

# AIRMON 2017

11–15 June  
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## AIRMON 2017

The 9<sup>th</sup> International Symposium on Modern Principles  
of Air Monitoring and Biomonitoring

– Programme and abstracts –

# **9<sup>th</sup> International Symposium on Modern Principles of Air Monitoring and Biomonitoring**

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## Updated programme

Start	Title	Chair/Speaker
<b>Sunday, 11<sup>th</sup> June 2017</b>		
16:30	Registration	
18:00	Welcome reception	
<b>Monday, 12<sup>th</sup> June 2017</b>		
8:30	Registration	
10:00	Opening and welcome	Prof. Dietmar Reinert, Prof. Yngvar Thomassen, Prof. Dietmar Breuer
10:15	<b>Opening speech:</b> Risk- and health-based limit values for carcinogenic metal compounds: Developments, approaches and future challenges	Prof. Andrea Hartwig
11:00	<b>Opening session</b>	Prof. Dietmar Breuer, Prof. Yngvar Thomassen
11:00	Biomonitoring applied to look at the characteristics of U.S. population with the lowest and highest blood metal concentrations from NHANES 2011-2014	Kathleen L. Caldwell PhD
11:20	10 years of National Biomonitoring in Canada: A unique dataset with novel tools to inform public health policy	Annie St-Amand
11:40	Workers' external and internal exposure to mercury during collection of discarded energy saving lamps in municipal collecting points	Ralph Hebisch PhD
12:00	Lunch	
13:00	<b>Keynote – Session 2: Aerosols 1</b> Experimental assessment of respiratory tract deposition of inhaled particles	Jakob Löhndahl PhD
13:00	<b>Session 2: Aerosols 1</b>	Alois Gutzwiller PhD, Martin Harper PhD
13:30	Revision of health-related sampling conventions	Göran Lidén PhD
13:50	Bioaerosols and quartz dust in potato and vegetable processing plants	Patrick Steinle PhD
14:10	Allergen and bioaerosol exposure assessment in different areas of a veterinary faculty – using stationary sampling equipment	Prof. Monika Raulf
14:30	Size fractionation of endotoxin from organic waste	Catherine Rolph PhD
14:50	Coffee break and poster exhibition	
16:00	<b>Keynote – Session 3: Aerosols 2</b> Development of samplers for aerosol fractions deposited in two regions of the respiratory tract – the gas-exchange region and the posterior head airways	Göran Lidén PhD
16:00	<b>Session 3: Aerosols 2</b>	Carsten Möhlmann, Simon Aubin
16:30	A cyclone with narrow-diameter particle deposition for end-of-shift quartz measurement	Taekhee Lee PhD
16:50	Towards better particle characterization in industrial workplaces	Balazs Berlinger PhD
17:10	Direct-reading gravimetric airborne nanoparticle monitor based on an electrostatic silicon microcantilever	Erik Uhde PhD
17:30	Risk assessment of handling rigid carbon nanotubes at a technical centre in Berlin	Bianca Oeffling

## Updated programme

Start	Title	Chair/Speaker
<b>Tuesday, 13<sup>th</sup> June 2017</b>		
8:30	<b>Keynote – Session 4: Biological monitoring – Bioaerosols</b> Biological monitoring without limits	John Cocker PhD
9:00	<b>Session 4: Biological monitoring – Bioaerosols</b>	Prof. Monika Raulf, Heiko Kafferlein PhD
9:00	Temporal variations of size distribution of bioaerosols at occupational settings	Philippe Duquenne PhD
9:20	Evaluation of bioaerosol samplers for biological sampling efficiencies under controlled conditions	Prof. Joseph Strauss
9:40	Measurement of fragments and spores for fungal exposure assessment	Anani Afanou PhD
10:00	Coffee break	
10:30	Biological monitoring of naphthalene in workers in the production of abrasives	Wolfgang Zschiesche PhD
10:50	Measurement of Staphylococcus species in sedimented and airborne dust in Danish homes	Anne Mette Madsen PhD
11:10	Bioaerosol measurements with an automated sampler – Experiences and results	Marcus Clau PhD
11:30	Association between exposure to airborne noroviruses and gastroenteritis among wastewater workers	Katrine Uhrbrand PhD
11:50	Lunch	
13:00	<b>Keynote – Session 5: Mixed phases – measurements</b> Characterization of emissions from bitumen with antistripping additives	Simon Aubin
13:30	<b>Session 5: Mixed phases – measurements</b>	Goran Lidn PhD, George Dragan PhD
13:30	IFA and INRS comparison on bitumen fumes sampling and analysing methods	Benjamin Sutter PhD
13:50	NovaCarbTM-Denuders as a vapour-particle partitioning tool for the occupational sampling of aerosols from semi-volatile organic compounds	Vesta Kohlmeier
14:10	Exposure to polycyclic aromatic hydrocarbons during recycling of railway sleepers and remediation of contaminated soil	Anja Baumgartel PhD
14:30	Exposure to air pollutants in pizza restaurants with wood-fired ovens	Pernilla Almerud PhD
14:50	Workplace formaldehyde exposure in the anatomical institutes of German universities	Ingrid Thullner
15:10	Characterisation of particle and volatile organic compound emissions from desktop fused filament fabrication three dimensional printers using real-time and analytical techniques	Samantha Hall
15:30	Coffee break and poster exhibition	
16:30	<b>Workshops</b>	
16:30	Workshop: Sampling of health-related aerosol fractions in occupational hygiene	Peter Gorner PhD
16:30	Workshop: Characterization of the size distribution of bioaerosols	Annette Kolk PhD, Philippe Duquenne PhD
16:30	Workshop: Odours in indoor and environmental air	Kirsten Sucker PhD
16:30	Workshop: Proficiency testing	Owen Butler

Start	Title	Chair/Speaker
<b>Wednesday, 14<sup>th</sup> June 2017</b>		
8:30	<b>Keynote – Session 6: Measurements</b> Low-cost sensors and citizen science: Prospects, pitfalls, and paradigm shifts	Prof. John Volckens
9:00	<b>Session 6: Measurements</b>	Owen Butler, Ralph Heibisch PhD
9:00	Workplace monitoring of diisocyanates at construction sites	Christoph Emmel PhD
9:20	Performance of various passive samplers for 15 minute short term exposure assessment	Eddy Langlois
9:40	Further advances in air quality monitoring in aircraft cabins	Andreas Bezdold PhD
10:00	Poster session (see also page 55)	
11:00	Analysis of end-exhaled air to study exposures to volatile organic compounds	Prof. Paul Scheepers
11:20	Development of an air monitoring method for diacetyl in the workplace	Ian Pengelly
11:40	Development and optimization of the plunger assisted solvent extraction (PASE) method for multi-channel silicone rubber traps	Chiedza Munyeza PhD
12:00	Accuracy and comparability of lung deposited surface area monitors	Christof Asbach PhD
12:20	Lunch	
13:30	<b>Keynote – Session 7: Asbestos and dust</b> Naturally occurring asbestos (NOA): a new issue for hygienists	Martin Harper PhD
14:00	<b>Session 7: Asbestos and dust</b>	Peter Görner PhD, Balazs Berlinger PhD
14:00	Asbestos measurements during processing of serpentinite rocks in Switzerland	Markus Schafer PhD
14:20	The Shaker Dustiness Test for High Aspect Ratio Materials	Dirk Broßell PhD
14:40	Thoracic aerosol sampling by the FSP cyclone sampler	Peter Görner PhD
16:00	<b>Social programme (excursion and conference dinner)</b>	

Start	Title	Chair/Speaker
<b>Thursday, 15<sup>th</sup> June 2017</b>		
8:30	<b>Keynote – Session 8: Exposure modelling, Biological Monitoring II and Bioaerosols I</b> Evaluation of tier exposure assessment tools for use under REACH (Inhalation)	Eun Gyung Lee PhD
9:00	<b>Session 8: Exposure modelling, Biological Monitoring II and Bioaerosols I</b>	Eun Gyung Lee PhD, Prof. Dietmar Breuer
9:00	Variability in exposure level – implications for measuring and modelling exposures	Dorothea Koppisch PhD
9:20	Dermal Penetration of N-Phenyl-2-naphthylamine in vivo	Stephan Koslitz
9:40	Urinary bisphenol A (BPA) concentrations among workers in industries that manufacture and use BPA in the United States	Cynthia J. Hines
10:00	Urinary concentrations of benzene metabolites of 1076 subjects living in Central Italy determined by HPLC/MS/MS	Giovanna Tranfo PhD
10:20	Coffee break	
10:50	<b>Keynote – Session 9: Bioaerosols II</b> The challenges of assessing bioaerosol-related health risks	Prof. Caroline Herr
11:20	<b>Session 9: Bioaerosols II</b>	Annette Kolk PhD, Xavier Simon PhD
11:20	Endotoxin measurement at the workplace: comparison of two personal sampling methods	Olivier Schlosser
11:40	Real time characterization of bioaerosols emissions from industrial sources	Zaheer Ahmad Nasir PhD
12:00	One year follow up of microbial biodiversity in French waste sorting plant	Jodelle Degois
12:20	Investigation of recovery efficiencies in bioaerosol analyses with filtration	Inken Schulze-Hessing
12:40	Closing remarks	Prof. Dietmar Breuer, N. N.
13:00	Lunch	

## Organisation



Dietmar Breuer



Anika Decker



Margrit Zube



Eva Windemuth



Sabine Fischer

## International Scientific Committee

- Lena Andersson, Örebro University Hospital, Sweden
- Balazs Berlinger, National Institute of Occupational Health (STAMI), Norway
- Dietmar Breuer, Institut für Arbeitsschutz der DGUV (IFA), Germany
- Owen Butler, Health and Safety Laboratory (HSL), United Kingdom
- George-Constantin Dragan, Helmholtz-Zentrum München, Germany
- Alois Gutzwiller, Schweizerische Unfallversicherungsanstalt (SUVA), Switzerland
- Martin Harper, National Institute of Occupational Safety and Health (NIOSH), USA
- Ralph Hebisch, Bundesanstalt für Arbeitsschutz und Arbeitsmedizin (BAuA), Germany
- Heiko Käfferlein, Institut für Prävention und Arbeitsmedizin der DGUV, Institut der Ruhr-Universität Bochum (IPA), Germany
- Kai Savolainen, Finnish Institute of Occupational Health (FIOH), Finland
- Xavier Simon, Institut National de Recherche et de Sécurité (INRS), France
- Silvia Springer, Allgemeine Unfallversicherungsanstalt (AUVA), Austria
- Yngvar Thomassen, National Institute of Occupational Health (STAMI), Norway

## Members from Institut für Arbeitsschutz der DGUV (IFA), Germany

- Frank Bochmann
- Yvonne Giesen
- Annette Kolk
- Dorothea Koppisch
- Markus Mattenklott
- Carsten Möhlmann
- Eberhard Nies
- Wolfgang Pflaumbaum

# Opening session

## Opening speech

### Risk- and health-based limit values for carcinogenic metal compounds: Developments, approaches and future challenges

Andrea Hartwig  
Karlsruher Institut für Technologie (KIT), Germany

The carcinogenicity of several metals and their compounds including nickel, cobalt, cadmium, arsenic and chromium(VI) has been recognized for some decades. They have been classified as human or animal carcinogens by the IARC, by SCOEL and by the German MAK commission. In Germany, up to the year 2005, exposure has been limited via Technical Guidance Values (TRK), according to technical and economical feasibility. Since then legislation requires health- or risk-based exposure limits also for carcinogens. Respective assessments should be based on the knowledge of the modes of action, which appear to be complex and are not completely understood at present. While with the exception of chromium(VI) direct DNA damage seems to

be of minor importance, interactions with DNA repair processes, tumor suppressor functions and signal transduction pathways have been identified in case of many other metal compounds. Additionally, non-cancer adverse health effects need to be taken into account, for example lung toxicity in case of nickel and kidney toxicity in case of cadmium. Altogether derived risk-based or health-based limit values are considerably lower as compared to TRK values, mostly in the low  $\mu\text{g}/\text{m}^3$  range. Nevertheless, many questions still need to be resolved with respect to toxicologically relevant interactions in the very low dose range. Furthermore, the compliance with the exposure limits will be an important challenge.

### Biomonitoring applied to look at the characteristics of U.S. population with the lowest and highest blood metal concentrations from NHANES 2011-2014

Kathleen L. Caldwell, Po-Yung Cheng, Jeffery M. Jarrett, Cynthia D. Ward, Robert L. Jones  
Centers for Disease Control and Prevention, USA

The Centers for Disease Control and Prevention's Environmental Health Laboratory in the Division of Laboratory Sciences measures elements and elemental species for the National Health and Nutrition Evaluation Survey (NHANES). Lead, cadmium, mercury (total), mercury species (ethyl mercury, methyl mercury and inorganic mercury), manganese and selenium are all measured in the blood of participants age 1+ in the survey. These data are used by U.S. policy makers to help inform national, state and local public health policy (e.g. National Childhood Blood Lead Reference Level). We present for the first time the 2.5 and 97.5 percentiles for selenium and the 97.5 percentile for lead, cadmium, manganese and mercury (total and species) in blood from the NHANES 2011-2014 survey results. We applied multiple logistic regressions and assessed the demographics of people who had blood concentrations at the highest and lowest percentiles.

We found that people who smoke have a 99-fold increased risk of having a blood cadmium at the 95 percentile or higher. Smoking is the most significant risk factor contributing to people having the highest blood cadmium concentrations. Smokers have a 2.76 fold increase risk of having lead in the 95 percentile or higher. Those individuals in the construction occupation class had a significant association with having blood lead and cadmium in the 90 percentile or higher. People having a blood mercury at the 95 percentile or higher were of higher income and higher education, and primarily male. This data provides an opportunity to look at the demographics of the U.S. population that have the highest and lowest amounts of toxic elements like lead, cadmium and mercury or essential elements like selenium that are actually found in people.

## 10 years of National Biomonitoring in Canada: A unique dataset with novel tools to inform public health policy

Annie St-Amand, Julie Yome, Kate Werry, Cheryl Khoury  
Government of Canada, Canada

Since 2007, Health Canada has conducted human biomonitoring as part of the Canadian Health Measures Survey (CHMS), which is the most comprehensive, direct health measures survey conducted in Canada. This ongoing survey operates in two-year cycles in which approximately 6 000 Canadians are selected to participate. So far, almost five cycles have been completed, collecting blood and urine samples from approximately 30 000 participants aged 3 to 79 years from 81 sites across the country.

These samples have been analysed to determine concentrations of hundreds of environmental chemicals including metals, persistent organic pollutants, volatile organic compounds (VOCs), fluoride, environmental phenols, acrylamide, pesticides, polycyclic aromatic hydrocarbon (PAH) metabolites, phthalates and alternate plasticizer metabolites, and tobacco biomarkers. The results obtained from this survey are representative of approximately 96% of the Canadian population and include vulnerable populations such as children as young as three years of age. In the first three cycles, half of the chemicals measured were above the limit of detection in 60% of individual blood and urine samples. Indoor air and tap water samples have also been collected in selected cycles.

Over the past decade, Health Canada has also developed tools to interpret and communicate human biomonitoring data in a public health context. Reference values (RV95) are statistical tools that allow the identification of individuals with increased exposure. RV95s derived from the CHMS, have been proposed for heavy metals, as well as persistent and non-persistent chemicals. Biomonitoring equivalents (BEs) are risk-based tools to prioritize chemicals. BEs have been derived for a number of chemicals and are used to calculate hazard quotients to identify priority chemicals for further follow up. Health-based guidance values are the most sophisticated tools to assess risk and proposing new values for various chemicals, such as urinary arsenic, is currently being examined.

The experience gained over the past ten years has made Canada a world leader in human biomonitoring. This decade-long effort has not only provided baseline concentrations in the Canadian population but it has, in turn, been used to inform regulatory risk assessment and improve evidence-based decision making in public policies aiming to reduce exposure to toxic chemicals and to protect the health of Canadians.

## Workers' external and internal exposure to mercury during collection of discarded energy saving lamps in municipal collecting points

Ralph Hebisch, Anja Baumgärtel, Roland Paul  
Bundesanstalt für Arbeitsschutz und Arbeitsmedizin (BAuA), Germany

Filament bulbs that have been used over the last century are nearly completely substituted by energy saving lamps such as compact fluorescent lamps and fluorescent tube lamps in Europe. Their disadvantage is the contained mercury, which requires a disposal as hazardous material after their life time. A large amount of these discarded lamps is collected in municipal collecting points before recycling. The workers of these enterprises are in contact with hazardous mercury which might be related to potential health risks.

To assess workers' exposure during collection of these lamps air monitoring and biological monitoring of external and internal exposure have been performed, respectively. For this purpose a new measurement procedure has been developed and validated to perform measurements of mercury in workplace air. For a two hour sampling period combined with quick sample treatment and atomic absorption determination a limit of quantification of  $0.01 \mu\text{g}/\text{m}^3$  could be reached. This enables reliable workplace measurements to monitor the Occupational Exposure Limit (OEL) of  $20 \mu\text{g}/\text{m}^3$  in Germany.

Measuring results for 10 enterprises indicated very low exposures to mercury. The measurements have been performed during stationary and mobile collection of discarded lamps and when picking up the collection containers by transport companies for transfer to recycling enterprises. In almost all cases the concentration found for mercury was less than 5% of the OEL. About two third of the measuring results correspond to the background concentration of mercury in the order of  $0.01 \mu\text{g}/\text{m}^3$  for urban areas. During loading lorries using a forklifter increased exposures up to  $3.4 \mu\text{g}/\text{m}^3$  have been determined as a consequence of busted lamps.

The internal load was measured by the quantification of mercury in urine corrected for creatinine. The mercury content for 61 workers of the municipal collecting points was found to be comparable to the reference value of  $0.75 \mu\text{g}/\text{g}$  creatinine for adults without amalgam fillings.

Despite these low exposures some recommendations for practice have been given to the enterprises. They are aimed to lower the exposure especially due to broken lamps.



## **Session 2: Aerosols 1**

## Keynote

### Experimental assessment of respiratory tract deposition of inhaled particles

Jakob Löndahl  
Lund University, Sweden

To determine the respiratory tract deposition of inhaled particles is a key link to understand their health effects during exposure. The deposition probability of particles in the lungs varies almost an order of magnitude, from around 10% to almost 100%, depending on physical and chemical properties of the particles as well as on breathing pattern and physiology of the exposed individual. Considering also variations in inhaled volumes, there are large variations in delivered dose between different people in different exposure situations. In addition, the region of deposition in the lungs varies substantially, with particles smaller than a few micrometers having a substantial ability to reach the peripheral lung and larger particles primarily depositing in the extrathoracic region and upper airways.

The available experimental data on respiratory tract deposition of airborne particles is limited and not fully consistent. Most studies have been performed on small groups of healthy male subjects, often with controlled standardized breathing patterns. Data is scarce for vulnerable subgroups such as children, elderly or people with respiratory diseases. Typically, little information is provided about the physiology of the investigated subjects. Normally hydrophobic particles have been used, although it is well known that ambient particles often are hygroscopic and that hygroscopicity alters the deposition substantially. Furthermore, many of the experimental studies on respiratory tract deposition have notable uncertainties in methodology.

We have, at Lund University, developed a technique to measure deposition probabilities of inhaled real-world particles. Extensive efforts have been made to minimize measurement errors, among other things by a careful review of previously described deposition experiments. With our set-up we have measured the

respiratory tract deposition of aerosols for around 160 subjects, including children, elderly and patients with chronic obstructive pulmonary disease. Different particle types have been investigated: hydrophobic spheres, hygroscopic particles, biomass combustion, diesel exhaust, traffic emissions, welding fumes and candle smoke. We have also specifically measured the alveolar deposition of nanoparticles in a cohort of 800 subjects.

Our data generally confirm the established deposition models (e.g. ICRP and MPPD) for healthy adults. The largest deviation between experimental studies and models was found for particles in the range 1-5  $\mu\text{m}$ . Ambient particles were observed to have an altered deposition due to hygroscopicity – the only exception being fresh traffic exhaust particles that mainly consist of hydrophobic soot. Children appear to have an increased deposition of inhaled particles, especially in relation to body size. Patients with respiratory disease may have both increased and decreased deposition depending on particle size and physiological parameters. For instance, subjects with emphysema had a decreased deposition of nanoparticles, but an increased deposition of particles larger than 0.2  $\mu\text{m}$ . In fact, we have found that respiratory disease can be identified based on the deposition of nanoparticles – a technique we have named AiDA, Airspace Dimension Assessment by nanoparticles.

In conclusion, the respiratory tract deposition and dose of ambient particles is complex to determine with high precision. However, a reasonable estimate can usually be made if information is available about the aerosol size distribution, particle hygroscopicity and density, and breathing pattern of the subjects.

## Revision of health-related sampling conventions

Göran Lidén<sup>1</sup>, Darrah Sleeth<sup>2</sup>, Peter Görner<sup>3</sup>

<sup>1</sup> Stockholm University, Sweden

<sup>2</sup> University of Utah, USA

<sup>3</sup> Institut National de Recherche et de Sécurité, France

In the early nineties, CEN, ISO and ACGIH agreed on common definitions of the sampling conventions for the respirable, thoracic and inhalable health-related aerosol dust fractions. Subsequent research demonstrated that in workplace environments with low wind speeds (lower than approximately 0.25 m/s), the aspiration of airborne particles as a function of particle aerodynamic diameter into a breathing human mannequin is higher than in workplace environments with higher wind speeds (exceeding approximately 0.5 m/s).

For some time the relevant working groups of the European and International organisations for standardisation (CEN/TC137/WG3 and ISO/TC146/SC2/WG1) have discussed how to amend the existing sampling conventions to incorporate the higher inhalability in low-wind workplace environments compared to the high-wind workplace environments into the set of existing sampling conventions.

The following principal decisions have been taken:

1) To separate the definition of the thoracic and respirable sampling conventions from the current inhalable sampling convention. Instead of, as currently, being defined as sub-fractions of the inhalable fraction, they are given complete definitions on

their own. The proposed new definitions will, numerically, be almost identical to the current definitions.

2) Look into the data for the inhalability in moving air, in order to see if a function can be found that both explains the existing experimental data as effectively as the current inhalable sampling convention, and also better matches the current convention to the aspiration efficiency of a sampler, especially in the particle size range with almost no inhalability data.

3) A new sampling convention for the inhalable fraction in low-wind workplaces shall be defined. It shall be based on the experimental results of Aitken et al. (1999) and Sleeth and Vincent (2011). The exact definition is expected to be decided at a meeting in February 2017.

The intention is not that the occupational hygienist needs to know whether a workplace is low-wind or high-wind. It is expected that a sampler for the inhalable fraction must be able to sample correctly in both low- and high-wind workplace environments. Available data on the performance of inhalable samplers in low- and high-wind environments show that personal samplers designed to be mounted with their inlets facing horizontally, either forward or omni-directionally, have such good performance.

## Bioaerosols and quartz dust in potato and vegetable processing plants

Patrick Steinle

Schweizerische Unfallversicherungsanstalt (SUVA), Switzerland

Potatoes and other vegetables such as onions, carrots and lettuce are usually washed, sorted and packaged in large plants, before delivery to point of sale. Measurements showed high levels of bioaerosols and quartz dust in such plants, especially in the areas where storage products are fed to the production lines and in the washing and sorting sections.

Personal and area sampling was performed, in order to assess both possible emission sources and time weighted average concentrations. Bacteria and molds were sampled as inhalable dust on polycarbonate filters with the PGP-GSP system (flow rate 3.5 L/min), desorbed and plated onto Caso- (bacteria) and DG18- (molds) agar. Colonies were counted after 5 days of incubation at 30 / 25°C, selected colonies were identified by MALDI-TOF (bacteria) or microscopy (molds). Endotoxin concentrations were measured in inhalable dust, sampled on glass fiber filters and analyzed with a chromogenic kinetic LAL-assay. Respirable quartz was sampled with the PGP-FSP device (flow

rate 2 L/min) and analyzed gravimetrically and with powder X-ray diffractometry.

Quartz dust concentrations were in the range of 0.02 to 0.50 mg/m<sup>3</sup> and often exceeded the Swiss permissible exposure limit (PEL) of 0.15 mg/m<sup>3</sup>, bioaerosol concentrations were usually in the range of 1E4 to 1E6 colony forming units (CFU)/m<sup>3</sup> for both molds and bacteria, and between 10 and 850 endotoxin-units (EU)/m<sup>3</sup>. Bacterial flora was dominated by gram-positive cocci, whereas molds were dominated by different species of *Penicillium*.

Unfortunately, control measures such as higher ventilation rates and installation of local exhaust ventilation systems did not prove to be very efficient, as shown by measurements prior and post installation of such controls.

The authors will present data from 15 measurement campaigns in 8 different plants in Switzerland.

## Allergen and bioaerosol exposure assessment in different areas of a veterinary faculty – using stationary sampling equipment

Monika Raulf<sup>1</sup>, Eva Zahradnik<sup>1</sup>, Christina Walther<sup>2</sup>, Norbert Schäl<sup>3</sup>, Verena Liebers<sup>1</sup>, Ingrid Sander<sup>1</sup>, Thomas Brüning<sup>1</sup>, Ingrid Thullner<sup>2</sup>

<sup>1</sup> Institut für Prävention und Arbeitsmedizin der DGUV, Institut der Ruhr-Universität Bochum (IPA), Germany

<sup>2</sup> Unfallkasse Hessen, Germany

<sup>3</sup> Justus-Liebig-Universität Gießen, Germany

Veterinarians and coworkers are potentially exposed to various occupational hazardous agents such as allergens from animals, plants, microbial agents (e.g. endotoxins or  $\beta$ -glucans) and chemical substances. Exposure to animal allergens has been implicated as major risk factor for sensitization and development of allergic symptoms. Studies among laboratory animal workers exposed to rodents showed that allergies can develop very early after first exposure. Thus, veterinary medical students might be at risk of developing allergy during their education. So far only little is known concerning health and exposure among veterinary students during their education. Therefore, we investigated as one aspect of a longitudinal study focusing on the health and exposure of veterinary students, air concentrations of various allergens, endotoxin and  $\beta$ -glucan at different places at the university campus.

Stationary airborne dust samples were collected using GSP-sampling heads for inhalable dust and air samplers at a flow rate of 10 L/min for allergen and  $\beta$ -glucan and 3.5 L/min for endotoxin determination. Allergen levels were measured with enzyme immunoassays against allergens from domestic mites (DM) and against major allergens of cat (Fel d 1), dog (Can f 1),

horse (Equ c 4) and cattle (Bos d 2). Additionally  $\beta$ -(1–3)-glucan concentrations were determined using enzyme immunoassay and endotoxin activity using LAL test. Exposure measurements were performed three times (July 2014, July 2015 and April 2016) at 14 places where veterinary students are working (campus and teaching/research farm). In total, 124 samples were collected.

Fel d 1 and Can f 1 levels were found at worksites where cat and dogs were examined, but also in social rooms. Equ c 4 was measured with the highest concentrations in rooms where horses were examined (median 17.6 U/m<sup>3</sup>), but also in social rooms (median 0.16 U/m<sup>3</sup>). The highest levels of Bos d 2 were determined in cattle stables (median 608 ng/m<sup>3</sup>). High DM levels were measured in the poultry house (median 231 ng/m<sup>3</sup>). Endotoxin activity and  $\beta$ -glucan were detectable in all samples, with the highest levels in the poultry house (median endotoxin: 1113 EU/m<sup>3</sup> and  $\beta$ -glucan 1184 ng/m<sup>3</sup>) and in cattle and sheep stables. Our data demonstrate that allergen, endotoxin and  $\beta$ -glucan exposure occurs during veterinarian's education. By using sensitive assays for quantification, allergen transfer into places without presence of animals was detectable.

## Size fractionation of endotoxin from organic waste

Catherine Rolph, Toni Gladding  
Open University, United Kingdom

Endotoxin, lipopolysaccharide molecules from the cell wall of gram negative bacteria, are a known pro-inflammatory agent. When released from organic waste sites such as composting facilities as a bioaerosol, airborne endotoxin can cause respiratory effects in exposed workers. There are currently few guidelines on the emissions of endotoxin from waste facilities and limited research on the potential exposure of surrounding populations. It is likely that even small concentrations (<50 EU m<sup>-3</sup>) can have health impacts.

This study comprehensively size fractionated endotoxin from compost under controlled and real-world conditions using an eight stage non-viable Andersen sampler. High endotoxin concentrations (>1000 EU m<sup>-3</sup>) were detected in a controlled environment chamber after aerosolising compost. Sampling was also undertaken at bio-waste facilities to further understanding

of how endotoxin may spread and to help inform endotoxin risk modelling for nearby communities. Detailed size fractionation helped to characterize the endotoxin, particularly as the finer fraction is more likely to travel further and penetrate deeper into the lung. It has been observed that endotoxin is largely associated with a coarse size fraction, however elevated concentrations which may have health impacts were also regularly detected in the fine fraction (<2.1  $\mu$ m). Endotoxin concentrations were compared to viable bioaerosols and particulates in order to help identify any proxies for high concentrations. Currently, standardisation of the endotoxin assay is limited, so key parameters such as sampling, extraction and storage methods were also optimised to ensure reliable and repeatable detection. Overall this work provides an important step in the full characterization of endotoxin in the environment and the risks it may pose to exposed communities.

## **Session 3: Aerosols 2**

## Keynote

### Development of samplers for aerosol fractions deposited in two regions of the respiratory tract – the gas-exchange region and the posterior head airways

Göran Lidén  
Stockholm University, Sweden

The ICRP model for deposition of airborne particles in human respiratory tract – sub-divided into the Extra-Thoracic1 (ET1), Extra-Thoracic2 (ET2), Tracheo-bronchial (BB), Bronchiolar (bb) and Alveolar regions (Alv) – is a mathematical model based on two mechanisms, diffusion and aerodynamics. The model is mainly based on experimental determinations of deposition of airborne particles. Extra-Thoracic1 consists of the anterior unciliated part of the nose. Extra-Thoracic2 consists of the posterior ciliated part of the nose and mouth airway. ET1 and ET2 constitute the head airways. The bronchiolar region consists of the bronchioles and the terminal bronchioles. Another common name for the Alveolar region is the Gas-Exchange region.

CEN and ISO have produced a standard with 5x2 sampling conventions for the aerosol fractions depositing in the five regions by diffusion and aerodynamics, respectively. Each sampling convention is the average of the deposition by males and females, nasal and oral breathing and sitting, light and heavy exercise activities.

Currently commercially available methods to measure any of these particle fractions are:

- Number-weighted spectrometers based on the (electrical) mobility equivalent diameter (Differential Mobility Aerosol Spectrometers – DMAS)

- Number-weighted spectrometers based on the aerodynamic equivalent diameter (Aerodynamic Particle Sizer – APS)
- Mass/chemical compound-weighted spectrometers based on the aerodynamic/diffusive equivalent diameters (AeroSelect)
- Surface area of the fraction depositing in the alveolar or tracheo-bronchial/bronchiolar regions
- Mass/chemical compound of all particles depositing in the respiratory tract by diffusion

Only the last sampler and some instruments for the surface area of the fraction depositing in the alveolar region can be used as personal samplers/monitors. The first three are too bulky for that and can only be used as static spectrometer monitors/samplers.

The development of two samplers for airborne particles depositing in the gas-exchange region and the posterior part of the nose will be presented. The fractions depositing by diffusion and aerodynamics are collected on different substrates. These two regions were selected because the content of particles deposited there may (after dissolution in the case of the gas-exchange region) end up in the brain.

The design, testing and validation of the samplers for the two fractions will be presented.

### A cyclone with narrow-diameter particle deposition for end-of-shift quartz measurement

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The National Institute for Occupational Safety and Health (NIOSH) is conducting research to develop field-ready instrumentation capable of an end-of-shift (EoS) measurement for respirable crystalline silica. Field-portable FTIR spectrometer gives relatively accurate analyses of filter samples using a direct-on-filter (DoF) analysis of samples.

However, there is a difference between the FTIR beam diameter (6-mm) and particle deposition diameter of 10 mm nylon cyclone (34-mm) so that it is necessary to account for the varying particle deposition profile across the filter. A new size selective sampler, based on the concept of the GS3 cyclone, was constructed using a 3-dimensional printer loaded with ABS-M30 polymer material. The internal dimensions of the GS3 cyclone were scaled according to empirical equations for sampler design. Sampling efficiency of the EoS cyclone was determined using polydisperse glass sphere particles and a time-of-flight real-time direct reading instrument in a calm air chamber. Five prototype

EoS cyclones were tested at flow rates of 1.1 and 1.2 L min<sup>-1</sup>. The measured performance for the EoS cyclone was compared to the international respirable convention. Average cut off diameters of the EoS cyclone at flow rates of 1.1 and 1.2 L min<sup>-1</sup> were 4.4±0.06 and 4.1±0.15 µm, respectively. Bias of the EOS cyclone ranged -4-10% at 1.1 L min<sup>-1</sup> and -16-4% at 1.2 L min<sup>-1</sup>. The EoS cyclone provided respirable dust mass concentration results similar but significantly larger (5%) than those obtained from samples collected with 10-mm nylon cyclones. The sensitivity of the DoF-FTIR analysis in estimating quartz was found to be increased more than 10 times when the samples were collected with the EoS cyclone. The average filter deposition diameter was 8.8 mm in sixty samples.

Further investigation is on-going to compare quartz measurements using the portable FTIR when samples are collected with the EoS cyclone to standard sampling and analysis procedures, especially in field applications.

### Towards better particle characterization in industrial workplaces

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Exposure to airborne particulate matter (PM) is a major risk factor for development of respiratory and cardiovascular diseases. Epidemiological and experimental studies have shown that particle size and physical and chemical properties of the PM are of importance, with possible increased toxicity of the smallest particles. Many industrial workers are exposed to agglomerates/aggregates composed of primary ultrafine particles (<0.1 µm). These primary particles are unintentionally formed, e.g. in thermal processes used in the production of metals/alloys, by welding and by mechanical grinding of clinker in cement factories.

The aim of the present study is to characterize the PM in workplace air during various industrial processes with regard to particle size distribution, morphology, chemical composition and solubility/bioavailability. PM formed in recycling and casting of precious metals, production of cement, aluminum, silicon,

silicon carbide, ferroalloys (silico- and ferromanganese, ferro-silicon) and nano zinc metallic powder, in different welding techniques and other hot processes such as plasma and thermal cutting and air carbon arc applications are under characterization.

The applied sampling and analytical methods include the use of personal and stationary cascade impactors for subsequent characterization of the particle fractions by gravimetric analysis, electron microscopy (SEM, ESEM, TEM) and atomic spectrometry (ICP-OES, ICP-MS).

In this presentation the characteristics of PM present in workroom air during production of manganese alloys and silicon carbide with respect to particle size (mass and number) distribution, morphology, chemical composition and solubility/bioavailability will be discussed.

### Direct-reading gravimetric airborne nanoparticle monitor based on an electrostatic silicon microcantilever

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Air pollution by particulate matter (PM) has become a topic of highest public awareness and economic relevance. Nanoparticles (NP) are regarded as most problematic, since they are small enough to reach the deepest regions of the lung. To protect e. g. workers from exposure, portable direct-reading instruments have been proposed to support occupational PM and NP monitoring using stationary equipment. Low-cost portable devices, which are based on optical scattering, are available, but have an insufficient response to NPs. Efficient PM sampling including the NP size range can be done by electrostatic precipitation (ESP) of charged particles.

Based on ESP we designed a direct-reading gravimetric NP monitor by implementing ESP within a micro electro mechanical system (MEMS) consisting of an electrothermal piezoresistive silicon micro cantilever. Charged NPs from particle-laden airstream precipitate on the cantilever operated as a resonant mass balance. Induced by its mass increase, the cantilever's resonance frequency shifts at a rate proportional to the airborne NPs mass concentration. Possible issues of this technology include the size-selectivity of NP sampling and the saturation (including the need for cleaning) of the MEMS device after long-term operation or extremely high-concentrations – both were studied in some detail.

The size-selectivity of NP sampling was investigated with aerosols of carbon, silica, and titania, which represent technically

relevant air pollutants in industrial environments. Uniform concentrations and size distributions of airborne NPs were generated in a sealed chamber and controlled in real time (1 s) with a standard laboratory NP monitoring system (Fast Mobility Particle Sizer, FMPS, TSI 3091, size range: 5.6 nm to 560 nm, 32 bins). NP mass concentrations were determined for each size bin assuming a spherical shape and a uniform density of the NPs. We found bimodal size distributions with a dominating enhancement mode having distinctly different mean diameters for the investigated aerosols depending, e.g., on the aerosol suspension liquid. Excellent agreement with the FMPS ( $R^2 = 0.996$ ) in a range from 0 to 800  $\mu\text{g}/\text{m}^3$  was obtained for the direct-reading gravimetric MEMS-based airborne NP monitor. Size-selectivity of NP sampling was found as expected for a tube-wire ESP assuming size-independent particle charge.

Sensor saturation after long-term use is indicated by instable readings. The cantilever can be completely regenerated by removing excess NPs from the micro cantilever in an ultrasonic bath. However, for easy use cleaning methods performed without demounting the fragile MEMS from the sampling head have to be developed. Large agglomerates could be removed at switched-off sampling voltage in clean air as indicated by a back-shift of the resonant frequency after 1 hour of purging. Further improvement is expected using, e. g., reverse electrostatic poling of the cantilever during purging.

### Risk assessment of handling rigid carbon nanotubes at a technical centre in Berlin

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The safety of handling aluminium or silicon wafers that were coated with different kinds of rigid carbon nanotubes was questioned by a laboratory. The first step of a risk assessment is the collection of information. The material safety data sheets (MSDS) from the manufacturer were insufficient to answer this question of a safe handling procedure. So we examined material samples under a scanning electron microscope (SEM) and simulated some work tasks and process parameters like air streams and physical impact in a glove box to see if a release of carbon nanotubes (CNT) was possible. Air samples over approximately 60 hours were evaluated under SEM analysis and showed that in case of careless handling emission is possible. Some CNT agglomerates even fitted to the so-called WHO criteria for hazardous fibres (aspect ratio 3:1, length  $> 5\mu\text{m}$ ).

As a result we advised some improvements of handling the CNT coated wafers towards a safer use and measured subsequently the possible emission and exposure at the workplace in a laboratory. For this purpose we applied a measurement strategy by stationary sampling in the near field, far field, background and at the person. We also modified the SEM analysis procedure (parameter adjustment to compare to the reference sample, e.g. accelerating voltage, operating distance etc.) to be able to compare the results with a suggested occupational exposure limit value of 10000 fibres per cubic meter. In that way the limit of detection of the sampling and counting method reached a value well below the limit value.

The results using our adapted measuring method show that during this improved handling operations no emission and thus no exposure took place at the workplace.

# **Session 4: Biological monitoring – Bioaerosols**

## Keynote

### Biological monitoring without limits

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Biological monitoring is a useful tool for assessing systemic exposure. It has a particular role for substances absorbed through the skin or where control of exposure relies on respiratory protection and therefore air monitoring alone may not give a complete picture of exposure.

Many organisations around the world propose biological monitoring guidance values (BMGVs) but recognising biological variation and that there are no 'bright lines' between safe and unsafe levels, several organisations avoid the word 'limits' when considering BMGVs. In America the ACGIH has Biological Exposure Indices and Germany has Biologische Arbeitsstoff-Toleranzwerte. Where a health-based BMGV is not possible for substances like non-threshold carcinogens or sensitisers a non-occupational exposed background or reference value may be proposed. Exceeding such a reference value then indicates the likelihood of occupational exposure and possibly the need to review workplace controls.

Great Britain has an alternative approach based on the 90<sup>th</sup> percentile value of biological monitoring data from workplaces following good occupational hygiene practice. First applied in 1987 to the aromatic amine and human carcinogen

4,4'-methylene-bis-2-chloroaniline (MbOCA), it was called a biological action level. It was not health-based and exceeding it simply indicates a need to review, and possibly improve controls. Such BMGVs were later established for hexavalent chromium, glycerol trinitrate, methylenedianiline, polyaromatic hydrocarbons and diisocyanates.

In addition to workplace surveys HSE's laboratory also analyses biological samples from external occupational health professionals and over the last 20 years has accumulated results from 240,000 samples. The external samples are not representative of industry as a whole. The data may be biased upwards from workplaces experiencing difficulties controlling exposure or may be biased downwards if samples come from workplaces with good control and/or little exposures. Ninetieth percentile data for 15 substances with over 100 samples each over a 3 year period show results generally below GB and international guidance values. The utility of the 90<sup>th</sup> percentile approach provides a pragmatic bridge between what is desirable (background/low level exposure) and what is achievable with current good practice and appropriate use of this approach should drive sustainable reduction in harmful exposures over time.

### Temporal variations of size distribution of bioaerosols at occupational settings

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Measurements of the size distribution of airborne microorganisms (SDAM) provide helpful data for removing airborne particles from contaminated air, verifying the consistency of biocollectors performances against the studied bioaerosol and predicting the deposition of microbial entities in lungs. SDAM has been documented in a multitude of occupational environments but usually with a limited number of measurements. Indeed, the variability of SDAM in time and space is scarcely known and additional research is needed in order to establish the relevance of the published data. The aim of the study was to investigate the temporal variability of SDAM in time at occupational settings.

Bioaerosols were studied over one year in a waste sorting plant (WSP) treating household waste in France. Samples were collected every month in a sorting cabin and in a grinding area for the measurement of culturable bacteria/fungi and gravimetric dust. Sampling was performed with the Marple 290 cascade impactor [2.0 L/min], the closed-face cassette [2.0 L/min], and the CIP 10-I [10.0 L/min] for five hours. The Optical Particle Sizer (OPS) Model 3330 [1.0 L/min] was also used.

The results revealed a complex behaviour of airborne microbial particles in the WSP over the year. In the sorting cabin, particles carrying airborne fungi had a median diameter from 2.9 to 7.2  $\mu\text{m}$  (mean=4.2  $\mu\text{m}$ , n=12) with a dominant mode between 3.0 and 7.0  $\mu\text{m}$ . The airborne dust were larger in size, with a median diameter from 8.8 to 12.5  $\mu\text{m}$  (mean=10.5  $\mu\text{m}$ , n=12) and a dominant mode between 6.0 and 10.0  $\mu\text{m}$  or between 10.0 and 20.0  $\mu\text{m}$ . Airborne bacteria varied in a wider range of size over the year with a median diameter from 3.2 to 23.0  $\mu\text{m}$  (mean=14.5  $\mu\text{m}$ , n=12). Similar trends were observed in the grinding area with greater variations for bacteria and inhalable dust. Bioaerosols were mainly polydisperse and the SDAM was not significantly affected ( $p < 0.0001$ ) by climatic parameters. The OPS measurements revealed a large number population of sub-micron particles that may contain microbial fragments.

The results show that SDAM vary over time/space and suggest different aggregate states for airborne bacteria and fungi in WSP. They support performing several overtime measurements for a relevant characterisation of SDAM at occupational settings with a microbial characterisation of submicron particles. The presentation also addresses methodological issues for SDAM measurements and lungs deposition of microbial particles.

## Evaluation of bioaerosol samplers for biological sampling efficiencies under controlled conditions

Joseph Strauss

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To date, bioaerosol sampling devices are only calibrated for physical sampling efficiencies of standardized inorganic or organic particles, but biological validation of these samplers under controlled conditions has proven difficult due to the high variability of bioaerosol particles.

We report here the development and application of a novel type of bioaerosol test chamber which is used to generate bioaerosol particles of living microorganisms with defined and constant cell numbers and viability. The system comprises of an aerosol generator, a testing chamber with controlled laminar airflow of 1 m/min in a roughly 1 m<sup>3</sup> chamber and in-built measurement devices to record particle counts, particle size distribution, temperature, humidity and provides space for at least two bioaerosol samplers. The whole system was physically validated for constant particle size distribution in the presence of operating bioaerosol samplers (Konlechner et al., 2013, GRdL 73: 471)

For the biological validation of the system we established three control points and in each of them we monitored the cell number and viability of microbes

(i) in the original material, which is fed into the bioaerosol generator

(ii) after aerosolization with a liquid sparkling aerosol generator as well as

(iii) during the operation of the laminar flow.

This set-up allowed us to firmly define the constant concentration of total and viable microbial cells per m<sup>3</sup> of air and thus to test how many of these bioaerosol particles can subsequently be detected by commercial sampling devices. The biological validation was carried out with different concentrations and viabilities of conidial spores of *Trichoderma longibrachiatum* and the MAS-100 sampler). The extensive evaluation provided solid evidence that this system is adjustable at each experimental control point, generates highly reproducible results in dozens of independent biological repetitions and is thus suitable for the determination of biological sampling efficiencies of bioaerosol sampling devices.

The results of this extensive comparison show that enormous differences prevail in CFU numbers when different samplers are tested with different type of organisms under these controlled conditions. Implications of these results on the interpretation of bioaerosol field measurements are discussed.

## Measurement of fragments and spores for fungal exposure assessment

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People dwelling or working in heavily mold contaminated environments can be exposed to high levels fungal particles bearing large amounts of allergens, antigens and toxins. Inhalation of these particles in occupational settings has been associated with immune diseases such as chronic obstructive pulmonary diseases (COPD), allergy and asthma. In order to reduce the morbidity and mortality associated with exposure to fungal particles, it is important to monitor exposure levels in suspected environments so that appropriate actions could be taken when levels of concern are observed. For decades, fungal exposure assessment has been mostly based on the measurement of spores or spore related biochemical constituents, such as ergosterol, (1-3)-beta glucans and fungal antigens. However, the observed levels in indoor environments with damp problems, especially, are relatively low and cannot explain the observed health outcomes. The discovery of the release of large numbers of airborne submicronic fungal fragments in in-vitro aerosolization studies, suggested that these fragments have been overlooked in environmental samples.

Overall, airborne fungal particles comprise spores from reproductive structures and fragments in different sizes from vegetative mycelial mass. Furthermore, it is possible that colonized substrate materials impregnated with fungal antigens and toxins become airborne increasing as such the fungal exposure load. Exposure assessment based on the measurement of both spores and fragments has been suggested to improve the characterization of fungal exposure load in various environments as the immune system reacts differently toward spores as compared to hyphal/mycelial particles.

Recently an immunodetection method was developed for measurement of fungal particles in Scanning Electron microscope (SEM) that allows direct enumeration of nanogold labelled fragments as well as spores in environmental samples. In the present paper, we have used this novel method to assess the levels of fungal fragments and spores in town house basements with mold problems and in sawmills recognized for high fungal spore exposure.

## Biological monitoring of naphthalene in workers in the production of abrasives

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Naphthalene is a solid chemical that easily sublimates at room temperature. It is used in the production of abrasives due to its positive effects on the formation of pores. Based on irritant effects in animal experiments, the Occupational Exposure Limit (AGW) in Germany was reduced in 2011 to 0.5 mg/m<sup>3</sup> (0.1 ppm). In the majority of other EU countries including Austria the Occupational Exposure Limit is 50 mg/m<sup>3</sup> (10 ppm). There is no exposure limit value in biological materials in Germany but a reference value (BAR: Sum of 1- and 2-naphthol = 35 µg/L urine). The aim of the study was to provide solid knowledge of the external and internal exposure in the abrasives industry for assessment of possible dose-dependent irritative effects in this industry.

### Methods:

We examined 39 exposed and 22 non-exposed non-smoking male subjects from 5 abrasives producing plants in Germany and Austria, where naphthalene is used in open handling procedures.

For biological monitoring, each day from Monday to Thursday of a working week spot urine samples were collected before and after shift. Urine samples were analyzed for the content of 1-naphthol and 2-naphthol.

Air monitoring including personal shift measurements was performed on Thursday of this week.

### Results:

In the reference group, all urine specimens at all days showed naphthol concentrations below the BAR. In the exposed groups, a sawtooth-like increase of the naphthol concentrations during

the week was found, and the values did, in the average, not drop below the BAR until next morning. In the highly exposed group the median naphthol concentrations raised from 331 µg/L urine on Monday morning to 1,099 µg/L urine on Thursday after shift.

The personal air measurements showed median (range, mg/m<sup>3</sup>) shift concentrations in the reference group of 0.13 (0.05-0.36), in the moderately exposed group (mainly bystanders) of 0.59 (0.20-1.22) and in the highly exposed group in the mixing/sifting and the molding/pressing areas of 6.30 (2.46-11.58).

The post-shift naphthol concentrations in urine showed a good correlation with the values from personal air sampling on Thursday ( $R^2 = 0.768$ ).

Subjects of the highly exposed group who started the working week after a break of at least 2 weeks showed naphthol concentrations all below the BAR on Monday morning.

### Conclusions:

Subjects who handled naphthalene in open procedures exceeded the allowable German exposure limit in air as well as the German urinary reference value of naphthols in the general population significantly. We observed a slight increase of urinary concentrations over the working week confirming a biphasic elimination kinetic of several hours and ca.17 hrs resp. Biological monitoring proves to be a suitable tool for monitoring naphthalene-exposed subjects.

### Measurement of *Staphylococcus* species in sedimented and airborne dust in Danish homes

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*Staphylococcus aureus* is an opportunistic human pathogen which can be antibiotic resistant (methicillin-resistant *S. aureus* called MRSA). Other *Staphylococcus* species can also be opportunistic pathogens and may play a role in horizontal transfer of genes for antimicrobial resistance.

This study aimed to identify airborne *Staphylococcus* species in Danish homes, including MRSA (methicillin-resistant *S. aureus*) as measured using different sampling methods. Airborne dust collected from: 1) 2 farm-related homes using Electrostatic Dust Collectors (EDCs), 2) 54 city-flats using EDCs, 3) 5 city-homes in four seasons using EDCs and stationary GSP-samplers, 4) 7 homes repeatedly using stationary and personal GSP-samplers, and 5) 1 office repeatedly using personal and stationary GSP and Andersen six stage sampler (ASSS) were analysed for concentration of bacterial species using two agar media (NA: Nutrient Agar and *Staphylococcus* Selective Agar: SA) and MALDI-TOF MS. The *Staphylococcus* species richness on NA versus SA was not significantly different. *S. aureus* was found in two of 68 homes. *S. aureus* from a farmer's home was identified as

MRSA (t034), while *S. aureus* from a city-home belonged to spa type t509. *S. capitis*, *S. epidermidis*, *S. hominis*, and *S. warneri* were found in 13-25%, *S. cohnii*, *S. pasteurii*, and *S. saprophyticus* in 5-10%, and *S. caprae*, *S. cohnii*, *S. equorum*, *S. haemolyticus*, *S. kloosii*, *S. lugdunensis*, *S. pettenkoferi*, *S. simulans*, and *S. xylosus* in less than 3% of 134 dust samples. Species-richness was high in the farmer's home, and *S. equorum* and *S. kloosii* were found only in that home. Season had a significant effect on *Staphylococcus* with lowest concentration and richness in winter. Concentration of *Staphylococcus* correlated negatively with the concentration of other genera. Concentrations of *Staphylococcus* and other bacteria as well as bacterial richness were higher when measured using personal GSP compared to stationary GSP, but concentrations correlated significantly. In conclusion, *Staphylococcus* species constituted a considerable proportion of the airborne bacteria. However, *S. aureus* and MRSA had very low incidences no matter whether long-term sampling using EDCs, or active stationary or personal GSP samplers, or ASSS were used and during all seasons. Thus, transmission of *S. aureus* through the air in Danish homes seems to be limited.

### Bioaerosol measurements with an automated sampler – Experiences and results

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The concentrations of micro-organisms in the air usually show large spatiotemporal variations. Seasonal fluctuations of the natural background were in the range of 4 to 8000 CFU/m<sup>3</sup> for airborne bacteria for example as given in Kolk et al. (2009). Only few data are available for diurnal fluctuations of airborne microbial concentrations. For this reason an automated bio-aerosol sampler for the continuous sampling of airborne micro-organisms, based on a standardized AGI-30 Impinger (Clauß 2015), was developed and constructed. The performance of this system was tested under field conditions in different environments and workplaces. In ambient air variations of the concentration of airborne bacteria of up to one power of ten were observed within a period of 24 h with a mean concentration of 50 CFU/m<sup>3</sup>. In different animal houses for poultry, pigs, goats and cattle much higher bio-aerosol concentrations were found and much higher fluctuations could be observed. In an aviary for laying hens the fluctuation range was even up to three powers of ten over a period of 48 h. The measured mean concentrations of airborne bacteria varied between 10<sup>6</sup> CFU/m<sup>3</sup> at daytime and about 10<sup>5</sup> CFU/m<sup>3</sup> at nighttime. In goat houses lower concentrations of airborne bacteria and also lower fluctuations were found,

followed by cattle and pigs. All diurnal courses show clearly lower concentrations at night times or rest periods respectively. A possible explanation for this finding could be the different activity of the animal species and, if assumed that most of the micro-organisms are emitted from the body surface of the animals, the different surface-area-to-volume ratio (feathers with a very large surface area for poultry vs. pig skin with only few bristles). The system will be further modified to conduct long-term measurements for the ascertainment of emission factors for different bio-aerosol emitting facilities.

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### Association between exposure to airborne noroviruses and gastroenteritis among wastewater workers

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An increased incidence of acute gastroenteritis (AGE) has been reported among workers at wastewater treatment plants (WWTPs). The cause is unknown but the symptoms are consistent with AGE caused by norovirus (NoV) infection. The objective of present study was to investigate if exposure to airborne NoVs is the cause of the increased incidence of AGE reported among WWTP workers.

Personal exposure to airborne enteric viruses was examined monthly among 14 WWTP workers during a one-year study period. Air sampling was performed throughout a working day using personal air samplers mounted in the inhalation zone of the workers. Gastrointestinal symptoms were reported by workers and their stool samples screened for NoV Genogroup (G)I and GII, sapovirus, adenovirus 40/41, astrovirus, rotavirus, enteric bacterial pathogens and protozoa.

NoV genomes were detected in approximately 47% of all personal air samples (n=106), albeit mostly in low concentrations. NoV was not detected in any of the reference air samples taken upwind from the WWTP. Quantifiable levels of NoV GI were found in 4.7% of the personal air samples with exposure levels ranging from 832 to 2384 genome copies (GC)/m<sup>3</sup> air, while 13.2% of air samples contained quantifiable levels of NoV GII in exposure

levels ranging from 82 to 2284 GC/m<sup>3</sup> air. The dose response of exposure to NoV is unknown, but with an estimated oral ID<sub>50</sub> reported to be as low as 18 viral particles the measured airborne exposure could potentially pose a risk to the workers.

Asymptomatic infection with NoV GI was observed in one of the 14 WWTP workers in two consecutive months (January and February). Both NoV GI and GII were detected in the personal air sample from this worker in February, but no airborne NoV exposure was observed on the sampling day in January. However, genotyping of NoV in the air sample showed the exposure to be from NoV GI.4 and not GI.3, which was found in the stool sample. In addition to NoV, *G. intestinalis* was detected in the stool sample of this worker in August, but infection was asymptomatic and self-limiting. No other enteric pathogens were detected in the stool from the WWTP workers.

The majority of WWTP workers were exposed to airborne NoV on several occasions, but exposure seldom correlated with gastrointestinal symptoms and infections. Although NoV infection following airborne exposure to NoV was seen in one worker, genotyping could not establish a direct association between exposure and infection.

# **Session 5: Mixed phases – measurements**

## Keynote

### Characterization of emissions from bitumen with antistripping additives

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Bitumen fumes are a complex mixture of different types of chemical compounds in both the particulate and the vapor phase. Semi-specific methods have been put forward to measure exposure, such as the IFA 6305(1) and INRS M-2(2), but little is known about the contribution of the additives that are almost always present in the bitumen to improve its viscoelastic properties. In Québec, an appreciable improvement in the adhesion properties of strip-resistant bitumen has been demonstrated, and its use has increased accordingly. However, complaints of irritating effects have been reported by paving workers when strip-resistant bitumen is applied, and little is known about the specific emissions generated by this kind of bitumen.

The purpose of this study was to characterize, in the laboratory, the fumes emitted at asphaltting temperature by bitumen with antistripping additives and by bitumen without these additives and to compare the emissions profiles for identification of chemical irritants or sensitizers in the bitumen with the additives. The knowledge acquired from this characterization will make it possible to develop sampling and analytical methods for assessing the risk of irritation associated with emissions of substances derived from using antistripping additives in bitumen.

Two approaches were used to generate the bitumen fumes: direct headspace generation together with gas chromatography mass spectrometry (GC/MS), and generation by a reactor in a test chamber under controlled temperature, humidity and UV-Vis radiation conditions.

Characterization of the additives alone demonstrated presence of a number of chemicals of different families, including amines, glycols, glycol ethers and aldehydes. Some of these compounds also showed up in the characterization of emissions from bitumen mixed with the additives in the proportions used in asphaltting. Relative amounts of the compounds identified depending on the different variables studied are reported. The results will be used to develop new methods of assessing exposure that will contribute to a better understanding of the irritating effects of fumes emitted when bitumen containing antistripping additives is used.

1) IFA-Arbeitsmappe “Messung von Gefahrstoffen”. 40. Lfg. IV/2008, 6305/1 und 6305/2. Hrsg.: Deutsche Gesetzliche Unfallversicherung (DGUV), Berlin. Erich Schmidt, Berlin

2) Metropol M-2, “Fumées de bitume”, Institut national de recherche et de sécurité, France, 2016

### IFA and INRS comparison on bitumen fumes sampling and analysing methods.

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In Europe, no consensus exists on a method that samples and analyses bitumen fumes on road constructions sites, essentially for historical and practical reasons. Thus, different samplers' design (GGP vs 37 mm cassette + XAD-2 sorbent tube), extraction solvents (tetrachloroethylene vs n-heptane), and analytical techniques (FT-IR vs GC-FID) were preconized leading to theoretically different results. Starting from that point, the Institute for Occupational Safety and Health of the German Social Accident Insurance (IFA) and the French Institut National de Recherche et Sécurité (INRS) wanted to compare their methods to correlate them to each other.

The comparison study was conducted in two steps: laboratory and workplace assays. During the laboratory assays, a bitumen fume generation system developed at INRS was used to simultaneously expose 6 IFA and 6 INRS samplers to controlled fume in terms of vapours and particles concentrations, humidity, temperature and homogeneity. Masses of fumes collected on each collection substrates of the samplers were determined and then compared. It was found that the GGP samples 9% more

fumes than the INRS system due to a better sampling efficiency of the inhalable fraction. Terchloroethylene extracted 9% and 29% more mass than n-heptane did on filter and XAD-2 sorbent bed, respectively. It was also highlighted that the sensitivity of the FT-IR and FID was different in function of the quality of the matter analysed. But globally, when the masses quantified on filters and XAD-2 beds are summed up giving the total mass concentration of fumes, there is a strong correlation between the methods. Those observations issued from the laboratory assays needed to be confirmed on workplaces where the concentrations and environmental conditions are not controlled and where bitumens should be different from those used in laboratory – even if the laboratory bitumens were certified as representative of the actual consumption in Germany and France. Workplace assays confirmed the laboratory correlation between the methods even if dramatically different environmental conditions were encountered during those assays. Thus, this unique equation  $C_{IFA} = 1,7646 C_{INRS} \pm 0,39$  should be applied to convert IFA quantifications to INRS ones and vice versa.

### NovaCarb™-Denuders as a vapour-particle partitioning tool for the occupational sampling of aerosols from semi-volatile organic compounds

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<sup>3</sup> University of Rostock

Aerosols from hazardous semi-volatile organic compounds (SVOC) may occur in workplace air and can simultaneously be found as particle and vapour phase (Breuer et al., 2015). For health risk assessment it is necessary to collect particles and vapours separately. This can be achieved by using a denuder for vapour collection, combined with a filter and an adsorbent cartridge for particle collection. The study focused on the suitability of NovaCarb™ carbon monolith denuders (MastCarbon International Ltd., Guilford, UK) to achieve particle-vapour separation. Particle transmission efficiency experiments were performed with polystyrene latex (PSL) particles (size range 0.51-3 µm), while the time dependent vapour collection efficiency was analysed for polar and nonpolar SVOC (mass concentrations 7-10 mg/m<sup>3</sup>) over 2 h at 5 or 10 L/min. The experimental vapour collection efficiency was also compared with values obtained from calculations according to de Santis, 1994.

For n-hexadecane (C16), the vapour collection efficiency was 75-90% for one denuder and 88-98% for two denuders, while for diethylene glycol (DEG) values in the range of 69-84% for one denuder and 81-97% for two denuders were determined. At 5 L/min higher vapour collection efficiencies were achieved than at 10 L/min. The deviations between the theoretical and experimental vapour collection efficiencies were around 2% for C16

and 15% for DEG. Since the theoretical efficiency depends on the geometric shape and length of the denuder, flow rate and diffusion coefficients of the tested substances, the obtained values define an upper limit which could be reached (de Santis, 1994). Regarding the particle transmission through the denuders, the use of one denuder showed transmission efficiencies around 98% for 1-3 µm particle diameters. The use of three denuders resulted in transmission efficiencies from 97-93% for the same particle sizes.

In summary, NovaCarb™-Denuders are well applicable for sampling aerosols of polar/nonpolar substances with particle diameters ≤ 3 µm and flow rates of 5 L/min or lower. These properties and their compact size make them suitable for use in personal aerosol samplers.

This work is supported by the German Social Accident Insurance (DGUV), research contract FP371.

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De Santis, F. (1994) Anal. Chem. 66, 3503-3504.

## Exposure to polycyclic aromatic hydrocarbons during recycling of railway sleepers and remediation of contaminated soil

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In the past, tar oils were widely used for the impregnation of wooden parts, such as railway sleepers. Once removed from service, they have to be handled as a hazardous waste because they contain polycyclic aromatic hydrocarbons (PAH). Furthermore, these substances are also present in soil from renaturation of contaminated industrial areas. Recycling of railway sleepers and remediation of contaminated soil is performed by specialised enterprises.

One of the critical components in the large group of PAHs is benzo[a]pyrene due to its carcinogenic potency. Based on a substance-specific exposure-risk relationship (ERR), according to the Technical Rule for Hazardous Substances (TRGS) 910, so-called acceptable as well as tolerable concentrations have been derived for benzo[a]pyrene. Related to a lifetime exposure these are specified to be 70 and 700 ng/m<sup>3</sup>, respectively. The workplace exposure by inhalation shall be assessed using these assessment criteria. According to the respective risk, the graduated concept of risk control measures (TRGS 910) shall be applied. Additionally, dermal exposure must be taken into account.

Accompanied by interventions to decrease the exposure, comprehensive air monitoring of external exposure and biological monitoring of internal exposure were performed. As shown by workplace measurements, the tolerable concentration was exceeded up to three times at critical tasks and workplaces. During soil remediation, this was the case during the delivery of contaminated soil and feeding of the decontamination device, as well as during daily inspections or maintenance of the systems. Regarding the recycling of railway sleepers, the highest concentrations were found when shredding.

Simultaneously performed biological monitoring, using 1-hydroxy-pyrene (1-OHP) as marker, did not show any correlation with air measurements. However, it did provide information about the efficiency of protective measures. Estimated 1-OHP concentrations in urine were found between 0.1 and 350 µg/g creatinine.

As an impressive example, it was shown that both internal and external exposure strongly decreased when demounting of old railway sleepers was performed in an air conditioned cabin with protective ventilation instead of performing the task in a large working hall without any controlled ventilation.

## Exposure to air pollutants in pizza restaurants with wood-fired ovens

Pernilla Almerud, Gunilla Runström, Bo Strandberg, Sandra Johannesson  
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### Introduction:

Wood burning is an important source of air pollution indoors as well as outdoors. Some restaurants use wood for cooking and baking, e.g. pizzerias with wood-fired ovens. The aim of this study was to measure exposure to air pollutants generated from these type of ovens, for the workers and in the restaurant.

### Methods:

The study included seven restaurants. The wood-fired ovens were located in a working area in the restaurants. Personal exposure to fine particles (PM<sub>2.5</sub>), benzene and 1,3-butadiene was measured on two workers at each restaurant. PM<sub>2.5</sub> was collected on teflon filters using a cyclone connected to a pump (4 L/min). Mass concentration was determined gravimetrically, and the particle mass was analysed for benzo(a)pyrene (B(a)P) using GC-MS in SIR mode. Benzene and 1,3-butadiene was measured with active sampling (30 ml/min) using Perkin-Elmer samplers filled with Carbo-pack X 60/80, and analysed with ATD GC-MS. One of the workers also wore a personal sampler for black carbon (BC), MicroAeth Model AE51 (AethsLab).

Stationary sampling equipment for PM<sub>2.5</sub>, benzene, 1,3-butadiene and formaldehyde (Sep-Pak, 100 ml/min) was placed near the oven and near the dining tables. Particle number concentration (PNC) in the size range 10-1000 nm was measured with a Condensation Particle Counter (CPC 3007, TSI). All samplings

were performed for 8 hours (about 11:30 to 19:30) on two days at each restaurant.

### Results:

Median personal exposure to PM<sub>2.5</sub> and B(a)P for the 26 workers was 27 µg/m<sup>3</sup> (range: 13-76 µg/m<sup>3</sup>) and 0.13 ng/m<sup>3</sup> (range: 0.01-2.6 ng/m<sup>3</sup>), respectively. For benzene and 1,3-butadiene median exposures were 1.3 µg/m<sup>3</sup> (range: 0.9-4.5 µg/m<sup>3</sup>) and 0.3 µg/m<sup>3</sup> (range: 0.09-0.8 µg/m<sup>3</sup>). Stationary levels were similar to the personal exposure concentrations. Median formaldehyde concentration was 7 µg/m<sup>3</sup>. There was no statistically significant difference between concentrations measured near the ovens and in the dining area for any of the air pollutants.

Median personal BC exposure varied between 0.5 and 4.1 µg/m<sup>3</sup>. In general, BC exposure was higher during lunch and evening rush hours. The measured PNC varied across a wide range between the restaurants, with mean concentrations from about 20 000 up to 170 000 particles/cm<sup>3</sup>.

### Conclusion:

The workers' exposure to benzene, 1,3-butadiene and B(a)P were well below the OELs. Particles generated from the wood-fired ovens gave rise to high number concentrations; however, the measured particles mass concentrations were low.

## Workplace formaldehyde exposure in the anatomical institutes of German universities

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Formaldehyde is a principle chemical, used for tissue fixation and preservation in anatomy. The Committee for Hazardous Substances defined in November 2014 a threshold value for formaldehyde at workplaces. This threshold value has to be adhered to at workplaces of the anatomical institutes of German universities. In addition, since 1<sup>st</sup> of January, 2016 formaldehyde is classified in the Regulation of Chemicals as hazardous in the categories carcinogen/category 1B and mutagenicity/category 2.

Studies from German social accident insurance institutions show that the threshold value for formaldehyde is often exceeded both at fixation of body donations and during anatomical training. Therefore, the project "Reduction of Formaldehyde Exposure during Anatomical Training" was initiated under the direction of the Institute for Occupational Safety and Health of the German Social Accident Insurance (IFA). As there are only limited possibilities for substituting formaldehyde in the above-named applications, technical and organizational arrangements have to be met in order to ensure that the threshold value will not be exceeded. After extensive determination and research it was discovered that detecting hazardous substances at the

source of origin through suctioning the dissecting tables was often practically non-existent, and that the existing measures concerning ventilation and air conditioning function inadequately. The efficacy of these measurements depends on both systems being available and well-coordinated. In this research project particular technical approaches to solve the problem of reducing formaldehyde contamination were worked out.

In this lecture the results of the exposure measurements during fixation of body donations and anatomical training will be described, subject to technical and organizational boundary conditions.

Thullner, I.; Stockmann, R.; Hohenberger, L.: Gefahrstoffe – Reinhalt. Luft 75 (2015), 219-228

Dahncke, M.; Hohenberger, L.; Klusmann, H.; Stockmann, R.; Thullner, I.: Gefahrstoffe – Reinhalt. Luft 76 (2016), 387-397

## Characterisation of particle and volatile organic compound emissions from desktop fused filament fabrication three dimensional printers using real-time and analytical techniques

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Potential inhalation exposures associated with the use of fused filament fabrication (FFF) desktop three-dimensional printers were investigated by a combination of two techniques. An enclosure test chamber and real time aerosol instruments allowed emissions to be characterised by number concentration, size distribution and lung deposited surface area. Pyrolysis testing was a fast repeatable way of identifying volatile organic compounds released from the filament in temperatures comparable to those of a printer nozzle.

For the enclosure testing, three desktop, FFF printers were chosen as they were considered representative of printers used in the education sector and small businesses. The two most commonly used filament materials are acrylonitrile butadiene styrene (ABS) and polylactic acid (PLA). These were chosen for testing alongside more exotic examples. Different combinations involving the three printers and four filament materials were used to print a standardised object. For all filament materials tested, average particle sizes were typically <100 nm and many were consistently < 20 nm. Particle emissions rates were found

to vary dramatically due to the filament material as well as other user variable parameters such as nozzle temperatures.

Pyrolysis testing allowed a wide range of filament materials to be analysed in a short space of time compared to completing a print with each material. It was a repeatable method, which replicated conditions comparable to those of the printer. The pyrolysis results also provided a strong correlation between heating temperature and the emissions observed. Different filament materials and increased temperatures influenced the measured weight loss and the pyrolysis testing found that for some filament material, it was not only the temperature but also the heating time which was critical.

The findings have informed a safe practise fact sheet to highlight the health and safety risks and associated controls for use by educational establishments and industry end users of FFF 3D printers.

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# Workshops

## Workshop: Sampling of health-related aerosol fractions in occupational hygiene

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Atmospheric aerosol sampling is necessary to assess concentration, composition, size distribution, etc., of airborne particles. Representative particle sampling in the workplace air helps to assess personal exposure to health-related aerosol fractions. They are defined in international conventions by probability of particle penetration in respiratory airways as a function of their aerodynamic diameter.

After a brief remainder of physical basis of particle movement in an airstream, a historical approach will be outlined to define health-related aerosol fractions. A notion of particle inhalability and its thoracic and alveolar penetration will be explained using a dichotomous model of human airways.

A short revue of historical definitions of health-related aerosol fractions will be done leading to their modern CEN-ISO definitions.

Different methods of sampling efficiency measurement in laboratory conditions will be reviewed. A notion of sampler's performance will be defined and calculation of sampling bias and accuracy explained.

A critical revue of various workplace particle samplers will be made on the basis of their efficiency measurement in experimental wind tunnels using aerosol generators.

A likely evolution of health-related aerosol sampling in near future will be mentioned.

## Workshop: Characterization of the size distribution of bioaerosols

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Significant advances were made during the last decade in the field of bioaerosol science and contributed to a better understanding of bioaerosols at the workplace. However, a large body of research is still needed to further improve the evaluation and the management of risks linked to the exposure to airborne biological agents at occupational settings. Among these fields, the measurement of the size distribution of airborne microorganisms (SDAM) remains an important issue in occupational hygiene. SDAM Data are needed to confirm the sampling efficiency of biosamplers for the bioaerosols present at workplaces. They might give useful information for the design of technical prevention measures and, for health effects purposes, to predict the deposition of microbial particles in lungs.

The aim of the workshop is to state the actual knowledge about SDAM at occupational settings, to share experience about SDAM measurements and to discuss the demand of further research on that topic.

The following aspects should be discussed:

- Relevance of SDAM for occupational hygiene
- Knowledge of SDAM at occupational settings
- Methods used for SDAM measurements
- Usability of cascade impactors (handling, particles bounds etc...)
- Presentation of data from SDAM measurements
- Deducing deposition of microbial particles in lungs from SDAM measurement data
- What's up with microbial fragments?

## Workshop: Odours in indoor and environmental air

Kirsten Sucker

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Reports of unusual odours should be taken seriously, as they can be an indicator of problems with air quality or other disturbing factors. Often, the perception of odours is associated with a possible impairment of health. The recurring question then is if the physical symptoms are the result of an immediate harmful effect, or a consequence of the annoyance reaction.

It is currently being discussed whether odour effects should be taken into account in the determination of indoor air parameters. For odours in ambient air, a range of national, regional and municipal odour regulations already exist including standards on measurement and evaluation.

We would like to invite you to discuss the following topics with us in this workshop:

- Current case law and its impact on practice
- Current development in the standardization of measurement methods
- Practical examples from case studies and projects.

### Odors at the workplace: challenges for research

Kirsten Sucker<sup>1</sup>, Simone Peters<sup>2</sup>, Yvonne Giesen<sup>2</sup>

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Against the background of the EU Energy Efficiency Directive and the conflict between growing energy saving measures and declining air exchange rates, the question is discussed at EU level as to whether a poor indoor air quality can harm human health. The World Health Organization is working on the development of health directives for frequently occurring indoor pollutants.

“Fresh, clean air” is a characteristic of the perceived quality of the air. Despite the use of low-emission building products, odours can occur in indoor workplaces. The perception of an odour is often interpreted as an indication of exposure to pollutants and cause concern to workers about a possible harmful effect.

If workers complain about disturbing odours or health problems such as headache, burning eyes or respiratory irritation usually indoor air pollutants are measured and evaluated using guidelines, reference or odour guide values. Occupational exposure limits for airborne pollutants are not applied to indoor workplaces as there are no activities with hazardous substances.

In recent years, the German Social Accident Insurance (DGUV) has made some efforts to standardize the procedures for the determination and assessment of chemical contamination in the air of indoor workplaces, to establish reliable indoor workplace reference values for indoor air pollutants and especially in offices, and to help with the assessment and evaluation of health complaints.

To date, unpleasant and annoying odours do not play a role in limiting workplace exposure as long as the annoyance is not inappropriate. It is currently being discussed whether odour effects should be taken into account in the determination of – so far not legally binding – indoor air parameters.

A standardized procedure for “Sensory testing of indoor air” in order to quantify the odour situation in a room is provided by DIN ISO 16000-30 (2015). In order to avoid unwanted odours in indoor air, building products can be subjected to an odour test using DIN ISO 16000-28 (2012) “Determination of odour emissions from building products”. In the Scandinavian region, odour emission tests are already part of well-established test seals.

### IPA/IFA-Project: Effect and evaluation of odours at indoor workplaces

Simone Peters<sup>1</sup>, Yvonne Giesen<sup>1</sup>, Kirsten Sucker<sup>2</sup>,

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The occurrence of unusual or unexpected odors at indoor workplaces often raises concerns and inquiries about a possible exposure to pollutants. In recent years, the accident insurance institutions (UVT) have made some efforts to standardize the procedures for the determination and assessment of chemical contaminants in the air of indoor workplaces and to provide assistance in the recording and evaluation of health complaints.

However, pollutant measurements in indoor air and the evaluation by means of guide or reference values do not always lead to satisfactory solutions. In addition, it is often difficult to find the causes of odors or health problems. So far, there are no criteria for the assessment of the complaints covered by questionnaires, and no uniform approach to objectifying complaints about annoying odors. Therefore, two of the research institutes of the German Social Accident Insurance (DGUV) – the Institute for Prevention and Occupational Medicine (IPA) and the Institute for Occupational Safety and Health (IFA) – have launched a joint project to assess and evaluate odors at indoor workplaces.

A preliminary study was conducted in offices of the DGUV in 2016. In addition to the employee surveys, indoor air measurements of volatile organic compounds (VOC), aldehydes and

carbon dioxide (CO<sub>2</sub>) concentration as well as measurements of air temperature and humidity were carried out. The first results show that the questionnaire is suitable for capturing user satisfaction with indoor air quality.

The aim of the main study in 2017 is a survey in office rooms without known indoor air problems in the UVT member companies. Reference values are derived from the frequency of complaints about the indoor environment, health problems and data on odor perception and odor annoyance. In order to ensure that no air contamination is present in the air, accompanying indoor air and climatic measurements are carried out. In a first step, only office workplaces should be examined. Extending to other indoor workplaces, e.g. schools and kindergartens are conceivable in a follow-up project.

The questionnaire developed within the framework of the project can be used to answer the following specific questions: examination of complaints, consideration of the necessity and/or effectiveness of measures, e.g. before and after a renovation (reorganization control) and, where appropriate, assessment of (new) buildings (certification).

### Workshop: Proficiency Testing

Owen Butler

Health and Safety Laboratory (HSL), United Kingdom

Proficiency testing (PT) is a key part in the laboratory accreditation process as it enables laboratories to monitor the quality of their analytical results so fulfilling a key requirement of ISO/IEC 17025. Participation in PT enables laboratories to demonstrate analytical competence to their customers, assists in the training of analysts, the implementation of new methods and supports instrument qualification studies. In the field of workplace air monitoring for chemical agents there are well established PT schemes in countries such as France, Germany, United Kingdom and the United States.

The aims of this PT workshop are two-fold. In the first part, through a number of short presentations, participants will hear

about latest PT developments such as innovations in the preparation of PT test samples and developments in PT data interrogation and reporting tools. In the second part, an open forum is planned where participants will be encouraged to share their opinions on topics such as:

- what new PT test samples are required in this arena?
- is more sampling PT required?
- is it possible to use PT to assess the performance of those scientists that undertake workplace air measurements using in-situ portable real-time instruments and sensors?

## Proficiency tests for the measurement of aldehydes in workplace air samples at the IFA

Franziska Nürnberger, Krista Gusbeth, Brigitte Maybaum, Birgit Heinrich, Heinz Assenmacher, Dietmar Breuer  
Institut für Arbeitsschutz der DGUV (IFA), Germany

Due to increasingly high quality requirements for laboratories and their analytical methods there is a growing demand for methods of external quality control. One common method of external quality control is participating in proficiency testing (PT) schemes. The Institute for Occupational Safety and Health of the German Social Accident Insurance (IFA) offers round robin tests for a wide range of analytes since 1989.

Since 2009 PTs for the measurement of aldehydes in air samples are provided. As analytes formaldehyde, acetaldehyde, propionaldehyde and butyraldehyde are used. The participants can choose whether they want to perform the sampling on their own at the IFA or have the samples sent to them. The samples are prepared at the dynamic test gas facility of the IFA which enables the production of realistic workplace and indoor air samples respectively.

The test gas consists of purified, humidified air as main gas with a flow of approximately 3.8 m<sup>3</sup>/h. The formaldehyde test gas is prepared by heating para-formaldehyde in a permeation oven with a make-up gas flow of approximately 0.2 m<sup>3</sup>/h. For the

production of the test gas containing acetaldehyde, propionaldehyde and butyraldehyde a cooled (0 °C) methanolic solution is directly introduced into the test gas facility with the help of a syringe doser at a heated transfer point which guarantees the instant and complete vaporisation of the aldehydes. Both methods ensure a high precision with excellent variability less than 2% for the analytes' concentration in the test gas.

In recent years the PT schemes for aldehydes had the highest number of participants within the IFA's PTs. The attendance numbers are constantly increasing. In 2016 the maximum number of participants of 76 in total (for two PTs with on-site sampling and one without own sampling) was reached.

Participant performance data since the implementation of this PT show a constant improvement of the participants' results. It can be observed that the frequency and length of a laboratory's participation in the PT schemes has a positive impact on the performance in many cases. The attendance in PT schemes can reveal errors within the sampling or the analytical method.

## Testing scheme for sampling and analysis method validation

Eddy Langlois  
Institut National de Recherche et de Sécurité (INRS), France

### Different strategies for the production of individual reference materials

Yvonne Giesen<sup>1</sup>, Christian Monsé<sup>2</sup>, Franziska Nürnberger<sup>1</sup>, Brigitte Maybaum<sup>1</sup>, Christian Monz<sup>3</sup>, Cornelia Hagemann<sup>1</sup>, Nils Lamm<sup>1</sup>, Ann-Kathrin Mühlberg<sup>1</sup>

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Reference materials are becoming increasingly important to ensure the validity of analytical results and methods. Owing to the complexity of their manufacture, reference materials for substances occurring at workplaces are expensive and available only on a limited scale and for a small number of substances. Therefore their fast and cheap production is an important aim. Reference materials that are suitable for use flexibly and under practical conditions in particular are in demand from both laboratories and accrediting bodies.

The Institute for Occupational Safety and Health (IFA) currently pursues two strategies for the production of reference materials. One strategy is the usage of a piezoelectric micro dispensing system for non-contact metering of extremely small substance quantities with high reproducibility. For loading a high number of samples the dispensing system is coupled to a semi-automated assembly unit. This system is used for metering the inorganic acids phosphoric and sulfuric acid onto quartz fibre filters. Daily series of 100 samples were performed. The target value of relative standard deviations below one percent was achieved. Comparison of the results gained on different days shows higher variability. But after adjusting daily the number of droplets to

the current droplet volume series with an adequate number of samples (> 500) were realised.

For preparation of metal oxide loaded filters a fundamentally different strategy is used. The particulates are generated by a nanoparticle generator by injecting an aqueous metal salt solution into a hydrogen/oxygen flame where the metal salts are pyrolyzed into nano-scaled metal oxide dust. This nanoparticle dust is introduced into a large sampling chamber (20 m<sup>3</sup>) via a dust tunnel (20 m). An eight-fold sampling system was developed for standard GSP sampling heads. The constancy of the flow rate is assured by critical orifices. Up to twelve of these systems can be operated simultaneously to produce 96 samples in parallel. Extensive series of tests have demonstrated that the filter loading is homogeneous. So far the system was tested for Zn, Cu, Pb, Co and Ni but it should work with all metals obtainable as soluble metal salts.

Both strategies show a high flexibility and a wide range for adaptation to different requirements. That holds the promise of various applications for the future.

### Possible reference materials for proficiency tests for emission chamber tests

Wolfgang Horn

Bundesanstalt für Materialforschung und -prüfung (BAM), Germany

### Evaluating PT and method validation data with PROLab and InterVAL Plus

Bertrand Colson

Quodata, Germany

### Discussion to inform future PT requirements and outputs

Open Forum

# **Session 6: Measurements**

## Keynote

### Low-cost sensors and citizen science: prospects, pitfalls, and paradigm shifts

John Volckens  
Colorado State University, USA

The advent of low-cost sensors for air quality monitoring provides an attractive prospect for environmental and occupational health. These devices, which typically generate real-time data, may be distributed at scales that offer unprecedented levels of spatial and temporal resolution. Both gas and particle sensors exist. When combined with other low-cost devices (e.g., wireless communications, microprocessors), these technologies show potential for enabling a paradigm-shift in the science and application of air quality measurement. Furthermore, when deployed in a crowdsourced (or citizen-science) framework, a compelling case can be made for revolutionary changes in how we conduct air quality monitoring.

A flood of such low-cost sensors has permeated our field over the past few years. However, with these new sensors come age-old performance issues that have confounded measurement science for decades, namely: reliability, bias, repeatability, and specificity. This presentation will discuss the prospects and pitfalls of the growing low-cost sensor revolution, highlight recent research efforts in this area, and will provide recommendations for further development and implementation of these technologies to improve our ability to study air quality and its adverse effects on health.

### Workplace monitoring of diisocyanates at construction sites

Christoph Emmel<sup>1</sup>, Klaus Kersting<sup>1</sup>, Reinhold Rühl<sup>1</sup>, Petra Heckmann<sup>2</sup>, Jens-Uwe Hahn<sup>2</sup>, Gabriele Leng<sup>3</sup>

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Isocyanates are widely-used in the construction industry. The applications include e.g. usage in adhesives, coatings, foams and gaskets. To produce polyurethane systems mainly diisocyanates like HDI (1,6-hexane diisocyanate), TDI (tolylene-2,4-diisocyanate and tolylene-2,6-diisocyanate) and MDI (2,2'-methylenediphenyl diisocyanate, 2,4'-methylenediphenyl diisocyanate and 4,4'-methylenediphenyl diisocyanate) are used. Together with alcohols isocyanates form so-called polyurethanes (PU) due to the amount of arising urethane groups.

Diisocyanates can trigger respiratory and skin sensitisation. Furthermore some (TDI, MDI) are suspected for causing cancer. Consequently occupational exposure limits (OEL) have been defined.

Since 2004 dimers and oligomers were additionally taken into account. Still containing isocyanate groups they also cause toxic effects. For the evaluation of isocyanates based on the total concentration of reactive isocyanate groups (TRIG) an exposure orientation value (Expositionsleitwert, ELW) has been established.

Since the 1980s the BG BAU conducts isocyanate workplace assessments for

- parquet laying (using parquet adhesives and parquet seals),
- manual surface coating,
- building of sports flooring,
- spray coating,
- usage of PU foams,
- usage of anticorrosive coatings.

Nearly 1800 isocyanate-results were obtained until the end of 2015. In 90% results were below the limit of determination. Only 11 times the OEL was exceeded.

Since 2004 about 200 TRIG measurements were conducted with 75% of the results going below the level of determination. Less than 1% of the samples exceeded the ELW.

High values were detected when the products had been sprayed (building of sports flooring, spray coating, anticorrosive coatings) however personal protective equipment (protective clothes, gloves, respiratory protection) is already standard when those works are performed.

Due to the dermal exposition, parallel biomonitoring procedures were done before and after a shift, inter alia, when parquet adhesives and seals were used.

These confirm that parquet laying and sealing does not lead to a significant exposure of the used diisocyanates.

### Performance of various passive samplers for 15 minute short term exposure assessment

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Passive sampling is known to be an efficient and a very convenient technique for the long term exposure assessment. On the other side, the efficiency of the passive sampling for the short term assessment is poorly studied and documented whereas it could be a very convenient tool likewise. In a previous study, we proved that passive samplers are able to follow exposure peaks in very fluctuant concentration atmosphere. Comparisons were carried out between active and passive sampling in a controlled test atmosphere with some common pollutants.

The aim of this study is to confirm the efficiency of numerous passive samplers for the short term exposure assessment and to define the appropriate strategy for the use of passive samplers for this assessment. We performed simultaneous active and passive sampling on field in various actual professional situations where activities can generate short term and intense exposure. Seven different commercial passive samplers were used to assess concentration. Substances of interest for the study were organic substances with short term exposure limit (STEL) in the French regulation, therefore sampling time never exceed 15 minutes. Workers were although equipped with photo-ionisation detectors (PID) to confirm the exposure peak occurrence.

Results of sampling analysis show that sampler behaviour for short term are very different according to the type of geometry. Indeed, sampling surface is a critical parameter for the sampling efficiency. A too low sampling surface implies low quantities of sampled substance, and then a poor sensibility for the analysis. On the other hand, a too large diffusion surface makes the sampler sensible to drops projection. Furthermore, the beginning and the end of the sampling time have to be well controlled by the operators because even small extra sampling time can lead to significant bias in the results. Sampler has to be easily installed and removed from the worker and quickly recapped in order to stop instantaneously the sampling.

It is therefore very important, in addition to the technical sampler performance assessment, to provide relevant advices for the use of passive sampler for short term exposure assessment. This study gives information about the right sampler to according to the type of professional activity to assess and gives clues for the sampling strategy for the 15 minute sampling in order to perform an accurate STEL comparison.

### Further advances in air quality monitoring in aircraft cabins

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At cruise altitudes for commercial aircraft between 36,000 and 43,000 feet, conditions of very low temperature and pressure, elevated ozone concentrations and the lack of humidity constitute a hostile environment to human beings. In order to create a life-supporting atmosphere inside the aircraft, environmental control systems provide appropriate regulation of pressure, temperature and air exchange in the cabin. During flight pressurized outside air is taken from the compressor stage of the engines ("bleed air") passing a pre-cooler unit and entering the "air conditioning pack" with a temperature of approximately 200°C. The air conditioning pack cools the air to the required temperature, is mixed with filtered recirculated air and distributed in the aircraft cabin. During last decades concerns have been raised in particular with regard to contamination of hot bleed air with jet engine lubricating oil. Although many studies were performed including in-flight measurements with reported odours and laboratory studies on thermal decomposition of jet engine lubricating oil, still little is known about the specific contaminant pattern in the bleed or cabin air and its chronological sequence during an odour occurrence related to jet engine oil contamination compared to other flight conditions. Some data exists

for semi volatile organophosphates like TCP in correlation with confirmed events of oil contamination mainly on military aircraft. However, unfortunately other contaminants like aldehydes or other volatile organic species were not addressed during these measurements. Traditional analytical methods often may not be sensitive enough to detect clear markers of odour nuisances as these can be perceivable at extremely low concentrations of contaminants, which are difficult to detect in a sufficiently time resolved manner, particularly not in a challenging environment like an aircraft cabin.

A sophisticated sampling and measurement system that was used in order to identify and trace airborne contaminants to investigate the contamination pattern of artificially provoked engine oil contamination during flight and on ground to further narrow down the main specific pollutants introduced by such contamination.

Based on the results, a number of partially specific contributing organic pollutants were identified, which may be used as marker substances for identification of such pollution.

## Analysis of end-exhaled air to study exposures to volatile organic compounds

Paul Scheepers, Gwendolyn Beckmann, Rob Anzion  
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### Background:

Most volatile substances that are primarily taken up by inhalation will also be excreted via the lungs, unchanged or sometimes after biotransformation. Analysis of exhaled air can therefore be considered as an alternative to analysis of body fluids, such as blood or urine.

### Objective:

Validate a non-invasive method for biomonitoring of a wide range of ubiquitous volatile organic compounds (VOC) in different settings (at home, in a shop and in industry).

### Materials and methods:

Study participants were instructed to exhale completely in a BioVOC (Markes). Samples of end-exhaled air were transferred to AirTox tubes (Camsco) immediately after sample collection in the field. In the laboratory the organic compounds were desorbed from the adsorbent tubes during 15 min at 250-275 °C on a thermal desorber system (Markes) connected to a gas chromatograph mass spectrometer (Thermo) equipped with a RXi-5 MS column (30 m, 0.25 mm internal diameter and 0.5 µm film thickness) for analysis using electron impact ionization.

### Results:

Exhaled air of 34 volunteers was analyzed for decamethylcyclopentasiloxane (D5) before and after using a deodorant in their own bathroom. The median (range) concentration of D5 increased in 10 minutes from 10 (3-294) ng/L to 284 (15-1544) ng/L. In a second application in bookshop on the location of a former dry cleaning shop and petrol station the exhaled air of 2 retail workers was analyzed for benzene, toluene, ethylbenzene and xylenes (BTEX) and chlorinated hydrocarbons (VOCL). BTEX concentrations were not above the 95th percentile values earlier reported for non-smoking workers. Concentrations of perchloroethylene (PER) increased from 12.4 and 15.1 ng/L on Monday morning to 65.3 and 58.4 ng/L, respectively, on Friday afternoon. In a third application in a metal workshop 6 production workers were exposed to dichloromethane and BTEX. Benzene exposure was primarily influenced by smoking habits. For the other substances work tasks explained the observed pattern in exhaled air from pre-shift, to mid-shift and to post-shift.

### Conclusion:

End-exhaled air collection is a noninvasive method to obtain samples for analysis of a variety of volatile organic compounds in residents, white collar and blue collar workers. Concentrations in exhaled air reflect primarily recent exposures but for substances with longer half-lives accumulation over a week may occur.

## Development of an air monitoring method for diacetyl in the workplace

Ian Pengelly  
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Diacetyl, and the related compound 2,3-pentanedione, are potentially harmful chemicals which are used as artificial flavourings in the food industry and which may also be generated during processing of natural products, in particular coffee roasting and grinding. In Europe, the European Commission Scientific Committee on Occupational Exposure Limits (SCOEL) has proposed an 8-hour time weighted average occupational exposure limit (TWA-OEL) for diacetyl of 20 ppb and a short-term exposure limit (STEL) of 100 ppb. In the USA, NIOSH has proposed a TWA-OEL for diacetyl of 5 ppb and a 15-minute STEL of 25 ppb. NIOSH has also proposed a TWA-OEL of 0.0093 ppm and a 15-minute STEL of 0.031 ppm for 2,3-pentanedione.

A simple and reliable measurement method for diacetyl and 2,3-pentanedione, capable of achieving the required levels of sensitivity, has been developed and evaluated. The sampling method uses sorbent tubes, which may be used in active or passive mode, with analysis by thermal desorption, gas chromatography and mass spectrometry. Diacetyl was found to be stable on Tenax TA sorbent for at least 7 months but samples

collected on Chromosorb 106 were found to require analysis within a week. Storage stability was not significantly affected by humidity or the presence of acetic acid. Diffusive uptake rates for diacetyl and 2,3-pentanedione on Tenax TA have been determined. For active sampling, the safe sampling volume for diacetyl on Tenax TA is around 3 litres. Consequently, for long-term sampling, in particular personal monitoring, passive sampling is the preferred option. The typical limit of detection for diacetyl was 0.2 ng which, for an 8-hour passive air sample, equates to an airborne concentration of around 0.3 ppb.

Field trials at a coffee manufacturer showed airborne concentrations of diacetyl of up to 400 ppb in the grinding area. Long-term passive samplers worn by workers in the plant showed personal exposures to diacetyl of 30 to 65 ppb. 2,3-Pentanedione was also detected at airborne concentrations around half of those for diacetyl. In addition, the samples identified the presence of a significant number of other volatile organic compounds at sub-ppm concentrations.

## Development and optimization of the plunger assisted solvent extraction (PASE) method for multi-channel silicone rubber traps

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Polycyclic aromatic hydrocarbons (PAHs) are widely distributed in the environment and are well known for their carcinogenic and mutagenic properties. They are produced from widespread sources such as diesel vehicle emissions, biomass burning and domestic fires. Due to the potential adverse effects of these organic compounds on human health, PAHs have received much research attention and they have been monitored in many matrices including water, air, soil, food and beverages. Multi-channel silicone rubber traps consisting of 22 parallel polydimethylsiloxane (PDMS) tubes have been developed for semi-volatile organic air pollutant monitoring, with the traps being thermally desorbed for sample analysis. In this work, a novel Plunger Assisted Solvent Extraction (PASE) method for multi-channel silicone rubber trap samplers has been developed and evaluated for the extraction of the 16 priority PAHs. Extraction parameters which are capable of influencing extraction efficiency of target analytes such as choice of extraction solvent, number of sequential extractions and trap orientation, were investigated and optimized. After extraction, the liquid extracts were injected

into a gas chromatography-mass spectrometry (GC-MS) system for analysis utilising a Restek Rxi-PAH column. The optimized PASE extraction method utilized small solvent volumes (1 mL of n-hexane per extraction). The proposed extraction method was fast (1 min per extraction with two sequential extractions recommended per trap), simple and presented an advantage over thermal desorption in that samples could be re-analyzed, as only a portion of the extract was injected. Extraction efficiencies were good (from 66% for acenaphthylene to 98% for anthracene). Additionally, this approach can be applied in laboratories which do not have thermal desorption systems, hence allowing for the more widespread use of these PDMS traps. The method has been successfully applied to domestic fire air emission samples at 10 and 20 min after ignition, using a sampling flow rate of  $500 \text{ mL} \cdot \text{min}^{-1}$  for 10 min in each case. The samples were found to contain primarily naphthalene (maximum concentration of  $9.5 \mu\text{g} \cdot \text{m}^{-3}$ , 10 min after ignition), as well as fluorene, anthracene, phenanthrene, fluoranthene and pyrene.

## Accuracy and comparability of lung deposited surface area monitors

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Exposure to airborne particles including nanomaterials is usually assessed by means of particle mass concentrations. However, several toxicological studies have shown that the particle number concentration or the lung deposited surface area (LDSA) concentration may be better indicators for possible health effects than particle mass. LDSA concentration will therefore be included in a new EN standard on metrics to be used for assessing exposure to airborne nanomaterials, which is currently under preparation in CEN TC 137/WG3. The LDSA concentration is the fraction of the airborne particle surface area concentration that upon inhalation would deposit in the alveolar region of the human lung. Currently available monitors for measuring LDSA concentrations use a unipolar corona discharge to electrically charge the aerosol particles. Eventually, the total current, induced by the charged particles is measured, which at least in a limited size range, happens to be proportional to the LDSA concentration. Currently available monitors that determine LDSA concentrations are Nanoparticle Surface Area Monitor (TSI NSAM model 3550), partector (naneos), DiSCmini (Testo AG) and nano-Tracer (oxilixity).

A large study on the accuracy and comparability of the available LDSA monitors has been conducted as pre-normative research for the aforementioned upcoming standard. The accuracy has been studied using monodisperse particles of known sizes and number concentrations. The data clearly show that the monitors are only able to adequately measure LDSA concentrations in a size range from approximately 20 to 400 nm. Within this size range the monitors can be expected to be at least  $\pm 30\%$  accurate. The comparability was investigated by simultaneously challenging several specimens of each instrument type with well-defined polydisperse aerosols of different modal particle sizes, materials, morphologies and concentrations. The results show that the determined accuracy of  $\pm 30\%$  also applies to the comparability of the instruments. It was also found that the same degree of comparability can be expected for agglomerated particles, when these are assumed to be spherical.

The presentation will include an introduction to the concept of LDSA concentration. Experimental set ups for the study on accuracy and comparability along with the results will be presented and discussed in view of standardization.



# **Session 7: Asbestos and dust**

## Keynote

### Naturally occurring asbestos (NOA): a new issue for hygienists

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When considering the hazard presented by natural occurrences of asbestos and other elongate mineral particles it is important to realize that there is very little evidence that undisturbed natural occurrences lead to disease. Where clusters of human disease associated with elongate mineral particles (fibers) in the environment have been found in the past, there has been an associated disturbance of the natural environment resulting in the release of fibers into the air. This included the use of rocks in building construction and soils for whitewash as well as the deliberate mining of fibrous minerals. The most important industry sectors with worker exposure to natural occurrences are mining, as should be expected, but also construction. In construction the appearance of elongate mineral particles may come as a surprise when the construction is not taking place in areas of known asbestos mining activity. One of the rocks hosting asbestos is serpentine and serpentine is so common in California that it is considered the official State rock. Given the widespread occurrence of serpentine and the generally dry climate, the Californian experience has been important in developing management strategies for natural occurrences of asbestos in construction. While serpentine typically hosts the

mineral chrysotile, amphiboles may also be encountered in a fibrous habit, i.e. asbestiform or intermediate. A particular suite of amphiboles is regulated because these minerals were most commonly mined for asbestos, but other compositions exist with different names and these can also be problematic. Finally, unrelated non-asbestos minerals also can exist as fibers in dimensions similar to asbestos. This presentation will examine situations of concern in the USA where elongate mineral particles have been encountered, including: deposition of chrysotile in homes and farms from floodwaters in WA, a dam construction project which encountered fibrous glaucophane in CA, a road construction project through rocks and soils with previously unnoticed fibrous actinolite in NV, and the presence of erionite, a fibrous zeolite, in SD. These occurrences in the western States of the USA provide lessons in management that can be applied to situations encountered elsewhere.

Disclaimer: The findings and conclusions in this presentation have not been formally disseminated by the Centers for Disease Control and Prevention and should not be construed to represent any agency determination or policy.

### Asbestos measurements during processing of serpentinite rocks in Switzerland

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In 2013, dust deposits containing small quantities of asbestos were discovered in several rock processing facilities in Switzerland. These discoveries prompted Suva to carry out a series of asbestos measurements during the manual and mechanical processing of rocks, in particular serpentinites, which were suspected to contain asbestos.

From a mineralogical perspective, it is evident that rigorous application of the SEM/EDX-based measuring protocol (DGUV Information 213-546) may lead to a massive overestimation of asbestos fiber concentrations in geogenic environments. This is particularly true for serpentinites containing the asbestos mineral chrysotile, but also the other two chemically identical minerals of the serpentine subgroup, antigorite and lizardite. A new approach was thus developed for distinguishing between fibers that are definitely or very likely to qualify as asbestos (= type 1) and fragments unlikely to qualify as asbestos (= type 2). This approach is based on specific morphological criteria that supplement the standard WHO dimensional criteria.

In 2015, Suva collaborated with the Swiss Natural Stone Association in performing comprehensive asbestos emission tests on three common serpentinites. Different operations were

investigated by means of stationary and personal dust and fiber measurements taken in a 40 m<sup>3</sup> asbestos remediation zone. The procedure for identifying the mineralogy of the fibers and measuring their concentration involved not only standard SEM but also systematic TEM analyses.

For grinding, drilling and engraving, asbestos exposures in the range of approx. 1–10 million fibers/m<sup>3</sup> were measured with dust levels of 1–10 mg/m<sup>3</sup>. Milling produced values of 20–100 million fibers/m<sup>3</sup>. The TEM analyses demonstrated that the approach developed for SEM for distinguishing between “definite/very likely” and “unlikely” asbestos fibers is reliable. The proportion of asbestos fibers verified by TEM in relation to the total number of WHO-compliant fibers ranges between 10 and 76%.

Apart from these asbestos emission tests, a total of eight asbestos measurements have been carried out in rock processing facilities since 2007. The detected concentrations tended to be lower than during the emission experiments, i.e. between 100,000 and 1 million fibers/m<sup>3</sup>. The proportions of asbestos types 1 and 2 were found to vary widely. The proportion of “definite/very likely” asbestos fibers was generally substantial (20–60%).

### The shaker dustiness test for high aspect ratio materials

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We have developed a dustiness test for powdery high aspect ratio materials (HARM), in particular for their nanoscale form (e.g. carbon nanotubes). In the so-called Shaker method, a laminar air stream with a low volume flow rate passes through a vertically vibrating powder column which results in powder fluidization. Vibration is required to overcome adhesive forces between powder grains that would otherwise hinder fluidization. The procedure generates continuous fibre dust emissions that are monitored and characterized with instruments for ultra-fine and fine aerosols to determine the so-called dustiness coefficients for the test material. Collective dust samples are analysed with the help of scanning electron microscope to perform morphology classification on the collected particles to enable material characterization in regard to both exposure and hazard potential.

Dust generation depends on the energy input on the powder column, adjustable by changing the vibration frequency, vibration amplitude and the flow rate. Compared to similar dustiness test methods like continuous drop and rotating drum, the amount of test material required is far less (in the range of 300 mg), which is beneficial towards costs and safe handling. In addition, the experimental setup is entirely made of commercially available parts, so a full-scale replica of the setup and application of the Shaker method by others is easily achievable.

Using a standard operation procedure, we performed dustiness tests on ca. 20 commercially available carbon nanotubes and carbon nanofibres. The results lead to material rankings based on the dustiness coefficient and the propensity to emit single fibres that fit the so-called WHO-criteria identifying hazardous fibres (aspect ratio 3:1, length > 5µm).

### Thoracic aerosol sampling by the FSP cyclone sampler

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In German workplaces, a modified Cossey and Vaughan cyclone (C.&V., 1987) operated at 10 Lpm is used as a high-volume aerosol sampler FSP (Feinstaubprobenahme) to collect respirable airborne particles. A stainless steel version of the cyclone was developed and the original (C.&V., 1987) experimental cut point-flow rate function ( $D_{50}=68.7/Q^{1.15}$ ) was used with the intention of sampling the thoracic aerosol ( $D_{50}=10\ \mu\text{m}$ ) at a flow rate of 5.34 Lpm (Breuer et al., 2012).

In this study, we verified the sampling efficiency of the FSP cyclone at 10 Lpm in laboratory conditions using a horizontal low speed wind tunnel with solid polydisperse aerosol, and then measured its efficiency at 5.3 Lpm. The experimental method is described elsewhere (Görner et al., 2001, 2008). At 10 Lpm an efficiency close to the value reported by C.&V. (1987) was found ( $D_{50}\approx 4.0\ \mu\text{m}$ ) as expected, assuming fair sampling of respirable aerosol. In contrast, the FSP efficiency measured at 5.3 Lpm yielded  $D_{50}=7.4\ \mu\text{m}$  only, what is far from the required 10-µm cut point for thoracic aerosol sampling. To achieve the target value, we progressively reduced the flow rate and continued to measure cyclone efficiency. The following results were found:

Q [Lpm]	10.0	8.0	5.3	4.0	3.5	3.0	2.5
D50 [µm]	3.9	5.0	7.4	8.7	10.5	10.2	-

The requisite 10-µm cut point is approached at 3.5 Lpm, in accordance with the recent study of Lee et al. (2016) who reached the 10-µm cut point at 4 Lpm using monodisperse fluorescein particles. At 3.0 Lpm the  $D_{50}$  is even closer to 10 µm, but the shape of the efficiency curve becomes irregular. This irregularity indicates that the flow rate is too low for the cyclone to maintain a steady vortex. At 2.5 Lpm the vortex collapses and particles transit directly from the inlet to the filter. This phenomenon is identical to that initially described by Vaughan (1988) as “a marked kink in the penetration curve for the lowest flow rate”.

Thus, the best performance in thoracic sampling with the FSP can be achieved at a flow rate of 3.5 Lpm, where the separation curve provided by the cyclone remains sharp. Log-normal fitting of experimental data yields:

$$D_{50}=10.5\ \mu\text{m}\ \text{with}\ \text{GSD}=1.3$$

In conclusion, the bias map calculated using previous parameters shows that operating the FSP thoracic cyclone at a flow rate of 3.5 Lpm provides a fair sampling performance with Bias Performance Criterion BPC equal to 85%.



**Session 8:  
Exposure modelling, Biological  
Monitoring II and Bioaerosols I**

## Keynote

### Evaluation of tier exposure assessment tools for use under REACH (Inhalation)

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Recently, one comprehensive validation study (as a part of ETEAM project) was conducted for inhalation tools (Tier 1-ECETOC TRAv2, TRAv3, EMKG-EXPO-TOOL, and MEASEv1.02.01, Higher tier-Stoffenmanager@v4.5) for use under REACH, but one limitation was the use of existing measurement data. The present study was conducted to address this limitation using exposure measurements and contextual information gathered specifically for this exercise. The same inhalation tools tested in the ETEAM project plus ART were used in this study. From NIOSH field surveys, 53 exposure situations (ESs) were developed based on tasks/chemicals. For each ES, applicable tools were then used to generate exposure estimates based on the contextual information which were translated into input parameters based on a consensus approach. The evaluation results were reported in six exposure categories: Aqueous solutions, Liquids with a vapor pressure (VP)  $\leq 10$  Pa, Liquids with a VP  $> 10$  Pa, Metal processing, Powders, and Solid objects. For the tier 1 tools, the level of conservatism of the tool estimates was defined as high if the percentage of measurement (M) that exceeded the tool estimates (T) ( $\%M>T$ )  $\leq 10\%$ , medium if  $10\% > \%M>T \leq 25\%$ , and low if  $\%M>T > 25\%$ . As results, for the liquids with VP  $> 10$  Pa category having sufficient number of exposure measurements, the EMKG-EXPO-TOOL showed a high level of conservatism, whereas the

TRAv2 and TRAv3 resulted in either a medium or low level of conservatism. For the higher tools, accuracy and robustness were evaluated. For all exposure categories with an exception of solid objects, the Stoffenmanager appeared to be accurate and robust to predict exposures. For the ART, although the 90th percentile prediction appeared to be accurate for all exposure categories, the  $\%M>T$  were  $> 25\%$  for all exposure categories (except for the powders), indicating underestimation of exposures. These findings suggest there may be a need to review the underlying tool algorithms. Except for liquids with VP  $> 10$  Pa, the findings of other exposure categories were based on the limited number of exposure situations and measurements with low exposure ranges. Thus, further validation studies are still necessary. Using the tool-specific descriptive exposure information recorded along with the collection of measurements leads to a stronger validation study than previous studies using preexisting data and it is recommended that the same approach be applied to further studies.

DISCLAIMER: The findings and conclusions in this report are those of the authors and do not necessarily represent the official position of the Centers for Disease Control and Prevention.

## Variability in exposure level – implications for measuring and modelling exposures

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For the assessment of workplace health risks due to inhalation, the exposure of the workers to hazardous substances must be known. This can be difficult because of the between- and within-worker variability of the exposure level due to variation in time, space, process and intensity of the activity.

Two main reasons for exposure assessment exist: One reason is the risk assessment for a specific workplace. This exposure assessment can be executed for future, current or historic exposure scenarios. Examples are compliance testing or investigations on occupational diseases. The second main reason is an exposure assessment within epidemiological studies for the approval of the relation between exposure and disease or for the derivation of occupational exposure limits (OELs).

In the case of compliance testing it is important to protect all workers, so the maximum exposure, (called worst case) or the reasonable worst case (often defined as the 95. percentile of the exposure distribution) should be assessed. In the case of epidemiological studies it is on one hand important to get information about the exposure of an average worker, described by the mean or the median of the exposure distribution. On the other hand for the derivation of OELs it is important to know the lowest

exposure that can cause a disease, which means that the lower percentiles are relevant.

These considerations show that exposure measurements and modelling in the field of occupational hygiene should include not only a point-estimate for the exposure level. In contrast it would be better to provide estimates for the mean or median of the exposure distribution as well as for the variation so that higher and lower percentiles can be estimated. Using a set of several hundred measurement values it will first be pointed out during the talk that even a sample size of 10 or 25 measurements can be too small to yield the whole range of possible exposures for one exposure scenario.

In a second step possibilities for taking into account variability during modelling are presented. An example from modelling dust exposure during filling, mixing, cleaning and plastering with Stoffenmanager® will be shown. For this dataset of 390 data points model estimates and measured values correlate with a Spearman coefficient of 0.46 and it can be shown that the modelled values cover the whole range of the measured values ( $\chi^2=13.90$ ,  $p>0.05$ ).

Finally implications for the validation of models will be derived.

## Dermal penetration of N-phenyl-2-naphthylamine in vivo

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### Objective:

Until the 1990's, N-phenyl-2-naphthylamine (P2NA) was widely used as an antioxidant. P2NA is metabolized to carcinogenic 2-naphthylamine in vivo. Recently, it has been demonstrated in vitro that P2NA does both, accumulates in the skin and penetrates the skin. Here, we tested whether or not skin penetration and skin accumulation of P2NA can also be observed in vivo.

### Method:

Four pigs were exposed to a 1% P2NA solution in dichloromethane (DCM)/oil (96/4, v/v) on a 200 cm<sup>2</sup> skin area. First, animals were exposed for one hour under occlusive conditions. In a second experiment, a selected amount of the P2NA solution was applied four times/day on five consecutive days using non-occlusive conditions. This application scenario was quite similar to exposure situations in the printing industries between 1970 and 1990 where rubber-coated printing cylinders were manually cleaned for short periods of time (minutes) using ~1% P2NA solutions in DCM and without the use of gloves. Pig blood samples and skin punches of the exposed areas were taken up to 14 days after the end of exposure. P2NA was quantified in all samples by means of gas chromatography with isotope dilution mass spectrometry.

### Results:

P2NA could be detected in blood after single applications and under occlusive conditions with a maximum concentration of 3.2 µg/L (Range: 0.8-5.8 µg/L) and 48 h post application. No P2NA was detectable in blood after 14 days (LOQ: 0.1 µg/L). The elimination half-life in blood was estimated to be 58 h. In the repeated non-occlusive experiments we observed an increase of the mean blood concentration from 0.2 µg/L (0.1-0.3 µg/L) after the first application to 2.3 µg/L (1.2-4.0 µg/L) after the 5<sup>th</sup> application cycle. P2NA was also detected in the upper skin compartments (maximum levels after single and repeated dosing: 19.3 and 56.0 mg/g skin) as well as in the subcutaneous fat tissue (1.5 and 0.7 mg/g skin, respectively).

### Conclusion:

The results show that dermal contact to P2NA under non-occlusive conditions and similar to former exposure scenarios at the workplace can lead to a relevant dermal uptake into the skin and the blood in vivo which subsequently results in the formation of carcinogenic 2-naphthylamine. Therefore, dermal penetration has to be considered when retrospectively assessing exposures to P2NA and in risk assessment of P2NA-associated work-related diseases.

### Urinary bisphenol A (BPA) concentrations among workers in industries that manufacture and use BPA in the USA

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#### Background:

Exposure to bisphenol A (BPA) and its toxicity to humans has been the subject of considerable scientific debate. Most studies have focused on general population exposure to BPA, while published occupational exposure data for BPA are limited.

#### Methods:

In 2013-2014, 77 workers at six U.S. companies making BPA, BPA-based resins, or BPA-filled wax provided seven urine samples over two consecutive work days (151 worker-days, 525 samples). Participant information included industry, job, tasks, personal protective equipment used, hygiene behaviors, and canned food/beverage consumption. Total (free plus conjugated) BPA, quantified in urine by mass spectrometry, was detected in all samples.

#### Results:

The geometric mean (GM) creatinine-adjusted total BPA (total BPACR) concentration was 88.0 µg/g (range 0.78-18,900 µg/g), nearly 70-times higher than adults in the U.S. National Health and Nutrition Examination Survey 2013-2014 (1.68 µg/g). GM total BPACR increased during Day 1 (26.6 µg/g to 127 µg/g), decreased by pre-shift Day 2 (84.4 µg/g) then increased during

Day 2 to 178 µg/g. By industry, baseline and post-baseline total BPACR was highest in BPA-filled wax manufacturing/reclaim (GM=111 µg/g) and lowest in phenolic resin manufacturing (GM=6.56 µg/g). By job, total BPACR was highest at baseline in maintenance workers (GM=157 µg/g) and post-baseline in those working with molten BPA-filled wax (GM=441 µg/g). Workers in the job of flaking a BPA-based resin had the lowest total BPACR concentration at baseline (GM=4.81 µg/g) and post-baseline (GM=23.2 µg/g). In multiple regression models, at baseline, industry significantly predicted increased total BPACR ( $p=0.0248$ ), post-baseline, handling BPA containers ( $p=0.0035$ ), taking  $\geq 3$  process/bulk samples with BPA ( $p=0.0002$ ) and wearing a Tyvek® coverall ( $p=0.0042$ ) significantly predicted increased total BPACR (after adjusting for total BPACR at baseline, time point and body mass index).

#### Conclusion:

Several work-related factors, including industry, job, and certain tasks performed, were associated with increased urinary total BPACR concentrations in this group of manufacturing workers. The potential for BPA-related health effects among these workers is unknown.

### Urinary concentrations of benzene metabolites of 1076 subjects living in Central Italy determined by HPLC/MS/MS

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The use of benzene concentrations greater than 0,1 % is prohibited by REACH, but exposure still occurs from industrial use, motor fuels and natural gas, and combustions of organics. Human biomonitoring is the tool used in surveys to assess the integrated exposure to xenobiotics of the population from different sources. As a part of the "ABC Human Biomonitoring study", the benzene urinary metabolite SPMA and the nicotine metabolite cotinine were measured in 1076 subjects living in Central Italy and tTMA in 735 out of 1076, using HPLC/MS/MS. Results were stratified by gender (58% males), age (35 – 65 divided in 4 classes) and occupation (5 classes). Mean (SD) and median (5 – 95 % range) values are presented. As the main determinant for benzene exposure is cigarette smoking, data were divided into smokers (urinary cotinine  $>100$  µg/g of creatinine, 25%) and non. Median SPMA value for smokers is 1.13 µg/g of creatinine, while for non-smokers it is 0.10, with a ratio of about 10. tTMA median values for smokers and non-smokers are respectively 78.88 and 40.51 µg/g of creatinine, with a ratio of about 2. SPMA median values for smoking males and females are respectively 0.68 and 1.81, in non-smokers males 0.07 and in females 0.10 µg/g of creatinine. tTMA values are 66.27 in male smokers,

and 83.69 in women, 36.12 in non-smoking males and 42.83 in women. Women always present higher concentration of metabolites both if normalized for the creatinine or not (µg /L), even if creatinine concentrations are lower than in men. The age stratification was done only for SPMA as it is the most sensitive and specific marker, on 1076 subjects. The highest level is in smokers, class 55-64, both genders, while in non-smokers differences are small. Small differences were also found in non-smokers among occupational classes: employed, autonomous workers, unemployed, housewives, retired. The benzene concentration inhaled from the population can be extrapolated considering the relationship between the ACGIH TLV-TWA for benzene (1.6 mg/m<sup>3</sup>) and the SPMA BEI (25 µg/g of creatinine). Considering that the median SPMA value on non-smokers is 0.10 µg/g of creatinine, the calculated benzene concentration inhaled would be 5 µg/m<sup>3</sup>. In conclusion, in the studied population the main source of exposure to benzene is active smoking, and the median exposure to airborne benzene correspond exactly to the limit of 5 µg/m<sup>3</sup> stated by the Directive 2008/50/EC on air quality for Europe.

# **Session 9: Bioaerosols II**

## Keynote

### The challenges of assessing bioaerosol-related health risks

Sandra Walser, Doris Gerstner, Bernhard Brenner, **Caroline Herr**  
Bayerisches Landesamt für Gesundheit und Lebensmittelsicherheit, Germany

Airborne microorganisms occur ubiquitously in the ambient air. Besides allergic and irritative-toxic effects they can cause infections after inhalation. Occupational studies have shown that an increased incidence of respiratory diseases is found in exposed workers. In studies from environmental medicine, respiratory diseases have also been observed in residents living in the vicinity of livestock facilities

Currently, there is a lack of health-related exposure limits for airborne microorganisms released from such facilities. Environmental risk assessment can be performed on the basis of the guideline VDI 4250 part 1, which relies on an excess of natural background concentration by facility-specific immissions. For the approval practice, the „LAI-Leitfaden Bioaerosole“ is a uniform, standardized method for determination and assessment of bioaerosol exposure. The LAI guideline provides orientation values for facility-based indicator parameters. For example, staphylococci as environmental-relevant sum parameter can be used for evaluation of bioaerosol immissions, including *Staphylococcus aureus* as a major human pathogen. If an orientation value for a facility-based indicator parameter is exceeded by a factor of 2 to 3, this has to be evaluated very critically. In this case, adverse environmental effects cannot be excluded with sufficient probability.

In addition to respiratory diseases, severe specific infections can also occur following exposure to bioaerosols in particular cases, e.g. in case of a hantavirus infection which can be recognized as an occupational disease. Evaporative cooling towers can pose an infection risk by inhalation of legionella-contaminated aerosol emitted from such systems. However, the infectious potential of legionella may be underestimated by detection of free-living legionella in water by currently used standard culture-based methods. Culture-dependent analyses cannot capture the stressed and non-cultivable legionella (VBNC status) as well as only partially those legionella contained in amoebae. Thus, it is not certain whether future outbreaks can be avoided with these investigations.

In indoor spaces, only a few mold types such as *A. fumigatus* are able to trigger infections by local or systemic infection of the human organism. In particular, persons with immune deficiency or allergies must be informed about the risks of mould exposure in indoor air. In general, mould growth in indoor spaces is a hygienic problem and must not be accepted as a matter of principle.

### Endotoxin measurement at the workplace: comparison of two personal sampling methods

Olivier Schlosser, Samuel Robert, Catherine Debeaupuis  
SUEZ, France

In a lot of occupational environments, bacterial endotoxin, as a high pro-inflammatory potency compound, is a key biological agent for bioaerosol exposure monitoring and associated health risk management. However, there is no international standardized protocol for the measurement of endotoxin exposure in the work environment. Even if filtration is the most commonly used sampling method for airborne endotoxin, other collection methods of interest can be applied for personal exposure assessment, and particularly task-based measurements. The aim of this study was to compare, at a sludge composting plant, two endotoxin collection devices for personal exposure measurement: with CIP 10-M (Tecora, France), which collects airborne particles into a liquid in a rotative cup, and with IOM system (SKC, UK), which collects airborne particles onto a glass-fiber filter. In addition, we aimed at estimating the effect of the tension-active agent Tween 20 0.05% on endotoxin measurement results, when added to pyrogen-free water (PFW) in the CIP 10-P cup and in the extraction solution when IOM filtration system was used.

Measurement results with the two devices were highly correlated, either with or without use of Tween. High correlation was

also observed between measurement results with and without addition of Tween in PFW, for each of the two devices. Estimated concentration of endotoxin was significantly higher in samples collected with CIP 10-M than with IOM. This increase in CIP 10-M collected samples was higher when Tween was added to PFW (resulting in a 7.9-fold-higher estimated endotoxin concentration) than when no Tween was added (resulting in a 2.8-fold-higher estimated concentration). Addition of Tween to CIP 10-M PFW collection liquid increased estimated endotoxin concentration by a 1.9 factor ( $P=0.004$ ). In contrast, addition of Tween to the extraction solution had no significant effect on the concentration of endotoxins from collection onto filters. This finding may be explained by immediate immersion of filters into solution after sampling.

On the field, the selection of the type of sampler will depend on the aim of the sampling campaign. The use of both sampling devices may give answer to most issues health and safety representatives and operations managers face to with regard to endotoxin exposure at the workplace.

### Real time characterization of bioaerosols emissions from industrial sources

Zaheer Ahmad Nasir, Sean Tyrrel  
Cranfield University, United Kingdom

There has been increasing concerns about public health risks from bioaerosols emissions due to increasing industrial sources such as waste treatment and intensive agriculture facilities. The existing monitoring methods for bioaerosols quantification are off-line, suffer from the considerable time delay between sampling and quantification, offer only snapshot data and thus cannot capture temporal variability in bioaerosols concentrations. Techniques that are capable of reliably measuring and characterizing bioaerosols loads, in real time, are crucial, not only to guide bioaerosols risk assessment methodologies for regulatory science but also to develop and advance numerical models to predict their transport and dispersion at different spatio-temporal scales. The recent advancement of detection technologies and modelling methods can greatly contribute to our capabilities to implement real time/near real time detection and modelling to advance bioaerosol exposure estimates and to characterize public health risk. This paper aims to investigate the potential of a novel fluorescence based bioaerosol sensor unit with highly resolved fluorescence intensity measurements (Spectral Intensity Bioaerosol Sensor – SIBS) to detect and characterize bioaerosols emissions in real time from green

waste composting. The SIBS is capable of performing a range of measurements (size, number, shape, and resolved emission fluorescence) on single particles, in real-time. SIBS uses two excitation wavelengths (280 nm and 370 nm) and records fluorescence emission across the 16 wavelength bands, covering from 288 nm-735 nm. Sampling was carried out during day time downwind of the source at a green waste composting site. Four repeated measurements were made on different days. A large temporal variability in both number and mass concentration of total and fluorescent particles were recorded over the sampling period. Highest concentrations were found during activity periods (turning/screening). Significant differences were also seen in emission spectra during different emission scenarios at the site (i.e. activity and no activity). This study offers evidence that SIBS fast response and capability to differentiate biological/non-biological particulate along with size, morphology and resolved emission spectra in real time can significantly contribute to advancing the existing state of knowledge on bioaerosols detection and emissions characteristics from different industrial sources.

### One year follow up of microbial biodiversity in French waste sorting plant

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Waste sorting activities are source of occupational bioaerosol exposure that was associated with several health disorders as rhinitis, asthma and hypersensitivity pneumonitis. So far, the microbial biodiversity data published in this occupational environment were obtained by cultivation of microorganisms on nutrient media prior to identification. Due to the well-known limits of cultural methods, these biodiversity measurements underestimate the real microbial taxon richness. Recent advances in molecular biology provided powerful methods for biodiversity studies such as high-throughput sequencing. The aim of the study was to assess of bioaerosol biodiversity in a waste sorting plant (WSP) during one year and to investigate the main factors of variability of this biodiversity. Bioaerosol biodiversity was assessed in a French WSP sorting journal newspapers, papers, cardboards, food packaging and other sorting waste. The WSP employed about 50 workers mainly dedicated to manual sorting in two cabins. Every month during one year, static sampling was performed in five areas in the plant, using closed-face cassettes (10 L/min) with polycarbonate membranes. To compare the

composition of related-task bioaerosols and control bioaerosols, two references were sampled: one indoor and another one in outdoor reference. Environmental data were measured (temperature, relative humidity) or collected (climatic conditions ...). Microbial DNA was extracted and microbial biodiversity was performed using high-throughput sequencing (bacterial 16S, fungal ITS2). All bioaerosols were composed of four main phyla: Actinobacteria, Bacteroidetes, Firmicutes and Proteobacteria. The proportion of Actinobacteria and Firmicutes was higher in bioaerosol emitted in WSP (10% and 35% respectively) than in reference bioaerosols (2% and 15% respectively). At the family rank, Staphylococcaceae was the family in the higher proportion in the WSP (10% to 20% depending on the sample). The first results showed that the composition of bioaerosols in WSP was different from the references. The composition of bioaerosols in WSP was also different from an area to another one. In the presentation, fungal biodiversity as well as the influence of environmental parameters will be discussed.

## Investigation of recovery efficiencies in bioaerosol analyses with filtration

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### Background:

The impact of bioaerosols on ecosystem dynamics and human health, especially at workplaces in animal husbandry, is becoming increasingly evident [1, 2]. Therefore, the microorganism concentration and the community structures in bioaerosols in the environment as well as on work places were intensively studied using different sampling methods (filtration, impingement and impaction). Furthermore various approaches for further analyses like culture-based methods, total cell counting (TCC) and molecular approaches were used. However studies determining the efficiency of bioaerosol sampling and sample processing methods are rare.

### Material and Methods:

In this study we determined the recovery of different cell species after sampling by filtration with either polycarbonate, quartz fibre or glass fibre filters. A fixed number of cells was spiked on filters, the sampling process was simulated and the recovery efficiency was investigated via TCC with the fluorescent DNA stain 4',6-diamidino-2-phenylindole or DNA extraction and quantification of the DNA amount by fluorometric measurements. For these analyses four different bacteria species, namely *B. subtilis subsp. subtilis*, *M. luteus*, *P. nitroreducens* and *S. capitis subsp. capitis* as well as the yeast *S. cerevisiae* were used.

### Results and Conclusion:

Using polycarbonate filters the recovery was usually higher than with quartz fibre or glass fibre filters, which have a much coarser surface. Moreover the recovery was generally higher after TCC compared to the molecular approach with DNA-extraction, probably due to additional effects concerning the recovery during DNA extraction. Nevertheless the differences between the recoveries of various cell species were much more significant. *B. subtilis* and *S. cerevisiae* showed much higher recovery efficiencies than *M. luteus*, *S. capitis* and *P. nitroreducens* e.g. after filtration with glass fibre filters and TCC the recoveries varied between 76% (*S. cerevisiae*) and 1,9% (*S. capitis*). If these results are transferable one-to-one to real bioaerosol analyses, problems in community analyses by concealing the real composition can be assumed. So the results of this study clearly show that efficiencies of bioaerosol sampling and analyses methods have to be specified to verify the significance of an investigation.

[1] Martin, E. et al. (2013) Environ. Sci.: Processes Impacts 15: 478-484.

[2] Bowers, R. M. et al. (2009) Appl. Environ. Microbiol. 75: 5121-5130.

# Poster Session

## Control banding for risk assessments in accordance with GHS – Example GESTIS-Stoffmanager/Stoffenmanager®

Mario Arnone

Institut für Arbeitsschutz der DGUV (IFA), Germany

In occupational safety and health risk assessments for the handling of hazardous substances have to be performed. Next to measurements also non-measuring methods can be applied in this risk assessment. Especially if there is no limit value for the hazardous substance under concern or if there are a lot of work places to screen, a control banding approach is helpful.

Control banding classifies the hazard, the exposure and the risk arising from the handling of hazardous substances in categories (bands). The hazard band is derived from the classification of the hazardous substance. With the introduction of the Globally Harmonized System (GHS) the rules for the derivation of hazard bands in existing control banding schemes have to be adapted to the new legislation (e.g. H statements). In order to do so, at first general rules for the assignment of hazards to hazard bands are set up.

As a first rule the H statements and the dilution rules for mixtures from the GHS are the basis for the assignment of hazard bands. All H statements are assigned to six hazard bands with respect to the severity of the underlying health hazard. These hazard bands range from n.a. = “not applicable” through A = “low hazard”, B = “moderate hazard”, C = “high hazard” and D = “very high hazard” to E = “extremely high hazard”. The

dilution rules from GHS are applied for the assignment of hazard bands to self-diluted mixtures of hazardous substances.

The second rule is that the H statements are assigned specifically to the route of exposure concerned in the respective H statement. For an exposure route not concerned in the H statement the hazard band n.a. is assigned. This is done to enable the user to adjust risk management measures to the specific uptake route.

Rule three finally claims that the hazard banding has to support the important principle of substitution. Therefore proven carcinogens or mutagens are assigned to hazard band E, while all less severe hazards are assigned at worst to hazard band D. Also the graduated assignment of acute toxic substances to hazard bands from D to B with respect to their severity supports substitution.

These rules are implemented in the hazard banding scheme of the control banding module of GESTIS-Stoffmanager/Stoffenmanager®. In my presentation I will use this tool as an example how the GHS hazard banding scheme is applied in control banding and can help to perform a risk assessment for the occupational handling of hazardous substances.

## Risk assessment applying the information system on hazardous substances of the German accident insurance institutions

Mario Arnone, Dorothea Koppisch, Stefan Gabriel

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The employer is obliged to take all necessary measures to protect employees from health hazards during activities with hazardous substances. Therefore risk assessments for the handling of hazardous substances have to be performed. In different companies however, the knowledge on hazardous substances and their risks can vary a lot. To assist companies with the risk assessment the Institute for Occupational Safety and Health of the German Social Accident Insurance (IFA), the BG for the raw materials and chemical industry (BG RCI) and the BG for the building and construction sector (BG BAU) have established an information system on hazardous substances. This “Gefahrstoff-informationssystem (GESTIS/GIS)” consists of several online databases and tools.

With these GESTIS/GIS tools a stepwise approach to the risk assessment is possible. Each step corresponds to a certain level of knowledge in the company and the duties for the risk assessment that have to be fulfilled on this level. The first step is raising awareness for hazardous substances in the company. Here the GESTIS substance database from the IFA, GISBAU from the BG BAU and GISChem from the BG RCI can give support by informing about hazardous substances and their identification. After

knowing which hazardous substances exist in the company, the hazards that can arise from these substances have to be determined. Here GESTIS-Stoffmanager can give assistance applying its control banding module. Also GISChem and GISBAU offer information on the hazards of sector specific products. The next step is the exposure assessment. In addition to measurements the quantitative module of GESTIS-Stoffmanager or the exposure descriptions in GISBau can be applied as nonmeasuring methods for this purpose. With information about the hazards and the exposure of employees, risks can be assessed and proper control measures can be derived. Here the GESTIS/GIS tools can help to find proper substitutes for very risky substances.

In addition with GESTIS-Stoffmanager the effectiveness of possible risk management measures can be estimated before installing them. The last step is the documentation and the validation of the results. The company has to keep an index of their hazardous substances, instruct their employees and register employees that have contact to carcinogenic or mutagenic substances. The central exposure database (ZED) was established to aid the companies with this registration duty. The poster presents this stepwise approach.

## Aerosol Test Chamber

Christiane Behrens-Gütschow, Frank Haverland, Stefan Köhne  
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The anthrax attacks in 2001 and recent events put a focus on protection systems against the threat of biological warfare agents for both civilian and military applications. Biological warfare agents of greatest concern are those that can be deployed as aerosol. For physiological reasons the average particle diameter of aerosolised agents will be in the range of 1 to 10 microns. Particles of this size pose the highest threat to humans as they are able to reach the alveoles and even small numbers of inhaled particles cause a high risk of infection.

During the last decade several systems using specific detection technologies have been developed to be able to identify/detect biological warfare agents. To test and to evaluate this equipment a variety of non-harmonised testing practices exists in different international test facilities. As a consequence the testing activities can not be coordinated and synchronised across national boundaries.

One aspect of our work is to take an active part in the national (e. g. Commission on Air Pollution Prevention VDI and DIN – Standards Committee KRdL) and international (European Defence Agency, EDA) efforts to define a common international standardisation set of equipment and procedures, so that only comparable methods will be used in the future. As an example of this effort our Aerosol Test Chamber (ATC) is presented. Within this ATC (12 m<sup>3</sup>) we are able to test and evaluate biological detection technologies and sampling devices under well defined conditions. Test instruments can be placed completely inside or partly outside of the chamber. The ATC allows the operator to independently generate different kinds of aerosol backgrounds and additional biological particles. For the testing of aerosol samplers the concentration of biological particles can be kept constant at very low concentrations for up to several hours.

## Multiple uses of a controlled atmospheric chamber; decontamination methods and air cleaning devices

Alan Beswick  
Health & Safety Executive (HSE), United Kingdom

The Microbiology Team at HSE's laboratory in Buxton, England, have used a Controlled Atmospheric Chamber facility for over ten years. This is a 34 m<sup>3</sup> controlled environmental room with air handling that allows control of temperature and relative humidity. When the air handling is switched off and ventilation ducts closed the facility provides a sealed unit into which bioaerosols and/or vapour phase fumigants can be safely introduced and contained. The room can be used as a simple, empty test chamber, or can be configured to mimic a setting relevant for the measurements being undertaken, e.g. domestic, office, laboratory or hospital side room settings.

A wide range of projects have been undertaken in the chamber. Bacteria, fungi and viruses deposited onto various surfaces

or aerosolised in to the room air have been used to measure microbiological log reduction following airborne disinfection treatments within the chamber. Such work provides valuable validation data to those interested in deploying fumigation systems for the decontamination of laboratories, healthcare premises, pharmaceutical areas or for biosecurity purposes following malicious release of chemicals or microorganisms. A number of air purification devices have also been assessed and compared side by side using bioaerosol, diesel particulate and organic chemical airborne challenges.

This presentation will summarise some of the results using a number of examples, and describe the anticipated future direction of work with the chamber facility.

### Alkanolamines from water-miscible metal working fluids in workplace air

Morten Blaskowitz, Petra Heckmann, Dietmar Breuer  
Institut für Arbeitsschutz der DGUV (IFA), Germany

Water-miscible metal working fluids often contain alkanolamines as additives. Because of the continuous progression of the metal working fluids in a lot of different areas of application, the composition of the additives is different and always changing. In recent years occupational exposure limits for several alkanolamines were set and published in Germany. In 2015 and 2016 the IFA analysed more than 300 workplace air samples on alkanolamines.

The alkanolamines were sampled on a quartz fibre filter which was fully impregnated with a 0.313 mol/L methane sulfonic acid (MSA) solution. The samples were analysed by ion chromatography with conductivity detection and MSA as eluent. The method is applicable for 11 alkanolamines frequently used in metal working fluids, including the most important compounds ethanolamine, diethanolamine and triethanolamine.

In 83% of the more than 300 workplace air samples in 2015 and 2016 no alkanolamines above the limit of quantification (LOQ)

were found. With 29 samples, the most frequently found alkanolamine in air samples above the LOQ was ethanolamine in a concentration range of 0.25 mg/m<sup>3</sup> to 0.84 mg/m<sup>3</sup>. Diethanolamine was found in only two samples, both with a concentration of 0.14 mg/m<sup>3</sup>. In 15 samples triethanolamine was detected in a range of 0.50 mg/m<sup>3</sup> to 2.7 mg/m<sup>3</sup>. Furthermore the following alkanolamines were quantified above the limit of quantification: 1-amino-2-propanol (3 samples: 0.65 mg/m<sup>3</sup> to 1.4 mg/m<sup>3</sup>), 2-amino-2-methylpropan-1-ol (5 samples: 0.38 mg/m<sup>3</sup> to 0.80 mg/m<sup>3</sup>), 2,2'-methyliminodiethanol (9 samples: 0.30 mg/m<sup>3</sup> to 0.89 mg/m<sup>3</sup>) and 2-(2-aminoethoxy)ethanol (11 samples: 0.088 mg/m<sup>3</sup> to 0.87 mg/m<sup>3</sup>).

In comparison to the occupational exposure limits only a very few measurements exceed these values. In none of the samples 2-amino-2-methyl-1,3-propanediol, 4-amino-1-butanol, 3-amino-1,2-propanediol and 2-(dimethylamino)ethanol above the LOQ were detected.

### Preparation and certification of two new bulk welding fume reference materials for use in laboratories undertaking analysis of occupational hygiene samples

Owen Butler, Darren Musgrove, Peter Stacey  
Health and Safety Laboratory (HSL), United Kingdom

Welding is a universal endeavour. In Europe, it is tabulated that there are approximately 750,000 workers engaged in welding whilst in the US the numbers employed is estimated to be around 340,000. Workers can be exposed to fume arising from welding activities that contain toxic metals and metalloids. For assessment purposes, sampling fume onto a filter for subsequent laboratory analysis using inductively coupled plasma-atomic emission spectrometry (ICP-AES) and inductively coupled plasma-mass spectrometry (ICP-MS) is often used.

An inherent difficulty however with ICP-based analytical techniques is that samples typically require digesting before analysis

i.e. dissolution of a welding fume filter sample in strong mineral acids. The increasing use of high performance closed vessel microwave assisted digestion systems helps but nevertheless this step does still rely heavily upon the skill and experience of the analyst involved.

In summary, the aim of this poster is to summarise the approach taken at the Health and Safety Laboratory to prepare and certify two new bulk matrix matched welding fume reference materials that can be routinely used by analysts to assess the performance of the digestion procedures that they employ in their laboratories when undertaking welding fume on filter analysis.

## Development of a semi-automated system for the spiking of thermal desorption sorbent tubes with volatile organic compounds for subsequent use as proficiency test or reference material samples

Owen Butler, Veronica Brown, Ian Pengelly, Neil Plant  
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Thermal desorption (TD) gas chromatography is a widely used analytical method for measuring airborne concentrations of volatile organic compounds (VOCs) collected using sorbent tube samplers. The technique has greatly improved sensitivity over classical solvent desorption, which allows TD samplers to be used for passive (diffusive) sampling, even in scenarios where concentrations are likely to be very low. The technique is now widely used in the ambient, fence line, indoor and workplace air monitoring environments. Calibration and internal quality control check samples are generally prepared by end user laboratories by spiking individual sorbent tubes with microliter liquid quantities of VOCs in a carrier solvent such as methanol. Given

the minute quantities involved this can be an error-prone step resulting in biased results.

We have developed, through a number of iterations, a computer controlled standard atmosphere system, based upon specifications set out in ISO 6145 part 4, which is now capable of spiking sorbent tubes from the gas-phase thus replicating real-life air sampling. This system is capable of spiking 60 samples simultaneously and through a combination of on-line system monitoring and adaptive feedback protocols, can repeat this process with a between lot precision of < 0.5%. Attributes of this system will be described in this poster.

## Exposure assessment to plicatic acid in woodworkers

Mariella Carrieri<sup>1</sup>, Eun Gyung Lee<sup>2</sup>, Taekhee Lee<sup>2</sup>, Martin Harper<sup>2</sup>, Giovanni Battista<sup>1</sup>

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<sup>2</sup> National Institute for Occupational Safety and Health (NIOSH), USA

Wood dust exposure has long been linked with respiratory disease including occupational asthma. Plicatic acid (PA), a natural constituent, appears to be the compound responsible for Western Red Cedar (WRC) asthma. PA concentration in WRC is around 3-4%, but Eastern white cedar (EWC) contains it in significant proportions as well. A study carried out in a sawmill where EWC was used reported a prevalence of occupational asthma comparable with that one in subjects exposed to WRC.

A HPLC-DAD method to quantify PA in cedar dust was developed in order to assess the occupational exposure to this substance and to investigate the use of PA as a chemical marker of occupational exposure to cedar dust when other types of dust are involved. The method was simple, fast and sensitive (LOD 0.003 mg/L, LOQ 0.010 mg/L). The chromatographic resolution was good and the detector response against PA concentration was linear in the range 0.01-100 mg/L. The method was tested on bulk samples of five wood (three WRC and two EWC) from different sources. The percentages by weight of PA in the three WRC samples were 0.08±0.00%, 0.52±0.03%, and 3.71±0.05 while in the two EWC samples were equal to 3.34±0.16% and 0.04 ±0.00%, respectively. The method was validated also by

the analysis of cedar dust samples collected in an exposure chamber.

A total of 68 samples were collected (with three different samplers) in the range of mass loadings between 0.265-3.501 mg by IOM (n. 35), 0.292-7.794 mg by button sampler (n. 18) and 0.900-2.941 mg by closed-face cassettes (n. 15) corresponding to a dust exposure between 1.104-14.588 mg/m<sup>3</sup>, 0.608-16.238 mg/m<sup>3</sup>, 3.750-12.254 mg/m<sup>3</sup> respectively, for a sampling time of 2 hours in a workplace. A very strong correlation was found between PA and the cedar dust collected in the exposure chamber independently from the different wood or different samplers used.

On the basis of these results this method could be applied to assess the exposure to PA and could be very useful to study the dose-response relationship in order to determine a level of exposure that can be considered "safe" for sensitization, especially when WRC or EWC are not the only wood used. The large variation in PA content between wood samples could be a reason for considering a limit value based on PA, if PA is the active compound or if the active compounds (or health effects) correlate with PA content, and not on the WRC dust.

### Tenacity studies of airborne micro-organisms under ambient conditions in a bioaerosol chamber

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The airborne state is suboptimal for most micro-organisms because they are exposed to a variety of environmental stressors e. g. uv radiation or low humidity levels. The survival rate of airborne micro-organisms significantly depends on their tenacity. The tenacity can be very different depending on the species as well as on meteorological factors and the concentrations of ozone, free radicals and ozone-olefin reaction products. The biocide effects of these compounds are summarized in the so-called "Open Air Factor" (OAF).

In the majority of cases the tenacity of airborne bacteria has been investigated in different types of enclosed bioaerosol chambers in the last 50 years (Springorum & Clauß 2016). The previous studies have been limited in reproducing actual outdoor conditions since mostly just single parameters were examined and no real outside air conditions existed in the test systems used for the experiments. Especially the compounds responsible for the OAF are extremely unstable. In enclosed systems they disintegrate by reactions with particles or surfaces within minutes. For this reason we developed and constructed a novel bioaerosol chamber in which the tenacity of airborne micro-organisms can be investigated under ambient

air conditions for the first time. The chamber consists basically of an UV transparent foil balloon which is inflated continuously with fresh ambient air. The air volume inside the chamber doubles per time unit. With start volume of 100 L air inside the chamber and an air volume doubling every 2.5 min the chamber is fully inflated after 25 min with an end volume of approximately 40 m<sup>3</sup>. First tests showed that air temperature, humidity and radiation in the spectral range from 300 nm to 750 nm inside the chamber were nearly equal to the outside conditions. The measured ozone concentrations were relatively constant during the experiments at about 75% of the outside ambient air concentrations. This shows how fast ozone disintegrates and hence the OAF is reduced.

The next step is to evaluate the bioaerosol chamber with microorganisms.

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### Biological tracer-particles for the validation of dispersion models for bio-aerosols

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Estimating airborne contamination is an important topic in environmental and health protection. Several mathematical dispersion models are used for the prediction of the airborne spread of micro-organisms. For the calculation of concentrations and transport length measures such as sedimentation velocity or deposition velocity, both depending on the aerodynamic diameter of the particles, are needed. In most cases the aerodynamic diameter for these estimations has an assumptive value based on dust particle data. To strengthen the knowledge on the aerodynamic properties of airborne micro-organisms biological tracer-particles for the validation of dispersion models for bio-aerosols could be a helpful tool. The non-pathogenic yeast *Saccharomyces cerevisiae*, which is widely used in the food and beverage industry, was used as test microorganism. An optical brightener, which is normally used in the textile industry was used as a fluorescent marker. Whitening agents, such as the stilbenes, are classified as harmless to health in the concentrations used and are already present in the environment, for example in ground water monitoring. The selected dye Tinopal CBS-x is characterized by good stability, very good water solubility and

very low toxicity. Also, there is no evidence in the literature of mutagenic effects. Tinopal CBS-x is also the most recommended and used tracer dye in hydrogeology and also for use in drinking water. To improve the dyeing properties and to protect the fluorescent signal from "fading-out" in the outside air under light and oxygen, ascorbic acid (vitamin C) was added in the dyeing procedure. Tracer particle solutions produced showed well-separated cells and an intense and clear coloring of the cell structures. In the field experiments the detected particle concentrations correspond very well to the projected dilutions during the aerogenic transport. Even in the case of strong solar irradiation during field tests, clear fluorescence signals could still be determined during the later examination under the fluorescence microscope. The tracer particles are stable in the concentrations used and are safe for human health and the environment. The good separation and aerosolisability of the particles as well as a long shelf life and the permanently clear fluorescence signal make the preserved tracer particles a good tool for the investigation of aerogenic transport of microorganisms under different conditions.

## Testing and validation of personal samplers and methods used for SVOC aerosol measurements

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Aerosols of Semi-Volatile Organic Compound (SVOC) origin represent an important challenge to industrial hygienists due to toxicological as well as sampling issues. Such SVOCs can be found in the particulate as well as the vapour phase of an aerosol and are often measured using personal samplers equipped with fibrous filters. However, due to evaporation-condensation processes, personal samplers do not reflect the particle-vapour-distribution of SVOC aerosols accurately. If a sampler fails to collect both phases of an aerosol, it could lead to significant underestimation of airborne pollutants. For the development of personal samplers and methods for the analysis of SVOC aerosols, many laboratories resort to “filter spiking” experiments as a way to simulate sampling of SVOC aerosol. This gives an indication if the tested SVOC should be sampled as particulate phase on filters, as vapour phase on adsorbers or mixed-phase aerosol on combined filter-adsorber personal samplers. Although broadly used, scarce information can be found regarding the comparability of “filter spiking” to that of aerosol sampling. In that regard, comparisons for two personal samplers and several SVOC were undertaken in stable, temperature-controlled laboratory conditions.

This study had two main goals:

1) determine and model the factors (vapour pressure, droplet size, temperature, concentration, relative humidity) that affect the evaporation rate of SVOC collected on fibrous filters.

2) determine the accuracy of filter-adsorber partitioning using the “filter spiking” technique, compared to the more realistic mixed-phase aerosol sampling.

Our results show that, for SVOC aerosols, the evaporation rate from filters can be accurately predicted by the model. The aerosols' particle size and the flow rate through the sampler did not influence the rate of evaporation. On the other hand, the evaporation from spiked filters is far more variable and difficult to predict, as the sampling flow rate and spiking pattern play an important role. Differences in filter-adsorber partitioning occurred in every comparison between spiking and aerosol sampling. The differences were largely within a 15 to 50% range for the SVOC tested. The spiking technique always overestimated the amount of SVOC that remained on filters.

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## Development of tools to measure the gas-particle partitioning of aerosols

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Semi-volatile organic compounds (SVOC) can often be found as aerosols in a multitude of workplace environments. SVOC are usually partitioned between an aerosols' vapour and particulate phases. The particulate and gaseous phases can lead to different toxicological effects upon inhalation. Separate measurement of the two phases can therefore provide additional information regarding the occupational exposure to mixed-phase aerosols and risk assessment.

Occupation monitoring of SVOC aerosols is usually undertaken using personal samplers with integrated filter cassettes and/or adsorber cartridges. However, SVOC trapped on filter surfaces are likely to evaporate therefrom. The evaporation of particles can cause misleading results and possibly lead to misinterpretation of the occupational exposure to the particulate phase. A tool to separate gas-from particle phase can prove to be extremely useful for occupational hygienists. One way of achieving gas-particle separation is to make use of inertial forces. Particles have a higher inertia and drag coefficient compared to gas molecules. Therefore, with increasing size, fewer particles will be able to change their trajectories and follow the direction

of a minor, lateral flow. The presented separation tools take use of this and separate a nearly particle-free lateral flow for the determination of the SVOC concentration in the gas phase. Two experimental setups were used to test the capability of separating a particle-free flow. The first setup uses a metallic membrane that is on the one hand permeable to vapours and on the other hand acts as a barrier for particles. A minor flow is taken after the metallic membrane to separate vapours from particles. The second, T-shaped setup uses a nozzle to axially accelerate particles while sampling the gas phase through a much lower flow, perpendicular to the particle flow direction.

Our results show that sampling of the gas phase through a minor flow can be a useful alternative for sampling mixed-phase aerosols. Separation through the metallic membrane proved to be the most efficient method, with less than one percent of the particles passing in the minor flow.

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### Occupational exposure to BTEX in an oil refinery: comparison between standard work and special clean-up

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Mixed exposures to chemical products are topical issues for occupational health. The evaluation of occupational exposures to VOCs can be done interestingly through the analysis of unmetabolized VOCs in urine. Dynamic headspace system linked to a mass spectrometer is a sensitive method, suitable for trace analysis (LOQ about 10 ng/L) and avoids time-consuming preliminary samples processing, usually required by metabolites analysis. Exposures to BTEX (benzene, toluene, ethylbenzene and xylenes) were investigated in an oil refinery through 4 field campaigns. Two of them occurred during standard weeks of work (closed system, few suspected exposures), and the others during major clean-up weeks, when activities were supposed to be more exposing. Each time, about 30 workers (plus controls) gave urine samples before and after work shift during five days. At least, 886 urines from exposed workers and 356 from controls were collected. Workers were classified into 7 (clean-up weeks) or 9 (standard weeks) Homogenous Exposure Groups (HEGs). Smoking effect is statistically significant in both functioning modes. Smokers BTEX excretions are always significantly higher for control or exposed workers. Indeed, the tobacco

smoke contains a lot of aromatic hydrocarbons, most especially benzene and toluene. Different profiles of BTEX excretions also appeared for the two functioning modes, depending of exposition and moment of urine collection (pre- or post-shift). During the two standard weeks, only a few HEGs led to BTEX excretions after work-shifts significantly higher than before work-shifts, especially to benzene. These differences were greater during the two clean-up weeks and more HEGs were concerned. This study also showed that, for control workers (even non-smokers) and low-exposed workers, urinary excretions after work-shifts are significantly lower than before work-shifts. It could be explained by a probably cleaner atmosphere in the refinery working area (except for exposing HEGs) than outside air or domestic indoor atmosphere (positive pressure buildings, air cleaning system, non-smoking area). Indeed, the comparison of post-shift urinary concentrations for exposed and control workers seems more relevant than the usual comparison of pre- and post-shift urinary concentrations. It highlights the necessity for the study to include controls working in the same plant.

### Modeling the evaporation of semi-volatile organic compounds

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Semi-Volatile Organic Compounds (SVOC) are often present in the air of industrial workplaces. Sampling and estimation of its health risks needs a theoretical understanding of the process of particle evaporation. Here a theoretical description and comparison with experimental data is presented. Evaporation of a single liquid aerosol particle is described by a quasi-stationary transport equation (Fuchs, 1964). Important parameters affecting evaporation are particle diameter, temperature, diffusion coefficient of the SVOC in air and its vapor pressure at the particle surface and in air. An exact solution exists for the lifetime of a single droplet as well as for the concentration of monodisperse particles that can saturate the air.

In all other cases a solution can be obtained by iteration only. The transport model is extended to deal with:

- the change of vapor concentration of SVOC in air,
- mixture of SVOC in the droplet (Law of *Raoult*),
- polydisperse particle size distribution,
- interaction of SVOC with water,

- change of the temperature of the particle upon evaporation.

The model to predict SVOC aerosol evaporation has been implemented by a computer program written in the "C", which runs on a Unix or Linux computer. A version of the program limited to alkanes is available via the internet (Ferron). The model has been tested for quasi-monodisperse droplets. The model is presently extended to several SVOC like alcohols, glycols, phthalates and amines. We will report on a comparison with experimental data on the evaporation of monodisperse diethylene glycol particles and its interaction with water.

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## Comparison of the determination and evaluation of quartz exposure and exposure levels at European workplaces

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### Introduction:

Quartz is employed as an agent or is released in the form of quartz dust in a range of work processes. All over Europe, the prevention of respirable quartz exposure is a key issue in the regulatory sphere. In view of this, there is a need for a general comparison of studies of quartz exposure in Europe.

### Quartz measurement and measurement strategies:

This study investigates whether the exposure data sourced from different countries like Austria, Finland, Germany and Switzerland for use in epidemiological studies are in fact directly comparable. It describes the measurement convention (DIN EN 481/ Johannesburg Convention), sampling, the analytics employed and the accompanying collection of data. The correlation was found to be close in this case. Sampling is carried out by means of defined standard methods. In addition to sampling, the participating institutions systematically determine and collect company and exposure data. Efforts are made to determine and describe all factors that may have an effect on the measurement result and to store all data on the situation in the work area at the time of measurement. The analytical methods available for this purpose are in principle X-ray diffraction and infrared spectroscopy. Significant differences are however observed between measurement strategies. Do the measurement strategies influence the exposure level significantly?

### Comparison of exposure data and discussion:

Round about 4.200 quartz exposure data from the following industrial sectors and work areas were selected and assessed for comparison.

- Extraction of stones: explosive blasting, drilling, loading for transport, transport
- Processing of minerals and earth: splitting, sanding, sawing, grinding, impact drilling, chiselling, kernelling, charring, scabbling,
- Quarrying of gravel and sand: preparing, screening, mixing, crushing, control panel, silo, loading for transport, weighing, filling.

### Conclusion:

The sampling, analytics and accompanying collection of data are comparable among the participating institutions. Different measurement strategies give rise to different exposure levels in comparable work areas. Investigations into the comparability of measurements from different countries can only be carried out with specialised knowledge of the sector of industry. General conversion factors cannot be derived.

### Development of a real-time sensor for ozone exposure monitoring

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Exposure assessment to volatile pollution in professional environment is currently performed by sampling on solid adsorbing materials or filters for 15 minutes or 8 hours and differed analysis in laboratory for comparison with the threshold limit value (TLV). Since several years, much attention has been focused on various chemical sensors for gases as they may be a convenient alternative to traditional sampling. Also their capability to detect toxic compounds in real time is very useful for occupational exposure assessment. As an air pollutant, a major concern with ozone is its effect on human health (TLV-8h = 0.1 ppmv and TLV-15min = 0.2 ppmv). Because of its potential oxidizing capacity, ozone is extremely irritating for the respiratory system [1]. It can cause lung damage and chronic respiratory disease [2].

This study is focused on the development of a real time system for ozone sensing in air. A chemical gas sensor is composed of a sensitive material deposited on a substrate connected to a measuring device. The quartz-crystal microbalance (QCM) is chosen as a transduction system. The vibration frequency of the oscillating piezoelectric crystal can be decreased by the adsorption of a gaseous compound on the sensitive coating. The interaction of ozone with phthalocyanine or polyaniline (PANI) was tested in controlled atmospheres generated in a dedicated test device [3]. Those materials are of interest for monitoring

airborne ozone [4]. The thin films of phthalocyanine were spray-coated from a chloroform solution. The sensor showed a response to ozone, the QCM frequency decreasing when exposed to 400 ppb of ozone. The initial sensor response could be recovered after purging the measurement cell with air, but the kinetic of the phenomenon had to be improved. Further investigations are currently performed to evaluate PANI response and regeneration in the 0-400 ppb range of ozone. We also study the influence of humidity on the sensor response, with the goal to eliminate the interference of water.

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### Exposure to nanoparticles at workplaces in food industry

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Various papers are published within the scope of (possible) use of nanotechnology applications in food industry. The most common food additives are silica (E551) and titanium dioxide (E171) used as flow aid and anticaking agent or food colorant. It is known from literature that these materials are (partly) in nanoscale size but no more detailed information is given about the specification and manufacturer of these materials. Currently specific information on the physicochemical characteristics of nanomaterials is not reported in material safety datasheets.

How could an employer estimate the hazard if information of the size range is lacking?

Due to the large knowledge gaps regarding the exposure of nanoparticles at workplaces in food industry one needs additional information:

- Manufacturer of common powdered food products
- Additives used in this branch of industry and the manufacturer of these additives

- Types and amounts of processed nanomaterials in food industry
- Workplaces atmosphere during handling with nanomaterials
- Processes whereby nanomaterials could be released
- Metrological determination of the exposure
- Assessment of the exposure level

This contribution should demonstrate the difficulties to acquire necessary information for preparing a risk assessment. Different workplaces have been selected (manual weighing and filling powder mixers) and the additives synthetic amorphous silica and titanium dioxide were identified and particle size determined. Particle number concentration (workplace and background) as well as the average particle diameter of the aerosols have been determined (DiscMini, CPC 3007). Representative results of workplace investigations in different companies should illustrate the difficulties for metrological determination of the exposure and their interpretation.

## Recycling of batteries, cells and accumulators: biological monitoring of occupational exposures to metals

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The number of batteries, cells and accumulators used in Europe increases each year. These compact energy sources are collected and recycled, when they can no longer supply power to electric cars, remote controls, smartphones and a multitude of other industrial and consumer products. France recycles a third of European batteries at its 17 specific recycling plants. After collection, these spent energy sources are sorted according to their composition: mercury button cells, lead acid batteries, alkaline cells, etc. They are then ground into powders, which are recycled using different thermal or chemical processes. Each recycling step potentially exposes operators to high concentrations of toxic metals, which can be harmful to the kidneys, lungs or blood. The organism may respond by producing early-effect biomarkers of recent exposure in advance of possible irreversible health effects.

The main aim of this study is to provide a biomonitoring-based description of occupational exposure to metals during pyrometallurgy and hydrometallurgy: two processes used to recycle any cell, battery or accumulator except lead batteries and mercury button cells. Urinary metal exposure biomarkers will be measured to identify the most exposing tasks and the effectiveness

of personal protective equipment. A secondary aim of our study is to detect the presence of early-effect biomarkers, which could conceivably be associated with occupational exposure. We will focus on nine French industries and will recruit approximately 150 volunteer employees from the pyrometallurgy and hydrometallurgy battery recycling sector as study subjects. These individuals will be classified into homogeneous exposure groups: operators, workshop visitors, administrative staff and battery crushers. Urinary samples will be collected to evaluate biomarker levels during their working week. This biological data will be complemented by exposure assessment based on atmospheric, surface and skin sampling. We will then perform statistical comparisons of exposure in the different groups and during the different tasks.

We expect to establish which processes and tasks lead to the highest metal exposures. We will also evaluate which biomarkers are the most sensitive in each industry. We believe our study will assist occupational health services in implementing biomonitoring for occupational exposure assessment during recycling of batteries, cells and accumulators.

## Cadmium-plated components of weapon systems within the German armed forces

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Cadmium compounds are likely to cause cancer when entering the human body; furthermore such compounds are highly toxic to marine organisms with long lasting environmental effects. Research studies are carried out to evaluate the possible threat of cadmium exposure to Bundeswehr employees and the environment.

Inspections of Bundeswehr aircrafts revealed the presence of corroded cadmium-plated parts, such as plug connectors. Therefore, cadmium exposure during disassembly of these aircrafts cannot be ruled out. In fact, measurements showed significant cadmium exposure levels during the disassembly of a weapon system, or during the washing process of a rocket launcher after field trials. Cadmium concentrations were determined below the threshold value, with an acceptance concentration of  $0.16 \mu\text{g}/\text{m}^3$ . Components within the rocket launcher are made of aluminium materials with a cadmium surface coating. During

rocket launches the surface coating is affected by emitted chlorine gas, or rather by mists of hydrochloric acid. The accumulated cadmium reaction products are washed off by the mandatory washing procedure; hence waste water has to be classified as harmful to the environment. The corresponding cadmium threshold value is  $0.1 \text{ mg}/\text{L}$  according to the waste water ordinance. The analysis confirmed a significant cadmium contamination of the waste water after the washing procedure: cadmium concentrations between  $1$  and  $56 \text{ mg}/\text{L}$  were determined. A few older weapon systems within the German armed forces contain cadmium-plated components. Soldiers and civil employees are usually safe from exposure due to the utilisation of protective clothing, e.g. respiratory filters and skin protection, during routine activities. The applied washing procedure of the rocket launcher does not pose a hazard to soldiers or civil employees. However, the cadmium containing waste water is harmful to the environment and must be professionally disposed of.

## Evaluation of material emissions for museum equipment – BEMMA-Scheme

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Museums worldwide are equipped with different display cases. Exhibit display cases should protect cultural objects from dust as well as from mechanical and physical damage. To ensure a stable climate inside the display cases, a low air exchange rate is maintained. Typically air exchange rates are often smaller than  $0.1 \text{ d}^{-1}$ , which can result in rising concentrations of potential harmful immissions inside of the display cases due to emissions from materials. Especially high concentrations of organic acids, which can emit from e.g. sealing materials, can produce damage of cultural objects.

In 2012 BAM introduced a procedure which is called BEMMA-Scheme (Bewertung von Emissionen aus Materialien für Museumsausstattungen) which stands for: "Assessment of Emissions from Materials for Museum Equipment". Micro chambers are used for VOC emission tests of display case construction materials, e.g. textiles, plastics, sealing material, coatings and others. Each sampling procedure is carried out in duplicate. Emissions like formic acid, acetic acid, formaldehyde and oximes are excluded and the sum of emissions of VVOCs, VOCs and SVOCs

is limited. For a positive assessment all listed criteria must be fulfilled; otherwise the display construction material fails the BEMMA scheme.

The BEMMA scheme is not a guarantee for an emission free display case, but a necessary requirement for the choice of suitable materials for emission and immission reduced display cases. The basic evaluation for the values used for first assessments were a ZIM-project with nearly 100 tested materials. In-between more than 100 new materials were tested and enlarged the knowledge about material emissions from display case materials. Mainly silicone sealing materials were tested due to the fact that this group of material have the highest emissions. With regard to the testing procedure only construction materials were evaluated, not the display cases their self. Nevertheless in combination with the certificate also designed by BAM additionally the further steps of construction can be taken into account. So other factors such as age and storage time of materials, tightness respectively air change rate, air condition or ventilation of display cases can be included in the evaluation.

## Airborne trichloramine levels in indoor swimming pools in Sweden

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Trichloramine is a disinfection by-product formed when chlorine reacts with nitrogen-containing contaminants in the pool water. Trichloramine can then evaporate from water to indoor air. Exposure to trichloramine can cause irritation in the airways, eyes, nose and throat of workers and swimmers. There is yet no Occupational Exposure Limit for trichloramine in Sweden.

Air levels of trichloramine were measured in altogether 41 indoor swimming pools located in different parts of Sweden. All swimming pools used sodium hypochlorite for water disinfection. The majority of the swimming pools (N=29) were traditional public swimming pools with a 25 m pool for training and recreational swimming, and many facilities also had an instruction pool for swimming schools and children. In addition, there were 7 adventure swimming pools and 12 rehabilitation pools. Stationary air samplings were carried out next to the pools at about 1.3 m above the floor. Air was pumped (1 L/min) through a filter impregnated with sodium carbonate and arsenic trioxide, and

the filters were analysed with ion chromatography. The sampling time was usually 2-3 hours, but varied from 1 up to 8 hours. The number of sampling days per swimming pool varied (from 1 up to 6 days), however, in most of the swimming pools samplings were performed on at least two different days. In total, about 400 air samples of trichloramine were collected.

For the traditional public swimming pools, the geometric mean (GM) concentration of trichloramine in air was  $0.13 \text{ mg/m}^3$ . In the swimming pool with the highest levels, the GM was  $0.29 \text{ mg/m}^3$ , and in the pool with the lowest levels GM was  $0.02 \text{ mg/m}^3$ . In the adventure swimming pools, air levels of trichloramine were generally higher with a GM of  $0.20 \text{ mg/m}^3$  (range:  $0.03$  to  $0.40 \text{ mg/m}^3$ ). Measured air levels of trichloramine were considerably lower in the rehabilitation pools, with a GM of  $0.03 \text{ mg/m}^3$ , however, the levels varied across a wide range between the pools ( $0.005$  –  $0.33 \text{ mg/m}^3$ ).

### A rotating drum for the ageing of semi-volatile particles

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Particles at industrial workplaces are frequently composed of semi-volatile organic compounds (SVOC) from production or combustion processes. Particles from machining and milling processes are commonly micrometer-sized fine or coarse particles. After their release into the surrounding air, they change their characteristics due to ageing processes (such as sedimentation, coagulation, evaporation). To study these processes under controlled conditions, particles have to be kept airborne for a prolonged time interval of minutes to hours; it mainly depends on the vapour pressure of the SVOC, particle-composition and -size. Therefore, storages for fine particle ageing usually need large volumes to avoid premature particle loss by wall contact or sedimentation. A more lab-scale setup for ageing studies is the “rotating drum storage” (RDS) where particles are retained in a rotating cylinder for the ageing process. There, particles are kept airborne while letting them settle in a horizontally mounted cylinder rotating gently around its axis. After an initialization time, particles are settling on a circular track with a radius depending mainly on particle aerodynamic diameter and cylinder rotation rate. Assuming there are neither coagulation nor wall losses, particles can be kept airborne

infinitely. Prior to construction, a theoretical model [1] was set up to balance operational parameters, physical dimensions, production effort and weight. Test measurements were carried out using diethylene glycol (DEG) particles from a Sinclair-LaMer type condensation generator as a SVOC model aerosol and using an optical particle counter (Welas digital 3000, Palas, Karlsruhe, Germany) with two identical sensors to account for differences in number concentration and particle size. Sensors were found to coincide within 2% in concentration and size. RDS functional ability was tested with 2.5 µm DEG particles, an ageing time of 1 hour and inlet and outlet connectors closed. When filled with model particles, 60 – 100-fold more particles were found thereafter in the rotating drum compared to the stopped drum. Modal particle diameter in the rotating drum was 1.3 µm; shrinking was assigned to DEG evaporation into the nitrogen of 85% relative humidity used as a dilution gas. In the non-rotating drum the particle concentration was identical with background and no micron-sized model particles were registered.

[1] R. L. Gruel, C. R. Reid and R. T. Allemann, J. Aerosol Sci., 1987, 18, 17-22

### Estimation of cumulative exposure to manganese using the exposure database MEGA and occupational histories of male participants of the Heinz Nixdorf Recall Study

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#### Objective:

The German Occupational Exposure Limit (AGW) was recently reduced to 200 µg/m<sup>3</sup> of inhalable manganese (Mn). We took advantage of a large collection of Mn concentrations and ancillary data compiled in the MEGA database to estimate occupational exposure to Mn of male participants of the prospective Heinz Nixdorf Recall Study (HNRS) in order to assess neurotoxic effects.

#### Methods:

This analysis was based on 4,635 measurements of inhalable Mn in the breathing zone of workers from 1989 to 2015. We assigned the measurements to at-risk occupations according to a supplemental questionnaire. Welding was categorized by major welding process and Mn content of the materials. Mixed-effects models were applied to the log-transformed Mn concentrations to calculate the annual geometric means (GMs) of shift exposure in at-risk occupations. We linked the exposure estimates with the occupational histories of 354 male participants of HNRS to calculate cumulative exposure to Mn as the sum of the exposure

levels in all periods working in at-risk occupations using the product of the job-specific GM and the corresponding duration.

#### Results:

The median of Mn concentrations was 33 µg/m<sup>3</sup>. Twenty percent were above AGW. GMs > 200 µg/m<sup>3</sup> were observed in gas welding and gas metal arc welding with materials of Mn content ≥ 5%. We did not observe time trends of exposure to Mn. Median cumulative exposure to Mn was 58 µg/m<sup>3</sup> years in all 354 participants but 1,121 µg/m<sup>3</sup> years among 26 welders enrolled in HNRS.

#### Conclusion:

Welding was frequently associated with exposure to Mn above the German AGW. In welders, exposure was strongly influenced by the major technique and the Mn content of the processed material. We recommend therefore to collect information using a supplemental questionnaire in addition to the job title in community-based studies like HNRS when estimating the health effects of occupational exposure to Mn or other metals.

## The suitability of multi-channel silicone rubber traps for particle-vapour separation of aerosolised semi-volatile organic compounds

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Currently used personal samplers are not able to achieve an artefact-free separation of particle and vapour phases of aerosols from semi-volatile organic compounds (SVOC). However, since aerosols from hazardous SVOC may occur in workplace air and can lead to occupational diseases, a simultaneous differential sampling of both phases is necessary. One promising approach towards particle-vapour partition and the collection of SVOC vapours is the use of multi-channel silicone rubber traps introduced by Ortner and Rohwer, 1996.

Our study focused on the suitability of silicone rubber traps as denuders to achieve separate analysis of particle and vapour phases. The particle size dependent transmission efficiency was analysed by using polystyrene latex (PSL) particles in the size range of 0.3-2 µm, while the time dependent vapour collection efficiency was investigated for polar and nonpolar SVOC (mass concentrations ~9 mg/m<sup>3</sup>) at a sampling flow rate of 0.5 L/min. The experimental vapour collection efficiency was compared with the theoretical predictions calculated according to Possanzini et al., 1983. For n-hexadecane (C16), the vapour collection efficiency was 96% over 135 min. If dimethyl phthalate (DMP) was applied, the vapour collection efficiency remained at

99% over 135 min. In contrast, diethylene glycol (DEG) led to a decrease of the vapour collection efficiency from 94 to 49% after the same time period. Calculations predicted theoretical vapour collection efficiencies of 81 % (C16), 86% (DMP) and 94% (DEG). Regarding the particle transmission through the denuders, transmission efficiencies from 91-100% were observed for PSL particles with diameters from 0.3-2 µm. In conclusion, our study shows that multi-channel silicone rubber traps are well suited for SVOC sampling of aerosols with particle diameters < 2 µm at flow rates of 0.5-1 L/min or lower. These characteristics as well as their small size and easy handling enable the use of multi-channel silicone rubber traps as denuders in low flow rate personal samplers.

This work is supported by the German Social Accident Insurance (DGUV), research contract FP371.

Ortner, E. K. and Rohwer, E. R. (1996) *J. High Resol. Chromatogr.* 19, 339-344.

Possanzini, M., Febo, A. and Liberti, A. (1983) *Atmos. Environ.* 17, 2605-2610.

## „(Ultra)fine particle emissions“ – Small intruders with huge effects

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Small particles from, for example, diesel engine exhausts or welding smoke pose a large risk to human health since they can enter into the respiratory tract or even overcome the blood-brain barrier. The maximum diameter is 100 nm. Therefore, a large part of the particulate content cannot be identified with conventional measuring techniques. While the existing values for dust exposure levels still have to be recorded, new methods for the measurement of ultrafine particulate dusts are needed. The effect of ultrafine particulate dusts is governed by the number of particles and the available surface. The established measurement methodology for the evaluation of dust and emissions from diesel engines is based on the determination of the total mass of the particles (gravimetric analysis). In the truest sense of the word, superfine particles barely carry any weight. Therefore with this technique, ultrafine particles do not contribute adequately in the risk evaluation of particulate dust. It is not the mass that needs to be evaluated but rather the number of particles. In a normal size distribution, 80% of the particles are smaller than 100 nm, their fraction of the entire mass of the particles is below 1%. Their properties, especially their mobility, depend predominantly on their geometric diameter and the particle shape

(simple sphere, chains, or agglomerates). The effect of ultrafine particulate dust is governed more by the number of particles and the surface concentration than by their weight. The absorption surface area is relatively huge and due to other hazardous substances being present in the air (such NO<sub>x</sub>), the particulate dust acts like a transport vehicle for these substances into the human body and hence presents an additional health risk.

To date, in order to determine the dust concentration in air, special filters are used to collect the airborne matter. The particle mass concentration is then obtained by correlating the collected total particulate mass to the total air-flow volume through the filter. The mass of the fine and ultrafine particles only contributes to a minor extent to the total mass content in a sample. Their number, however, may be large. Due to the complexity of measurement on one hand, and the setting of appropriate reference standards on the other, it is not expected that a legal limit value will be introduced in the near future.

### Estimation of factors influencing endotoxin activity measurement

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Quantification of endotoxin activity is widely used in hygiene and pyrogen controls as well as a surrogate marker for microbial exposure in environmental and occupational settings. Although in the 1970s, the Limulus Amoebocyte Lysate (LAL) test, which is an in vitro test (with the haemolymph of the horseshoe crab) was established for the specific detection of endotoxin activity, so far no international accepted standard protocol for the measurement exists. Therefore comparison of results of different studies is difficult. Not only strategies for collecting the samples, but additionally, extraction procedure and using test equipment from different companies influence the results. As reported before, especially the usage of Tween-20 as detergent in the extraction buffer resulted in higher values of endotoxin activity compared to measurement without Tween.

Therefore, the aim of our study was to estimate the effect of different extraction procedures and calculate conversion factors for better comparison of endotoxin results obtained under different extraction conditions. For this purpose we used dust collected with 102 electrostatic dust samplers for 14 days in private

households. Each sampler was equipped with two cloths which were extracted with 20 ml Aqua iniectionabilia with or without 0.05% Tween-20 in parallel. Endotoxin activity was measured with the chromogen-kinetic LAL-Test (Charles River, Sulzfeld, Germany). Samples extracted without Tween-20 showed lower endotoxin activities than samples extracted with Tween-20 (0.02 to 8020 EU/mL versus 0.16 to 29764 EU/mL) with significant correlation ( $r_s = 0.95$ ,  $p < 0.0001$ ). Neither the recovery rate (median value with and without Tween 109% versus 112%) nor the variation coefficient (5.7% for both) were significantly different. The standard curve (0.005 to 50 EU/ml) was significantly elevated with Tween, resulting in higher values of endotoxin activity. Using linear regression two conversion factors to estimate the Tween effect could be calculated: for values below 10 EU/mL Tween extraction leads to two times higher values and for values above 10 EU/mL Tween extraction resulted in threefold higher values. If these conversion factors are valuable for other dust sampling strategies has to be verified. However, such calculations may help to compare data from different studies using different extraction procedures.

### Priority pollutants from weapon emissions: methodology of selection

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Human risk assessment during the use of weapon systems is a key step to protect military servants during and after fire. During the use of many weapon systems, there is a smoke emission which could present a risk for exposed military. Fumes are generally composed of plenty of pollutants.

However, all these pollutants cannot be measured because of technical (and/or financial) limitations. As a consequence, a selection has to be made in order to establish a prioritized list of toxic substances representative of the smoke mixture hazards. The pollutants have to be selected with some specific criteria and toxicity of these pollutants has to be representative of the mixture toxicity which composes weapon smoke. A methodology to select relevant marker pollutants among all the chemicals emitted by weapon systems has been established by toxicologists and pharmacists from the French Ministry of Defense.

The first step is to identify a list of all the pollutants in the weapon smoke (gas and particles). Then, specific criteria are proposed to select toxic markers in this list. A hazard score, given to each pollutant is based on:

- French occupational exposure levels
- CMR classification – estimated concentrations
- Toxicological profile of each pollutant (target organs)
- Possible cumulative effects on common organs/systems

When the substance score is important, the substance is selected as a toxic marker of the weapon smoke mixture. The final list of selected substances is validated by a commission of experts. An example of weapon smoke pollutants will be presented to show how this methodology can be applied.

### Survival of MRSA and *Staphylococcus aureus* in sedimented swine farm dust

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Methicillin-resistant *Staphylococcus aureus* (MRSA) is an antibiotic resistant bacterium, which can cause serious human infections. MRSA CC398 is a specific clone that have adapted to livestock, and which is widespread in Danish pig farms. Transmission of MRSA CC398 has been shown to occur from pigs to humans and even between humans. People working in pig stables are exposed to MRSA CC398 directly by contact with the pigs, but also indirectly via the environment. Dust has been shown to contain MRSA CC398, and hence dust can be a vector for transmission both through aerosolized particles and through particles settled at surfaces.

The purpose of this study was to determine the rate of decay for *S. aureus* and MRSA in dust. Electrostatic dust fall collectors (EDCs) were used for passive sampling of settling airborne dust in 11 barn sections from 6 different pig farms. Extraction and enumeration of cultivable *S. aureus* and MRSA from the EDCs were performed for a period of 0-30 days post sampling. Appropriate dilutions of the extraction were plated on chromogenic agar plates selective for MRSA (Brilliance MRSA 2 agar, Oxoid)

or for *Staphylococcus* (SaSelect, Bio-Rad). After 24 hours of incubation isolates resembling MRSA and *S. aureus* were further identified using MALDI-TOF-MS and counted. A large variation in the initial concentration of MRSA was represented in the EDC samples from the different swine farms, but also between stable sections within the same farm. *S. aureus* was found in all samples, but in dust from one farm MRSA was below the detection limit. The concentrations of *S. aureus* and MRSA in stable dust collected from swine farms were significantly ( $P < 0.01$ ) reduced in response to storage time of the dust. A total of 138 quantitative measurements of *S. aureus* and MRSA survival in dust from all farms, were used to estimate the exponential decay constant  $\lambda$ , according to a model for exponential decay,  $N(t) = N_0 \times e^{-\lambda t}$ . The data fitted well to the model and the mean half-lives were between 4 and 5 days. The survival of *S. aureus* and MRSA is interesting in relation to re-aerosolisation of dust from surfaces in the stable environment, but also in relation to dust transported to other areas as the home environment and working vehicles.

### Two-fraction aerosol sampler PGP-EA 10 using a porous foam

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A simultaneous aerosol sampling of more than one health related dust fraction can be realized by using porous foams. Its application allows a simplified personal sampling procedure with information on two or even three dust fraction concentrations. The personal sampler PGP-GSP 10 (10 L/min) for the inhalable dust fraction was equipped with a porous foam plug of polyurethane and cell diameter 480  $\mu\text{m}$ . Its diameter was chosen at 30 mm, covering the same collection area as the underlying membrane filter (cellulose nitrate, pore size 8  $\mu\text{m}$ ). Several plug thicknesses (8 to 14 mm) were tested in order to optimize the penetration of the respirable dust fraction. Tests were performed with NaCl and oil droplets in a size range from 1 to 10  $\mu\text{m}$  aerodynamic diameter. A calculation of the bias maps according to EN 13205 (2001) gave most promising results for a 8 mm thick foam plug with bias values below 20% for all relevant size distributions. This combination of conical aspiration orifice with 13 mm opening, 8 mm foam plug plus membrane filter is called PGP-EA 10. Laboratory comparisons were carried out using welding fume below 5  $\text{mg}/\text{m}^3$  in average and reference instruments (FSP 10, MPG II, GSP 10, GSP 3,5) in a small chamber (2 · 2 · 2.5  $\text{m}^3$ ) in calm air (sampling times 2 to 8.5 h). Sampling

ratios were found to be 1.0 for the inhalable fraction in comparison with GSP 10, 0.92 for the respirable fraction and FSP 10, 1.0 with MPG II. Calculation of the accuracy criterion according EN 13205 (2001), Part B, gave in all cases the required accuracies below or equal to 30%. Currently there is no need for a correction factor. Additional field tests were conducted and showed equivalence of PGP-EA 10 with FSP 10 and GSP 10. The handling of the sampler, the foam and filter cassettes was positively proven.

The application of the PGP-EA 10 will be limited to welding workplaces, as the clogging effect for the foam can occur when sampling coarse particles. It is hard to decide for the user at which dust load the foam will change its penetration efficiency and deviate considerably from the respirable fraction. Besides the mass concentration by weighing foam and filter, the composition of the dust is of interest. Further investigations on elemental blank values, cleaning and selection procedures for the foam material are necessary and underway in order to reach a comprehensive sampling method.

## Generation, characterization and online-monitoring of airborne substances in an exposure unit for human inhalation challenges

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Exposures to vapors and particles pose important health hazards at workplaces. Human inhalation studies provide a wide variety of real-life conditions and facilitate the measurement of multiple endpoints of relevance. Particularly for the setting of occupational exposure limits controlled exposure of the respiratory tract yields valuable information. One of the main goals is to add experimental approaches in humans to the currently existing mosaic of in-vitro, animal and epidemiological studies, and thus to achieve a more comprehensive understanding of the complex nature of adverse health effects of air contaminants.

An exposure laboratory (ExpoLab) at our institute enables inhalation studies for up to 4 subjects simultaneously. In an adjacent preparation room we generate and characterize the atmospheres of airborne chemicals like gaseous substances (i. e. ethyl acrylate, ozone) or nanoparticles (zinc oxide). The air exchange rate of the ExpoLab can be set between 4 to 16 times. The temperature is adjustable between 20 and 25 °C and the relative humidity can be set 40% or higher. The distribution of the laden air is realized at the bottom of the unit and extraction under the ceiling thus guaranteeing an even spatial distribution

throughout the chamber. The generation of gaseous atmospheres is performed with a test gas generator equipped with an evaporation unit. This device evaporates pure solvents and mixes the vaporized material with nitrogen in a pre-chamber made of a 300 L glass vessel. The enriched atmosphere passes through a T-piece in the air conditioning flow of the ExpoLab to reach its desired concentration. The main analyzer of the gaseous atmospheres is a chemical ionization mass spectrometer. This device has a very fast analysis time with 1 scan per second. Analysis of multi-component mixtures without chromatographic separation is possible down to the lower ppb range. Metal oxide nanoparticles can be generated via flame spray pyrolysis of aqueous precursor solutions in a hydrogen-oxygen flame. Size distribution of the particles is measured via SMPS. Airborne particle mass can be analyzed with a TEOM device. Results of profile measurements using sulfur hexafluoride and zinc oxide nanoparticles showed that the technical setup at ExpoLab enables a highly homogeneous and timely stable spatial distribution of gases and particles which, in turn, offers unique possibilities to study the health effects of chemicals in humans using experimental settings.

## Proficiency testing for the measurement of hazardous substances in air at the IFA

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Since laboratories and their analysis methods have to satisfy increasingly strict quality requirements, there is a growing demand for methods for external quality control. Participation in proficiency testing (PT) schemes is a popular way of checking the quality of one's own measurement results and demonstrating it towards third parties as accrediting bodies and customers. IFA has been an established provider of international PT schemes for many years.

Since 1989, the IFA offers PTs for a wide range of analytes. In recent years PTs for five different substance groups were performed: organic solvents, volatile and non-volatile inorganic acids, volatile organic compounds (VOC), metals and aldehydes. Sampling is one possible source of error within a measurement method.

Therefore the IFA offers PTs with on-site sampling. The participants can choose whether they want to perform the sampling on their own at the IFA or have the samples sent to them. The PTs for non-volatile inorganic acids and metals are only offered without own sampling because the preparation of the samples cannot be accomplished at the test gas facility.

At the IFA, the samples are prepared at the large dynamic test gas facility which enables the production of realistic workplace samples. It has a length of 15 m and a tube diameter of 50 mm and is suitable for parallel sampling for up to 13 participants. The test gas facility is composed of three different units: test gas preparation and conditioning, section for active sampling and metrology for online control of the test gas. The test gas consists of a basic gas, purified, and if necessary humidified air with a gas flow of 1-6 m<sup>3</sup>/h, and a secondary gas flow which contains the particular analytes. The secondary gas is introduced into the basic gas at a heated transfer point. Different methods for the production of the secondary gas flow are used at the IFA: calibration gas generator with push-pull syringe or peristaltic pump, permeation oven and syringe doser. These systems allow a large variability of substances that is necessary e.g. for simulating an indoor air sample with volatile and semi-volatile substances in parallel. All different systems guarantee a high precision with excellent variability of less than 2% for the test gas. The PT schemes offered by the IFA enjoy great popularity. The attendance numbers are consistently high. In 2016 a total of 231 participants from 18 different countries took part in the PTs of the IFA.

### Determination of health-related aerosols and volatile organic compounds generated from room care cleaning sprays

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Professional cleaning is a common occupation in Norway with more than 60.000 workers employed in 2016. Professional cleaners in Norway self-reports the highest occurrence of airway symptoms compared with the general population.

Professional and domestic cleaning is associated with work-related asthma (WRA). A recent systematic review of 24 epidemiological studies on cleaning work and risk of asthma and rhinitis reported that increased risk of asthma and rhinitis had been shown in 79% of the included epidemiological studies. Cleaning sprays, bleach, ammonia, disinfectants, mixing products, and specific job tasks have been identified as specific causes and/or triggers of asthma. However, there are only limited reports of quantitative exposure assessment in studies of cleaning products and respiratory disorders and to our knowledge no studies have determined the health-related aerosol fractions generated by cleaning sprays.

The aim of this study was to determine the health-related aerosol fractions and volatile organic compound generated by cleaning sprays. Seventeen different room care cleaning products and seven different trigger sprayers from the two largest suppliers in Norway were investigated. Samples of health-related aerosol fractions and volatile organic compound were collected in a standardized laboratory experiment. In addition workroom air samples of the thoracic aerosol fraction and volatile organic compounds were collected during professional cleaning tasks.

The results showed that an exposure reduction of health-related aerosol fractions of more than 90% can be achieved by replacing the most common trigger sprayer in Norway with pressure sprayers. Furthermore, the results showed that an even larger exposure reduction can be achieved by using trigger sprayers producing foam.

### Permeation measurements in preclinical medical training (anatomy)

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During preclinical medical education (anatomy) extensive studies concerning the formaldehyde exposure in the air at the workplace were conducted. These studies are a topic of a presentation at this year's Airmon. Concurrently the skin exposure of the employees and students to formaldehyde-containing fixatives and body donations was investigated.

Usually nitrile, vinyl or even latex based disposable gloves are used, which are supposed to protect not only against infection, but also against body fats and the used fixatives and preservation chemicals. Generally fixatives, containing – aside from formaldehyde – ethanol and phenoxyethanol, are being used during preparation, while the preservation solutions only contain formaldehyde. It is also likely that additional substances, with which the students and employees may come in contact with, are being released by the preserved body donations. Considering the expected spectrum of substances permeation studies have been conducted on different disposable and protective gloves under the exposure of fixatives and preserved

specimen of pig meat. A standard measurement method according to DIN EN 374-3, which cannot differentiate substances, was used. This was complemented by a special method which is able to distinguish various substances. It has been shown that the permeation is dominated by formaldehyde and ethanol. Other substances that have been detected in the fixative and preservation solution are irrelevant for the permeation. Depending on the material and quality of the used gloves relevant permeating amounts of substances were detected on the inside of the gloves after only a few minutes, suggesting a limited wearing time.

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## Evaluation of ozone-initiated VOC and particle emissions from a carpet deodorizer

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Indoor use of fragranced consumer products (e.g. cleaning products, air fresheners) may pose health hazards and discomfort for building occupants due to inhalation exposure to product constituents and to secondary pollutants.

1. Several studies highlighted that unsaturated reactive Volatile Organic Compounds (VOCs), such as terpenes included in the formulations as fragrances, undergo gas-phase and surface reactions with oxidants such as ozone and nitrogen oxides leading to the formation of a variety of ozone-initiated products.

2. The main objective of the present work was to investigate the ozone-initiated reaction products of terpenes emitted from a carpet deodorizer. Investigations were performed inside a full-scale climate chamber in absence and presence (50 ppb) of ozone and under near-realistic user conditions in order to mimic user pattern behavior. Experimental activity involved the characterization of VOCs emission (primary emission) from the carpet deodorizer and the identification of ozone-initiated reaction products by GC/MS and HPLC-UV and the evaluation of Secondary Organic Aerosol (SOA) formation. Experiments were carried out both onto an inert surface and onto a carpet with the main purpose, in the latter case, to investigate the extent of

both heterogeneous reactions onto carpet's surface and homogeneous reactions in the gas-phase (after the application of the product) and to evaluate the real exposure scenario. Emission testing of the carpet deodorizer onto the inert surface in the presence of 50 ppb ozone showed the formation of oxidation products (i.e. acetaldehyde, acetone and 6-MHO) and of SOA, confirming experimental results obtained in previous investigations.

This study provides also additional evidence of the potential of the carpet to significantly remove ozone resulting in an increase in the gas-phase concentration of secondary formed aliphatic aldehydes.

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## Development of a Nano Exposure and Contextual Information Database (NECID)

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### Objectives:

Research in exposure to nanoparticles requires sufficient and detailed data on occupational exposure. In addition to a uniform and harmonised way to collect and store information, data sharing and the connection to other sources of information is a key factor to increase the quality and amount of data. Only with a sufficient number of datasets of high quality the next steps in risk assessment and also the deduction of future limit values will be feasible.

### Methods:

Under the leadership of IFA and TNO a working group of PEROSH institutes developed and tested a database software called NECID (Nano Exposure and Contextual Information Database). In addition to measurement data of individual instruments the collection and documentation of work conditions is a focus of this project. The NECID software includes a nanomaterial specific exposure database, as well as features for data sharing and data assessment. The software runs locally on a computer but also offers a web-based, central database for the exchange of information. As far as possible NECID uses a harmonised ontology to

enable a link to other databases. A direct link to the database of the EU project eNanoMapper is projected.

### Results:

The first version of the software was realised and has been tested by PEROSH members and three external partners. It is planned to offer the software to organisations, which perform exposure measurements for nanomaterials, and companies that produce or use nanomaterials. Aim is to enlarge the number of users and datasets and thus enhance the benefit for the users. Participating companies e. g. can benchmark themselves amongst their peer group. Scientific users can enlarge data pools to strengthen statistical conclusions or validate their measurement results with reference data. Finally public access shall be enabled to consolidated and anonymised information.

### Conclusion:

Due to the limited amount of data in the field of exposure to nanomaterials, a harmonised exposure database linked to other databases, e. g. on material or toxicological properties, is able to accelerate the improvement in occupational safety.

## Next level of air monitoring: latest developments and applications in real-time gas analysis with PTR-TOFMS

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Proton Transfer Reaction – Mass Spectrometry (PTR-MS) is a well-established direct injection trace gas analysis method with numerous advantages: high sensitivity, low detection limits, no sample preparation and online quantification. Atmospheric research and indoor air analysis have always been among the most important fields of application of PTR-MS [1]. Hence, here we present some of the latest instrumental developments, which evolve real-time air monitoring to the next level. The transfer region between the chemical ionization chamber and the Time-Of-Flight (TOF) mass analyzer is one of the most critical parts of a PTR-MS instrument. By installing a Quadrupole ion guide (Qi) in this area we could improve the overall sensitivity by more than a factor of 20. Measurement data obtained with certified gas standards prove that the sensitivity of this PTR-QiTOF can reach up to 4700 cps/ppbv at a mass resolution of about 7000 m/Δm [2]. However, a different approach of optimizing ion transmission in the transfer region is the use of ion funnels. An ion funnel consists of a series of lenses with successively smaller apertures with applied RF voltages. We present a modular version of an ion funnel, which can be installed e.g. in the compact PTR-TOF 1000 and increases the sensitivity by up to one

order of magnitude. Importantly, in contrast to known PTR-MS ion funnel implementations, the ionization conditions are not negatively affected, i.e. branching ratios remain comparable to PTR-MS instruments without an ion funnel. Both implementations of sensitivity enhancing measures considerably improve the signal-to-noise ratio and, thus, measurement speed and sample throughput.

This project was supported the EU IMPACT (GA 674911) and the Land Tirol via an FuEul project and by the Austrian Research Promotion Agency (FFG) via a Basisprogramm and an ASAP project.

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## Mite allergen exposure in offices in comparison to homes

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### Background:

Mite allergens are presumably the most important cause of allergic asthma all over the world. Allergen exposure is not restricted to the living area but might occur also at the workplace. Aim of study was to compare domestic mite allergen (DM) exposure in offices to homes.

### Methods:

Electrostatic dust collectors (EDCs) which are developed for passive sampling of airborne particles and are useful in large population studies were placed for 14 days four times a year in five office buildings in Hamburg and Berlin (67 rooms, 435 EDCs), and in parallel in the office workers' homes (145 rooms, 403 EDCs). In addition, floor dust was sampled by vacuuming 0.4 m<sup>2</sup> carpet in the office rooms also four times a year (437 samples). Allergens were quantified in all samples with an immunoassay based on polyclonal antibodies to DM. The detection limit for DM on EDC was 35.9 ng/m<sup>2</sup> and on floors 1.9 ng/m<sup>2</sup>.

### Results:

In homes, 360 EDCs (89%) contained DM (interquartile range 124-1356 ng/m<sup>2</sup>), whereas in offices only on 199 EDCs (46%) DM could be found (upper quartile 85 ng/m<sup>2</sup>). This difference in DM

concentrations on EDCs between offices and homes was highly significant (Mann Whitney test, p<0.0001). On the office floor, DM load was at median 100 ng/m<sup>2</sup> and the DM concentration in dust 1334 ng/g. DM load on EDCs and floors in the same office room were moderately correlated (Spearman r = 0.39). Removal of carpet within three years before sampling reduced dust and DM loads per square meter significantly. In addition, dust and DM loads per square meter were significantly lower in offices without or with sporadic customer visits only. These differences were more pronounced for dust loads than for allergen loads. In consequence the ratios, DM concentrations per gram dust, were higher in rooms without customer visits and in rooms with new carpets. However, DM loads on EDCs corroborated lower DM exposure in rooms with new carpets and without customers.

### Conclusions:

DM exposure in offices seems to be much lower than DM exposure in office workers' homes. Daily customer contact and old carpets seem to increase exposure. Exposure assessment by measuring allergen concentrations per floor dust could result in misleading prevention recommendations.

### Non-selective VOC air sampling using canisters

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Radboudumc, Netherlands

#### Background:

Canisters are rigid stainless steel spheres, drawn vacuum for non-selective collection of air samples. This technique was developed during the space shuttle program to allow chemical characterization of spacecraft air quality. Collection of an air sample does not require a pump and no reagent or adsorption tube or filter. The sampled air is transferred from the canister directly to a thermal desorption gas chromatograph mass spectrometer (TD-GC-MS) for analysis. We applied this method to characterize indoor quality in a variety of indoor environments such as operation rooms, offices, laboratories and homes.

#### Objective:

To chemically characterize indoor air atmospheres for VOC by canister sampling and analyze these samples with TD-GC-MS for exploration purposes in clean environments. Materials and methods canisters were equipped with flow restrictors (Entech) were calibrated to allow sample collection over periods of a few hours up to one week. An air server (Series 2, Markes) is used to extract a gas sample of 100-250 mL from the canister. Gas cylinders with VOC mixtures of known composition (TO14 and TO15) were used for calibration. For the analysis we used a thermal desorber (Markes) combined with a gas chromatograph mass

spectrometer (Thermo), equipped with a RXi-5 MS column (30 m, 0.25 mm internal diameter and 0.5  $\mu\text{m}$  film thickness). Sample extraction took 7 to 17 minutes at a rate of 15 mL/min. The TD trap temperature was increased from -10°C to 300°C in 5 min.

#### Results:

We applied canisters in situations where conventional adsorbent sampling was not expected to perform very well because of extreme short-term (minutes) and long-term sampling (7 days) and situations where extremely low concentrations were anticipated. In the operating room of a hospital environment we studied infiltration of organic vapors from helicopter and diesel engine emissions. In a residence we identified traces of chlorinated aromatic hydrocarbons due to infiltration from a historic soil contamination related to dry cleaning and a gasoline station.

#### Conclusion:

Canisters can be used as alternative for adsorption tubes or filters for exploring extremely low concentrations of yet unidentified VOC. We demonstrated detection with satisfactory precision at concentrations below 0.05  $\mu\text{g}/\text{m}^3$ .

### Grouping of nanomaterial characteristics and work process parameters for a simplified control banding

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The current state of knowledge on the hazard of nanomaterials towards protected persons or the environment is quite complex. The grouping approach can structure this situation. It has been used only in special cases (e.g. for fibres) and can be applied in areas such as occupational health and safety, product identification, and regulation, which presently still must rely on individual case studies.

The German nanoGRAVUR project (nanostructured materials – grouping for occupational health, consumer and environmental protection and risk mitigation) is going to develop different criteria catalogues for a grouping of nanomaterials according to the respective potentials for exposure, hazard and risk. A control banding approach to estimate the risk requires the allocation of exposure and hazard into a few classes in order to derive the severity of risk in terms of low, medium and high risk and facilitate the assessment of a workplace as well as subsequent control measures. Exposure depends on material properties, process parameters and transfer characteristics from the source to the recipient. Additionally to existing knowledge on these parameters, further tests are being done to determine missing

values. Hypotheses for grouping are prepared and tested using existing data and experimental tests. Material properties like the particle shape (fibre – platelet – compact particle), the kind of material (powder, compound material, coating), the propensity for dispersion into air (dustiness), their dispersion into compound materials by using different matrix materials (polypropylene, epoxy resin, aluminium, concrete) and the kind of processing (energy input at grinding, sawing, drilling) is going to be tested for the degree of release and exposure.

Additionally the toxicity is tested for grouping effects, depending on physical and chemical properties. Carbon black, graphene, carbon nanotubes, WS<sub>2</sub> nanotubes, SiO<sub>2</sub>, TiO<sub>2</sub>, copper phthalocyanine, activated cement additive are under investigation and are representatives for different groups.

The resulting and simpler tools for risk assessment shall facilitate the choice of protective measures during use of nanomaterials for all kind of applications in companies, but also for end users and the environment.

## Laboratory and field comparisons of four bioaerosol samplers: collection onto a filter in a closed-face cassette vs. liquid-based collectors

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Assessing exposure to bioaerosols using culture-based methods presents drawbacks and provides qualitative rather than quantitative results. Nonetheless, it is still widely used by occupational hygienists to differentiate “uncontaminated” areas from higher concentrated workplaces in which reducing exposure needs to be addressed. Previous laboratory experiments showed that stress-sensitive microorganisms, especially vegetative cells, may lose culturability due to desiccation when sampled by filtration in a closed-face cassette (CFC), which may lead to severe underestimation of culturable bacteria concentrations. Liquid-based collectors use a gentler sampling process and are supposed to provide better microorganisms recovery. However, their use in field studies is very limited and comparisons with CFC are not documented.

Our objective was to compare culturable microorganisms concentrations obtained with CFC (2 L/min) to those measured with three liquid-based samplers filled with a phosphate buffered solution: BioSampler (BS, 12.5 L/min), CIP 10-M (10 L/min) and Frit-Bubbler (FB, 4 L/min). Fungi were cultured on MEA and bacteria on TSA, EMB and McConkey media (25°C for 5 days). First,

laboratory experiments were performed in a test bench where samplers were compared by pairs (60 min) using an experimental bioaerosol of *Escherichia coli*. Results confirmed that liquid-based samplers perform better than CFC in preserving culturability of airborne *E. coli* cells, e.g. CFC concentrations were 10 to 10 000 times lower than those measured with BS or FB, depending on the operating conditions. Side-by-side static comparisons (5 h) were also performed in occupational atmospheres. As expected for hydrophobic spores, culturable fungi concentrations by liquid-based samplers were systematically lower than those measured by CFC. However, culturable bacteria concentrations measured by liquid-based samplers in a waste sorting plant were also significantly lower than those measured by CFC ( $p < 0.05$  Poisson regression model). This bacterial concentrations behavior, which contrasts with laboratory results, is confirmed to a lesser extent in wastewater treatment plants. Key factors such as particle size distributions (aggregates vs. single cells), physical sampling efficiencies of the samplers tested and differences between experimental (*E. coli* model) and complex occupational bioaerosols (mixing of wild species and other particles) will be discussed to interpret these new results.

## Latest efforts in harmonizing the measurement of particle number concentration in ambient air

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Measuring the particle number concentration of airborne particles is a different approach compared to gravimetric air quality measurements of metrics such as PM<sub>2.5</sub> or PM<sub>10</sub>. Ultrafine particles (UFPs) in particular can be present in large numbers both indoors and outdoors due to local sources such as traffic, residential heating, and other processes, yet they contribute very little to the mass of airborne particles. While the measurement of particle number concentration has successfully been used to assess the effectiveness of low emission zones, data were only comparable when using the exact same measurement setup and equipment. Monitoring networks like NABEL (EMPA, 2000) and GUAN (Birmili, 2015) use condensation particle counters (CPCs) to supplement gravimetric air quality measurements with a time resolved measurement of particle number concentration. However, different CPCs can have different lower detection limits and can work with different fluids, which can make it difficult to compare data.

As a first step of harmonizing the continuous measurement of particle number concentration in ambient air, the European Committee for Standardization (CEN) drafted Technical Specification CEN/TS 16976, which describes a standardised method

by defining a set of requirements for the Condensation Particle Counter (CPC), its sampling system, the measurement procedure and the reporting of measurement results. Recently, a new CPC and a dedicated sampling system, both of which are fully compliant with CEN/TS 16976, have been introduced (model 3772-CEN, TSI Inc., Shoreview, USA). As required, this CPC is a full-flow, butanol-based device that counts airborne ultrafine particles from 7 nm in diameter at an aerosol flow rate of 1.0 L/min. It uses an optimized coincidence and dead time correction method to count particles in single count mode up to concentrations of 50,000 particles/cm<sup>3</sup>. Other advancements include a pulse height analyzer that monitors wick health, super-saturation state, and instrument status. With these improvements, the 3772-CEN CPC brings the same technology and accuracy to atmospheric monitoring that the EEPCs used in automotive type approval testing according to Euro 5b/6 legislations rely on.

We will introduce the CEN/TS 16976 and show performance data of the 3772-CEN CPC and its dedicated sampling system, as well as data from selected measurements.

### Exposure to hazardous substances in saunas during pouring of diluted sauna essences on hot stones

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The use of mixtures containing essential oils diluted in water poured on the hot stones has acquired importance in commercial saunas. The high temperatures of the sauna stoves give rise to pyrolytic and oxidative processes in the organic constituents of the mixtures. The substances produced in this process include various aldehydes and ketones. The release of formaldehyde is of particular importance for the assessment of chemical exposure in saunas, owing to the classification\* of formaldehyde as a carcinogen (K1B), its suspected mutagenic effect (M2) and its skin-sensitizing effect (H1).

The aldehyde and ketone emissions from selected essences were determined in laboratory studies at defined temperature stages between 200 °C and 500 °C. Exponentially rising concentrations of aldehydes and ketones were detected.

Workplace analyses of aldehydes and ketones in eight unoccupied sauna rooms yielded a spectrum of exposure to the sauna employees when the mixture was poured on the hot stones under normal operational and simulated, controlled conditions. Measurements were conducted with stationary equipment both in the breathing zone of the employee when pouring the mixture and simultaneously on the sauna bench. Surface temperatures

were measured by means of a contact thermometer and an infrared camera.

Formaldehyde was the only substance to be assessed. Other aldehydes and acetone were negligible with respect to their occupational exposure limits. It was shown that background exposure to formaldehyde already occurs in the hot sauna rooms and that additional exposure occurs when the mixture is poured on the hot stones. Formaldehyde concentrations complied with the occupational exposure limits\*\* if the doses declared by the manufacturers of the essences and the recommendations of the German Society for Bathing (DGfDB) were observed. Formaldehyde concentrations exceeding the permissible short term limit value may occur when stove designs allow the mixture to enter hot parts of the stove, the essences in the water are overdosed and the mixture is poured rapidly.

\*Regulation (EC) No 1272/2008 of the European Parliament and of the Council

\*\*time weighted average (0,37 mg/m<sup>3</sup>) and short term limit value (0,74 mg/m<sup>3</sup>) stated in the TRGS 900 technical rules (occupational exposure limits)

### Taking ambient air monitoring to the next level – Multiple applications with the Fidas® technology for fine and ultrafine particles measurements

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Air pollution due to particulate matter and the related negative effects (health problems, economic damages) has become one of the major problems our society is faced with today. In order to be able to investigate and to assess the real exposition of the general public in a comprehensive way, the performance of precise and accurate measurements of particulate matter is an essential part of air pollution control.

The Fidas® sensor applies the well-approved measurement technology of optical light scattering on single particles and is equipped with a polychromatic LED light source with long-term stable output. The scattered light intensity is detected under 90° through a patented aperture technology, thus preventing border-zone error and enabling for precise coincidence detection. The implemented approach allows for an easy field calibration as well as a permanent online-monitoring of the calibration status. Due to its modular design, the Fidas® sensor technique

has been adapted to specific devices to cover a large range of possible applications, which will be highlighted in this presentation. It includes regulatory monitoring of PM<sub>2.5</sub> and PM<sub>10</sub> in official networks by the type-approved and EN/MCERTS-certified Fidas® 200, indoor and workplace measurements with the portable Fidas® FROG or due to the lightweight sensor technology also installations on flight robots or drones for assessment of line and area sources are possible. Results from the latest approval campaigns will be discussed. Since the Fidas® sensor delivers also total number concentration and particle size distributions with a high time resolution, this can be valuable for e.g. source appointment, prognosis models or the detection of condensation and droplet formation. For the monitoring of ultrafine and engineered nanoparticles, the Fidas® is combined with an Universal-SMPS to measure from 8 nm to 40 µm to get a comprehensive picture of the air pollution. The overlapping region of the two systems can then be used for extended characterisation.

### Exposure to mite and mammalian allergens in homes of veterinary students

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Exposure to animal allergens is a major risk factor for allergic airway diseases. Apart from ubiquitous mites, the most important animal allergens are derived from mammals. The main sources of allergens are animal hair and dander. Based on their aerodynamic properties, mammalian allergens easily become airborne, attach to human clothing and hair, and are spread from one place to another. Particularly in the veterinary field, high exposure to various animal allergens and allergen transfer from work to home can be expected. However, concentrations of transferred allergens are mostly unknown. Therefore, we investigated the allergen levels in homes of veterinary students from the begin of their studies in a longitudinal design.

Dust sampling was performed using electrostatic dust fall collectors (EDCs). The EDCs were placed once a year (November to January) in the students' apartments for 14 days about 1.5 m above the floor in a horizontal position and collect airborne dust that has settled on electrostatic cloths. So far the measurements were carried out in three consecutive years (n=67 in 2013, n=62 in 2014, n=52 in 2015). Allergen levels were measured with enzyme immunoassays against allergens from domestic mites and against major allergens of cat (Fel d 1), dog (Can f 1), horse (Equ c 4) and cattle (Bos d 2).

In the first year, allergens from domestic mites were detected most frequently (96%, median: 199 ng/m<sup>2</sup>), followed by Fel d 1 (72%, median: 24 ng/m<sup>2</sup>), Can f 1 (70%, median: 37 ng/m<sup>2</sup>) and Equ c 4 (37%, median: <LOD). The bovine allergen Bos d 2 was only measurable in two samples (3%). In the following years, no considerable changes were found in mite, cat and dog allergen levels or detection frequencies. The detection rate and concentration of horse allergen increased in 2014 (90%, median: 40 ng/m<sup>2</sup>), but remained constant in 2015 (87%, median: 39 ng/m<sup>2</sup>). The most significant change was observed for Bos d 2. The percentage of positive samples increased from 3% in 2013 to 74% in 2014 and to 96% in 2015, and the median Bos d 2 concentration increased from 24 ng/m<sup>2</sup> (2014) to 66 ng/m<sup>2</sup> (2015).

The increase of horse and bovine allergens on EDCs indicates allergen transfer from the university campus to students' homes. Exposure measurements in the students' homes as well as at the campus will be carried out over the entire study period. Future research aims to investigate the relationship between airborne allergen exposure and veterinary students' health.

### Stationary and personal air monitoring of naphthalene in the abrasives production – shift and short time measurements

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Naphthalene is a solid chemical that easily sublimates at room temperature. In an open way, it is for example used in the production of abrasives due to its positive effects on the formation of pores. In 2011, the Occupational Exposure Limit (AGW) in Germany was lowered to 0.5 mg/m<sup>3</sup> (0.1 ppm), based on irritant effects in animal trials. In the majority of other EU countries including Austria the Occupational Exposure Limit is 50 mg/m<sup>3</sup> (10 ppm). Aims of the study are: 1) Application of a newly developed air monitoring method under the conditions of a field study, and 2) Providing a solid base of the exposure situation in the abrasives industry for assessment of possible dose-dependent irritative effects in this industry.

We examined 39 exposed and 22 non-exposed non-smoking male subjects from 5 abrasives producing plants in Germany and Austria, where naphthalene is used in open handling procedures. Ambient and personal air sampling were performed over the shift. We applied a device that simultaneously sampled both the particle and the volatile naphthalene fractions. In addition, we performed short-term measurements over about 15 minutes. The personal air measurements showed median (range, mg/m<sup>3</sup>) shift concentrations in the reference group of 0.13 (0.05-0.36), in the moderately exposed group (mainly bystanders) of 0.59

(0.20-1.22) and in the highly exposed group in the mixing/sifting and the molding/pressing areas of 6.30 (2.46-11.58).

The respective stationary values showed naphthalene concentrations in the same ranges with a strong correlation of R<sup>2</sup> = 0.841. No naphthalene was found on the particle filters.

The short-term measurements showed mainly naphthalene concentrations within the range of the shift averages. In some cases, they reflected the naphthalene content of the abrasive tool recipes. In situations such as sifting of pure naphthalene, values up over 100 mg/m<sup>3</sup> were measured.

The naphthalene exposure format in the investigated workplaces occurs solely via the gaseous phase. Subjects who handled naphthalene in open procedures exceeded the allowable German exposure limit in air significantly but were within the higher Austrian exposure limit. Short-term measurements reflected the ongoing workplace activities in a reliable way. Overall, the air monitoring method proved to be suitable in field measurement.

## Comprehensive real-time air monitoring using dual-polarity SIFT-MS

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<sup>2</sup> Department of Chemistry, University of Canterbury, New Zealand

This paper introduces a multi-purpose analytical technique for atmosphere research and routine atmospheric monitoring applications: Selected Ion Flow Tube Mass Spectrometry (SIFT-MS). SIFT-MS is a real-time analytical technique that rapidly analyses air to ultra-trace levels for volatile organic compounds (VOCs) and inorganic compounds (Prince et al., 2010).

SIFT-MS utilises three positively charged reagent ions ( $\text{H}_3\text{O}^+$ ,  $\text{NO}^+$  and  $\text{O}_2^+$ ) and five negatively charged reagent ions ( $\text{OH}^-$ ,  $\text{O}^-$ ,  $\text{O}_2^-$ ,  $\text{NO}_2^-$  and  $\text{NO}_3^-$ ) to provide very selective analysis via gas-phase chemical separation coupled with mass spectrometric detection. The reagent ions are created from a microwave discharge through moist or dry air and subsequently mass-selected using a quadrupole mass spectrometer. The mass-selected reagent ions are then injected into the flow tube, where they react with the air sample introduced directly and continuously through the sample inlet. Reagent and productions are separated using

a second mass spectrometer and detected with a particle multiplier. SIFT-MS provides a unique ability to conduct highly selective analysis in real-time, by applying multiple rapidly switchable reagent ions and mass spectrometric detection. The outcome is that gaseous pollutants in air are typically monitored at part-per-trillion levels within one second.

We will present data that demonstrate the ability of SIFT-MS to monitor a diverse range of VOCs and inorganic gases. Data will illustrate the flexibility of the technique, including its ability to be used in full scan mode to identify and quantify non-targeted species.

### References:

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## **Invited speakers**

## Prof. Andrea Hartwig

Andrea Hartwig is full Professor and Chair of Food Chemistry and Toxicology at the Karlsruhe Institute of Technology (KIT). In addition she is actively involved in chemical risk assessment. Since 2007, she is president of the „Senatskommission der Deutschen Forschungsgemeinschaft zur Prüfung gesundheitsschädlicher Arbeitsstoffe“ („MAK Commission“), member of the “Scientific Committee on Occupational Exposure Limits” (SCOEL) and serves as an expert for the European Food Safety Authority (EFSA).

Main research areas are the impact of carcinogenic metal compounds, metal-based nanoparticles, essential trace elements and bioactive food ingredients on the stability of the genome and oxidative stress.



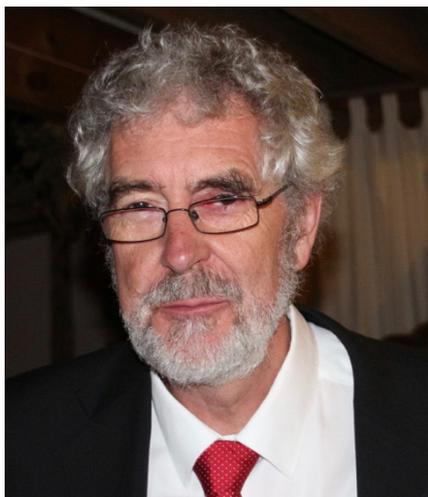
## Simon Aubin

Simon Aubin received his Bachelor degree in chemistry at Université Laval (Québec City) and completed his Master degree in analytical chemistry at McGill University (Montréal) in 2000. He is also an occupational hygienist recognized by the Canadian Registration Board of Occupational Hygienist and the American Board of Industrial Hygiene. At the beginning of his career, he worked on different air sampling and analysis projects involving the provincial public health division and the Canadian National Defence. In 2004, he joined the Institut de recherche en santé et en sécurité du travail (IRSST, Montréal, Québec) as the chemist in charge of organic and gravimetric analyses in the Laboratory Division. Simon has been involved in numerous research projects on isocyanates, flour dust, diesel particulates, asphalt fumes, etc. Simon has been a member of ASTM and ISO committees involved in sampling and analytical methods. Since the beginning of 2017, Simon is the convenor of an ISO working group on workplace air quality/organic vapours.



## John Cocker PhD

John Cocker is a Fellow at the UK Health & Safety Laboratory with over 43 years experience in biological monitoring and over 100 peer-reviewed publications. He is a member of the ACGIH Biological Exposure Indices Committee, a member of the European Scientific Committee on Occupational Exposure Limits and an occasional advisor to the World Health Organisation. He is an assistant editor for the Annals of Occupational Hygiene and a passionate advocate of biological monitoring.



## Martin Harper PhD

Dr. Harper recently retired from the National Institute for Occupational Safety and Health (NIOSH, USA) where he served for 14 years, to take a position as Scientific Research Manager with Zefon International. His first degree was in Geology from Oxford University and he has a Post-Graduate Diploma in Environmental Pollution Controls; a Master of Science in Earth Sciences and the Environment; and he obtained his PhD from the Department of Occupational Health, London School of Hygiene and Tropical Medicine. He has a Higher National Certificate in Advanced Analytical Chemistry and he is a Chartered Chemist (CChem) and Fellow of the Royal Society of Chemistry (FRSC), and he is Certified in the Chemical Practice of Industrial Hygiene (CIH) and a Fellow of the American Industrial Hygiene Association (FAIHA). He has over 130 peer-reviewed publications in exposure assessment and his interests include sampling and analysis of aerosols, such as wood dusts, metals, metalworking fluids, mineral fibers (asbestos), silica and nanoparticles; active and diffusive gas and vapor sampling; indoor air chemistry; quality assurance of measurements; and exposure assessment strategies and models.



## Prof. Caroline Herr

Caroline Herr is head of unit for Occupational and Environmental Health, Epidemiology at the Bavarian Health and Food Safety Authority, Munich. Furthermore she is president of the Gesellschaft für Hygiene, Umweltmedizin und Präventivmedizin (GHUP) (Society of Hygiene, Environmental and Public Health Sciences). She chairs Community committee bioaerosols and biological agents of the Commission on Air Pollution Prevention of VDI and DIN – Standards Committee (KRdL) as well as the CEN/TC 264/WG 28 “Measurement of bioaerosols in ambient air and emissions”. Besides further editorial activities, she is member of the advisory board of the Journal of Hygiene und Environmental Health, Elsevier.

Caroline graduated in the field of human medicine and holds a professorship “Environment-Related Health Protection and Prevention” at the Institute and Outpatient Clinic for Occupational, Social and Environmental Medicine, Clinical Centre of the Ludwig Maximilian University Munich, Germany. Her research activities are presently mainly focusing on environmental health protection (bioaerosols, noise and childrens health).



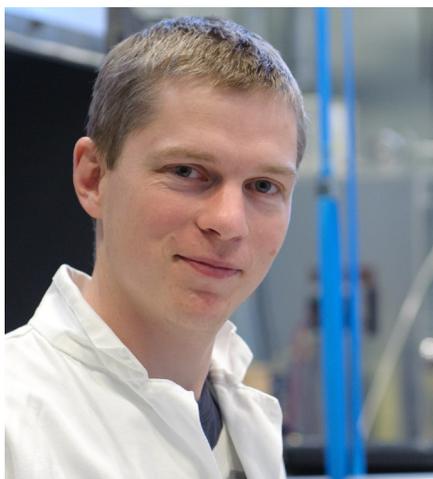
## Eun Gyung Lee PhD

Eun Gyung (Emily) Lee is an Environmental Health Scientist at the National Institute for Occupational Safety and Health in the US. She has worked on several research studies involving exposure measurements and modelling evaluation of airborne chemicals, development of sampling pumps corresponding to human breathing rates, and comparison of sampling strategies between different sampling and analytical methodologies. She has been Secretary of ISO Technical Committee 146 on Air Quality/Sub-Committee 2 on Workplace atmosphere since 2009 and is currently a case-column editor of Journal of Occupational and Environmental Hygiene.



## Prof. Jakob Löndahl

Jakob Löndahl is Associate Professor in aerosol technology at the Department of Design sciences at Lund University and CEO of JP Respiratory Technology. He has an MSc in engineering physics and in 2009 he received a PhD on experimental analyses of inhaled aerosols. In 2010-11 he carried out postdoctoral studies on biological aerosol particles at McGill University, Canada, and Aarhus University, Denmark. Since 2012 his research is mainly focused on health related aspects of aerosol particles, such as exposure to airborne contamination and medical applications of inhaled nanoparticles. Together with Prof. Per Wollmer he is inventor of the Airspace Dimension Test (ADT), which is a novel instrument for diagnosis of pulmonary emphysema.



## Prof. Volckens

Dr. John Volckens is a professor of Mechanical Engineering at Colorado State University. His research involves aerosols, air quality, and air pollution-related disease. He is a founding member of the CSU Partnership for Air Quality, Climate, and Health – an organization that seeks to develop practical, science-vetted solutions to the intertwined problems of air quality, climate, and health that we face as a society.

He earned his B.S. in Civil/Environmental Engineering from the University of Vermont (1996) and M.S./Ph.D. degrees from the University of North Carolina (1999, 2003). He then went on to a Postdoctoral position at the U.S. EPA's National Exposure Research Laboratory. In 2004, he joined Colorado State University, where he pioneered the development of several new sensor technologies – resulting in three patents. Dr. Volckens is the recipient of the 'Best Paper' award from the American Industrial Hygiene Association Journal (1999) and the Journal of Indoor Air (2013).





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