strategy Committee of ACI EUROPE (Airports Council International). ACI EUROPE would like to thank all the airports involved in this study for their time and dedication, in particular Zurich Airport's Environmental Department which contributed significantly to the execution and completion of the study.

## **About ACI EUROPE**

ACI EUROPE, the voice of Europe's airports, is the European region of Airports Council International, the only worldwide professional association of airport operators. ACI EUROPE represents over 400 airports in 46 European countries. Member airports handle 90% of commercial air traffic in Europe, welcoming nearly 1.5 billion passengers each year.

For more information, visit [www.aci-europe.org](http://www.aci-europe.org)

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[robert.omeara@aci-europe.org](mailto:robert.omeara@aci-europe.org)  
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## Management Summary

Studies and subsequent conclusions in 2010 at Copenhagen airport in Denmark have raised concerns about health related impacts from ultrafine particles from airport activities. As ultrafine particles are currently not regulated in terms of emissions or concentrations, the overall understanding and coverage of the topic deserves additional efforts to gain a better understanding. The Environmental Strategy Committee of ACI EUROPE has taken the initiative to further investigate the topic of ultrafine particles at airports. To this end, this report first introduces the scientific aspect of ultrafine particles (nature, origin, health effects and current regulations).

Current air quality activities at airports covers all aviation related sources with emissions, concentration measurements and modelling as well as mitigation planning for regulated criteria air pollutants (e.g. NO<sub>x</sub>/NO<sub>2</sub>, HC, PM). However, first studies for ultrafine particles in aviation were carried out in 2000 for aircraft engines, later also to include some airport related measurements.

Several airports, many of which are in Europe have recently addressed the topic of ultrafine particles, either in the light of initiatives at Copenhagen Airport or independent from it. Some of the studies are presented in this report while other programs are still on-going and will be published later.

Some of key findings of the studies are as follows:

- Ultrafine particle (UFP) concentrations in terms of average (and median) tend to be relatively high at airports (30,000-100,000), but a very high variability in number concentrations and particle sizes has been observed
- It seems that UFP from aircraft turbines on average tend to be smaller in size (10-16 nm) than from standard diesel/gasoline combustion engines (10-300 nm) but higher in numbers; as such, a source discrimination appears to be possible; aircraft turbine particle emissions also correlate with the sensory cognition of the typical aircraft exhaust smell
- The measurement setup (equipment, location) has a very significant impact on the results

In conclusion, any single measurement campaign is insufficient to properly describe the average UFP concentrations at an airport. Instead, only multiple long-term measurement campaigns at airports (e.g. like at Copenhagen) would be sufficiently robust to provide a clearer picture of UFPs' behaviour.

As a further conclusion, it can be stated that the current understanding of average, long-term concentrations of ultrafine particle at airports, particular in terms of dose exposure and human response is insufficient to conclude any dose-effect relationships. This also includes the question of linearity between particle number concentrations and possible human effects as well as the effects of various particle properties (e.g. surface properties).

Many activities are emitting ultrafine particles and people in their environment are subject to the resulting concentrations. The following figure displays some activities and/or measurement locations with UFP number concentrations with information on measurement duration or frequency. As can be seen, the concentrations measured at airports are comparable to those measured from other activities and there are no significant higher results from airport locations.

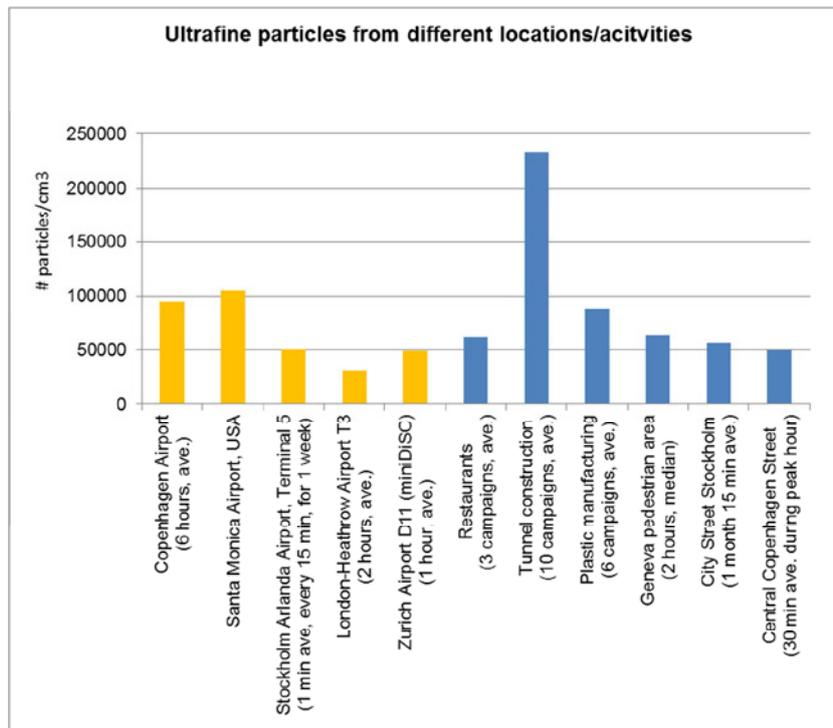


Fig 1: UFP emissions from various locations/activities

Experience from the various measurement campaigns has demonstrated the need for a very careful planning and execution of ultrafine particle concentration measurements. The range of the obtained results has further revealed that many effects contribute to the outcome of measurements: meteorological conditions or choice and location of the monitoring equipment. To this end, multiple measurement campaigns over longer periods of time and with multiple devices simultaneously are strongly recommended.

In the context of the discussion around ultrafine particles from aviation, the topic of regulations or definition of standards has been raised. Currently, there are no regulations pertaining to ultrafine particles. The main requirements for any standard setting process are:

1. Parameters to be regulated: For ultrafine particles, the question will be which parameters should be used, e.g. the mass weight, particle numbers, particle surface, physical-chemical properties of the surface (volatile or non-volatile) or the formation of reactive oxygen species
2. Standardization of measurement: Harmonization of measurement guidelines and standardization of measurement equipment (methods and technologies)
3. Standard-setting: Relevant for establishing standards are known dose-effect relationships, if possible on the basis of epidemiological and experimental studies. This requires both longer-term measurements and health impact studies
4. Applicability: Any new standards have to be applicable over the whole range of the relevant emission sources from all activities (transportation, manufacturing, etc)

There are three domains within which standards could be defined: emissions, ambient concentrations or workplace concentrations. For each domain, different regulatory entities may be responsible and different – already existing – tools and regulations can be used to potentially add text and standards for ultrafine particles. In the first place, usually the concentrations are being regulated as they are impact relevant. Subsequently and if needed, then emission standards for certain sources are developed and implemented.



## Ultrafine particles over Germany – an aerial survey

By WOLFGANG JUNKERMANN<sup>1\*</sup>, BERNHARD VOGEL<sup>2</sup> and MAX BANGERT<sup>2</sup>, <sup>1</sup>*Institute of Meteorology and Climate Research, IMK-IFU, Garmisch-Partenkirchen, Germany*; <sup>2</sup>*Troposphere Research, IMK-TRO, Eggenstein-Leopoldshafen, Germany*

(Manuscript received 23 July 2015; in final form 9 February 2016)

### ABSTRACT

Ultrafine particles in the atmosphere may have important climate and health effects. As they are below visible size and not visible for remote sensing techniques, the majority of observations thus come from ground-based measurements. Some of those observations indicate elevated sources for ultrafine particles. Here we present for the first time airborne measurements of number concentration and size distributions of ultrafine particles along defined flight paths across Germany, allowing to derive background concentrations and to identify major single sources. A significant impact of fossil fuel-related emissions on background and maximum concentrations was found. Maxima reaching up to 90 000 particles  $\text{cm}^{-3}$  were encountered in plumes of single large sources extending over more than 200 km. Modelling shows that about 10–40 % of Germany were continuously affected by such plumes. Regional-scale transport and boundary layer dynamics were identified as major factors controlling spatial and temporal patterns of size and number distributions.

*Keywords: ultrafine particles, source apportionment, budget, regional distribution, Germany, power station emissions*

### 1. Introduction

Ultrafine particles (UFPs) in the air are suggested to have significant impact on climate and health. Too small to be visible and undetectable for remote sensing techniques, they are affecting on a regional scale the number concentration of cloud condensation nuclei (CCN) and subsequently cloud optical properties and rainfall distributions (Laaksonen et al., 2005; Pierce and Adams, 2007; Junkermann et al., 2011b; Kerminen et al., 2012; Sporre et al., 2014; Junkermann and Hacker, 2015). Bister and Kulmala (2011) even hypothesised an impact of UFPs on upper tropospheric water vapour from nucleation mode particles.

Health issues of particulate mass are normally linked to fine particles like PM<sub>10</sub> and PM<sub>2.5</sub> (Oberdörster et al., 2005; Pope, 2007; Pope et al., 2008). However, although not yet confirmed, recently the ultrafine fraction (< 100 nm) was supposed to be probably even more important (Araujo, 2011; Franck et al., 2011).

Despite the potential health and climate hazard due to potential effects on rainfall, spatial, temporal and intensity distribution (Junkermann et al., 2011b) or cloud modification

important for radiation budgets (Paasonen et al., 2013), the knowledge of the tropospheric distribution of UFPs is limited as these particles are not included into routine atmospheric monitoring programs on a wider scale. For example, the German environmental agency (UBA) reports UFP number concentrations only from 13 out of 314 stations reporting PM<sub>2.5</sub> and PM<sub>10</sub> data. However, there are at least some attempts to overcome this gap. In 2008, a national ground-based measuring network was setup in Germany (GUAN, Birmili et al., 2009, 2015). More detailed ground-based measurements covering parts of Germany are available from campaign studies in different regions (Asmi et al., 2013; Birmili et al., 2013). However, all single ground-based stations encounter the problem whether they are representative for the wider region. Due to the high temporal and spatial variability of ultrafine aerosol sources, for example, traffic and several anthropogenic burning processes, and the high emission rate of certain single point sources such as power stations, which emit to elevated altitudes of the planetary boundary layer (PBL) (Junkermann et al., 2011a), the representativeness of ground-based measurements is not always guaranteed. Thus, three-dimensional measurements at larger scales, from local to regional or continental scale, and vertical profiles of UFP distributions, would be beneficial. This requires airborne mobile platforms (O'Dowd et al., 2007, 2009; Crumeyrolle et al., 2010;

\*Corresponding author.  
email: wolfgang.junkermann@kit.edu  
Responsible Editor: Kaarle Hämeri, University of Helsinki, Finland.

# Perspectives 3

January 2013

*Insights from HEI's research*



## Understanding the Health Effects of Ambient Ultrafine Particles

HEI Review Panel on Ultrafine Particles

HEALTH EFFECTS INSTITUTE

# CONTRIBUTORS

In Spring 2011, the Health Effects Institute appointed an expert panel to review and critique the scientific literature on the ultrafine particles — their sources, the role of automobile emissions, and their potential health effects at ambient levels of exposure. The panel consisted of scientists from a variety of disciplines and was chaired by Mark Frampton, a professor of medicine and environmental medicine at the University of Rochester

Medical School. HEI is indebted to the panel for its expertise, cooperation, and enthusiasm. The panel also received support from a team of HEI staff, under the leadership of Katherine Walker, Senior Scientist. A draft of the resulting report was submitted for outside peer review; the help of the peer reviewers in improving the quality of this document is gratefully acknowledged.

## HEI Review Panel on Ultrafine Particles

**Mark W. Frampton, Chair**, *Professor of Medicine and Environmental Medicine, University of Rochester Medical Center; member, HEI Review Committee*

**Michael Brauer**, *Professor, School of Population and Public Health, University of British Columbia; member, HEI Review Committee*

**Michael Kleeman**, *Professor, Department of Civil & Environmental Engineering, University of California–Davis*

**Wolfgang G. Kreyling**, *Biophysicist Emeritus, Institute of Lung Biology and Disease, Helmholtz Zentrum München, German Research Center for Environmental Health*

**Leonidas Ntziachristos**, *Assistant Professor, Laboratory of Applied Thermodynamics, Mechanical Engineering Department, Aristotle University Thessaloniki*

**Stefanie Ebel Sarnat**, *Assistant Professor, Department of Environmental Health, Rollins School of Public Health, Emory University*

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**Jonathan Levy**, *Professor of Environmental Health, Boston University School of Public Health*

**Morton Lippmann**, *Professor, Nelson Institute of Environmental Medicine, New York University Medical Center*

**Juha Pekkanen**, *Professor, Department of Environmental Health, National Institute for Health and Welfare, Unit of Public Health and Clinical Nutrition, University of Eastern Finland*

**Kent Pinkerton**, *Professor and Director, Center for Health and the Environment, University of California–Davis*

**Ira Tager**, *Emeritus Professor, School of Public Health, Division of Epidemiology, University of California–Berkeley*

**Clifford P. Weisel**, *Professor, Environmental and Occupational Health Sciences Institute, Rutgers University*

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# EXECUTIVE SUMMARY

## Understanding the Health Effects of Ambient Ultrafine Particles

### INTRODUCTION

Over the past 30 years, a large body of scientific literature has emerged that provides evidence of associations between short-term and long-term exposures to ambient particulate matter (PM) and increased mortality and hospitalization from cardiovascular and respiratory diseases. Most of the evidence is based on epidemiologic studies of human exposure to PM with aerodynamic diameters  $\leq 10$  micrometers ( $PM_{10}$ ) or  $\leq 2.5$  micrometers ( $PM_{2.5}$ ). However, scientists and regulators have long known that PM in the ambient air is a complex mixture including particles of different sizes and chemical composition. What has been less clear is whether certain characteristics of the ambient mixture are more harmful to public health than others and are therefore the most important to control. In its 1998 blueprint for a research program on airborne PM, the United States National Research Council identified improved understanding of ultrafine particles (UFPs) as a priority.

UFPs make up the smallest size fraction in what is a continuum of airborne particles with diameters ranging from a few nanometers to several micrometers. By convention, UFPs have been defined as particles that are 100 nanometers or less in diameter ( $\leq 100$  nm). Given their small size, UFPs contribute little to the mass of PM in ambient air, but they are the dominant contributors to particle number. Motor vehicles, especially those powered by diesel engines, have often been cited as a leading source of ambient UFP emissions and of human exposure.

The work of the HEI Review Panel on Ultrafine Particles was supported with funding from the United States Environmental Protection Agency (Assistance Award CR-83234701) and motor vehicle manufacturers. Support for the preparation and publication of this document was provided by the Federal Highway Administration (Grant DTFH61-09-G-00010). This report has not been subjected to peer or administrative review by any of the sponsors and may not necessarily reflect their views, and no official endorsement should be inferred.

Concern about UFPs developed from early evidence, primarily from animal and in vitro studies, that suggested that they could be inhaled more deeply into the lung and might be more toxic than larger particles. The first epidemiologic studies that included particle number measurements also suggested that UFPs might be associated with the same adverse effects in humans that have been attributed to larger particle size fractions. Scientists hypothesized that UFPs would have greater toxicity than larger particles in part because their vast numbers and small diameters mean that they have a high surface area, a potentially important interface through which to transmit any toxic chemicals that might be adsorbed.

In the decades since concerns were first raised about UFPs, the role they might play in the adverse health effects associated with exposures to air pollution has remained an important research target at institutions around the world, including HEI. National and local air quality authorities in the United States and in other regions of the world continue to assess the need for specific action on UFPs in reviews of ambient air quality standards and other regulatory programs. At the same time, under existing regulatory and technological changes, UFP emissions from motor vehicles are already changing. The resulting impacts on ambient concentrations, and ultimately on human exposures, are difficult to predict.

### TIME FOR A BROAD PERSPECTIVE

Given this context, HEI formed a special panel (see Contributors list) to review the scientific evidence available on UFPs and to present its evaluation in this third issue of the HEI Perspectives series: *Understanding the Health Effects of Ambient Ultrafine Particles*.

## Understanding the Health Effects of Ambient Ultrafine Particles

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The Panel structured its assessment of the scientific evidence regarding ambient UFPs as responses to three questions:

- Ambient UFPs — sources, emissions, and exposures: To what extent do motor vehicles contribute? (Chapter 2);
- Do UFPs affect health? What is the evidence from experimental studies in animals and humans? (Chapter 3);
- Do UFPs affect human health at environmental concentrations? What is the evidence from epidemiologic studies? (Chapter 4).

Chapter 2 explores the contribution of motor vehicles within the broader context of the multiple sources of ambient UFPs. It discusses in detail the changing profiles of mobile-source emissions, the spatial and temporal patterns of ambient UFP concentrations, and the implications of all these factors for the design and interpretation of studies of UFP exposure and health.

The next two chapters explore the health evidence on UFP exposures from a broad array of study designs using animal and human subjects. Chapter 3 focuses on the evidence from experimental studies in animals and in humans because they can directly test hypotheses about the causal role of specific exposures.

Chapter 4 focuses on observational epidemiologic studies of people exposed to UFPs in the environment, in mostly urban settings. Because they involve studies of people exposed to concentrations of air pollutants found in the real world, epidemiologic studies of UFPs have the potential to provide more direct evidence with which to determine whether UFPs affect human health at concentrations found in the environment.

Chapters 3 and 4 both focus on various measures of intermediate markers and health endpoints that represent the multiple hypothesized pathways for UFP effects. Most of these pathways are shared by PM generally, but some pathways may be especially relevant for UFPs.

In identifying experimental and epidemiologic studies for its assessment, the Panel made a number of choices to make sure that responses to the questions were most informed by studies relevant to the understanding of the potential risks of inhaling ambient UFPs, particularly those related to motor vehicle exhaust. For the experimental studies, it considered only studies involving exposures to UFPs via the inhalation route, which is physiologically relevant and directly comparable with the results of epidemiologic studies. The Panel therefore excluded *in vitro* studies or studies in which particles were directly instilled

into the lungs or airways. The Panel focused on exposures to combustion-related UFPs and therefore largely excluded the vast literature on engineered nanoparticles. The Panel also placed particular emphasis on both experimental and epidemiologic studies of UFPs that included analyses of exposures to copollutant gases and larger particle size fractions, because of the potential of such studies to provide insight into the role of UFPs themselves in any health effects observed.

Finally, Chapter 5 summarizes each chapter's main conclusions and attempts to identify some of the broader lessons, about both the specific health effects associated with exposures to UFPs and possible directions for future studies that could enhance our understanding of emissions, exposures, and effects of UFPs.

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## SUMMARY AND CONCLUSIONS

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A substantial body of literature has now been published on the sources of UFPs, their spatial and temporal distribution in ambient air, their inhalation and fate in the body, their mechanisms of toxicity, and their adverse effects in animals and in humans. The purpose of this issue of HEI Perspectives is to provide a broad assessment of what has been learned about UFPs and what remains poorly understood. The Panel's findings in response to the three questions posed at the outset of this Executive Summary are summarized briefly below.

### **AMBIENT UFPs — SOURCES, EMISSIONS, AND EXPOSURES: TO WHAT EXTENT DO MOTOR VEHICLES CONTRIBUTE?**

As products of combustion and secondary atmospheric transformations, ambient UFPs have multiple sources whose relative contributions to ambient concentrations vary with location, season, and time-of-day. However, in urban areas, particularly in proximity to major roads, motor vehicle exhaust can be identified as the major contributor to UFP concentrations. Diesel vehicles have been found to contribute substantially, sometimes in disproportion to their numbers in the vehicle fleet.

However, the absolute and relative contributions of different vehicle types to motor vehicle emissions are changing rapidly. On the one hand, under the force of regulations to reduce particle mass and number emissions from diesel and other vehicles, the emissions, and therefore ambient levels, of UFPs will decrease. On the other hand, this decrease may be partially offset by UFP emissions from the

## Research Article

# Vertical Profiles and Chemical Properties of Aerosol Particles upon Ny-Ålesund (Svalbard Islands)

**B. Moroni,<sup>1</sup> S. Becagli,<sup>2</sup> E. Bolzacchini,<sup>3</sup> M. Busetto,<sup>4</sup> D. Cappelletti,<sup>1,4,5</sup> S. Crocchianti,<sup>5</sup> L. Ferrero,<sup>3</sup> D. Frosini,<sup>2</sup> C. Lanconelli,<sup>4</sup> A. Lupi,<sup>4</sup> M. Maturilli,<sup>6</sup> M. Mazzola,<sup>4</sup> M. G. Perrone,<sup>3</sup> G. Sangiorgi,<sup>3</sup> R. Traversi,<sup>2</sup> R. Udisti,<sup>2</sup> A. Viola,<sup>7</sup> and V. Vitale<sup>4</sup>**

<sup>1</sup>SMAArt Research Center, University of Perugia, 06125 Perugia, Italy

<sup>2</sup>Department of Chemistry, University of Florence, 50019 Sesto Fiorentino, Italy

<sup>3</sup>POLARIS Research Center, DISAT, University of Milano-Bicocca, 20126 Milano, Italy

<sup>4</sup>Institute for Atmospheric Sciences and Climate, CNR, 40129 Bologna, Italy

<sup>5</sup>Department of Chemistry, Biology and Biotechnologies, University of Perugia, 06123 Perugia, Italy

<sup>6</sup>Alfred Wegener Institute, Helmholtz Centre for Polar and Marine Research, 14473 Potsdam, Germany

<sup>7</sup>Institute for Atmospheric Sciences and Climate, CNR, 00133 Rome, Italy

Correspondence should be addressed to B. Moroni; [b.moroni@tiscali.it](mailto:b.moroni@tiscali.it)

Received 25 December 2014; Revised 23 April 2015; Accepted 14 June 2015

Academic Editor: Richard Leitch

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Size-segregated particle samples were collected in the Arctic (Ny-Ålesund, Svalbard) in April 2011 both at ground level and in the free atmosphere exploiting a tethered balloon equipped also with an optical particle counter (OPC) and meteorological sensors. Individual particle properties were investigated by scanning electron microscopy coupled with energy dispersive microanalysis (SEM-EDS). Results of the SEM-EDS were integrated with particle size and optical measurements of the aerosols properties at ground level and along the vertical profiles. Detailed analysis of two case studies reveals significant differences in composition despite the similar structure (layering) and the comparable texture (grain size distribution) of particles in the air column. Differences in the mineral chemistry of samples point at both local (plutonic/metamorphic complexes in Svalbard) and remote (basic/ultrabasic magmatic complexes in Greenland and/or Iceland) geological source regions for dust. Differences in the particle size and shape are put into relationship with the mechanism of particle formation, that is, primary (well sorted, small) or secondary (idiomorphic, fine to coarse grained) origin for chloride and sulfate crystals and transport/settling for soil (silicate, carbonate and metal oxide) particles. The influence of size, shape, and mixing state of particles on ice nucleation and radiative properties is also discussed.

## 1. Introduction

The Arctic is the world region mostly affected by climate change [1, 2]. Herein, climate forcing is causing dramatic environmental changes in a complex cycle of feedback processes involving atmosphere, ocean, cryosphere, and land [3]. In particular, the Arctic is undergoing large changes in extension and thickness of the annual and permanent sea ice and in the permafrost superficial structure (e.g., [4]). Changes in temperature profiles along the uppermost seawater layers and in the tropospheric air column involve relevant variations of the marine and atmospheric circulation processes, which

are able on turn to significantly amplify the climate forcing on a hemispheric scale [5]. The increase in the Arctic cloud cover observed in the last decades may have significant effects too [6, 7]. These observations raised public interest on global warming, which is actually more evident in the Arctic [8].

Arctic aerosol is believed to play a relevant role in climate-environment feedbacks by scattering and absorbing the solar radiation and by altering cloud properties [9, 10]. Many of these effects remain poorly known, their quantitative evaluation is still limited [2], and this is one of the challenges of present aerosol research. For example, black carbon particles act as positive forcing agents because they

#### 4. Instrument capacity

<b>Abstract 4.01</b> A low Pressure drop preseparator for elimination of particles larger than 450 nm	<b>Page 131</b>	<b>Abstract 4.14</b> Determining the count median diameter of nanoaerosols by simultaneously measuring their number and lung deposited surface area concentrations	<b>Page 144</b>
<b>Abstract 4.02</b> A micro aerosol sensor for the measurement of airborne ultrafine particles	<b>Page 132</b>	<b>Abstract 4.15</b> Development and validation of a UAV based system for air pollution measurements	<b>Page 146</b>
<b>Abstract 4.03</b> Accuracy of electrical aerosol sensors measuring lung deposited surface area concentrations	<b>Page 133</b>	<b>Abstract 4.16</b> Enabling low-cost particulate matter measurement for participatory sensing scenarios	<b>Page 147</b>
<b>Abstract 4.04</b> Assessment of workplace exposure to carbon nanotubes with personal and stationary instruments	<b>Page 134</b>	<b>Abstract 4.17</b> Evaluation of a diffusion charger for measuring aerosols in a workplace	<b>Page 148</b>
<b>Abstract 4.05</b> Can we trust real time measurements of lung deposited surface area concentrations in dust from powder nanomaterials?	<b>Page 135</b>	<b>Abstract 4.18</b> Evaluation of the DiSCmini personal aerosol monitor for submicrometer sodium chloride and metal aerosols	<b>Page 149</b>
<b>Abstract 4.06</b> Characterization and response model of the PPSM aerosol sensor	<b>Page 136</b>	<b>Abstract 4.19</b> Field comparison of portable and stationary instruments for outdoor urban air exposure assessments	<b>Page 151</b>
<b>Abstract 4.07</b> Charge-based personal aerosol samplers	<b>Page 137</b>	<b>Abstract 4.20</b> High-throughput and label-free single nanoparticle sizing based on time-resolved on-chip microscopy	<b>Page 152</b>
<b>Abstract 4.08</b> Comparability of mobility particle sizers and diffusion chargers	<b>Page 138</b>	<b>Abstract 4.21</b> Influence of instruments performance and material properties on exposure assessment of airborne engineered nanomaterials	<b>Page 153</b>
<b>Abstract 4.09</b> Comparability of portable nanoparticle exposure monitors	<b>Page 139</b>	<b>Abstract 4.22</b> Mathematical description of experimentally determined charge distributions of a unipolar diffusion charger	<b>Page 155</b>
<b>Abstract 4.10</b> Comparative testing of a miniature diffusion size classifier to assess airborne ultrafine particles under field conditions	<b>Page 140</b>	<b>Abstract 4.23</b> Partially integrated cantilever-based airborne nanoparticle detector for continuous carbon aerosol mass concentration monitoring	<b>Page 156</b>
<b>Abstract 4.11</b> Comparison of measured particle lung-deposited surface area concentrations by an Aerotrak 9000 using size distribution measurements for a range of combustion aerosols	<b>Page 141</b>	<b>Abstract 4.24</b> Standard operation procedures for assessing exposure to nanomaterials, following a tiered approach	<b>Page 157</b>
<b>Abstract 4.12</b> Comparison of the DiSCmini aerosol monitor to a handheld condensat ion particle counter and a scanning mobility particle sizer for submicrometer sodium chloride and metal aerosols	<b>Page 142</b>	<b>Abstract 4.25</b> Variable field ion traps	<b>Page 159</b>
<b>Abstract 4.13</b> Design, calibration, and field performance of a miniature diffusion size classifier	<b>Page 143</b>		



## A Low Pressure Drop Preseparator for Elimination of Particles Larger than 450 nm

C. Asbach<sup>1\*</sup>, H. Fissan<sup>1,2</sup>, H. Kaminski<sup>1</sup>, T.A.J. Kuhlbusch<sup>1,2</sup>, D.Y.H. Pui<sup>3</sup>, H. Shin<sup>3,4</sup>, H.G. Horn<sup>5</sup>, T. Hase<sup>6</sup>

<sup>1</sup> Institute of Energy and Environmental Technology (IUTA) e.V., 47229 Duisburg, Germany

<sup>2</sup> Center for Nanointegration Duisburg-Essen (CeNIDE), 47057 Duisburg

<sup>3</sup> University of Minnesota, Minneapolis, MN 55455, USA

<sup>4</sup> now at: KOTEC, Bukgu, Ulsan 68337, Korea

<sup>5</sup> TSI GmbH, 52068 Aachen, Germany

<sup>6</sup> TSI Inc., Shoreview, MN 55126, USA

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### ABSTRACT

Measurement techniques which allow the detection of airborne nanoparticles are of great interest for e.g. exposure monitoring and quality control during nanoparticle production. An increasing number of commercial devices use a unipolar diffusion charger to charge the particles and determine the nanoparticle concentration and sometimes size. The analysis however may be biased by the presence of large particles. We therefore developed a preseparator that removes particles larger than 450 nm, i.e. the minimum in the range of particle lung deposition curves, but only causes a low pressure drop. The preseparator uses a total flow rate of 2.5 L/min and consists of two stages. The first stage is a virtual impactor that removes particles larger than approximately 1 µm with a minor flow of 1 L/min. Particles above 450 nm are removed from the remaining 1.5 L/min in the cyclone of the second stage. The combination of a cyclone with a virtual impactor was shown to reduce the pressure drop of the preseparator from 8.1 to 5.6 kPa compared with a cyclone alone and improve the sharpness of the separation curve for cut-off diameters around 450 nm. Furthermore the virtual impactor extends the cleaning intervals of the preseparator, because large particles are no longer deposited in the cyclone. Eventually the preseparator was tested with an opposed flow diffusion charger and it was shown that particle charging is not affected by the pressure drop.

**Keywords:** Cyclone; Virtual impactor; Diffusion charger; Nanoparticle.

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### INTRODUCTION

Nanoparticles, here synonymously also used for nanoplates and nanofibres, can be considered as important building blocks for nanostructured materials. There is concern that these engineered nanoparticles can be released into the environmental media air, water and soil, during their entire lifecycle, i.e. during synthesis, handling, downstream use or recycling (Mueller and Nowack, 2008; Som *et al.*, 2010). This may lead to exposure of human beings and the ecosystem with corresponding possible risks (Borm *et al.*, 2006; Warheit *et al.*, 2008). Inhalation is currently seen as the most important route of nanomaterial intake by humans (Oberdörster, 2010).

Online exposure related measurements of nanoparticle concentrations in air as well as off-line analysis of nanoparticle

properties after sampling on a substrate may be biased by larger particles and nanoscale particles from other sources. An increasing number of direct-reading instruments for the detection of nanoparticles use electrical sensors due to their ease of use, low power consumption and small size. Such electrical sensors normally comprise a corona discharge to produce unipolar ions, a chamber for diffusive ion attachment to the aerosol particles (Hernandez- Sierra *et al.*, 2003; Park *et al.*, 2007) followed by an ion trap to remove excess ions. The particles are eventually collected e.g. on an absolute filter and the particle induced current is measured with a Faraday cup electrometer (Fissan *et al.*, 2007; Marra *et al.*, 2010; Fierz *et al.*, 2011). These diffusion charger based electrical sensors are commonly used to infer total concentrations (number, length, active or lung deposited surface area) from the measured current. To do so, the average charge per particle has to follow the same size dependence as the wanted particle quantity. According to Fuchs' theory (Fuchs, 1963), however, the average charge level is proportional to the particle diameter squared in the free molecule regime and directly proportional to the

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\* Corresponding author. Tel.: +49 (0)2065 418-209;  
Fax: +49 (0)2065 418-211  
E-mail address: asbach@iuta.de

Article

# A Micro Aerosol Sensor for the Measurement of Airborne Ultrafine Particles

Chao Zhang <sup>1</sup>, Rong Zhu <sup>1,\*</sup> and Wenming Yang <sup>2</sup>

<sup>1</sup> State Key Laboratory of Precision Measurement Technology and Instrument, Department of Precision Instrument, Tsinghua University, Beijing 100084, China; zhangchao14@mails.tsinghua.edu.cn

<sup>2</sup> School of Mechanical Engineering, University of Science and Technology Beijing, Beijing 100083, China; wmyang@ustb.edu.cn

\* Correspondence: zr\_gloria@mail.tsinghua.edu.cn; Tel.: +86-10-6278-8935

Academic Editor: W. Rudolf Seitz

Received: 18 December 2015; Accepted: 16 March 2016; Published: 18 March 2016

**Abstract:** Particle number concentration and particle size are the two key parameters used to characterize exposure to airborne nanoparticles or ultrafine particles that have attracted the most attention. This paper proposes a simple micro aerosol sensor for detecting the number concentration and particle size of ultrafine particles with diameters from 50 to 253 nm based on electrical diffusion charging. The sensor is composed of a micro channel and a couple of planar electrodes printed on two circuit boards assembled in parallel, which thus integrate charging, precipitating and measurement elements into one chip, the overall size of which is  $98 \times 38 \times 25 \text{ mm}^3$ . The experiment results demonstrate that the sensor is useful for measuring monodisperse aerosol particles with number concentrations from 300 to  $2.5 \times 10^4 / \text{cm}^3$  and particle sizes from 50 to 253 nm. The aerosol sensor has a simple structure and small size, which is favorable for use in handheld devices.

**Keywords:** ultrafine particles; number concentration; particle size; micro aerosol sensor

## 1. Introduction

Airborne nanoparticles or ultrafine particles [1,2] distributed in the atmospheric, indoor and industrial environments seriously threaten human health [3,4]. The number concentration and particle size are the two key parameters used to describe exposure to airborne nanoparticles or ultrafine particles. The toxicology research results show that aerosol particles can deposit in different parts of the human respiratory organs [4–7] according to the sizes of the particles. The particles with sizes of less than  $10 \mu\text{m}$  can enter the nasal cavity, those smaller than  $7 \mu\text{m}$  can enter the throat, and if less than  $2.5 \mu\text{m}$ , they enter the lungs. Nanoparticles or ultrafine particles can enter into the human lungs and alveolar area, and further enter into the human blood circulation system [8,9].

Measurements of the size and concentration of aerosol particles mainly involve two kinds of methods based on optical and electrical mechanisms [1]. Optical measurements require a sensor or a particle detector in the detection zone; three of the most widely used sensors are the optical particle counter (OPC) [10], the laser particle counter (LPC) [11], and the condensation particle counter (CPC) [12]. However particle size detection by light scattering loses sensitivity when the size is less than the wavelength of the light or laser used, so OPCs or LPCs can only detect particle sizes larger than  $0.1 \mu\text{m}$  [1]. CPCs can detect particles with sizes less than  $0.1 \mu\text{m}$ , but to date the limitations of their compactness, portability and cost do not allow their application for personal monitoring. The particles with sizes ranging from 1 nm to 300 nm can be detected by electrical measurement. Electrical measurements can be classified into two groups, according to their specific measurement principle. One, exemplified by the Scanning Electrical Mobility Spectrometer (SEMS) [13] or Differential Mobility Analyzer (DMA) [14] techniques, is based on the fact that the electric mobility of charged particles is



Contents lists available at ScienceDirect

## Journal of Aerosol Science

journal homepage: [www.elsevier.com/locate/jaerosci](http://www.elsevier.com/locate/jaerosci)



# Accuracy of electrical aerosol sensors measuring lung deposited surface area concentrations



Ana Maria Todea, Stefanie Beckmann, Heinz Kaminski, Christof Asbach\*

Institut für Energie-und Umwelttechnik e.V. (IUTA), Air Quality & Filtration, Bliersheimer Straße 58-60, 47229 Duisburg, Germany

### ARTICLE INFO

#### Article history:

Received 16 April 2015  
Received in revised form  
6 July 2015  
Accepted 15 July 2015  
Available online 22 July 2015

#### Keywords:

Lung deposited surface area concentration  
Accuracy  
Diffusion chargers  
Monodisperse particles

### ABSTRACT

The accuracy of instruments measuring the alveolar lung deposited surface area (LDSA) concentration based on unipolar diffusion charging has been assessed. Monodisperse particles with sizes between 10 nm and 700 nm were used. The results indicate that the LDSA concentration can be measured with at least  $\pm 30\%$  accuracy for particle sizes between 20 nm and 400 nm. The LDSA concentrations of particles  $< 20$  nm are overestimated and of particles  $> 400$  nm increasingly underestimated by the instruments. The LDSA concentration of 685 nm particles was on average underreported by a factor of approximately 2. LDSA concentrations measured with agglomerated particles were consistently higher than those measured with spherical particles of the same electrical mobility diameter. The accuracy was, however, still mostly within  $\pm 30\%$  for a size range from 20 nm to 400 nm. Due to the strong and increasing deviation for large particles, the use of an appropriate preseperator is recommended when measuring LDSA concentrations.

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## 1. Introduction

The inhalation exposure to airborne nanoscale particles, including engineered nanomaterials needs to be assessed in view of worker protection and risk assessment. The discussion on suitable exposure metrics is still ongoing. While traditionally the particle mass concentrations have been measured for assessing exposure to airborne particles, the number and especially surface area concentration have recently raised increased attention, because they are more sensitive for nanoscale particles and have been reported to be more relevant in terms of possible health effects of insoluble and poorly-soluble particles (Oberdörster, 2000; Peters, Wichmann, Tuch, Heinrich, & Heyder, 1997). While the number concentration and mass concentration of airborne particles are well defined, the surface area concentration of particles lacks a clear definition. The total surface area of a particle may comprise only the outer shell of the particle or also inner surfaces, e.g. of pores in case of a structured particle (compare with BET surface area, Brunauer, Emmet, & Teller, 1938). Therefore, the definition of the surface area is only straightforward for compact, e.g. spherical particles, but more complex for agglomerated or porous particles. As of now, no measurement principle is known, able to measure the surface area concentration of airborne submicron particles according to the aforementioned definitions. BET surface area measurements are only available for powders and the geometric outer surface area can strictly only be determined for spherical particles by measuring their number size distribution and calculating the surface area concentration from it (Bau, Witschger, Gensdarmes, Rastoix, & Thomas, 2010; Ku, 2010; LeBouf et al., 2011). The only instruments available for measuring a

\* Corresponding author.

E-mail address: [asbach@iuta.de](mailto:asbach@iuta.de) (C. Asbach).

# Assessment of Workplace Exposure to Carbon Nanotubes with Personal and Stationary Instruments

Asmus MEYER-PLATH<sup>1</sup>, Barbara SIMONOW<sup>1</sup>, Daniela WENZLAFF<sup>1</sup>, Ana Maria TODEA<sup>2</sup>, Bertrand FAURE<sup>3</sup>, Christof ASBACH<sup>2</sup>, Simon CLAVAGUERA<sup>3</sup>, Nico DZIURWITZ<sup>1</sup>, Martin FIERZ<sup>4</sup>, A.S. FONSECA<sup>5</sup>, M. VIANA<sup>5</sup>, Sabine PLITZKO<sup>1</sup>, Carmen THIM<sup>1</sup>



<sup>1</sup>Federal Institute for Occupational Safety and Health (BAuA), Berlin, Germany,

<sup>2</sup>Institut für Energie- und Umwelttechnik (IUTA), Duisburg, Germany,

<sup>3</sup>Commissariat à l'Energie Atomique et aux Energies Alternatives (CEA), Grenoble, France,

<sup>4</sup>University of Applied Science Northwestern Switzerland, Windisch, Switzerland,

<sup>5</sup>Institute for Environmental Assessment and Water Research (IDÆA-CSIC), Barcelona, Spain.

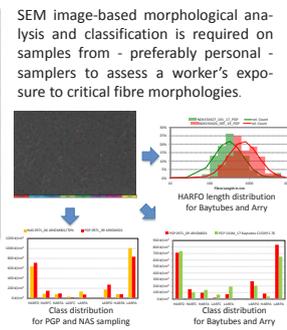
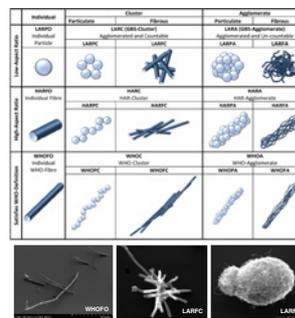
## Introduction

For nanocomposite production, large quantities of CNTs are synthesized and compounded in laboratories and manufacturing sites all over the world. Being a high-aspect material of WHO geometry, CNT and CNF raise fibre-toxicological concerns. In order to identify exposure to critical nanofibre morphologies, detection and quantification techniques for airborne nanofibres are required together with progress on their morphological classification and toxicological testing.

## Scope

The applicability of personal and stationary devices for the characterisation of CNT-containing aerosols was studied. The instruments were exposed to CNT aerosols in the laboratory under controlled conditions. The response of monitors and the collection efficiencies of sampling devices was compared to that of stationary devices. The measurements were conducted using a dedicated exposure chamber capable of providing high concentrations of individualized CNTs. The instruments were also tested in field measurements at workplaces where CNTs were handled. The instrument performance was assessed with respect to a classification of morphologies, an identification of nanotubes and detection sensitivity. The detection limits are discussed in relation to occupational exposure limits for granular and fibrous biopersistent dusts.

## Identification and Classification of Critical Fibre Morphologies



## Stationary Instruments for Exposure Assessment

The selection of stationary devices covered most of the metrics of the personal devices.



## Carbon Nanotube Aerosol Generation and Exposure



The BAuA exposure chamber for instrument testing has a volume of 400 litres and is equipped with 12 aerosol sampling lances. CNT aerosols are generated by Venturi injection of a volumetrically fed free-flowing mixture of glass beads and CNTs. The mixture is separated downstream by a cyclone. Well controlled aerosol concentrations, even exceeding 100000 fibres and agglomerates per cm<sup>3</sup> can be provided for several hours.



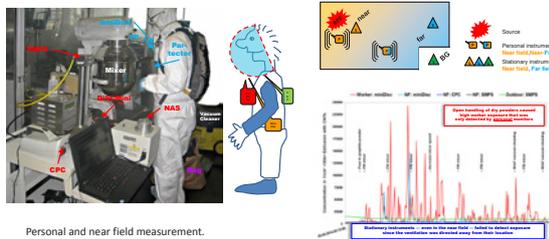
## Personal Instruments for Individual Exposure Assessment

The selection of personal nanoparticle monitors and samplers included commercial as well as prototype devices.



## Workplace Exposure Assessment

Field Measurements were conducted in companies and institutes handling CNTs. For personal exposure assessment, workers were equipped with several devices measuring in the breathing zone. The results were compared to stationary measurements in the near and far field of a potential emission source.



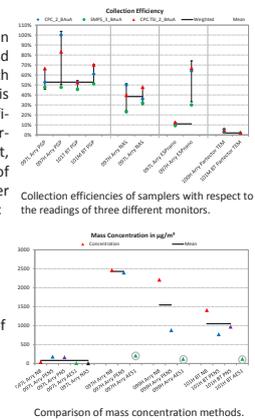
In real-world manufacturing scenarios, local airflow distribution may prevent both near and far field instruments to detect peaks of personal exposure to airborne nanoscale objects. This shows the importance of personal exposure assessment.

## Results

Significant discrepancies were observed between particle concentration determination by CPC-based monitoring and filter or substrate collection with SEM image-based particle counting. The reason is currently unclear. Significant filter membrane inefficiencies are not expected. Possibly, coincidence correction of CPCs kicks in for HAR objects. At present, only EM-based methods allow identification of critical fibre morphologies, but the fibre diameter defines the required EM resolution in a critical way:

SEM Image Size	20 MPixel	20 MPixel	20 MPixel
Area	85 x 64 µm	42.5 x 32 µm	5 x 3.8 µm
Resolution	16.7 nm/pixel	8.3 nm/pixel	1.0 nm/pixel
Images to find 1 CNT for 10 000/m <sup>3</sup>	218 images	817 images	2436 images
Images to find 1 CNT for 100 000/m <sup>3</sup>	23 images	88 images	244 images

For German OE limits for asbestos concentrations of 100 000 fibres/m<sup>3</sup> (tolerance level) and 10 000 fibres/m<sup>3</sup> (acceptance level) 1 000 fibres/m<sup>3</sup> (new acceptance level 2018) compliance testing can become very laborious for thin fibres.



## Acknowledgement

This work is part of the project nanoIndex and was supported by the French National Funding Agency for Research (ANR), the German Federal Ministry of Education and Research (BMBF), the British Technology Strategy Board (TSB) and the Swiss TEMAS AG, under the frame of SIINN, the ERA-NET for a Safe Implementation of Innovative Nanoscience and Nanotechnology.





## Can We Trust Real Time Measurements of Lung Deposited Surface Area Concentrations in Dust from Powder Nanomaterials?

Marcus Levin<sup>1,2\*</sup>, Olivier Witschger<sup>3</sup>, Sébastien Bau<sup>3</sup>, Elzbieta Jankowska<sup>4</sup>, Ismo K. Koponen<sup>2</sup>, Antti J. Koivisto<sup>2</sup>, Per A. Clausen<sup>2</sup>, Alexander Jensen<sup>2</sup>, Kristian Mølhavé<sup>1</sup>, Christof Asbach<sup>5</sup>, Keld A. Jensen<sup>2</sup>

<sup>1</sup> Department of Micro and Nanotechnology, Technical University of Denmark, Kgs. Lyngby, DK-2800, Denmark

<sup>2</sup> National Research Centre for the Working Environment, Lersø Parkallé 105, DK-2100 Copenhagen, Denmark

<sup>3</sup> Institut National de Recherche et de Sécurité, Rue du Morvan, FR-54500 Vandoeuvre les Nancy, France

<sup>4</sup> Centralny Instytut Ochrony Pracy – Państwowy Instytut Badawczy, Zakład Zagrożeń Chemicznych, Pyłowych i Biologicznych, ul Czerniakowska 16, PL-00701 Warsaw, Poland

<sup>5</sup> Institut für Energie- und Umwelttechnik (IUTA), 47229 Duisburg, Germany

### ABSTRACT

A comparison between various methods for real-time measurements of lung deposited surface area (LDSA) using spherical particles and powder dust with specific surface area ranging from 0.03 to 112 m<sup>2</sup> g<sup>-1</sup> was conducted. LDSA concentrations measured directly using Nanoparticle Surface Area Monitor (NSAM) and Aerotrak and were compared to LDSA concentrations recalculated from size distribution measurements using Electrical Low Pressure Impactor (ELPI) and Fast Mobility Particle Sizer (FMPS). FMPS and ELPI measurements were also compared to dust surface area concentrations estimated from gravimetric filter measurements and specific surface areas.

Measurement of LDSA showed very good correlation in measurements of spherical particles ( $R^2 > 0.97$ , Ratio 1.0 to 1.04). High surface area nanomaterial powders showed a fairly reliable correlation between NSAM and Aerotrak ( $R^2$  0.73–0.93) and a material-dependent offset in the ratios (1.04–2.8). However, the correlation and ratio were inconsistent for lower LDSA concentrations. Similar levels of correlation were observed for the NSAM and the FMPS for high surface area materials, but with the FMPS overestimating the LDSA concentration. The ELPI showed good correlation with NSAM data for high LDSA materials ( $R^2$  0.87–0.93), but not for lower LDSA concentrations ( $R^2$  0.50–0.72). Comparisons of respirable dust surface area from ELPI data correlated well ( $R^2 > 0.98$ ) with that calculated from filter samples, but materials-specific exceptions were present.

We conclude that there is currently insufficient reliability and comparability between methods in the measurement of LDSA concentrations. Further development is required to enable use of LDSA for reliable dose metric and regulatory enforcement of exposure.

**Keywords:** Lung deposited surface area; Exposure assessment; Aerosol measurement; Dustiness.

### INTRODUCTION

There is increasing evidence that the pulmonary toxicological response of ambient air-pollution and manufactured nanomaterials may, at least partially, be driven by the specific surface area dose of the test materials (Oberdorster, 2000; Maynard and Kuempel, 2005; Duffin *et al.*, 2007; Jacobsen *et al.*, 2009; Giechaskiel *et al.*, 2009;

Donaldson *et al.*, 2013; Saber *et al.*, 2014). Therefore, it is of high interest to include airborne particle surface area measurements to offer a potentially more biologically relevant metric in exposure and risk assessment. To meet these new developments, it is also of interest to include surface area measurements in dustiness testing; the latter tests are performed to rank the ability of powders to generate dust and used in e.g., new modeling approaches and regulatory exposure assessment (BS EN:15051, 2006; Aitken *et al.*, 2011; Jensen *et al.*, 2015).

The surface area of airborne dust particles may be determined by either direct or indirect methods. There are currently no commercially available real-time methods to determine the geometric surface area concentration of

\* Corresponding author.

Tel.: +4539165274; Fax: +4539165201

E-mail address: mle@nrcwe.dk



## Characterization and Response Model of the PPS-M Aerosol Sensor

Antti Rostedt,<sup>1</sup> Anssi Arffman,<sup>1</sup> Kauko Janka,<sup>2</sup> Jaakko Yli-Ojanperä,<sup>1</sup> and Jorma Keskinen<sup>1</sup>

<sup>1</sup>*Aerosol Physics Laboratory, Department of Physics, Tampere University of Technology, Tampere, Finland*

<sup>2</sup>*Pegasor Oy, Tampere, Finland*

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The Pegasor PPS-M sensor is an electrical aerosol sensor based on diffusion charging and current measurement without particle collection. In this study, the role and effect of each component in the instrument is discussed shortly and the results from a thorough calibration measurements are presented. A comprehensive response model for the operation of the PPS-M sensor was developed based on the calibration results and computational fluid dynamics (CFD) modeling results. The obtained response model, covering the effects of the particle charger, the mobility analyzer, and both diffusion and inertial losses, was tested in the laboratory measurements with polydisperse test aerosols, where a good correlation between the model and the measured results was found.

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### INTRODUCTION

The concern about the health effects of the exposure to fine particles has led to an increasing request for aerosol measurement and monitoring. Aerosol concentration measurement may be realized for various particle properties, such as particle number, mass, surface area, and volume (Kulkarni et al. 2011). Real time aerosol concentration instruments are usually based on the electrical or optical detection techniques. The optical instruments typically utilize light scattering or absorption of particles, while the electrical instruments are most commonly based on charging of the particles and subsequent measurement of the charge carried by the particles as an electrical current.

Particle charging is usually accomplished by unipolar diffusion chargers based on corona discharge, as reviewed, e.g., by Marquard et al. (2006) and Intra and Tippayawong (2009). Because of the simplicity, one of the most straightforward ways to produce an electrical aerosol detector is to combine unipolar diffusion charger with a faraday cup electrometer. The measured quantity is electrical current, which is related to

the particle number concentration and particle size. Ntziachristos et al. (2004) demonstrated such instrument for the real time monitoring of active surface area of particles emitted by a diesel engine. Fissan et al. (2007) introduced a similar instrument with a varying charging efficiency for the monitoring of the lung deposited particle surface area. Recent development of these diffusion charger-based instruments has focused on minimizing the size of the instruments to produce handheld instruments. The AeraSense Nanotracker (Marra et al. 2009) and Matter Aerosol DiSCmini (Fierz et al. 2011) are good examples of such instruments, the latter being even able to provide information on the average particle size of the measured aerosol. To make the instrument even smaller, micro-electromechanical (MEMS) techniques have been used by Lee et al. (2011).

All of the electrical instruments mentioned above are based on the collection of the particles after charging. Lehtimäki (1983) demonstrated electrical aerosol instrument without particle collection, based on measuring the charge escaping the charger with the charged particles. The idea has also been applied by Rostedt et al. (2009b). Recently, Fierz et al. (2014) described a non-collecting instrument based on induced current measurement.

The Pegasor PPS-M (Pegasor Oy, Tampere, Finland) sensor treated in this article is based on the escaping charge principle. The basic principle of the sensor has been presented by Lanki et al. (2011). Application of the sensor to engine exhaust measurements has been described by Ntziachristos et al. (2011, 2013). In this article, we present the first detailed calibration of the instrument, and a comprehensive model for the response of the instrument as a function of particle size together with laboratory test measurements.

### SENSOR COMPONENTS AND OVERALL RESPONSE

The operation of the PPS-M sensor is based on electrical charging and detection of the charged aerosol particles. The design combines a sheath air-assisted corona charger with an

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Received 17 April 2014; accepted 7 July 2014.

Address correspondence to Antti Rostedt, Aerosol Physics Laboratory, Department of Physics, Tampere University of Technology, P.O. Box 692, Tampere FI-33101, Finland. E-mail: antti.rostedt@tut.fi

RESEARCH ARTICLE

# Charge-based personal aerosol samplers

Martin Fierz, Alejandro Keller, and Heinz Burtscher

University of Applied Sciences Northwestern Switzerland, Windisch, Switzerland

## Abstract

There are several good reasons to use personal monitors for exposure control and health effect studies. But current personal monitoring methods are either not sensitive enough to measure typical ambient concentrations, work offline (masking short exposures to high concentrations), and/or require trained personnel to analyze the data, which makes them difficult to use. For this reason, we propose the use of a diffusion charging sensor as an online personal monitoring method, and present a miniaturized device (45 × 80 × 200 mm, 770 g) that works on this principle. Our device has a high time resolution and covers typically encountered ambient concentration ranges. It can measure very low particle concentrations of a few hundred particles per cubic centimeter even for ultrafine particles (i.e., two to three orders of magnitude more sensitive than rival technologies), while the upper detection limit is 1 million particles/cm<sup>3</sup>, which hardly ever occurs in ambient settings. While other methods measure a fixed quantity, the response of our device can be tuned to be proportional to the particle diameter to the power of  $x$ , with at least  $0.3 \leq x \leq 1.35$ . This opens up the possibility of giving more weight to smaller particles, which is a key feature, since on a per-mass basis, smaller solid particles have been shown to be more toxic than larger ones.

**Keywords:** Particulate matter; exposure; personal; monitoring; diffusion charging

## Introduction

Personal exposure monitoring serves two main purposes: In the field of occupational/industrial health, personal monitoring is used to measure the exposure of workers on a regular basis and to verify that no unwanted exposure occurs. For this application, it is desirable that the personal monitor is an online instrument; it can then warn exposed workers so that they can leave a polluted area immediately. Additionally, the instrument must be very robust and simple to use for this type of daily routine measurement. The prime example of personal monitoring in occupational health is the nuclear industry with the dosimeter. It is worth noting that nanoparticle detection always requires pumping air through a detection unit, and even for low flow rates (e.g., 1 L/min) this requirement makes personal aerosol samplers heavier and larger than their counterparts measuring radioactivity.

The second major application of personal monitoring is in studies of health effects: In vitro and in vivo studies are both necessary tools for studying toxicity; however, the link between in vitro or rodent studies and the human is not always straightforward. With a personal monitor, a direct link between exposure and effect (e.g., lung function) can be established. In this case, an online instrument is also

desirable: If the dose-response relationship is nonlinear, then a simple average may be misleading, and a more detailed analysis of the exposition is necessary. Figure 1 shows two expositions with the same average value, but a very different exposition profile. A priori it is not clear at all

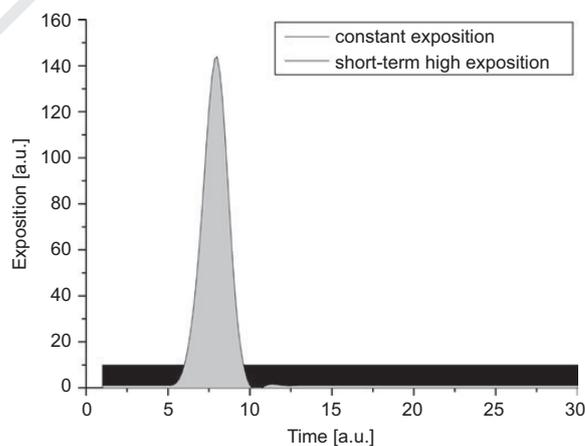


Figure 1. Two different exposition profiles with the same average exposition—is the response identical?

Address for Correspondence: Dr. Martin Fierz, Institut für Aerosol- und Sensortechnologie, Fachhochschule Nordwestschweiz, 5210 Windisch, Switzerland. E-mail: martin.fierz@fnw.ch

(Received 27 March 2009; accepted 02 April 2009)

ISSN 0895-8378 print/ISSN 1091-7691 online © 2009 Informa UK Ltd  
DOI: 10.1080/08958370902942632

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Journal of Aerosol Science

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## Comparability of mobility particle sizers and diffusion chargers



Heinz Kaminski<sup>a</sup>, Thomas A.J. Kuhlbusch<sup>a,f</sup>, Stefan Rath<sup>b</sup>, Uwe Götz<sup>b</sup>,  
Manfred Sprenger<sup>b</sup>, Detlef Wels<sup>b</sup>, Jens Polloczek<sup>b</sup>, Volker Bachmann<sup>c</sup>,  
Nico Dziurawitz<sup>c</sup>, Heinz-Jürgen Kiesling<sup>d</sup>, Angelika Schwiigelshohn<sup>d</sup>,  
Christian Monz<sup>e</sup>, Dirk Dahmann<sup>e</sup>, Christof Asbach<sup>a,\*</sup>

<sup>a</sup> Institute of Energy and Environmental Technology (IUTA) e.V., Air Quality & Sustainable Nanotechnology unit, Bliersheimer Str. 60, Germany

<sup>b</sup> BASF SE, 67063 Ludwigshafen, Germany

<sup>c</sup> Federal Institute of Occupational Safety and Health (BAuA), Nöldnerstr. 40–42, 10317 Berlin, Germany

<sup>d</sup> Bayer Technology Services GmbH, 51368 Leverkusen, Germany

<sup>e</sup> Institute for the Research on Hazardous Substances (IGF), Waldring 97, 44789 Bochum, Germany

<sup>f</sup> Center for NanoIntegration Duisburg-Essen (CENIDE), 47057 Duisburg, Germany

### ARTICLE INFO

#### Article history:

Received 25 July 2012

Received in revised form

4 October 2012

Accepted 15 October 2012

Available online 15 November 2012

#### Keywords:

SMPS

FMPS

Diffusion charger

CPC

Electrical mobility analysis

### ABSTRACT

A large study on the comparability of various aerosol instruments was conducted. The study involved altogether 24 instruments, including eleven scanning, sequential and fast mobility particle sizers (five Grimm SMPS+C, three TSI SMPS and three FMPS) with different settings and differential mobility analyzers (DMAs), twelve instruments based on unipolar diffusion charging to determine size integrated concentrations and in some cases mean particle size (five miniDiSCs of the University of Applied Sciences and Arts Northwestern Switzerland, four Philips Aerasense nanoTracers, two TSI Nanoparticle Surface Area Monitors and one Grimm nanoCheck) and one TSI ultrafine condensation particle counter (UCPC). All instruments were simultaneously challenged with particles of various sizes, concentrations and morphologies. All measurement results were compared with those from a freshly calibrated SMPS for size distributions and the UCPC for number concentration. In general, all SMPSs showed good comparability with particularly the sizing agreeing to within a few percent. Differences in the determined number concentration were somewhat more pronounced, but the largest deviations could be tracked back to the use of an older software version. The comparability of the FMPSs was shown to be lower, with discrepancies on the order of  $\pm 25\%$  for sizing and  $\pm 30\%$  for total concentrations. The discrepancies between FMPSs and the internal reference SMPS seemed to be influenced by particle size and morphology. Total number and/or lung deposited surface area concentrations measured with unipolar diffusion charger based instruments generally agreed to within  $\pm 30\%$  with the internal references (CPC for number concentrations; lung deposited surface area derived from SMPS measurements), as long as the particle size distributions of the test aerosols were within the specified limits for the instruments. When the upper size limit was exceeded, deviations of up to several hundred percent were detected.

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\* Corresponding author. Tel.: +49 2065 418 209; fax: +49 2065 418 211.

E-mail address: [asbach@iuta.de](mailto:asbach@iuta.de) (C. Asbach).

# Comparability of Portable Nanoparticle Exposure Monitors\*

CHRISTOF ASBACH<sup>1</sup>, HEINZ KAMINSKI<sup>1</sup>, DANIEL VON BARANY<sup>1</sup>,  
THOMAS A.J. KUHLBUSCH<sup>1</sup>, CHRISTIAN MONZ<sup>2</sup>, NICO DZIUIROWITZ<sup>3</sup>,  
JOHANNES PELZER<sup>4</sup>, KATJA VOSSEN<sup>4</sup>, KNUT BERLIN<sup>5</sup>, SILVIO  
DIETRICH<sup>5</sup>, UWE GÖTZ<sup>6</sup>, HEINZ-JÜRGEN KIESLING<sup>7</sup>, RUDOLF  
SCHIERL<sup>8</sup> and DIRK DAHMANN<sup>2</sup>

<sup>1</sup>Institute of Energy and Environmental Technology, 47229 Duisburg, Germany; <sup>2</sup>Institute for the Research on Hazardous Substances (IGF), 44789 Bochum, Germany; <sup>3</sup>Federal Institute for Occupational Safety and Health (BAuA), Berlin, Germany; <sup>4</sup>Institute for Occupational Safety and Health of the German Social Accident Insurance (IFA), 53757 Sankt Augustin, Germany; <sup>5</sup>Bayrisches Landesamt für Gesundheit und Lebensmittelsicherheit (LGL), 91058 Erlangen, Germany; <sup>6</sup>BASF SE, 67063 Ludwigshafen, Germany; <sup>7</sup>Bayer Technology Services, 51368 Leverkusen, Germany; <sup>8</sup>Institute for Occupational, Social and Environmental Medicine, University Munich, 80336 Munich, Germany

Received 05 April 2012; in final form 10 March 2012

Five different portable instrument types to monitor exposure to nanoparticles were subject to an intensive intercomparison measurement campaign. Four of them were based on electrical diffusion charging to determine the number concentration or lung deposited surface area (LDSA) concentration of airborne particles. Three out of these four also determined the mean particle size. The fifth instrument type was a handheld condensation particle counter (CPC). The instruments were challenged with three different log-normally distributed test aerosols with modal diameters between 30 and 180 nm, varying in particle concentration and morphology. The CPCs showed the highest comparability with deviations on the order of only  $\pm 5\%$ , independent of the particle sizes, but with a strictly limited upper number concentration. The diffusion charger-based instruments showed comparability on the order of  $\pm 30\%$  for number concentration, LDSA concentration, and mean particle size, when the specified particle size range of the instruments matched the size range of the aerosol particles, whereas significant deviations were found when a large amount of particles exceeded the upper or lower detection limit. In one case the reported number concentration was even increased by a factor of 6.9 when the modal diameter of the test aerosol exceeded the specified upper limit of the instrument. A general dependence of the measurement accuracy of all devices on particle morphology was not detected.

**Keywords:** CPC; diffusion charger; exposure; nanoparticle; number concentration; surface area concentration

## INTRODUCTION

The use of nanomaterials has significantly increased over the recent years. According to the Woodrow

Wilson Database (2011), the number of nanotechnological products has risen by  $>520\%$  between March 2006 and March 2011. Nanoparticles are considered as important building blocks for nanotechnologies (Rotello, 2004), but concerns have been raised about possible adverse health effects of nanoparticles (Oberdörster *et al.*, 2005). A risk may only arise from nanomaterials, such as nanoparticles, if exposure and hazard exist simultaneously (Krug and Klug, 2008).

\*Author to whom correspondence should be addressed.

Tel: +49 2065 418 209; fax: +49 2065 418 211

\*based on presentations at the INRS Symposium on Risks of Nanoparticles and Nanomaterials, Nancy, France, April 2011.



## Comparative Testing of a Miniature Diffusion Size Classifier to Assess Airborne Ultrafine Particles Under Field Conditions

Reto Meier, Katherine Clark, and Michael Riediker

*Institute for Work and Health, University of Lausanne and University of Geneva, Lausanne, Switzerland*

Miniature diffusion size classifiers (miniDiSC) are novel handheld devices to measure ultrafine particles (UFP). UFP have been linked to the development of cardiovascular and pulmonary diseases; thus, detection and quantification of these particles are important for evaluating their potential health hazards. As part of the UFP exposure assessments of highway maintenance workers in western Switzerland, we compared a miniDiSC with a portable condensation particle counter (P-TRAK). In addition, we performed stationary measurements with a miniDiSC and a scanning mobility particle sizer (SMPS) at a site immediately adjacent to a highway. Measurements with miniDiSC and P-TRAK correlated well (correlation of  $r = 0.84$ ) but average particle numbers of the miniDiSC were 30%–60% higher. This difference was significantly increased for mean particle diameters below 40 nm. The correlation between the miniDiSC and the SMPS during stationary measurements was very high ( $r = 0.98$ ) although particle numbers from the miniDiSC were 30% lower. Differences between the three devices were attributed to the different cutoff diameters for detection. Correction for this size dependent effect led to very similar results across all counters. We did not observe any significant influence of other particle characteristics. Our results suggest that the miniDiSC provides accurate particle number concentrations and geometric mean diameters at traffic-influenced sites, making it a useful tool for personal exposure assessment in such settings.

[Supplementary materials are available for this article. Go to the publisher's online edition of *Aerosol Science and Technology* to view the free supplementary files.]

### INTRODUCTION

Exposure to particulate matter (PM) is associated with adverse cardiovascular and pulmonary health effects (Pope et al.

1995; Brook et al. 2010). Traffic emissions are an important source of PM and traffic exposure has been directly linked to adverse health outcomes (Peters et al. 2004; Riediker et al. 2004). Recent publications suggest that ultrafine particles (UFP) play a critical role in triggering oxidative stress and inflammatory processes that provoke atherogenic and thrombotic effects and influence the autonomous nervous system (Schmid et al. 2009; Schneider et al. 2010; Peters et al. 2011). Detection and quantification of these particles is important and a first step to characterizing potential health hazards. UFP are usually measured in number-concentrations, as they do not contain significant mass for gravimetric quantification. State of the art UFP measurements are performed with condensation particle counters (CPCs) (Bricard et al. 1976). The basic working principle of a CPC is to condensate alcohol or water vapor on particles and to detect these droplets by light scattering. Miniaturized portable CPC devices, such as the P-TRAK, are used to measure UFP under real-world conditions in industry or environmental research. Recently, a miniature diffusion size classifier (miniDiSC) has been developed at the University of Applied Sciences Northwestern Switzerland. The working principle of this new handheld device is to label particles in a standard positive unipolar charger and to detect them in two electrometer stages: in a diffusion stage and a filter stage where the particles induce an electrical current (Fierz et al. 2011). In addition to number counts, the two detection stages allow an estimation of the geometric mean particle diameter. A laboratory comparison (Dahl et al. 2009) suggested that the miniDiSC correlates well to an SMPS; however, no studies compared these devices under real world conditions such as personal exposure campaigns.

With this comparative study, we wanted to assess how measurements of this new generation device correspond to the widely used CPCs and how useful they are for personal exposure assessment. Although the working principle differs from a CPC we expected to measure similar particle numbers. To compare UFP numbers of a miniDiSC with conventional UFP counters, we made simultaneous measurements with (1) a miniDiSC and a P-TRAK while following highway maintenance workers in western Switzerland; and (2) a miniDiSC, a P-TRAK

Received 30 March 2012; accepted 1 August 2012.

The authors thank the Swiss Federal Road Office for administrative support, the maintenance workers for their kind cooperation, and Martin Fierz for providing a miniDiSC. This study was funded by a grant from the Swiss National Science Foundation; the Grimm SMPS was partly sponsored by Loterie Romande.

Address correspondence to Michael Riediker, Institute for Work and Health, Rue du Bugnon 21, Lausanne CH-1011, Switzerland. E-mail: michael.riediker@hospvd.ch



## Comparison of Measured Particle Lung-Deposited Surface Area Concentrations by an AeroTrak 9000 Using Size Distribution Measurements for a Range of Combustion Aerosols

Anna Leavey,<sup>1</sup> Jiaxi Fang,<sup>1</sup> Manoranjan Sahu,<sup>2</sup> and Pratim Biswas<sup>1</sup>

<sup>1</sup>*Aerosol and Air Quality Research Laboratory, Department of Energy, Environmental and Chemical Engineering, Washington University in St. Louis, St. Louis, Missouri, USA*

<sup>2</sup>*Advanced Energy Technology Initiative, University of Illinois at Urbana-Champaign, Champaign, Illinois, USA*

Surface area in addition to mass concentration is increasingly being emphasized as an important metric representing potential adverse health effects from exposure to inhaled particles. Lung-deposited surface area (SA) concentrations for a variety of aerosols: coal, biomass, cigarette, incense, candle, and TiO<sub>2</sub> were measured using an AeroTrak 9000 (TSI Incorporated) and compared with those calculated from number size distributions from a scanning mobility particle sizer (SMPS). Three methodologies to compute the SA concentrations using the International Commission on Radiological Protection's (ICRP) Lung Deposition model and an SMPS were compared. The first method calculated the SA from SMPS size distributions, while the second method used lognormal size distribution functions. A third method generated a closed-form equation using the method of moments. All calculated SMPS SA data against which the measured SA data were compared were generated using the first method only; however, the SA concentrations calculated from each of the three methods demonstrated strong correlations with each other. Overall, results between measured and calculated lung-deposited SA indicated strong positive linear associations ( $R^2$  0.78 - > 0.99), moderately dependent on the type of aerosol. In all cases, the measured SA concentrations slightly underestimated those calculated from the SMPS data, with the exception of coal combustion particles. Although some dependency on aerosol material exists, the instrument measuring lung-deposited SA demonstrated consistent reliability across a range of concentrations for a range of materials. For optimal results however, applying a correction factor (CF) before taking the instrument to the field is recommended.

### INTRODUCTION

Indoor air quality issues have been receiving increasing attention over recent years, and it is estimated that around 3 billion people worldwide are exposed to harmful emissions from indoor cooking systems (Legros et al. 2009). In fact, the approximately 2 million excess deaths each year from lung-related illnesses such as Chronic Obstructive Pulmonary Disorder (COPD) and acute respiratory infections such as pneumonia are attributed to direct exposure to black carbon and other indoor air pollutants. The majority of those affected are women and children (Tsai et al. 2000; Legros et al. 2009). These emissions may also contribute significantly to global climate change (WHO 2008; Jacobson 2009). Mass-based dose parameters, especially PM<sub>2.5</sub>, have been used most often to characterize cookstove particle emissions in the field (Tsai et al. 2000; Chengappa et al. 2007; Dutta et al. 2007; Masera et al. 2007; Ryhl-Svendson et al. 2010; Zhang et al. 2012b). However, in recent years, it is the smaller size fraction of the emitted aerosol that is increasingly implicated in adverse health effects. Small particles have large surface areas (SAs) compared to larger particles for a given mass; therefore, their presence may be captured more reliably by a SA metric compared to traditional mass measurements.

Particles that deposit in the respiratory tract can cause adverse health effects. Using the particle size distribution and the International Commission on Radiological Protection's (ICRP) lung deposition curves (ICRP 1994), the fraction of particles depositing in the lung can be estimated. Aerosol size distribution measurement instruments have been in use for many decades at the laboratory scale (Liu et al. 1974; Knutson and Whitby 1975a, 1975b) and to a lesser extent in research field studies (McMurry and Zhang 1989; Covert et al. 1996; Woo et al. 2001). Only now are more robust size distribution measurement instruments being developed that will find broad scale use in the field (Qi and Kulkarni 2012). Thus, while the size distribution is a comprehensive descriptor, the SA concentration is an

Received 16 September 2012; accepted 22 April 2013.

This work was supported by a grant from the McDonnell Academy Global Energy and Environment Partnership. Partial support through a contract with Pegasus, Inc. funded by the USEPA is gratefully acknowledged.

Address correspondence to Pratim Biswas, Department of Energy, Environmental and Chemical Engineering, Washington University in St. Louis, One Brookings Drive, Campus Box 1180, St. Louis, MO 63130, USA. E-mail: pbiswas@wustl.edu

# Comparison of the DiSCmini Aerosol Monitor to a Handheld Condensation Particle Counter and a Scanning Mobility Particle Sizer for Submicrometer Sodium Chloride and Metal Aerosols

Jessica B. Mills, Jae Hong Park, and Thomas M. Peters

Department of Occupational and Environmental Health, University of Iowa, Iowa City, Iowa

*We evaluated the robust, lightweight DiSCmini (DM) aerosol monitor for its ability to measure the concentration and mean diameter of submicrometer aerosols. Tests were conducted with monodispersed and polydispersed aerosols composed of two particle types (sodium chloride [NaCl] and spark-generated metal particles, which simulate particles found in welding fume) at three different steady-state concentration ranges (Low,  $<10^3$ ; Medium,  $10^3$ – $10^4$ ; and High,  $>10^4$  particles/cm<sup>3</sup>). Particle number concentration, lung deposited surface area (LDSA) concentration, and mean size measured with the DM were compared with those measured with reference instruments, a scanning mobility particle sizer (SMPS), and a handheld condensation particle counter (CPC). Particle number concentrations measured with the DM were within 16% of those measured by the CPC for polydispersed aerosols. Poorer agreement was observed for monodispersed aerosols ( $\pm 35\%$  for most tests and  $+101\%$  for 300-nm NaCl). LDSA concentrations measured by the DM were 96% to 155% of those estimated with the SMPS. The geometric mean diameters measured with the DM were within 30% of those measured with the SMPS for monodispersed aerosols and within 25% for polydispersed aerosols (except for the case when the aerosol contained a substantial number of particles larger than 300 nm). The accuracy of the DM is reasonable for particles smaller than 300 nm, but caution should be exercised when particles larger than 300 nm are present. [Supplementary materials are available for this article. Go to the publisher's online edition of the Journal of Occupational and Environmental Hygiene for the following free supplemental resources: manufacturer-reported capabilities of instruments used, and information from the SMPS measurements for polydispersed test particles.]*

**Keywords** CPC, DiSCmini, nanoparticles, SMPS, welding fume

Correspondence to: Thomas M. Peters, University of Iowa, 102 IREH: Oakdale Campus, Iowa City, Iowa 52242; e-mail: Thomas-m-peters@uiowa.edu.

## INTRODUCTION

Worker exposure to submicrometer aerosols is a major concern in many occupations and particularly so in welding. Welding fume typically consists of high concentrations of metal particles smaller than 300 nm,<sup>(1)</sup> which have been referred to as very fine particles.<sup>(2)</sup> The small particle size and presence of metals such as manganese, chromium, and cadmium contribute to the toxicity of welding fume.<sup>(3)</sup> Welding fume exposures have been associated with a variety of adverse health effects, including adverse pulmonary responses,<sup>(4)</sup> impaired neurological function,<sup>(5)</sup> lung cancer,<sup>(6)</sup> and cardiovascular disease.<sup>(7)</sup>

Personal monitoring with a direct-reading instrument (DRI) can be useful in associating high exposures to a contaminant with a particular task. A worker's time-weighted average exposure may then be lowered by modifying worker behavior, implementing engineering controls, or requiring personal protective equipment for high-exposure tasks. Photometers have previously been used to perform task-based exposure monitoring, such as in the assessment of personal exposure to dust among swine barn workers.<sup>(8)</sup> More recently, photometers have been recommended for use in identifying sources of nanomaterials in production facilities<sup>(9)</sup> and to monitor personal exposures to carbon nanotube-containing composite material from surface grinding.<sup>(10)</sup> Photometers are, however, limited to measuring particles larger than 300 nm. Consequently, they are inadequate for use in personal monitoring of the very fine particles that typically dominate welding fume exposures.

A variety of instruments can be used to measure the number concentration and size of very fine particles (examples in online Table S1). Traditionally, the size distribution of submicrometer aerosols has been measured with a scanning



## Design, Calibration, and Field Performance of a Miniature Diffusion Size Classifier

M. Fierz, C. Houle, P. Steigmeier, and H. Burtscher

*University of Applied Sciences Northwestern Switzerland, Windisch, Switzerland*

Due to the increasingly widespread use of engineered nanoparticles and the increasing number of persons handling them, there is a need to monitor the personal exposure of these persons. Current gravimetric and optic methods are rather insensitive for nanoparticles (<~100 nm), and therefore not suitable for this task. To help solve this problem, we have miniaturized an instrument capable of measuring nanoparticles developed earlier by our group; the diffusion size classifier (DiSC). The instrument is now handheld (4 × 9 × 18 cm), and can easily be used for personal exposure monitoring, opening up applications for workplace exposure monitoring (for engineered nanoparticles but also for traditional workplace aerosols such as welding fumes or combustion exhaust) and medical studies. The DiSC measures the particle number concentration and the average particle diameter of an aerosol, however, like most simple instruments, it is nonspecific, i.e., it detects all nanoparticles and cannot distinguish between background aerosol and specific engineered nanoparticles. In this paper, we first present the instrument design and the calibration procedure for the miniature DiSC, followed by some results from comparisons with traditional aerosol instruments in the field.

### 1. INTRODUCTION

Engineered nanoparticles have novel properties (electronic, optic, catalytic, etc.) due to their small size. Besides some traditional uses (TiO<sub>2</sub> particles in paints, cosmetics and sunscreens, carbon black as additive for tires or printer toner), a lot of new applications have been proposed or realized which exploit the specific properties of nanoparticles—for example their higher catalytic efficiency (e.g., cerium oxide particles as fuel-borne catalysts), increased permeability through biological barriers (drug delivery), different optical properties (tunable absorption

by particle size changes), and so on. Nanoparticles are being incorporated into composites to improve material properties; in particular, carbon nanotubes with their excellent electrical conductivity and mechanical strength have promising applications. Silver nanoparticles have toxic properties which can be exploited in the medical sector but also in consumer products such as clothing that will not smell of sweat, or paints for building facades that have antialgal and antifungal properties.

Along with the larger number of available engineered nanoparticles and their applications, their potential detrimental health effects have received more attention. Airborne nanoparticles appear most critical, because of their easy uptake pathway through airways and lung. In particular, people handling these materials or working in plants where nanoparticles are being fabricated or processed are at risk of exposure. Because leaks in such plants are likely to be localized, stationary measurement equipment might not be at the right location to detect a leak, and a wearable device to measure the personal exposure is preferable. The nuclear industry has developed a tool for this purpose: the dosimeter. It is worn by potentially exposed persons, and their dose is monitored regularly. The need for similar tools in the nanoparticle industry is clear (Nel et al. 2006), and the development of a universal aerosol sampler for airborne nanostructure materials has been proposed as one of five big challenges on the road to safe nanotechnology, namely, such a universal sampler should be able to measure number, surface, and mass concentrations simultaneously, since it is not obvious which metric should be employed (Maynard et al. 2006). Toxicological studies suggest that particle surface area is best related to health effects (Aitken et al. 2006). Microscopically, this can be intuitively understood, at least for biopersistent particles: the particle surface is the area where interactions with the body take place, and it thus is to be expected that health effects scale with available particle surface area.

An ideal personal sampler would be robust, small, light, and cheap; it should be a direct-reading instrument to provide an alarm capability and finally it should be able to distinguish the ubiquitous background aerosol from the specific engineered nanoparticles in question (e.g., carbon nanotubes that may pose similar health risks as asbestos fibers). Unfortunately, this wish list is far from today's reality: a distinction between background

Received 27 May 2010; accepted 12 July 2010.

We thank Jürg Brunner and Susanne Schlatter of Umwelt- und Gesundheitsamt (UGZ) Stadt Zürich for their cooperation in the field measurements, and for sharing their CPC and SMPS data, and Christoph Hüglin (EMPA) for sharing 1 year of SMPS data of the Swiss NABEL network. We acknowledge funding by the Forschungsfonds Aargau.

Address correspondence to M. Fierz, University of Applied Sciences Northwestern Switzerland, 5210 Windisch, Switzerland. E-mail: martin.fierz@fnw.ch

# Determining the count median diameter of nanoaerosols by simultaneously measuring their number and lung deposited surface area concentrations

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*Brief communication*

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S. Bau<sup>1</sup>, O. Witschger<sup>1</sup>, F. Gensdarmes<sup>2</sup> and D. Thomas<sup>3</sup>

<sup>1</sup> *Institut National de Recherche et de Sécurité, Laboratoire de Métrologie des Aérosols, Rue du Morvan CS 60027, 54519 Vandoeuvre, France*

[sebastien.bau@inrs.fr](mailto:sebastien.bau@inrs.fr)

<sup>2</sup> *Institut de Radioprotection et de Sûreté Nucléaire (IRSN), PSN-RES/SCA/LPMA, Saclay, Gif-sur-Yvette, 91192, France.*

<sup>3</sup> *Laboratoire de Réactions et Génie des Procédés – Université de Lorraine, 1, rue Grandville - BP 20451, 54001 Nancy Cedex, France*

*Keywords: nanoaerosol; count median diameter; lung-deposited surface area concentration*

## Abstract

Due to the increasing use of nanomaterials in research and product development, it is probable that the number of situations of occupational exposure to them is also rising. The same is true for the number of workers. Although current research in nanotoxicology is far from conclusive, it is clear that relying on mass concentration and chemical composition alone is not appropriate in all cases and alternative measurement methods and approaches need to be developed.

In this work, we propose a method based on simultaneous size-integrated measurements of two particle concentrations (number and lung-deposited surface area, CNC/NSAM), and on the estimation of the average size of potentially inhaled particles from the combination of these measurements. The proposed method could be part of a measurement strategy that is practical as it would use field-portable, commercially available aerosol instruments. In the absence of instruments providing real-time size-resolved measurements, this original approach can be carried out as considering that the ratio of these concentrations is a monotonous function of particle size. Indeed, the latter function depends only on the geometric standard deviation of airborne particle number size distribution, assumed to be lognormal.

Compared to SMPS data for polydisperse aerosols having three chemical natures with count median diameters ranging from 64 to 177 nm, experimental results were obtained with acceptable relative discrepancies of  $\pm 30\%$ . Though the method proposed is less accurate than traditional instruments like SMPS, it can be used for workplace air monitoring or as a screening tool to detect the presence of airborne nanoparticles.



Article

# Development and Validation of a UAV Based System for Air Pollution Measurements

Tommaso Francesco Villa <sup>1</sup>, Farhad Salimi <sup>2</sup>, Kye Morton <sup>3</sup>, Lidia Morawska <sup>1,\*</sup> and Felipe Gonzalez <sup>3</sup>

<sup>1</sup> International Laboratory for Air Quality and Health (ILAQH), Queensland University of Technology (QUT), 2 George St, Brisbane QLD 4000, Australia; [tf.villa@hdr.qut.edu.au](mailto:tf.villa@hdr.qut.edu.au)

<sup>2</sup> Menzies Institute for Medical Research, University of Tasmania, Hobart, Tasmania 7000, Australia; [farhad.salimi@utas.edu.au](mailto:farhad.salimi@utas.edu.au)

<sup>3</sup> Australian Research Centre for Aerospace Automation (ARCAA), Queensland University of Technology (QUT), 2 George St, Brisbane QLD 4000, Australia; [kye.morton@hdr.qut.edu.au](mailto:kye.morton@hdr.qut.edu.au) (K.M.); [felipe.gonzalez@qut.edu.au](mailto:felipe.gonzalez@qut.edu.au) (F.G.)

\* Correspondence: [l.morawska@qut.edu.au](mailto:l.morawska@qut.edu.au); Tel.: +61-7-3138-2616

Academic Editor: Hans Tømmervik

Received: 23 November 2016; Accepted: 19 December 2016; Published: 21 December 2016

**Abstract:** Air quality data collection near pollution sources is difficult, particularly when sites are complex, have physical barriers, or are themselves moving. Small Unmanned Aerial Vehicles (UAVs) offer new approaches to air pollution and atmospheric studies. However, there are a number of critical design decisions which need to be made to enable representative data collection, in particular the location of the air sampler or air sensor intake. The aim of this research was to establish the best mounting point for four gas sensors and a Particle Number Concentration (PNC) monitor, onboard a hexacopter, so to develop a UAV system capable of measuring point source emissions. The research included two different tests: (1) evaluate the air flow behavior of a hexacopter, its downwash and upwash effect, by measuring air speed along three axes to determine the location where the sensors should be mounted; (2) evaluate the use of gas sensors for CO<sub>2</sub>, CO, NO<sub>2</sub> and NO, and the PNC monitor (DISCmini) to assess the efficiency and performance of the UAV based system by measuring emissions from a diesel engine. The air speed behavior map produced by test 1 shows the best mounting point for the sensors to be alongside the UAV. This position is less affected by the propeller downwash effect. Test 2 results demonstrated that the UAV propellers cause a dispersion effect shown by the decrease of gas and PN concentration measured in real time. A Linear Regression model was used to estimate how the sensor position, relative to the UAV center, affects pollutant concentration measurements when the propellers are turned on. This research establishes guidelines on how to develop a UAV system to measure point source emissions. Such research should be undertaken before any UAV system is developed for real world data collection.

**Keywords:** UAV remote gas sensing; downwash effect; air quality; hexacopter; optical sensor; air pollution; particle number concentration monitor

# Enabling Low-Cost Particulate Matter Measurement for Participatory Sensing Scenarios

Matthias Budde, Rayan El Masri, Till Riedel, and Michael Beigl  
{budde,rmasri,riedel,michael}@teco.edu

TECO, Karlsruhe Institute of Technology (KIT)  
Karlsruhe, Germany

**Abstract.** This paper presents a mobile, low-cost particulate matter sensing approach for the use in Participatory Sensing scenarios. It shows that cheap commercial off-the-shelf (COTS) dust sensors can be used in distributed or mobile personal measurement devices at a cost one to two orders of magnitude lower than that of current hand-held solutions, while reaching meaningful accuracy. We conducted a series of experiments to juxtapose the performance of a gauged high-accuracy measurement device and a cheap COTS sensor that we fitted on a Bluetooth-enabled sensor module that can be interconnected with a mobile phone. Calibration and processing procedures using multi-sensor data fusion are presented, that perform very well in lab situations and show practically relevant results in a realistic setting. An on-the-fly calibration correction step is proposed to address remaining issues by taking advantage of co-located measurements in Participatory Sensing scenarios. By sharing few measurement across devices, a high measurement accuracy can be achieved in mobile urban sensing applications, where devices join in an ad-hoc fashion. A performance evaluation was conducted by co-locating measurement devices with a municipal measurement station that monitors particulate matter in a European city, and simulations to evaluate the on-the-fly cross-device data processing have been done.

**Categories and Subject Descriptors:** B.4.M [Hardware]: Input/Output and Data Communications – *Miscellaneous*; H.1.2 [Information Systems]: Models and Principles – *User/Machine Systems*

**General Terms:** Design; Experimentation; Measurement; Reliability

**Keywords:** Novel Sensing; Particulate Matter; PM10; PM2.5; Participatory Sensing; Urban Sensing; Mobile Dust Sensor; Air Quality; Environmental Sensing; Wearable; Crowd Sensing.

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# Evaluation of a Diffusion Charger for Measuring Aerosols in a Workplace

Donna J. H. Vosburgh<sup>1\*</sup>, Bon Ki Ku<sup>2</sup> and Thomas M. Peters<sup>3</sup>

1. Department of Occupational and Environmental Safety and Health, University of Wisconsin-Whitewater, 800 West Main Street, Whitewater, WI 53190, USA

2. Division of Applied Research and Technology, National Institute for Occupational Safety and Health, 4676 Columbia Parkway, MS-R5, Cincinnati, OH 45226, USA

3. Department of Occupational and Environmental Health, The University of Iowa, S331 CPHB, 105 River Street, Iowa City, IA 52242, USA

\*Author to whom correspondence should be addressed. Tel: 1-262-472-1252; fax: 1-262-472-1091; e-mail: [vosburgd@uww.edu](mailto:vosburgd@uww.edu)

Submitted 16 August 2013; revised 21 November 2013; revised version accepted 12 December 2013.

## ABSTRACT

The model DC2000CE diffusion charger from EcoChem Analytics (League City, TX, USA) has the potential to be of considerable use to measure airborne surface area concentrations of nanoparticles in the workplace. The detection efficiency of the DC2000CE to reference instruments was determined with monodispersed spherical particles from 54 to 565.7 nm. Surface area concentrations measured by a DC2000CE were then compared to measured and detection efficiency adjusted reference surface area concentrations for polydispersed aerosols (propylene torch exhaust, incense, diesel exhaust, and Arizona road dust) over a range of particle sizes that may be encountered in a workplace. The ratio of surface area concentrations measured by the DC2000CE to that measured with the reference instruments for unimodal and multimodal aerosols ranged from 0.02 to 0.52. The ratios for detection efficiency adjusted unimodal and multimodal surface area concentrations were closer to unity (0.93–1.19) for aerosols where the majority of the surface area was within the size range of particles used to create the correction. A detection efficiency that includes the entire size range of the DC2000CE is needed before a calibration correction for the DC2000CE can be created. For diesel exhaust, the DC2000CE retained a linear response compared to reference instruments up to 2500 mm<sup>2</sup> m<sup>-3</sup>, which was greater than the maximum range stated by the manufacturer (1000 mm<sup>2</sup> m<sup>-3</sup>). Physical limitations with regard to DC2000CE orientation, movement, and vibration were identified. Vibrating the DC2000CE while measuring aerosol concentrations may cause an increase of ~35 mm<sup>2</sup> m<sup>-3</sup>, whereas moving the DC2000CE may cause concentrations to be inflated by as much as 400 mm<sup>2</sup> m<sup>-3</sup>. Depending on the concentration of the aerosol of interest being measured, moving or vibrating a DC2000CE while measuring the aerosol should be avoided.

**KEYWORDS:** diffusion charger; nanoparticles; surface area monitor

## INTRODUCTION

Nanoparticles are defined as particles with one or more dimensions <100 nm (ASTM International, 2006), and they occur in many workplaces. Regardless of age

or breathing pattern, diffusion causes nanoparticles to have high rates of deposition throughout the respiratory system (Daigle *et al.*, 2003; Kim and Jaques, 2005). Toxicological studies have found that some

EVALUATION OF THE DISCMINI PERSONAL AEROSOL MONITOR FOR  
SUBMICROMETER SODIUM CHLORIDE AND METAL AEROSOLS

by  
Jessica Breyan Mills

A thesis submitted in partial fulfillment  
of the requirements for the Master of  
Science degree in Occupational and Environmental Health  
in the Graduate College of  
The University of Iowa

May 2013

Thesis Supervisor: Associate Professor Thomas M. Peters

## ABSTRACT

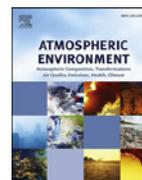
This work evaluated the robust, lightweight DiSCmini (DM) aerosol monitor for its ability to measure the concentration and mean diameter of submicrometer aerosols. Tests were conducted with monodispersed and polydispersed aerosols composed of two particle types (sodium chloride, NaCl, and spark generated metal particles, which simulate particles found in welding fume) at three different steady-state concentration ranges (Low,  $<10^3$ ; Medium,  $10^3$ - $10^4$ ; and High,  $>10^4$  particles/cm<sup>3</sup>). Particle number concentration, lung deposited surface area (LDSA) concentration, and mean size measured with the DM were compared to those measured with reference instruments, a scanning mobility particle sizer (SMPS) and a handheld condensation particle counter (CPC). Particle number concentrations measured with the DM were within 16% of those measured by the CPC for polydispersed aerosols. Poorer agreement was observed for monodispersed aerosols ( $\pm 35\%$  for most tests and  $+101\%$  for 300-nm NaCl). LDSA concentrations measured by the DM were 96% to 155% of those estimated with the SMPS. The geometric mean diameters measured with the DM were within 30% of those measured with the SMPS for monodispersed aerosols and within 25% for polydispersed aerosols (except for the case when the aerosol contained a substantial number of particles larger than 300 nm). The accuracy of the DM is reasonable for particles smaller than 300 nm but caution should be exercised when particles larger than 300 nm are present.



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journal homepage: [www.elsevier.com/locate/atmosenv](http://www.elsevier.com/locate/atmosenv)



# Field comparison of portable and stationary instruments for outdoor urban air exposure assessments



M. Viana <sup>a,\*</sup>, I. Rivas <sup>a,b,c,d</sup>, C. Reche <sup>a</sup>, A.S. Fonseca <sup>a</sup>, N. Pérez <sup>a</sup>, X. Querol <sup>a</sup>, A. Alastuey <sup>a</sup>, M. Álvarez-Pedrerol <sup>b,c,d</sup>, J. Sunyer <sup>b,c,d,e</sup>

<sup>a</sup> IDAEA-CSIC, Jordi Girona 18, 08034 Barcelona, Spain

<sup>b</sup> Centre for Research in Environmental Epidemiology (CREAL), Barcelona, Spain

<sup>c</sup> Universitat Pompeu Fabra (UPF), Barcelona, Spain

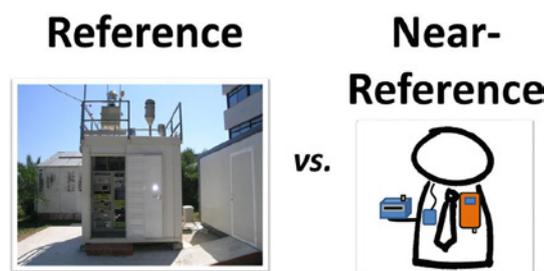
<sup>d</sup> CIBER Epidemiología y Salud Pública (CIBERESP), Spain

<sup>e</sup> Hospital del Mar Research Institute (IMIM), Barcelona, Spain

### HIGHLIGHTS

- Epidemiological studies highlight the need for exposure assessment studies.
- Portable and stationary monitors were compared for exposure assessment.
- Good agreements were found:  $R^2$  mostly  $>0.80$ ; relative differences  $<20\%$ .
- Relative differences were  $<10\%$  between different units of the same instrument.
- Parameters assessed were BC, N, LDSA and mean particle diameter, in outdoor air.

### GRAPHICAL ABSTRACT



### ARTICLE INFO

#### Article history:

Received 2 August 2015

Received in revised form

27 October 2015

Accepted 27 October 2015

Available online 31 October 2015

#### Keywords:

Intercomparison

Relative error

Uncertainty

Performance

Outdoor

Indoor

### ABSTRACT

The performance of three portable monitors (micro-aethalometer AE51, DiscMini, Dusttrak DRX) was assessed for outdoor air exposure assessment in a representative Southern European urban environment. The parameters evaluated were black carbon, particle number concentration, alveolar lung-deposited surface area, mean particle diameter,  $PM_{10}$ ,  $PM_{2.5}$  and  $PM_1$ . The performance was tested by comparison with widely used stationary instruments (MAAP, CPC, SMPS, NSAM, GRIMM aerosol spectrometer). Results evidenced a good agreement between most portable and stationary instruments, with  $R^2$  values mostly  $>0.80$ . Relative differences between portable and stationary instruments were mostly  $<20\%$ , and  $<10\%$  between different units of the same instrument. The only exception was found for the Dusttrak DRX measurements, for which occasional concentration jumps in the time series were detected. Our results validate the performance of the black carbon, particle number concentration, particle surface area and mean particle diameter monitors as indicative instruments (tier 2) for outdoor air exposure assessment studies.

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\* Corresponding author. IDAEA-CSIC, C/ Jordi Girona 18, 08034, Barcelona, Spain.

E-mail addresses: [mar.viana@idaea.csic.es](mailto:mar.viana@idaea.csic.es) (M. Viana), [irivas@creal.cat](mailto:irivas@creal.cat) (I. Rivas), [cristina.reche@idaea.csic.es](mailto:cristina.reche@idaea.csic.es) (C. Reche), [ana.godinho@idaea.csic.es](mailto:ana.godinho@idaea.csic.es) (A.S. Fonseca), [xavier.querol@idaea.csic.es](mailto:xavier.querol@idaea.csic.es) (X. Querol), [andres.alastuey@idaea.csic.es](mailto:andres.alastuey@idaea.csic.es) (A. Alastuey), [malvarez1@creal.cat](mailto:malvarez1@creal.cat) (M. Álvarez-Pedrerol), [jsunyer@creal.cat](mailto:jsunyer@creal.cat) (J. Sunyer).

<http://dx.doi.org/10.1016/j.atmosenv.2015.10.076>

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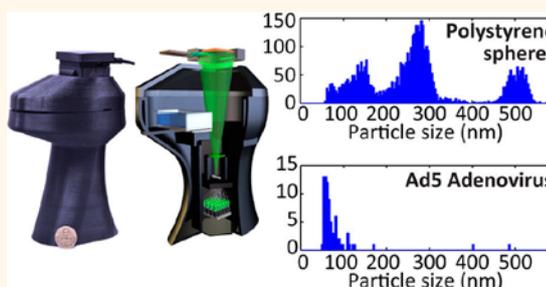
# High-Throughput and Label-Free Single Nanoparticle Sizing Based on Time-Resolved On-Chip Microscopy

Euan McLeod,<sup>\*,†,‡</sup> T. Umut Dincer,<sup>†,‡</sup> Muhammed Veli,<sup>†,‡</sup> Yavuz N. Ertas,<sup>‡</sup> Chau Nguyen,<sup>§</sup> Wei Luo,<sup>†,‡</sup> Alon Greenbaum,<sup>†,‡</sup> Alborz Feizi,<sup>‡</sup> and Aydogan Ozcan<sup>\*,†,‡,⊥,||</sup>

<sup>†</sup>Electrical Engineering Department, University of California, Los Angeles, California 90095, United States, <sup>‡</sup>Bioengineering Department, University of California, Los Angeles, California 90095, United States, <sup>§</sup>Chemistry & Biochemistry Department, University of California, Los Angeles, California 90095, United States, <sup>⊥</sup>California NanoSystems Institute, University of California, Los Angeles, California 90095, United States, and <sup>||</sup>Department of Surgery, David Geffen School of Medicine, University of California, Los Angeles, California 90095, United States

**ABSTRACT** Sizing individual nanoparticles and dispersions of nanoparticles provides invaluable information in applications such as nanomaterial synthesis, air and water quality monitoring, virology, and medical diagnostics. Several conventional nanoparticle sizing approaches exist; however, there remains a lack of high-throughput approaches that are suitable for low-resource and field settings, *i.e.*, methods that are cost-effective, portable, and can measure widely varying particle sizes and concentrations. Here we fill this gap using an unconventional approach that combines holographic on-chip microscopy with vapor-condensed nanolens self-assembly inside a cost-effective hand-held device.

By using this approach and capturing time-resolved *in situ* images of the particles, we optimize the nanolens formation process, resulting in significant signal enhancement for the label-free detection and sizing of individual deeply subwavelength particles (smaller than  $\lambda/10$ ) over a 30 mm<sup>2</sup> sample field-of-view, with an accuracy of  $\pm 11$  nm. These time-resolved measurements are significantly more reliable than a single measurement at a given time, which was previously used only for nanoparticle detection without sizing. We experimentally demonstrate the sizing of individual nanoparticles as well as viruses, monodisperse samples, and complex polydisperse mixtures, where the sample concentrations can span  $\sim 5$  orders-of-magnitude and particle sizes can range from 40 nm to millimeter-scale. We believe that this high-throughput and label-free nanoparticle sizing platform, together with its cost-effective and hand-held interface, will make highly advanced nanoscopic measurements readily accessible to researchers in developing countries and even to citizen-scientists, and might especially be valuable for environmental and biomedical applications as well as for higher education and training programs.



**KEYWORDS:** nanoparticles · particle-sizing · lensfree microscopy · field-portable

The ability to detect and size nanoparticles is extremely important in the analysis of liquid and aerosol samples for medical, biological, and environmental studies.<sup>1–8</sup> Some examples of nanoparticles that researchers have been interested in detecting and sizing include viruses,<sup>9–11</sup> exosomes,<sup>1</sup> metallic labels,<sup>12,13</sup> soot,<sup>6,14</sup> ice crystals in clouds,<sup>15</sup> and engineered nanomaterials,<sup>16</sup> among others. While there exist various nanoparticle detection and sizing methods, there is a lack of high-throughput instruments that can cover a large dynamic range of particle sizes and concentrations within a field-portable, cost-effective and rapid interface. Existing nonoptical methods,

such as transmission electron microscopy (TEM), scanning electron microscopy (SEM), and atomic force microscopy, are typically very accurate and provide a gold standard for particle sizing;<sup>1,4</sup> however they are bulky, require significant capital investment, can be slow in image acquisition, and provide extremely restricted fields of view (FOVs) that limit throughput for particle sizing. Optical techniques can be more cost-effective and rapid; however, it is in general difficult to overcome the challenge of obtaining a large enough signal-to-noise (SNR) ratio to detect and reliably size both individual nanoparticles and populations of nanoparticles.

\* Address correspondence to euanmc@ucla.edu, ozcan@ucla.edu.

Received for review January 18, 2015 and accepted February 17, 2015.

Published online February 17, 2015  
10.1021/acsnano.5b00388

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## **Influence of instruments performance and material properties on exposure assessment of airborne engineered nanomaterials**

**Levin, Marcus**

*Publication date:*  
2015

*Document Version*  
Publisher's PDF, also known as Version of record

[Link to publication](#)

*Citation (APA):*  
Levin, M. (2015). Influence of instruments performance and material properties on exposure assessment of airborne engineered nanomaterials. DTU Nanotech.

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## Abstract

Over the last decades, materials engineered of nanosized structures have increased tremendously, in terms of both produced tonnage and economic market share. This, together with the fact that some of these engineered nanomaterials have shown an increased toxicological effect in humans as compared to their bulk counterpart, has expanded the scientific field of exposure measurements to airborne nanoparticles. As the greatest potential for human exposure to engineered nanomaterials resides within the production, packaging and downstream powder-material handling, as well as at reworking/waste treatment facilities, exposure risk for workers has received great focus.

The studies described in this thesis come to four main conclusions: **1)** Mass-balance modeling of airborne engineered nanomaterials using dustiness index as a primary source term can be useful for assessment of material-specific exposure scenarios and in decision-making regarding powder choices. **2)** That such mass-balance modeling can, however, be highly sensitive to environmental conditions, especially humidity, during storage and use, which may cause a severe misrepresentation of the true emission if the conditions during dustiness testing differ from the modeled scenario. **3)** That particles with a geometrical mean diameter above 200 nm cannot be measured reliably with the Fast Mobility Particle Sizer (FMPS 3091, TSI Inc., MN, USA) but will instead be underestimated in terms of particle size and overestimated in terms of particle number concentration. Measured size distributions with particle modes above 150 nm should not be deemed reliable as they might arise from misclassification of larger size particles. **4)** That current methods for real-time measurement of lung-deposited surface area concentration for airborne engineered nanomaterials are cannot be relied upon to represent comparable levels for use in exposure assessments and for other regulatory purposes.

The work presented in this thesis provides understanding to improve assessment of airborne exposure to engineered nanomaterials in occupational settings. Based on conclusions drawn in this thesis, exposure assessment and control-banding models should review their use of dustiness index as a term of emission or ensure that the specific material of interest has been tested in relevant conditions. The work shows the limits of the capabilities of current techniques for measurement of airborne particle characteristics, and highlights necessary improvements for future adaptations of new metrics into regulatory testing and occupational exposure limits.



## Mathematical Description of Experimentally Determined Charge Distributions of a Unipolar Diffusion Charger

Heinz Kaminski,<sup>1</sup> Thomas A. J. Kuhlbusch,<sup>1,2</sup> Heinz Fissan,<sup>1,2</sup> Lavanya Ravi,<sup>1</sup>  
 Hans-Georg Horn,<sup>3</sup> Hee-Siew Han,<sup>4</sup> Rob Caldow,<sup>4</sup> and Christof Asbach<sup>1</sup>

<sup>1</sup>*Air Quality & Sustainable Nanotechnology Unit, Institute of Energy and Environmental Technology (IUTA) e.V., Duisburg, Germany*

<sup>2</sup>*Center for NanoIntegration Duisburg-Essen (CeNIDE), Duisburg, Germany*

<sup>3</sup>*TSI GmbH, Aachen, Germany*

<sup>4</sup>*TSI Inc., Shoreview, Minnesota, USA*

The charge distributions of an improved opposed flow unipolar diffusion charger were measured using a tandem differential mobility analyzer (DMA) set up in a size range of approximately 20–400 nm. The charger is intended to be used in a portable aerosol sizer to measure particle size distributions. The determined charge distributions were represented by lognormal distributions, and a set of equations and coefficients was developed to calculate the charge distributions. These equations can be easily implemented in software for size distribution measurements. The agreement between the mathematically derived and measured charge distributions is very good, with regression coefficients  $R^2 > 0.96$ . The investigations showed that approximately 55% of 20-nm particles remain uncharged, while up to 25 elementary charges need to be considered for multiple charge correction of 400-nm particles. Comparison with the Fuchs theory delivered satisfying agreement with the measured average charge levels, but charge distributions cannot be described by the Fuchs theory, likely caused by the charger geometry.

### INTRODUCTION

Engineered nanomaterials have been reported to be of possible health concern (Oberdörster 2000; Hoet et al. 2004; Nel et al. 2006; Poland et al. 2008). The highest possibility for exposure to engineered nanoparticles (the term “nanoparticle” is here synonymously also used for nanoplates and nanofibers) exists in occupational settings, where such particles are produced,

handled, or used otherwise (Schulte et al. 2008). Studies on the possible exposure to engineered nanoparticles in work environments have therefore raised increased attention in the past. Since inhalation is seen as the major uptake route, exposure to airborne nanoparticles needs to be assessed, e.g., in view of worker protection. The best estimate of a worker’s exposure can be derived from mobile, ideally personal measurements, taking aerosol samples in the breathing zone of the worker. Personal samplers for nanoparticles, however, are currently all more or less still at a research level (Azong-Wara et al. 2009; Furuuchi et al. 2010; Cena et al. 2011). Due to the lack of suitable personal measurement equipment, extensive measurement campaigns with a large set of bulky equipment are commonly carried out for a detailed assessment of possible exposure. Reviews of nanoparticle exposure measurements in industrial settings have recently been published by Brouwer et al. (2009) and Kuhlbusch et al. (2011). Those campaigns usually require extensive equipment and their data evaluation can be very time-consuming. Methner et al. (Methner, Hodson, and Geraci 2010; Methner, Hodson, Dames et al. 2010) and the German Chemical Industry Association (VCI 2011) recently published a tiered approach to assess possible exposure. The first tier foresees a rough assessment of the particle concentration by means of portable measurement devices. Requirements for such mobile nanoparticle exposure monitors are small size, low weight and power consumption. The discussion on the health relevance of different aerosol metrics, to be determined by such monitors, is still ongoing (Maynard and Aitken 2007; Oberdörster et al. 2007; Wittmaack 2007), and hence, a sophisticated exposure monitor should provide versatile information on the aerosol, i.e., the particle size distribution which under several assumptions can also be converted into size integrated number, surface area, or volume/mass concentrations. Besides the abovementioned requirements, a portable or personal workplace monitor must not use any harmful substances. Bipolar aerosol chargers using

Received 2 September 2011; accepted 26 December 2011.

The research leading to these results has received funding from the European Community’s Seventh Framework Programme (FP7/2007-2013) under grant agreement no. 211464-2.

Address correspondence to Christof Asbach, Air Quality & Sustainable Nanotechnology Unit, Institute of Energy and Environmental Technology (IUTA) e.V., 47229 Duisburg, Germany. E-mail: asbach@iuta.de



## Partially integrated cantilever-based airborne nanoparticle detector for continuous carbon aerosol mass concentration monitoring

H. S. Wasisto<sup>1,2</sup>, S. Merzsch<sup>1,\*</sup>, E. Uhde<sup>3</sup>, A. Waag<sup>1,2</sup>, and E. Peiner<sup>1,2</sup>

<sup>1</sup>Institut für Halbleitertechnik (IHT), Technische Universität Braunschweig, Braunschweig, Germany

<sup>2</sup>Laboratory for Emerging Nanometrology (LENA), Braunschweig, Germany

<sup>3</sup>Material Analysis and Indoor Chemistry Department (MAIC), Fraunhofer-WKI, Braunschweig, Germany

\*now at: Infineon Technologies AG, Munich, Germany

Correspondence to: H. S. Wasisto ([h.wasisto@tu-bs.de](mailto:h.wasisto@tu-bs.de))

Received: 27 November 2014 – Revised: 19 February 2015 – Accepted: 19 February 2015 – Published: 11 March 2015

**Abstract.** The performance of a low-cost partially integrated *cantilever-based airborne nanoparticle (NP) detector (CANTOR-1)* is evaluated in terms of its real-time measurement and robustness. The device is used for direct reading of exposure to airborne carbon engineered nanoparticles (ENPs) in indoor workplaces. As the main components, a miniaturized electrostatic aerosol sampler and a piezoresistive resonant silicon cantilever mass sensor are employed to collect the ENPs from the air stream to the cantilever surfaces and to measure their mass concentration, respectively. Moreover, to realize a real-time measurement, a frequency tracking system based on a phase-locked loop (PLL) is built and integrated into the device. Long-term ENP exposure and a wet ultrasonic cleaning method are demonstrated to estimate the limitation and extend the operating lifetime of the developed device, respectively. By means of the device calibrations performed with a standard ENP monitoring instrument of a fast mobility particle sizer (FMPS, TSI 3091), a measurement precision of ENP mass concentrations of < 55 % and a limit of detection (LOD) of < 25  $\mu\text{g m}^{-3}$  are obtained.

### 1 Introduction

Over the last few decades, nanotechnology, which covers a compilation of technologies and methods for manipulating material on the nanoscale (i.e., nanomaterial or nanoparticle (NP)), has been attracting immense attention in society and has been hailed by some scientists as the next industrial revolution. The possible interests in nanotechnology originate mainly from the novel properties and characteristics of the nanomaterials, which are not the same as bulk materials and may be unpredictable and unimagined as scale effects (Maynard, 2007; Hullman, 2007). Thus, this technology has rapidly been developed and used across a variety of industries (e.g., electronics, medicine, cosmetics, pharmaceuticals, food packaging, household appliances, and national defense), leading to increased economic growth and new job vacancies (Bekker et al., 2013).

Although nanotechnology provides society with enormous feasibilities, questions have also been raised about uncertainties concerning the risks to and potential health effects of released NPs on the environment. The formation and release of the NPs into indoor environments and workplaces can occur through both incidental (i.e., unintentional NPs) and planned manufacturing processes (i.e., engineered NPs (ENPs)) (Balbus et al., 2007). Moreover, much higher awareness should be given to the workers, who manufacture and handle NPs directly in large quantities during the line productions (Brouwer, 2010). Thus, a direct-reading airborne NP mass concentration detector is very useful for the assessment of personal- and location-dependent monitoring in workplaces and indoor environments.

For individual NP mass monitoring, the complete system relies on mini portable devices that can be held and carried easily by the workers. Currently, the already developed NP mass sensors based on microelectromechanical systems



## Standard Operation Procedures

For assessing exposure to nanomaterials, following a tiered approach

Date: June 26<sup>th</sup>, 2012

### Authors:

Christof Asbach<sup>1</sup>, Thomas A.J. Kuhlbusch<sup>1</sup>, Heinz Kaminski<sup>1</sup>, Burkhard Stahlmecke<sup>1</sup>, Sabine Pitzko<sup>2</sup>, Uwe Götz<sup>3</sup>, Matthias Voetz<sup>4</sup>, Heinz-Jürgen Kiesling<sup>4</sup>, Dirk Dahmann<sup>5</sup>

<sup>1</sup> Institute of Energy and Environmental Technology (IUTA) e.V., Duisburg, Germany

<sup>2</sup> Federal Institute of Occupational Safety and Health (BAuA), Berlin, Germany

<sup>3</sup> BASF SE, Ludwigshafen, Germany

<sup>4</sup> Bayer Technology Services GmbH (BTS), Leverkusen, Germany

<sup>5</sup> Institute for the Research on Hazardous Substances (IGF), Bochum, Germany

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# SOP-Tiered Approach

## Tiered Approach for the assessment of exposure to airborne nanoobjects in workplaces

Date

29<sup>th</sup> March 2012

Version

1.1 English

Scope

1	Scope	2
2	Tier 1 – Data Gathering	2
3	Tier 2 – Basic Assessment	2
4	Tier 3 – Expert Assessment	3
5	List of Standard Operation Procedures	5
5.1	Main SOPs	5
5.2	Sub-SOPs – Instruments	5
5.3	Sub-SOPs – Other	6



Contents lists available at ScienceDirect

# International Journal of Mass Spectrometry

journal homepage: [www.elsevier.com/locate/ijms](http://www.elsevier.com/locate/ijms)



## Variable field ion traps

Hrishikesh S. Sonaliker<sup>a</sup>, Atanu K. Mohanty<sup>a,b,\*</sup>



<sup>a</sup> Department of Instrumentation and Applied Physics, Indian Institute of Science, Bangalore 560012, India

<sup>b</sup> Supercomputer Education and Research Centre, Indian Institute of Science, Bangalore 560012, India

### ARTICLE INFO

#### Article history:

Received 5 July 2013

Received in revised form 2 September 2013

Accepted 3 September 2013

Available online 7 October 2013

#### Keywords:

Cylindrical ion trap

Split electrodes

Multipole coefficients

Field optimization

Ion trap capacitances

### ABSTRACT

This paper presents a technique to vary the electric field within a cylindrical ion trap (CIT) mass spectrometer while it is in operation. In this technique, the electrodes of the CIT are split into number of mini-electrodes and different voltages are applied to these split-electrodes to achieve the desired field.

In our study we have investigated two geometries of the split-electrode CIT. In the first, we retain the flat endcap electrodes of the CIT but split the ring electrode into five mini-rings. In the second configuration, we split the ring electrode of the CIT into three mini-rings and also divide the endcaps into two mini-discs. By applying different potentials to the mini-rings and mini-discs of these geometries we have shown that the field within the trap can be optimized to desired values. In our study, two different types of fields were targeted. In the first, potentials were adjusted to obtain a linear electric field and, in the second, a controlled higher order even multipole field was obtained by adjusting the potential.

We have shown that the different potentials required can be derived from a single RF generator by connecting appropriate capacitor terminations to split electrodes. The field within the trap can be modified by changing the values of the external capacitors.

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### 1. Introduction

This paper presents a technique to vary the field within an ion trap mass spectrometer while it is in operation. The technique we propose will be demonstrated on the three dimensional ion trap configuration.

The ideal geometry of the Quadrupole Ion Trap (QIT) [1] uses electrodes of hyperbolic shape. For ease of machining and to enable miniaturization, the QIT was simplified to the geometry of the cylindrical ion trap (CIT) [2–5] which is now widely used [6–11]. To compensate for the field inhomogeneities introduced by the simplification of the CIT, Wu et al. [11] optimized its geometry by experimentally testing candidate structures for their performance and choosing the one that had the best performance. In another simulation approach proposed by Tallapragada et al. [12], the stretch of CIT was numerically optimized to get the desired field. In both these methods however, once an ion trap is manufactured, the electric field of that ion trap is fixed and cannot be changed. As a result, the nonlinearities in electric field introduced by defects in manufacturing of an ion trap and misalignment of electrodes cannot be tweaked post-manufacture.

There are several reasons why an experimenter may want to have flexibility to alter field within the trap during its operation. First, this will enable correction of fields post-manufacture so that field inhomogeneities which are introduced by machining errors or misalignment in assembly can be taken care of. Another reason may be to alter the field for different modes of operation. For instance, a linear field is desired for mass selective boundary ejection experiments [13], whereas a weak octopole field would improve performance of the mass spectrometer in resonance ejection experiments [14–16]. Thus, with the ability to control the field within ion traps, an experimenter can choose the optimum field for performing different experiments using the same trap hardware configuration.

Several researchers have used multiple electrode structures as well as compensation electrodes to optimize the electric field within the ion trap [17–20]. Matsuda and Matsuo [21] have used 12 symmetrically arranged wires to eliminate 6th and 10th order components of potential to produce a better quadrupole field. Austin et al. [22,23] and Zhang et al. [26,25] have proposed a new ion trap geometry consisting of two electrode plates, each consisting lithographically printed concentric ring electrodes. Each ring is supplied with appropriate RF voltage so that required electric field is established inside the trap. Gerald [26] has shown the use of compensation electrodes to improve the accuracy of Penning traps.

Taking a cue from these earlier studies we have undertaken a computational study in which we have adopted different electrode configurations to tailor the field in ion traps. In this study we have considered the following two geometries for tailoring the field

\* Corresponding author at: Supercomputer Education and Research Centre, Indian Institute of Science, Bangalore 560012, India. Tel.: +91 80 22932979; fax: +91 80 23600135.

E-mail addresses: [hrishikeshsonaliker@gmail.com](mailto:hrishikeshsonaliker@gmail.com) (H.S. Sonaliker), [amohanty@serc.iisc.ernet.in](mailto:amohanty@serc.iisc.ernet.in) (A.K. Mohanty).

