

Airmon

15-19 June 2014

Marseille, France



Dear colleague,

Welcome to the eighth International Symposium on Air Monitoring and Biomonitoring, AIRMON 2014.

Air quality in the workplace and general environment is an important contributor to human health. Numerous air pollutants and mixtures thereof must be monitored and controlled to prevent potential health effects both in workers and the population at large.

The AIRMON symposium was initiated and first organized by occupational and environmental health researchers in the northern European countries in 1993. For more than twenty years it has been a platform for presenting and discussing recent scientific progress in air sampling, exposure assessment, analysis and identification of exposure biomarkers.

This eighth edition of the AIRMON symposium is organized by a consortium of occupational and environmental health institutes in collaboration with a number of universities from Europe and Northern America, for the first time extending beyond northern Europe.

The AIRMON 2014 program provides a comprehensive scientific overview of the current worldwide state of art in air monitoring and biomonitoring through eleven plenary lectures, fifty eight oral presentations and over one hundred poster presentations.

The scientific training tradition of the symposium will continue with six Short Courses on selected topics. During the symposium relevant scientific equipment will be on display and presented by a number of exhibitors.

All presentations (including posters) will be considered for “full paper, peer reviewed publication” in ENVIRONMENTAL SCIENCE: PROCESSES & IMPACTS, which is published in electronic form by the Royal Society of Chemistry, UK.

Last, but not least, an amazing social program has been planned to explore Marseille and the beautiful Mediterranean coast. We hope that you will be captivated by the history and culture of this region of France in addition to the natural beauty of the area. We also hope that meetings with old and new friends will complement our scientific endeavors.

On behalf of the organizers it is our pleasure to welcome you to AIRMON 2014. We wish you an exciting and memorable conference and stay in Marseille.

Symposium co-chairs

Peter Görner and Yngvar Thomassen

Information for Contributors

The official language is English. No simultaneous translation will be provided. Digital projection with PowerPoint software will be available in every lecture room. Lecturers are requested to deliver the PowerPoint files to the responsible chairman well before the start of the session.

Posters will be displayed from Sunday to Thursday in the Symposium Centre. Authors are requested to be at their posters on Monday between 18:00 and 20:00.

All contributions will be considered for publication in a special issue of The Royal Society of Chemistry (RSC) journal "Environmental Science: Processes & Impacts", after the conference, subject to the normal review procedures of the journal. Authors are kindly requested to hand in their manuscripts at the Symposium, the final deadline being 31 August 2014.

Scientific Programme

Oral Presentations

Invited plenary lectures and submitted oral contributions will be 40 and 20 minutes in length, respectively (including discussion).

Video projectors will be provided in every lecture room.

Posters

Posters should be mounted in the early morning on Sunday 15 June in the poster area located next to the lecture room. Materials for poster mounting are available either from the Conference Desk or in the poster mounting area.

Language

The working language of the Symposium is English.

Liability

The Organising Committee declines any responsibility whatsoever for injuries or damages to persons or their property during the Symposium.

Exhibition

An instrument exhibition will take place in Symposium Centre. It will be open Sunday – Thursday. The participants are encouraged to visit the exhibition. The following companies have registered for display and demonstration:

AGILENT
BERTIN
ECOMESURE
MCV
SUNSET
TECORA
TSI
ZEFON

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Social Programme

Saturday, June 14, 18:00-20:00 : Informal Get-together at Mercure Centre Hotel.

All delegates and accompanying persons are invited.

Sunday, June 15, 16:00: Marseille sightseeing tour:

Guided Tour of Marseille and of its main monuments:

- Vieux Port
- Corniche
- Notre Dame de la Garde
- The MuCEM
- Villa Méditerranée and Cathédrale Major

Ending at the Vieux Port (Old Harbour)

Walk back to the hotel for dinner at 20:30

Wednesday 18 June, 16:20: Symposium evening

Visit to wine cellars and tasting of local wines, followed by an excursion by boat to admire the Calanques de Cassis (Port Pin, En Vau, Sugiton, Morgiou) and dinner at the Presqu'île Restaurant overlooking the sea opposite the impressive cliff of Cap Canaille.



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COMMITTEES

Conference Co-Chairs

Peter Görner	INRS	France
Yngvar Thomassen	STAMI	Norway

INRS Organising Committee

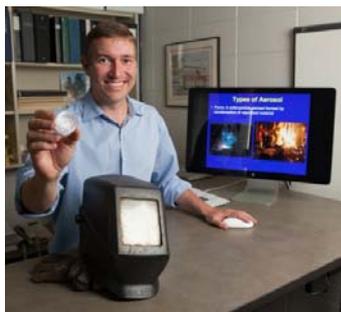
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Peter Görner
Dominique Mur
Lucile Poirot
Stéphane Vaxelaire

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Philippe Duquenne	Xavier Simon
Eddy Langlois	Alain Simonnard
Virginie Matéra	Olivier Witschger
Florence Pillière	

International Scientific and Programme Committee

Didier Baptiste	INRS	France
Dietmar Breuer	IFA	Germany
Oven Butler	HSL	United Kingdom
Peter Görner	INRS	France
Martin Harper	NIOSH	USA
Jan Olof Levin	Umea Univ.	Sweden
Marco Mecchia	INAIL	Italy
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Gerd Sallsten	Gothenburg Univ.	Sweden
Yngvar Thomassen	STAMI	Norway
Timo Tuomi	FIOH	Finland



John VOLCKENS - Associate Professor

**Department of Environmental and Radiological Health Sciences
Colorado State University, Fort Collins, CO, 80523, USA**

Dr. John Volckens is an Associate Professor and Associate Department Head of Environmental and Radiological Health Sciences at Colorado State University. His research interests involve human exposure to airborne particles, aerosol measurement, and air pollution-related disease. He received a PhD from the University of North Carolina at Chapel Hill in 2003 and then went on to Postdoc at the U.S. EPA's National Exposure Research Laboratory in Research Triangle Park, NC. Dr. Volckens is the recipient of the

AIHA Journal's 'Best Paper' award in 1999, has served two terms as Chair of AIHA's Aerosol Technology Committee, and is the former President of the Board of Directors for the Journal of Occupational and Environmental Hygiene. He has over 15 years of experience and has published over 40 manuscripts related to exposure science and air pollution.

Plenary lecture: 19th Century innovations for 21st century exposure science: how crayons, paper and pencils can revolutionize occupational/environmental health



Caroline DUCHAINE – Professor Université Laval

Centre de recherche de l'Institut Universitaire de cardiologie et de pneumologie de Québec, Université Laval, Quebec City, Canada

Since the beginning of her academic career in 2000, Prof. Duchaine has obtained, in addition to important equipment grants, over 50 operating grants and contracts from various sources (including FRSQ, IRSST, FQRNT, Canadian National defense, NSERC, EHSRC, INSPQ). She is the 2006 Young Investigator Awardee (international Agence Universitaire de la Francophonie). She was the expert of the Quebec Government for the management of mould-associated problems in homes after natural tragedies as well as expert-witness in several bioaerosol-associated court trials. She took part to international meetings aiming to set the basis for bioaerosol research (Iowa CAFO meeting, 2005; Skokloster Sweden organic dust meeting, 2003; Tromso Organic dust symposia 2010) and was invited by the NASA to the Workshop on life detection in extraterrestrial samples (2012). She co-authored a seminal chapter in the Manual of Environmental Microbiology (2007 and 2014) and is currently leading a strategic group on "Bioaerosols and Respiratory Viruses" within the Respiratory Health Network. Her main field of expertise is the characterization of bioaerosols, application and development of non-culture methods for bioaerosol characterization, as well as human exposure assessment. Her research involves the study of agricultural, domestic, industrial, and hospital environments. She is the author of over 300 manuscripts and abstracts.

Plenary lecture: Solving the puzzle of bioaerosol exposure: how conventional and modern meet.



Olivier WITSCHGER - Researcher

INRS - Institut National de Recherche et de Sécurité, 54519 Vandoeuvre lès Nancy, France - Laboratory of aerosol metrology

Olivier Witschger is an aerosol physicist at the Aerosol Metrology Laboratory at INRS and has over 20 years' experience in the measurement and characterization of airborne particles in the Workplace. Since 2004, Olivier is involved on the topic of risks associated with development of nanomaterials.

Olivier participates in different working groups at the French, European and international level dealing with aerosol metrology, characterization of occupational exposures and measurement strategy. In the framework of the European Commission Mandate M/461 to CEN, he is currently the project leader for the "Measurement of dustiness of bulk nanomaterials" prenormative research project.

Olivier and co-workers have published in various journals, in book chapters, and presented their research at scientific international conferences. He is a regular member of scientific committees for organizing international conferences on occupational health implications of nanomaterials. Recently, he was the chairman of the Nano2011 conference on the risks associated with nanoparticles and nanomaterials.

Plenary lecture: Occupational exposure to manufactured nanomaterials: available data, approaches and needs.



Kevin Ashley - Senior Research Chemist

US Department of Health and Human Services, Centers for Disease Control and Prevention,

NIOSH - National Institute for Occupational Safety and Health, 4676 Columbia Parkway, Mail Stop R-7, Cincinnati, Ohio 45226-1998, USA

Kevin Ashley was born in Hammond, Indiana in 1958 and grew up in Phoenix, Arizona. Ashley received his PhD in physical-analytical chemistry from the University of Utah in 1987 and then joined the chemistry faculty at San Jose State University in California. Since 1991 he has been a researcher with the National Institute for Occupational Safety and Health in Cincinnati, Ohio. Dr Ashley's work at NIOSH has focused on the development and evaluation of methods for elemental exposure monitoring in the workplace (e.g., lead, hexavalent chromium, beryllium and multi-element analysis). Author / co-author of over 100 scientific publications, Ashley and has also contributed to more than two dozen international voluntary consensus standards (ASTM and ISO). Some of the recognitions he has received include the ASTM Award of Merit, the ASTM Committee D22 Moyer D. Thomas Award, the NIOSH Alice Hamilton Award, Federal Award for Excellence in Technology Transfer, and the Japan Industrial Safety and Health Association Foreign Researcher Award. Dr Ashley chairs ASTM International Subcommittee D22.04 on Workplace Air Quality and was elected Chair of the Cincinnati section of the American Chemical Society (2014-2015).

Plenary lecture: NIOSH Manual of Analytical Methods; 5th Edition and Harmonization of Occupational Monitoring.



Martin Harper - Chief, Exposure Assessment Branch

NIOSH - National Institute for Occupational Safety and Health, 1095 Willowdale Rd. MS-3030, Morgantown WV26505, USA

Dr. Martin Harper has worked in NIOSH, Morgantown, WV, since 2002. Originally from the UK, his first degree was in geology from Oxford University, he has a Master of Science in Earth Sciences and the Environment, and he obtained his PhD from the London School of Hygiene and Tropical Medicine. He is a Chartered Chemist and Fellow of the Royal Society of Chemistry and he is certified in the Chemical Practice of Industrial Hygiene. Dr. Harper has published more than 100 peer-reviewed journal papers, book chapters, encyclopedia articles and standards. He has received several awards from the American Industrial Hygiene Association and the American Society for Testing and Materials. He served as Chair of the ISO Technical Committee 146, sub-Committee 2 (Workplace Air Quality) for six years, and for four years as an Editorial Board member for Journal of Environmental Monitoring, and he is currently Editor of the Analytical performance Issues column for Journal of Occupational and Environmental Hygiene. He has organized and chaired several international conferences on air sampling and analysis. His interests include sampling and analysis of aerosols, including wood dusts, metals, metalworking fluids, fibers (including asbestos), silica and nanoparticles; active and diffusive gas and vapor sampling; indoor air chemistry; quality assurance of measurements; and exposure assessment strategies and models.

Plenary lecture: Where occupational and environmental hygiene overlap.



Dietmar BREUER - Head of Unit Chemical Agents II

IFA - Institut für Arbeitsschutz der Deutschen Gesetzlichen Unfallversicherung. Institute for Occupational Safety and Health of the German Social Accident Insurance (IFA), 53757, Sankt Augustin, Germany

PhD in chemistry from University of Paderborn in Germany in 1988.

Since 1988 head of the section Analytical Chemistry II at IFA.

Research interests: Workplace air, indoor air, organic vapours, volatile organic compounds, sampling of vapour droplet mixtures, inorganic acids, hydroxides, complex organic analytes (e. g. metal working fluids, bitumen), gas chromatography, ion chromatography, infrared spectrometry, proficiency testing, preparation of test gas atmospheres.

Member of the working group “Analytical Methods” of the Senate Commission for the Investigation of Health Hazards of Chemical Compounds in the Work Area (MAK Commission).

Chairman of CEN Technical Committee 137 (CEN TC 137) “Assessment of workplace exposure to chemical and biological agents” and convener of Working Group 2 “General requirements for measuring procedures” of CEN TC 137

German delegate, ISO Subcommittee (TC 146/SC 2) on Workplace Air Quality, member of WG 2 “Inorganic particulate matter” and convenor of working group 9 “Sampling pump performance”.

Member of ASTM International Subcommittee D22.04 on Workplace Air Quality

Plenary lecture: Development and field testing of a miniaturized sampling system for simultaneous sampling of gazes and vapours.



Wolfgang Rosenberger IOM - Institute of Occupational Medicine, Hannover Medical School,

Carl-Neuberg-Straße 1, D-30625 Hannover, Germany

Birthday: 09 June 1965

Vocational Training:

1981 – 1985 Chemical engineering, Technical College, Werdohl, North Rhine-Westphalia

1996 – 1998 Health and Safety Officer, university of applied science, Berlin

Professional Career:

1986 – 1991 Analytical Laboratory of the German Federal Armed Forces, Hannover

Analysis of food, water, drugs and environmental samples

1991 – 2002 Institute for Indoor Hygiene, TÜV Nord, Hannover - Specialist for indoor air measurement,

2002 – 2010 Institute of Occupational Medicine, Hannover Medical School - Technical Assistant Chromatography, mass spectrometry, atomic absorption spectrometry, air monitoring

since 2004 Lecturer for measurement of hazardous substances, Hannover Medical School

since 2010 Laboratory head, Institute of Occupational Medicine, Hannover Medical School

Committee work:

since 2009

Member of the Working Group “Air Analyses”

Permanent Senate Commission for the Investigation of Health Hazards of Chemical Compounds

in the Work Area, Deutsche Forschungsgemeinschaft (DFG)

„Expert guest“, Indoor Air Hygiene Commission (IRK), German Federal Environmental Agency

Project work on aircraft indoor measurements since 2009

Plenary lecture: Air quality in aircraft cabins – in-flight measurements of organophosphates and other hazardous substances in different types of aero planes.



Yngvar Thomassen - Research Director

**STAMI - National Institute of Occupational Health
P.O. Box 8149 DEP, NO-0033 Oslo, Norway**

Yngvar Thomassen was born in Porsgrunn, Norway, on March 25, 1947. Thomassen's academic training (cand real) was obtained in the Department of Analytical Chemistry at the University of Oslo from where he graduated in 1973. He spent one year at the Norwegian Defense Institute before taking a post research associate position at the Department of Analytical Chemistry at the University of Oslo, where he conducted research for 2 1/2 years. In 1978 he visited The University of Toronto, Department of Environmental Studies and Geology, for one year with a Royal Norwegian grant (visiting scientist).

He is currently Research Director, Department of Chemical and Biological Work Environment, National Institute of Occupational Health in Oslo where he has spent 37 years of his professional life.

He is also appointed from 2004 as a professor in environmental chemistry, Department of Plant and Environmental Sciences, at the Norwegian University of Life Sciences outside Oslo.

Thomassen is the author or co-author of 160 scientific publications, the majority focusing on atomic spectrometry and other spectrometric methods for the determination of essential and toxic elements with special emphasis on electrothermal atomic absorption spectrometry. In recent years more focus has been given to other spectrometric methods as inductively coupled plasma atomic emission and mass spectrometry. His main scientific activity during the last ten years has been in the field of environmental and occupational exposure characterisation and assessment in human health studies. His research focuses on clinical aspects of analytical chemistry and the application of atomic spectroscopy within the context of environmental and occupational health.

Thomassen has served on the Editorial Boards of *The Analyst*, *Analytical Communication and Scandinavian Journal of Work, Environment and Health* and *Journal of Environmental Monitoring* and serves on the Board of *Journal of Trace Elements in Medicine and Biology*.

He has given over 275 presentations on various aspects of his research, of which 105 were invited lectures at major conferences and symposia. In the period 1983-91 he was a member of the Commission on Toxicology, International Union of Pure and Applied Chemistry (titular) member from 1986, where he initiated the development of human body fluids as quality assurance materials for the measurement of minor, trace and ultra-trace elements and organic metabolites. From 2011 he is elected as a titular member in the Analytical Chemistry Division.

Thomassen has organised a number of national, Nordic and international conferences on topics dealing with analytical chemistry, atomic spectroscopy and environmental and biological issues. His present research focuses on clinical aspects of analytical chemistry and the application of atomic spectroscopy within the context of environmental and occupational health.

Plenary lecture: Studies of the solubility and bioaccessibility of work-room aerosol.



George-Constantin DRAGAN - Junior Scientist

**Joint Mass Spectrometry Centre, Cooperation Group Comprehensive Molecular Analytics,
Helmholtz Zentrum München, Ingolstädter Landstr. 1, 85764 Neuherberg, Germany**

George-Constantin Dragan studied Chemical Engineering at the Technical University in Iasi, Romania. He is working since 2010 in aerosol sciences at the Helmholtz Zentrum in Munich, Germany where he is running a semi-volatile aerosol experimental facility. His main research interest is the study of dynamic particle-vapor mixtures on both experimental and theoretical modeling aspects. The investigation of sampling artefacts also plays an important role in his studies.

Plenary lecture: Semi volatile aerosols and evaluation of their impact on various workplace aerosol samplers in connection with air monitoring and human health.



Jaroslav Mráz - Head of the department

**Centre of Occupational Health, National Institute of Public Health,
Šrobárová 48, 100 42 Prague, Czech Republic**

Jaroslav Mráz, born 1960, studied analytical chemistry at the Faculty of Science, Charles University in Prague, Czech Republic. Following graduation in 1983 (RNDr. degree), his professional career was very simple. He joined the Department for assessment of occupational exposure to chemicals at the Centre of Occupational Health, National Institute of Public Health, Prague, where he had been working as a researcher and currently as a head of the department and head of the National reference laboratory for biological monitoring. In the meantime he finished external

PhD. studies in analytical chemistry at the Faculty of Science, Charles University in Prague (1993). In 1992 he obtained a fellowship in toxicology for a 1-year stay at Aston University, Birmingham, UK. Dr. Mráz's professional interests cover all aspects of biological monitoring of occupational exposure to chemicals, especially identification of new biomarkers, development of analytical procedures, and human volunteer studies. His current research projects focus on investigations of the blood protein adducts with xenobiotics and their use in biomonitoring. Partially he also involved in observing occupational health aspects of nanomaterials.

Plenary lecture: Biomacromolecules as in vivo dosimeters of cumulative exposures to chemicals.



Raymond VINCENT - Project Executive

**INRS - Institut National de Recherche et de Sécurité, 54519 Vandoeuvre lès Nancy, France
Direction for prevention applications**

Raymond VINCENT received an initial training in chemistry and has over 35 years of experience in the field of occupational chemical risks. After working in the oil industry, he joined INRS where he served as a research officer and responsible of laboratory within the Metrology department pollutants. His work has involved the development of methods of sampling and analysis, conducting national and international exposure surveys like SUMER, the French inventory of CMR chemicals, CAREX WOODRISK, Asbestos-META..., studies on sampling strategy, development and management of exposure databases and contributed to the development of national regulations ...'

He is currently project executive at the INRS direction for prevention applications and member of various national and international committees in charge of recommending limits and methodologies for assessing occupational exposure to chemical agents. He is currently a member of the French committee at ANSES for OELs and leads the TC 137 WG1 in charge of the revision of EN 689 on the sampling strategy.

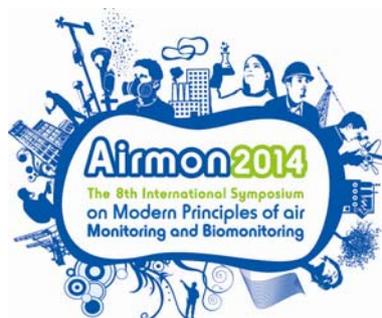
Plenary lecture: Measurement of occupational exposure to airborne chemical agents: which type of strategy.

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Programme

Saturday 14 June

16:00	Registration
18:00	Informal get-together

Sunday 15 June

08:00	Registration and welcome coffee
09:30	Opening session
09:30	Didier Baptiste, INRS Scientific Director
09:40	Yngvar Thomassen, Airmon 2014 Co-Chair
09:50	Dietmar Breuer, Airmon 2017 Chair
09:55	Harpal Minhas, Editor in Chief of Journal ESPI
10:05	Dominique Mur, Symposium Coordinator
10:10	Peter Görner, Airmon 2014 Co-Chair
10:20	Session 1 - Sampling and measurement of aerosols and bioaerosols Chair: John Volckens - Colorado State University, USA; Philippe Duquenne - INRS, France
	Plenary lecture: 19th century innovations for 21th century exposure science: how crayons, paper and pencils can revolutionize occupational/environmental health <i>John Volckens - Colorado State University, USA</i>
11:00	Coffee break
11:20	Highly time resolved aerosol sampling needs appropriate analytical methods – In-situ derivatization thermal desorption for analysis of non-polar and polar organic matter <i>J. Orasche, J. Schnelle-Kreis, G. Abbaszade, G.-C. Dragan, R. Zimmermann</i>
11:40	Comparing the UNC passive sampler to particle counters in the Swedish mining industry <i>M. Shirdel, B. M. Andersson, H. Wingfors, I. Liljelind</i>
12:00	Development of a sampler to measure the nasal deposition fraction of inhaled particles <i>D.K. Sleeth, S. Balthaser</i>
12:20	Realistic emission testing of consumer products risk assessment of a kitchen cleaning agent and an air freshener <i>A.W. Nørgaard, J.D. Kudal, V. Kofoed-Sørensen, I.K. Koponen, P. Wolkoff</i>
12:40	Lunch
13:40	Session 2 - Sampling and measurement of aerosols and bioaerosols Chair: Caroline Duchaine - Laval Hospital, Quebec; Anne Oppliger - IST, Switzerland
	Plenary lecture: Solving the puzzle of bioaerosol exposure: how conventional and modern meet <i>Caroline Duchaine - Laval Hospital, Quebec, Canada</i>
14:20	Evaluation of bioaerosol exposures during hospital bronchoscopy examinations <i>J. Lavoie, G. Marchand, Y. Cloutier, S. Hallé, S. Nadeau, C. Duchaine, G. Pichette</i>
14:40	Exposure to bacterial and fungal bioaerosols in the facilities processing biodegradable wastes <i>S.K. Laitinen, M. Kontro, M. Kirsi, P. Jokela, K. Reijula</i>
15:00	Determination of endotoxin and pyrogenic activity in occupational settings using electrostatic dustfall collectors <i>V. Liebers, H. Stubel, M. Düser, S. Freundt, T. Brüning, M. Raulf</i>
15:20	Comparison of methods for sampling indoor microbial aerosols and influence of activities in the home on the measured exposure level <i>C. Jürgensen, M. Frankel, D. Imail, N. Hamza, E.W. Hansen, A.M. Madsen</i>
15:40	Exhibition/poster session/coffee break
16:00	Marseille sightseeing tour
20:00	Dinner at hotel

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Monday 16 June

08:00	Registration
08:30	Session 3 - Nano-aerosol sampling and measurements <i>Chair: Olivier Witschger – INRS, France; Göran Lidén – University of Stockholm, Sweden</i>
	Plenary lecture: Occupational exposure to manufactured nanomaterials: available data, approaches and needs <i>Olivier Witschger – INRS, France</i>
09:10	Laboratory study of the performance of the miniature diffusion size classifier (DiSCmini) for analyzing different aerosols in the range 15-400 nm <i>S. Bau, B. Zimmermann, R. Payet, O. Witschger</i>
09:30	The effect of particle surface coating on emission potential from calcium carbonate nanopowders <i>C. Bekker, A.M. Rodrigues Pires Gomes, W. Fransman, L.T. Kuijpers, R.C.H. Vermeulen</i>
09:50	Laboratory and field evaluation of a personal sampler for engineered nanoparticle exposures <i>D. Leith, D.D. Miller-Lionberg, A. Marchese, H. Lentz, T. Lersch, G. Casuccio, J. Volckens</i>
10:10	Exhibition/poster session/coffee break
10:40	Session 4 – Semi volatile organic compounds sampling and analysis <i>Chair: Kevin Ashley - NIOSH, USA; Eddy Langlois, INRS, France</i>
	Plenary lecture: NIOSH Manual of Analytical Methods 5th Edition and Harmonization of Occupational Exposure Monitoring <i>Kevin Ashley - NIOSH, USA</i>
11:20	ECOS-PM: A nationwide survey of semi-volatile organic compounds in indoor air <i>C. Mandin, F. Mercier, J-P. Lucas, O. Ramalho, O. Blanchard, N. Bonvallot, P. Glorennec, B. Le Bot</i>
11:40	Neurotoxic semi volatile organic compounds (SVOCs) in house settled dust: contamination and determinants <i>B. Le Bot, C. Warembourg, F. Mercier, E. Gilles, G. Raffy, O. Blanchard, N. Bonvallot, C. Chevrier, P. Glorennec</i>
12:00	Semi-volatile organic compounds in the air and dust of 30 French schools <i>G. Raffy, F. Mercier, O. Blanchard, M. Derbez, C. Dassonville, N. Bonvallot, P. Glorennec, B. Le Bot</i>
12:20	Lunch
13:20	Session 5 - Air sampling and air monitoring <i>Chair: Martin Harper - NIOSH, USA; Marco Mecchia – INAIL, Italy</i>
	Plenary lecture: Where occupational and environmental hygiene overlap <i>Martin Harper - NIOSH, USA</i>
14:00	Application of respondent-based sampling approach in a national indoor air survey in Canada <i>J. Zhu</i>
14:20	Validation of control guidance sheets for filling of containers with organic solvents – Worker's exposure to solvent vapours during these activities and efficiency of protective measures <i>R. Hebisch</i>
14:40	Development of ASTM international standards for occupational exposure monitoring <i>K. Ashley, Ph.D.</i>
15:00	Detection and quantification of short-time chemical exposures in some military activities <i>D. Saurat, M.-F. Cordat, A.-C. Guillard, J.-U. Mullot</i>
15:20	Biological particles of the air and their health impact <i>M. Thibaudon, G. Oliver</i>
15:40	Exhibition/poster session/coffee break
16:00	Development of a miniature sensor network for studying the impact of ventilation on indoor air quality <i>L. Robert, B. Galland</i>
16:20	Filter capture efficiency testing for the biological glove box in the international space station <i>P.T.J. Scheepers, G. Beckmann, S. Van Hout, P. Leenders, E. Van der Kroon</i>
16:40	Supercritical CO₂ desorption for air sampling analysis <i>E. Langlois, S. Mélin, E. Pelletier, C.Ravera</i>

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17:00	Dispersal of bioaerosols emitted on composting facility assessed using molecular techniques <i>N. Wéry, A. Gales, V. Bru-Adan, K. Delabre, H. Bacheley, J.-P. Steyer, J.-J. Godon</i>
17:20	Laboratory determinations of the penetration curve of respirable cyclones and workplace comparisons between different models of respirable cyclones <i>G. Lidén.</i>
17:40	Sampling, measurement and analysis of VOCs: what are the best tools for the job? <i>C. S. Widdowson, R. Green, H. Calder, J. Williams.</i>
18:00	Poster discussion with regional refreshment tasting

Tuesday 17 June

08:00	Registration
	Session 6 - Air sampling and air monitoring <i>Chair: Dietmar Breuer - IFA, Germany; Owen Butler – HSL, United Kingdom</i>
08:30	Plenary lecture: Development and field testing of a miniaturized sampling system for simultaneous sampling of gases and vapours <i>Dietmar Breuer - IFA, Germany</i>
09:10	Real-time ambient air monitoring using selected ion flow tube-mass spectrometry (SIFT-MS) <i>V.S. Langford, J. Vercammen, M.J. McEwan, D.B. Milligan, B.J. Prince</i>
09:30	Indoor aerosolized bacterial population characterization by culture and pyrosequencing <i>A. Gérard, S. Gabet, J.P. Gangneux, P. Le Cann</i>
09:50	Aerosol fungi in dwellings: evaluation of an air ERMI and comparison with NGS sequencing <i>P. Le Cann, D. Méheust, T. Reponen, Stephen Vesper, J.P. Gangneux</i>
10:10	Exhibition/poster session/coffee break
	Session 7 - Air sampling and air monitoring <i>Chair: Wolfgang Rosenberger – HMS, Germany; Xavier Simon - INRS, France</i>
10:40	Plenary lecture: Air quality in aircraft cabins – in-flight measurements of organophosphates and other hazardous substances in different types of aero planes <i>Wolfgang Rosenberger - Hannover Medical School, Germany</i>
11:20	Advances in air quality monitoring in aircraft cabins <i>A. Bezold, S. Mair</i>
11:40	Environmental and cultural heritage: development of an analytical protocol for sampling and analysis of air pollutants by solid phase micro extraction <i>S. Dugheri, A. Monti, I. Pompilio, A. Bonari, N. Mucci, G. Arcangeli, V. Cupelli</i>
12:00	ECOS-PER: semi-volatile organic compounds in indoor air and settled dust in 30 French dwellings <i>O. Blanchard, P. Glorennec, F. Mercier, N. Bonvallot, C. Chevrier, O. Ramalho, C. Mandin, B. Le Bot</i>
12:20	Lunch
	Session 8 - Exposure assessment-strategies, peak exposures, multi-exposures <i>Chair: Yngvar Thomassen - STAMI, Norway; Gerd Sallsten – Univ. of Gothenburg, Sweden</i>
13:20	Plenary lecture: Studies of the solubility and bioaccessibility of work-room aerosol <i>Yngvar Thomassen - STAMI, Norway</i>
14:00	Cumulative indoor exposures to semi-volatile organic compounds (SVOCS) in France: progression of the ECOS project <i>P. Glorennec, C. Mandin, F. Mercier, O. Blanchard, K. Fournier, O. Ramalho, J.P. Lucas, N. Bonvallot, B. Le Bot</i>
14:20	Occupational exposure to particulate matter in two Portuguese waste sorting units <i>S. Viegas, C. Viegas</i>
14:40	Tiered exposure assessment approach for human risk assessment <i>A. Sánchez Jiménez, M. van Tongeren</i>
15:00	Exposure to ultrafine particles and carbon monoxide in norwegian manganese and silicon smelters <i>B. Berlinger, B. Ulvestad, Y. Thomassen, H. Kjuus, M.D. Bugge</i>
15:20	Formaldehyde exposures in 5 major industrial sectors in France and Germany from 2002 to 2011 <i>M. Steinhausen, F. Clerc, N. Bertrand, R. Vincent, R. Van Gelder, S. Gabriel</i>
15:40	Exhibition/poster session/coffee break

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16:00	Peak exposure measurements for task analysis and toxicity studies <i>P.T. Walsh, R.D.R Clark, S. Coldrick, A. Kelsey</i>
16:20	Indoor exposure to chemical and biological contaminants: results from the Asthm'Child study on risk factors for childhood upper and lower airways inflammation <i>A. Dallongeville, D. Zmirou-Navier, B. Le Bot, P. Le Cann, C. Chevrier, N. Costet, S. Deguen, I. Annesi-Maesano, O. Blanchard</i>
16:40	Exposure assessment of military personnel to smokes and dust <i>I. Tuinman, M. van Hulst, L. Bischoff, J. Langenberg</i>
17:00	Safe use of nitrous oxide in delivery suites <i>B.C. Bäck, H. Veijalainen, R. Holopainen, M. Sainio</i>
17:20	Microbial species and enzymes in aerosols from grass seeds causing organic dust toxic syndrome versus from reference grass seeds <i>A.M. Madsen, A. Zervas, K. Tendal, V. Schlünssen, I. Heltberg</i>
17:40	Relationships between air and urinary concentrations of beryllium in Cu-foundry, Al foundry and Al-smelter workers <i>D. Rousset, F. Pillière, J. Devoy</i>
18:00	Reference material developments at the UK Health and Safety Laboratory <i>O. Butler, G. Burdett, L. Davies, D. Lomas Fletcher, D. Musgrove, I. Pengelly, P. Stacey</i>
18:20	Exhibition/poster session/coffee break
	SC1 - Short courses in parallel
18:40	Molecular methods to characterize airborne microorganisms <i>Anne Oppliger-Goudet, IST (CH) - Philippe Duquenne, INRS (F)</i>
	Generating, filtering and sampling semi-volatile aerosols <i>Benjamin Sutter INRS (F)</i>
	NIOSH aerosol sampling methods <i>Martin Harper, NIOSH, (US)</i>
20:00	Dinner at hotel

Wednesday 18 June

08:00	Registration
08:30	Session 9 - Active and passive sampling of organic and inorganic substances – Chair: George-Constantin Dragan – HZM Germany; Bo Strandberg, Univ. of Gothenburg, Sweden
	Plenary lecture: Semi volatile aerosols and evaluation of their impact on various workplace aerosol samplers in connection with air monitoring and human health <i>George-Constantin Dragan – Helmholtz Zentrum München, Germany</i>
09:10	Comparison of French and German methods for bitumen fumes sampling and analysis <i>B. Sutter, E. Langlois, E. Pelletier, W. Esteve, D. Breuer, M. Blaskowitz</i>
09:30	Adsorbent media for workplace nitrous oxide sampling <i>M. Guillemot, B. Castel, A. Nouveau</i>
09:50	Radiello diffusive sampler® for measurement of VOC emission from landfill biogas : influence of meteorological conditions <i>M. Verrièle, N. Allam, L. Depelchin, L. Le Coq, N. Locoge</i>
10:10	Exhibition/poster session/coffee break
10:40	Session 10 - Biological monitoring - biomarkers of exposure Chair: Jaroslav Mraz - SZU, Czech Republic; Alain Robert – INRS, France
	Plenary lecture: Globin adducts as in vivo dosimeters of cumulative exposure to chemicals <i>Jaroslav Mraz - National Institute of Public Health, Czech Republic</i>
11:20	Dermal absorption of cyclic siloxanes (D4/D5): implications for human risk assessment <i>J.W.H. Biesterbos, G. Beckmann, R.B.M. Anzion, N. von Goetz, M.I. Bakker, C.J.E. Delmaar, N. Roeleveld, A.M.J. Ragas, F.G.M. Russel, P.T.J. Scheepers</i>
11:40	Variance components of short-term biomarkers of manganese exposure in an inception cohort of welder trainees <i>M.G. Baker, C.D Simpson, L. Sheppard, B. Stover, J. Morton, J.Cocker, N.S. Seixas</i>

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12:00	Photonic portable detection system to evaluate the oxidative potential of airborne nanoparticles and related oxidative stress in exhaled air <i>G. Suárez, M. Riediker</i>
12:20	Lunch
13:20	Aniline exposure, methemoglobinemia and hemoglobin adducts <i>H.U. Käfferlein, H.C. Broding, J. Bünger, S. Koslitz; E.M. Marek, C. Monsé, T. Weiß, T. Brüning</i>
13:40	Phtalate exposure in school children and their parents <i>G. Tranfo, R. C. Bonanni, E. Paci</i>
14:00	Product emissions into indoor air: important factors for interlaboratory studies with emission test chambers <i>W. Horn, M. Nohr, O. Wilke, M. Richter, O. Jann</i>
14:20	Identification of work-related exposure to carcinogenic substances in Germany <i>S. Gabriel, M. Steinhausen, R. Van Gelder</i>
14:40	Exhibition/poster session/coffee break
14:50	SC2 - Short courses in parallel
	Sampling and analytical method validation <i>Kevin Ashley, NIOSH, (US)</i>
	Solvent-free desorption and extraction <i>Eddy Langlois, INRS, (F)</i>
	Biomonitoring of organic compounds <i>Jaroslav Mraz, SZU, (CZ)</i>
16:10	Coffee break
16:20	Symposium evening

Thursday 19 June

08:00	Check out
09:30	Session 11 - Exposure modeling <i>Chair: Raymond Vincent – INRS, France; Peter Görner – INRS, France</i>
	Plenary lecture: Measurement of occupational exposure to airborne chemical agents: which type of strategy <i>Raymond Vincent – INRS, France</i>
10:10	Emission profiles characterization for hand-held wood working machines <i>F. Chata, A. Taniere, E. Belut, F-X.Keller</i>
10:30	Modeling of exposure of welders to welding fumes: comparison of predicted concentrations with field measured concentrations <i>F. Jongeneelen, P. Kanters</i>
10:50	Modeling patterns of occupational exposure to formaldehyde for chronic health risk assessment <i>R. Persoons, J. Cat, A. Maitre, D.J. Bicut</i>
11:10	Use of the MEGA database for the validation of determinants of exposure to welding fumes derived from the WELDOX study <i>R. Van Gelder, B. Kendzia, B. Pesch, T. Bruening</i>
11:30	Closing session
	Concluding remarks <i>Peter Görner, Airmon 2014 Co-Chair</i> <i>Yngvar Thomassen, Airmon 2014 Co-Chair</i> <i>Dietmar Breuer, Airmon 2017 Chair</i>
12:00	End of the Symposium

OPENING SESSION

- *Didier Baptiste –Scientific Director, INRS, France*
- *Yngvar Thomassen, STAMI, Norway*
- *Dietmar Breuer - IFA, Germany*
- *Harpal Minhas, Editor of the Scientific Journal ESPI :
"Environmental Science: Processess & Impacts"*
- *Dominique Mur , INRS, France*
- *Peter Görner , INRS, France*

Airmon

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ORAL PRESENTATIONS

Airmon

15-19 June 2014

Marseille, France

Session 1:

Sampling and measurement of aerosols and bioaerosols

Chair:

John Volckens - Colorado State University, USA

Philippe Duquenne - INRS, France

Plenary lecture

19th Century innovations for 21st century exposure science: how crayons, paper, and pencils can revolutionize occupational & environmental health

J. Volckens

Department of Environmental and Radiological Health Sciences,
Colorado State University, Fort Collins, CO, 80523, USA

This lecture will highlight recent research at Colorado State University to advance the science of exposure assessment, with an emphasis on new sensor technologies for measuring aerosols and air pollution. Many of these technologies are designed to overcome classic limitations associated with personal exposure measurement: time, cost, usability, and scalability. These limitations have hindered our ability to survey hazards, to conduct epidemiology, and to design effective interventions to protect human health. The ultimate goal of this work is to simplify the process of exposure assessment and to challenge a longstanding paradigm in our field: that scientific measurements must be made solely by the scientific community.

Acknowledgement: This work was supported by grants from the National Institute for Occupational Safety and Health (OH010050) and the National Institute of Environmental Health Sciences (ES019264).

Highly time resolved aerosol sampling needs appropriate analytical methods –In-situ derivatization thermal desorption for analysis of non-polar and polar organic matter

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¹Joint Mass Spectrometry Centre, Comprehensive Molecular Analytics, Helmholtz Zentrum München, Germany

²Joint Mass Spectrometry Centre, Chair of Analytical Chemistry, University of Rostock, Germany

³HICE – Helmholtz Virtual Institute of Complex Molecular Systems in Environmental Health – www.hice-vi.eu

In recent years a range of analytical methods and instruments have been established for chemical characterization of carbonaceous aerosols such as the Aerodyne Aerosol Mass Spectrometer (AMS). Although the AMS has no chromatographic separation, it is well introduced in aerosol research due to its competence on highly time resolved online measurement. To support online air monitoring by the meaning of detailed chemical characterization the In-situ Derivatization Thermal Desorption (IDTD) followed by Gas Chromatography and Time-Of-Flight Mass Spectrometry (GC-TOF-MS) was developed, which allows derivatization of organic compounds directly on the filter (Orasche et al. 2011, Fig. 1).

The advantages of IDTD are the possibility of ascertaining of highly polar organic compounds like water soluble organic compounds (WSOC) as well as non-polar ones like polycyclic aromatic hydrocarbons (PAH) in only one measurement. The highly sensitive method works with very low quantities of filter material which allows ambient air monitoring with time resolutions of one hour per sample or even less. Therefore the high time resolution is useful for source apportionment to investigate the emitter of harmful substances, for the study of secondary organic aerosols (SOA) including reactive oxygen species (ROS) as well as for indoor measurements.

For elucidation and validation of air pollutants, responsible sources must be well indicated by suitable source tracer compounds. In a winter sampling campaign in the city of Augsburg, Germany, high resolution PM₁ filter sampling was done. By hourly filter changing 24 samples were collected a day – more than 90 samples during a period of almost four days. Compounds from wood combustion in ambient air which are highly degradable in the atmosphere were investigated. It is therefore important to examine their atmospheric reaction products, too, such as methoxyphenols and their reaction products with NO₃-radicals. Similar to a described smog chamber experiment (Liu et al., 2012) a clear dependency of nitration products to NO₃-radicals during night time was observed for the first time in ambient air (Fig. 2). The concentrations of nitrated products reached their maxima one to two hours later than maxima of precursors were observed.

The recent results indicate that in the future a more sensitive observation of harmful airborne substances will be possible. Moreover the health effects of compounds can be carefully investigated.

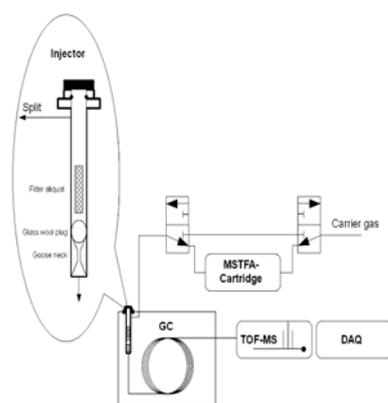


Figure 1 (left side). Scheme of the IDTD-GC-TOF-MS.

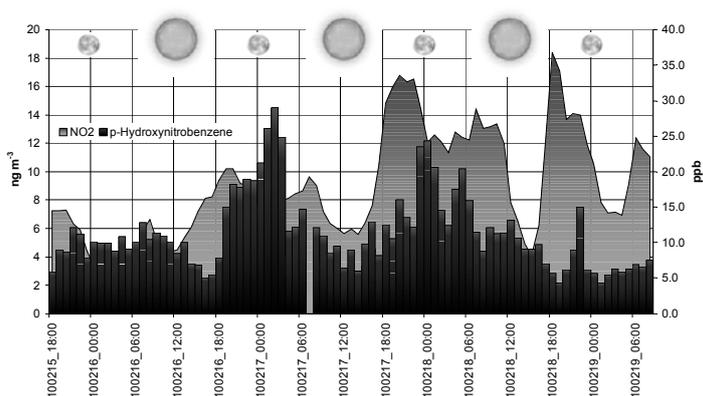


Figure 2 (right side). The relationship of p-Hydroxynitrobenzene and NO₂ during day- and night-time.

Acknowledgement: This work was supported by the Helmholtz Virtual Institute of Complex Molecular Systems in Environmental Health (HICE).

Liu et al., *Environmental Science & Technology*, 2012; Vol. 46, pp 13262-13269.

Orasche et al., *Atmospheric Chemistry and Physics* 2011, 11, 8977-8993.

Comparing the UNC passive sampler to particle counters in the Swedish mining industry

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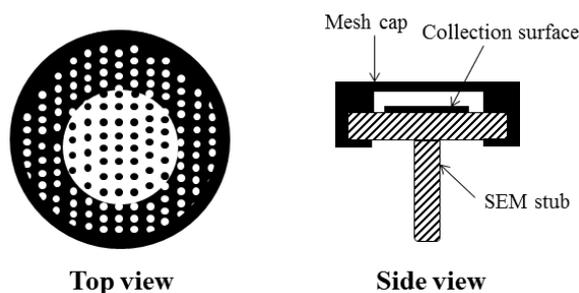
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Keywords: UNC passive sampler, particle, particle counters, Aitik mine

The Swedish mining industry is expanding, making it a good place to investigate the working environment, since the miners are exposed to chemical substances and particles (Ejdemo & Söderholm, 2011; Huertas *et al.*, 2012). To measure the particles in the Aitik mine (Northern Sweden) we used the UNC passive sampler (UPS), which collects particles by gravity and diffusion, as seen in Fig. 1. It has a mesh cap that protects the collection surface from large particles such as waste. The UPS has a diameter of 15 mm and weighs 1.7 grams resulting in a perfect candidate for particle sampling in the field (Wagner & Leith, 2001).

Figure 1. Top view of the UNC passive sampler, depicting the mesh cap. Side view of the sampler, depicting the mesh cap, collection surface, and Scanning Electron Microscopy (SEM) stub.



We used the UPS to investigate the airborne particles in the mining environment. We investigated four different microenvironments in the mine. The first microenvironment was the crushing station – crushes the ore. The second microenvironment was the drive station – drives the belt conveyor that transports the crushed ore. The third microenvironment was the concentrator – the ore is milled and the finished product is manufactured. The fourth microenvironment was the concentrate terminal – the copper concentrate is transported from here.

All of the microenvironments had stations where we placed 20 UPS at each station, but to be able to validate the results we also used four different particle counters: SidePak, P-trak, Climet, and Lighthouse; and a deployable particulate system. The deployable particulate system consisted of two samplers, one with a filter for PM₁₀ and one for PM_{2.5}. The filters and particle counters showed the highest particle mean concentration at the drive station with a PM₁₀, PM_{2.5} and respirable concentration of 6294 µg/m³, 437 µg/m³, and 305 µg/m³, respectively. The lowest particle mean concentration was at the concentrate terminal with a PM₁₀, PM_{2.5} and a respirable concentration of 79 µg/m³, 23 µg/m³, and 13 µg/m³, respectively.

The particle concentrations of four microenvironments in the Aitik mine were measured by six different particle samplers/counters and the results from five of the samplers/counters will be used as a comparison to the results analysed from the UPS. The results will give us valuable information about the precision and accuracy of the UPS as a stationary particle sampler. This is essential for a future reliable utilisation of the UPS as a personal particle sampler in the mining industry.

Acknowledgement: This work is supported by the Swedish Research Council for Health, Working life and Welfare under grant DNr 2012-0478.

Ejdemo, T., & Söderholm, P. (2011). *Resources Policy*, 36, 14-21.

Huertas, J.I., Huertas, M.E., & Solis, D.A. (2012). *The science of the total environment*, 423, 39-46.

Wagner, J., & Leith, D. (2001). *Aerosol Science and Technology*, 192, 186-192.

Development of a sampler to measure the nasal deposition fraction of inhaled particles

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Many commonly used aerosol samplers for occupational exposure assessment measure the fraction of particles that penetrate to given areas of the respiratory tract (i.e., inhalable, thoracic and respirable). It is well understood that some fraction of particles will be exhaled and not deposit in the body after inhalation. This has spurred interest in the development of aerosol samplers that instead measure the deposition fraction of inhaled particles. This should provide more biologically relevant exposure assessment data, which will be especially useful for epidemiological purposes.

A new sampler was developed to measure the fraction of inhaled particles that deposit specifically in the nasal region. It is based on the premise that the nasal deposition fraction proposed by Vincent (2005) is essentially identical to the complement of the respirable penetration curve (i.e., "inhalable minus respirable") adopted by the International Organization for Standardization (ISO, 1995). Therefore, it was hypothesized that a sampler that can simultaneously measure the inhalable fraction (i.e., the maximum available for deposition) and the respirable fraction could be utilized to also estimate the nasal deposition fraction.

In fact, IOM inhalable samplers are commercially available with polyurethane foam inserts that can accomplish this dual collection. In that sampler, the entire IOM cassette (with foam insert and filter) is weighed to provide the inhalable fraction and the filter is weighed on its own to provide the respirable fraction. Normally, the foam insert is discarded. However, for this study, separate gravimetric analysis of this foam insert was carried out to determine if it could be used to estimate the nasal deposition fraction. This involved repeated personal sampling tests on a rotating mannequin in a low speed wind tunnel ($U = 0.2$ m/s). Different sizes of narrowly graded powders of fused alumina were used as the test dust. Two isokinetic samplers were used during each test to measure the reference concentration.

Results showed good agreement with the nasal deposition curve proposed by Vincent (2005). Although foam is often considered difficult to use for gravimetric analysis, these foam inserts performed well, with good measurement precision within tests. It should also be noted that new ISO definitions for deposition sampling efficiency (ISO, 2012) are also available which separate the nasal (termed "extrathoracic") fraction into two separate regions (essentially, anterior and posterior). In order to meet these new criteria, modifications to the foam will be considered. However, considering the similarity in the shape of these various sampling efficiency curves, the results presented here provide a promising starting point for this future work.

Acknowledgement: This work was supported by the U.S. National Institute for Occupational Safety and Health (NIOSH) grant K01/OH010188.

International Organization for Standardization (ISO) (1995). *Air quality – Particle size fraction definitions for health-related sampling*, ISO Standard 7708, Geneva, Switzerland: ISO.

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Vincent J.H. (2005). *J. Environ. Monit.*, 7, 1037-1053.

Realistic emission testing of consumer products risk assessment of a kitchen cleaning agent and an air freshener

A.W. Nørgaard, J.D. Kudal, V. Kofoed-Sørensen, I.K. Koponen, and P. Wolkoff

National Research Centre for the Working Environment, Copenhagen Ø, Denmark

Indoor air pollution has been linked to increased reports of building related symptoms and illnesses since the 1970s and the advent of stricter energy efficiency measures. For instance, cleaning activities have been linked to adverse health effects in cleaning professionals, but also in residents by use indoors. However, it is unclear which of the compounds of cleaning products that may be associated with the reported respiratory effects.

Indoor use of consumer products that contain terpenes like limonene, and terpenoids like α -terpineol, react rapidly with the strong oxidizing ozone. These reactions, which occur in the gas-phase and on surfaces, produce a host of gaseous and particulate oxygenated compounds with potential adverse health effects in the eyes and upper and lower airways (Rohr, 2013). Some of the compounds have low vapor pressure leading to i.e. formation of secondary organic aerosols (SOA) as ultrafine particles.

Emissions of volatile organic compounds and ultrafine particles from a kitchen cleaning agent (cream) and plug-in air freshener were investigated in a 20 m³ walk-in climate chamber at low (0-5 ppb) and high ozone (~50 ppb) conditions, 0.6 air exchange rate, and 23 °C.

The products emitted terpenoids, inter alia limonene, α -terpineol, dihydromyrcenol, geraniol, linalool. Ozone-initiated reactions of these compounds were observed by air sampling on Tenax TA followed by thermal desorption GC-MS, air sampling on DNPH cartridges followed by liquid extraction and HPLC-UV analysis. Ultrafine and fine particle formation was monitored by FMPS and CPC.

A number of oxygenated and poly-oxygenated reaction products were identified at high ozone conditions and risk assessed: formaldehyde, acrolein, acetaldehyde, 4-acetyl-1-methylcyclohexene (4-AMCH), 6-methyl-5-heptene-2-one (6-MHO), 3-isopropenyl-6-oxo-heptanal (IPOH), and 4-oxo-pentanal (4-OPA).

These compounds generally increased initially at elevated ozone condition, while the terpenes decayed, and in part reflected in the ozone decay. The plug-in air freshener resulted in concentrations of formaldehyde, acrolein, and 4-OPA at the high ozone condition that gave rise to concern regarding sensory and respiratory effects; this is estimated to be even more pronounced by background adjustment.

The total particle concentrations peaked at 10⁵ – 10⁶ #/cm³ and the modal particles sizes developed progressively over time from ca. 6 nm to 100 nm, along with gradual increase of the mass concentration. The particles, in view of their chemistry and concentration, are not considered to cause concern of airway effects.

Emission testing under realistic conditions that mimics user pattern behavior is warranted to obtain acute and longer-term exposure data in context of ozone exposure, as opposed to testing in an artificial clean atmosphere; for risk assessment, additional source contributions should be considered.

Acknowledgement: This work was supported by the projects EPHECT (emission, exposure patterns, and health effects of consumer products in the EU), funded by European Union, Executive Agency for Health and Consumers under the sub-action: Healthy environments. 2010-2013 and “OFFICAIR” (on the reduction of health effects from combined exposure to indoor air pollutants in modern offices) funded by the European Union 7th Framework (Agreement 265267) under the Theme: ENV. 2010.1.2.2-1.

Rohr, A.C. (2013). The health significance of gas- and particle-phase terpene oxidation products: A review. *Environ Int* 60, 145-162.

Airmon

15-19 June 2014

Marseille, France

Session 2:

Sampling and measurement of aerosols and bioaerosols

Chair:

Caroline Duchaine - Laval Hospital, Quebec, Canada

Anne Oppliger - IST, Switzerland

Plenary lecture

Solving the puzzle of bioaerosol exposure: how conventional and modern meet

Caroline Duchaine

Professor Université Laval

Centre de recherche de l'Institut Universitaire de cardiologie et de pneumologie de Québec,
Université Laval, Quebec City, Canada

Despite their significant impact on respiratory health, bioaerosols remain understudied and misunderstood. Culture techniques, the main tools used for bioaerosol description in past years, allow for the recovery of only a small fraction of the real airborne microbial burden of bioaerosols. This is due mainly to inefficiencies of the culture methods. With the development of tools to detect and quantify non-culturable microorganisms, the study of bioaerosols has advanced significantly and these techniques have revealed a completely unexpected bioaerosol burden of non-culturable microorganisms, including archaea and viruses. However, scientists remain reluctant to use these techniques, given that there are relatively few studies in the literature and that the exposure-effects relationship is not easy to determine. This presentation will overview the knowledge regarding non-culture based bioaerosol content and will focus on the complementarity of using both culture and molecular approaches in bioaerosol exposure assessment studies.

Evaluation of bioaerosol exposures during hospital bronchoscopy examinations

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Keywords: Bronchoscopy, bioaerosols, UV-APS, fluorescent and non-fluorescent particles, modeling

During hospital bronchoscopy examinations, aerosols emitted from the patient's mouth or nose during coughing can be found suspended in the ambient air. The aerosols produced can contain pathogenic microorganisms such as mycobacteria, viruses and even moulds. These microorganisms can also be aerosolized during bronchoscope cleaning after the examination. Depending on the nature of these microorganisms, and the sizes and the masses of the bioaerosols that transport them, they can remain in the air for quite a long time and potentially cause infections in exposed workers. The main objective of this study was to measure the concentrations of the total and biological particles during bronchoscopy examinations, and to propose, if need be, preventive or corrective measures.

Two bronchoscopy rooms were studied. They met the recommendations of the American Society of Heating, Refrigerating and Air-Conditioning Engineers (ASHRAE) (2008). A TSI 3314 UV aerodynamic particle sizer (UV-APS) was used to establish in real time the concentrations and fine structures of the particles and bioaerosols present (before, during and after the bronchoscopy examinations). This instrument determines the aerodynamic diameter of the aerosols and can distinguish the original biological fraction. Reference concentrations were measured before the start of the examinations (control concentrations). They were used as comparison levels for the concentrations measured during and at the end of the bronchoscopies. The results obtained with the UV-APS were compared to other microorganism sampling methods, by impaction in a liquid using an AGI-30 impinger and a Coriolis sampler, and directly on agar using the Andersen impactor. These samples were analyzed with agar culture methods, and for samples in a liquid medium, by molecular biology methods. In parallel with the bioaerosol evaluations (concentration, identification, suspension time, as well as particle sizes), computational fluid dynamics (CFD) made it possible to isolate and understand different factors that can affect the contamination levels in bronchoscopy rooms.

The concentrations of the non-fluorescent and fluorescent particles (bioaerosols) were significantly higher ($p \leq 0.05$) than the reference concentrations (morning background noise) during the bronchoscopy examinations. For the studied factors, the bioaerosol concentrations were significantly higher during bronchoscope insertion tasks, followed by the bronchoscopy examination. Some of the opportunistic pathogenic aerosols classified in risk group 2 (e.g., *Streptococcus pneumoniae*) likely came from the patient and not the caregiving personnel. The bioaerosol concentrations during the cleaning operations performed in the reprocessing room were not higher than the reference concentrations. The time required at the end of the day for the bioaerosols to reach the morning reference concentrations was about fifteen minutes for both bronchoscopy rooms. Our models based on computational fluid dynamics (CFD) enabled us to observe the behaviour of bioaerosols for the different rooms. Under actual conditions, it is recommended that personnel wear disposable respiratory protection such as type N95 on a continuous basis during bronchoscopy examinations, in the framework of a respiratory protection program.

Acknowledgment: This work was supported by the IRSST under grant 099-8980.

ASHRAE (2008). Ventilation of Health Care Facilities. AINSI/ASHRAE/ASHE Standard 170-2008. Atlanta, Georgia.

Exposure to bacterial and fungal bioaerosols in the facilities processing biodegradable wastes

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Objectives

The aim of the study was to find bacterial and fungal risks for workers' health in the processes of the biodegradable waste treatment plants. Wastes contain high numbers of microorganisms, which can be harmful, like pathogenic, allergic, or toxic. Workers might expose to bioaerosols when microorganisms spread into air during handling of wastes.

Methodology

Occupational measurements were performed in seven composting plants, and in three biogas or bioethanol producing facilities. Bioaerosol samples were measured from workers' breathing zones and their nasal mucous membranes. Bacteria and fungi from the air were collected to MCE filters using Button samplers. Nasal samples from 30 workers were taken with nylon flocked swabs. The occurrence of DNA of *A. fumigatus*, *Bacillus cereus* group, *Campylobacter* spp., *Salmonella* spp., *Streptomyces* spp., and *Yersinia* spp. in air and nasal samples was determined by real-time PCR analysis. Bacterial airborne endotoxin was collected to glass fiber filters using IOM samplers and measured using a kinetic chromogenic LAL assay.

Results

Endotoxin concentrations were high in the air (up to 16 000 EU/m³), and they exceeded a health based recommended occupational exposure limit (OEL) of 90 EU/m³ in the most facilities processing biodegradable wastes. The high copy numbers of *A. fumigatus* (fungi) and *Streptomyces* spp (actinobacteria) DNA were measured from the air. The occurrence of DNA of these microorganisms in air correlated with the DNA findings of same microorganisms from nasal samples.

Especially, the DNA copy number of *A. fumigatus* in the nasal mucous membranes of workers was the greatest in those jobs and operations, where it was also in the air. Out of twenty humans examined in composting plants, 11 had fungus DNA after working day. Instead, one worker only had a positive nasal finding of *A. fumigatus* DNA in the biogas or bioethanol producing plants, where the fungus DNA was absent from air samples.

Streptomyces spp. DNA was found after the working day in almost all humans (19/20) who worked in composting facilities. Three of studied 10 persons had positive nasal findings of *Streptomyces* spp. DNA in the biogas or bioethanol producing plants. The difference in *Streptomyces* spp. DNA before and after the work shift was more difficult to detect than that of *A. fumigatus*.

Campylobacter spp. DNA was also common in the nasal mucous membranes of workers. Positive nasal samples were detected in 22 workers, although it could be detected only once from air samples. The sequencing of 16S rDNA of detected nasal *Campylobacter* DNAs indicated that strains were the same isolated earlier from skin. The conditions in composting facilities may enhance *Campylobacter* spp. growth in nasal mucous membranes.

Yersinia spp. DNA was found to be in the air of three composting plants and one biogas producing plant. Where there were large amounts of airborne *Yersinia* spp. DNA, one worker was found to have this bacterial DNA in his nose.

DNA of members of *B. cereus* group and *Salmonella* were detected from couple air samples, but not from nasal swab samples. This indicates that these two bacterial groups are not very easily growing in nasal mucous membranes and they are not common in the air.

Significance

The real-time PCR enabled to estimate the exposure to microbiological bioaerosols in various work environments. Taking a sample from the nasal mucous membranes of workers shows their actual inhalation of microorganisms. This helps to establish potential respiratory health risks and efficiencies of preventive measures and personal protection of workers.

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Determination of endotoxin and pyrogenic activity in occupational settings using electrostatic dustfall collectors

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Keywords: Bioaerosol, endotoxin, passive airborne dust sampling, pyrogenic activity

Exposure to airborne bioaerosol is an important risk factor for the development of respiratory diseases. Therefore information on the level of microbial components associated with dust particles is necessary to prevent adverse health effects. Collection of dust and characterization of the dust components associated with human health effects is a prerequisite to assess the health risk.

The aim of the study was to evaluate passive airborne dust sampling using electrostatic dustfall collectors (EDC) as suitable tool for dust collection and the subsequent determination of endotoxin and/or pyrogenic activity to characterize different exposure circumstances in occupational settings.

Dust sampling was performed with EDC which collected dust settling on the surface of a cloth (0.032 m² area) for 14 days. The cloths were rendered endotoxin-free before use by heating four hours at 200°C. EDC were placed in social rooms of composting plants (n = 31) and in domestic homes (n = 40). After shaking the EDC cloth for one hour in *Aqua iniectionabilia* without Tween 20 the extracts were frozen at – 80°C. After thawing endotoxin activity was determined with *Limulus amoebocyte lysate* (LAL)-assay (Charles River, Sulzfeld). Pyrogenic activity was measured by stimulation of cryo-preserved blood (Zwisler Laboratorium, Konstanz) in a whole blood assay and quantification of the interleukin (IL-)1 β -release as a marker of pyrogenic activity via specific ELISA. In addition, different alternative protocols of dust extraction were validated with 30 EDC loaded in occupational settings especially with the focus on the presence of Tween 20 and a second extraction step.

Endotoxin as well as pyrogenic activity could be determined on all collected EDC using the standard one-step extraction protocol in the absence of Tween 20 ($r_s = 0,85$; $p < 0.0001$). Significant differences were measured between social rooms of compost plants and domestic homes for endotoxin activity (median 1514 EU/m² versus median 620 EU/m²; $p < 0.0001$) and pyrogenic activity (786 ng_{IL-1 β} /m² versus 163 ng_{IL-1 β} /m²; $p < 0.0001$).

Validation of alternative extraction protocols for the quantification of endotoxin activity using 30 additional EDC showed that the first extraction step delivers more than 80% of the total endotoxin activity loaded on the EDC independent of the presence of Tween 20 in the extraction media. The presence of Tween 20 (0.05%) enhanced the disposal of the endotoxin activity around 3.8 fold (median; range 1.9 - 30.9 fold). Endotoxin activity quantified in the extracts obtained with and without Tween 20 was significantly correlated ($r_s = 0.92$; $p < 0.0001$).

In summary, EDC are valuable and easy to use equipment to collect settled dust passively over a time period of 14 days for characterization of bioaerosol exposure in areas with high as well as low microbial burden. Extraction of the EDC cloth for one hour is sufficient to recover approximately 80 % of the endotoxin activity load. Extraction procedure in the absence of Tween is suitable for the determination of both parameters endotoxin and pyrogenic activity, delivers reliable results and is therefore our favored extraction procedure.

Comparison of methods for sampling indoor microbial aerosols and influence of activities in the home on the measured exposure level

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Keywords: Bioaerosol sampling, personal versus stationary sampling, endotoxin, indoor air

Indoor microbial exposure has been related to allergy, inflammation and respiratory disorders (Doues *et al.* 2003). The lack of standardised sampling methods is problematic when investigating dose-response relationships between exposure and health effects. In this study, we have compared personal and stationary sampling of bioaerosols in indoor air. In addition, different sampling methods were compared regarding their assessment of microbial exposures, including fungi, bacteria and endotoxin, as well as the total inflammatory potential (TIP) of dust samples from Danish homes. Microbial species were identified using MALDI-TOF. The Gesamtstaubprobenahme (GSP) filter sampler, DGI-sampler (Gravimetric Impactor) and BioSampler were used for sampling of airborne dust, whereas the dust fall collector (DFC) and the electrostatic dust fall collector (EDC) were used for sampling of settling dust.

The GSP assessed significantly higher microbial levels than the BioSampler, yet measurements from both samplers correlated significantly. The DGI-sampler could only be used for short sampling periods as the survival of the microorganisms was reduced during a sampling period longer than 20 minutes. Higher levels of fungi, endotoxin, and TIP were found in the EDC compared with the DFC. The measurements from the EDC associated well with those from GSP. Settled dust from the EDC was most representative of airborne dust and may thus be considered as a surrogate for the assessment of indoor airborne microbial exposure (Frankel *et al.* 2012).

Personal and stationary measured exposure to fungi, bacteria and endotoxin using the GSP-sampler showed high variation but correlated significantly. Fungal and bacterial species in personal and stationary samples will be identified.

The DGI sampler sampled a high volume and could be used for activity specific sampling. Measurements before and during activities in homes revealed that work processes in homes, as e.g. bed making, caused a significantly higher exposure to endotoxin and bacteria. Other activities as work with vegetables in the kitchen could cause a significant increase in exposure to fungi.

Acknowledgement: This study was part of the Centre for Indoor Air and Health in Dwellings (CISBO) study, which was supported by the REALDANIA foundation.

Douwes J, Thorne P, Pearce N, Heederik D.(2003). *Ann. Occup. Hyg.* 47:187.

Frankel M, Timm M, Hansen EW, Madsen AM. (2012). *Indoor Air*; 22:405-414.

Airmon

15-19 June 2014

Marseille, France

Session 3:

Nano-aerosol sampling and measurements

Chair: Olivier Witschger - INRS, France

Göran Lidén – University of Stockholm, Sweden

Plenary lecture

Occupational exposure to manufactured nanomaterials: available data, approaches and needs

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Manufactured nanomaterials present new challenges to understanding, predicting, and managing potential risks to workers, consumers and the environment (Houdy *et al.*, 2011). In recent years, concerns about the risks associated with nanomaterials have led to a significant increase in toxicity studies (Stebounova *et al.*, 2012). The results of laboratory studies on various nanomaterials such as high aspect ratio nanoparticles (HARNs) have raised issues of concern. In addition, common materials, such as titanium dioxide, showed a greater biological activity when they were in nanostructured form. In that context, the prospective widespread usage of nanomaterials calls for an assessment of the possible release and exposure to workers in industrial and academic workplaces.

The aim of the plenary lecture is twofold: (i) to provide an overview of the occupational inhalation exposure in the workplaces where nanomaterials are manufactured and used and (ii) to identify the still existing shortcomings, according to our understanding, with the overall goal to propose strategies to overcome these shortcomings. The up-to-date overview relies mainly on an analysis of the 50 peer-reviewed publications that have been identified over the period 2004 – 2013, with more than half of them published in the last 4 years. The choice is deliberately focused on publications that describe studies based on real workplaces with potential exposure data on nanomaterials, not publications with potential exposure to incidental nanoparticles.

As an illustration, Figure 1 gives an overview of the distribution of the selected publications according to two factors: the main activity of the real workplaces visited and the type of nanomaterials (Brouwer *et al.*, 2013). Here, the main activity has been subdivided into: (i) production of nanomaterials, (ii) downstream use and (iii) research activity, with research activities that correspond to activities on bench-scale whether in industry or academia. As nanomaterials (NMs), they were divided into: (i) HARNs including carbon nanotubes, carbon fibres and other nanofibres, (ii) metal and metal oxides (M or MeO), e.g., titanium dioxide, zinc oxide, ferric oxide, etc., and (iii) miscellaneous NMs, e.g., carbon black, quantum dots, fumed silica etc.

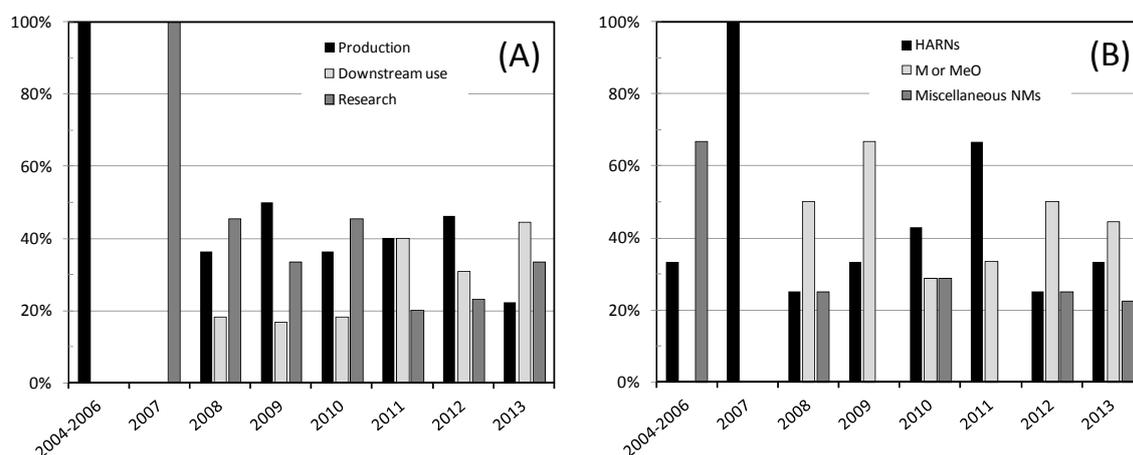


Figure 1. Overview of the distribution of publications according to the main activity of the visited workplaces (a) and the type of nanomaterials (b) for the period 2004-2013.

Many of the earlier studies have an explorative character, whether in terms of instruments used or approaches to measurement or analysis of the data, while the most recent studies provide more relevant information for the interpretation of the exposure.

Brouwer DH, van Duuren-Stuurman B., Berges M., Bard D., Jankowska E., Moehlmann C., Pelzer J., Mark D. (2013). *J. Nanopart Res*, 15, 2090-3004.

Houdy P, Lahmani M, Marano F (eds) (2011). *Nanoethics and Nanotoxicology*, Springer-Verlag Berlin Heidelberg, 620p.

Stebounova LV, Morgan H, Grassian VH, Brenner S (2012) *Wiley Interdisciplinary Reviews: Nanomedicine and Nanobiotechnology*, 4, 310-321.

Laboratory study of the performance of the miniature diffusion size classifier (DiSCmini) for analyzing different aerosols in the range 15-400 nm

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Due to the increasing use of nanomaterials in research and product development, the number of situations of occupational exposure to them is also likely to be rising. Recently published strategies indicate that, in addition to chemical composition, a variety of parameters is required for characterizing exposure to airborne nanomaterials. Among them, particle concentration and size play an important role since they provide information on both the quantity of nanoparticles inhaled and the region of the respiratory tract where they are deposited and may potentially interact.

Portable devices based on particle diffusion charging and sequential electrical measurement have been developed to provide airborne nanoparticle concentration and average size data with high time resolution (1 s). Of these, the DiSCmini (Matter Aerosol; Fierz *et al.*, 2011; Mills *et al.*, 2013) has been identified as a potential candidate for workplace exposure assessment. In the DiSCmini, particles are first positively charged by means of a diffusion charger; and are then collected either on diffusion grids or on the terminal filter depending on their diffusion equivalent diameter. Current measurements allow the real-time determination of particle mean size (20-200 nm) and number concentration (10^3 - 10^6 #/cm³).

Test nanoaerosols composed of different materials (C, Ag, CsCl, DEHS) were produced by means of different generators in the CAIMAN facility (Jacoby *et al.*, 2011). In a first step (monodisperse configuration), airborne particles of 15 nm to 400 nm equivalent mobility diameter were selected with a DMA (Differential Mobility Analyser, Grimm 'Vienna Type'). Number concentrations measured by the DiSCmini were compared to data from a CNC (Condensation Nucleus Counter, TSI model 3007); in parallel, average sizes from the DiSCmini were compared to DMA-selected sizes (Figure 1, left). No significant effect of particle composition or morphology can be noted.

The instruments were then challenged with polydisperse test aerosols of the same substances with count median diameters ranging from 15 nm to 300 nm and geometric standard deviations of between 1.38 and 2.70. Airborne particle number concentrations measured by SMPS ranged from $5 \cdot 10^3$ #/cm³ to 10^6 #/cm³. The lung-deposited surface area (LDSA) concentrations for the DiSCmini and NSAM (Nanoparticle Surface Area Monitor, TSI model 3550) were also compared. The DiSCmini results were found to be in agreement with those of the reference instruments.

Finally, instruments were exposed to a series of "real-life" (non-controlled) aerosols. Experimental data indicate a close agreement between the different devices (Figure 1, right).

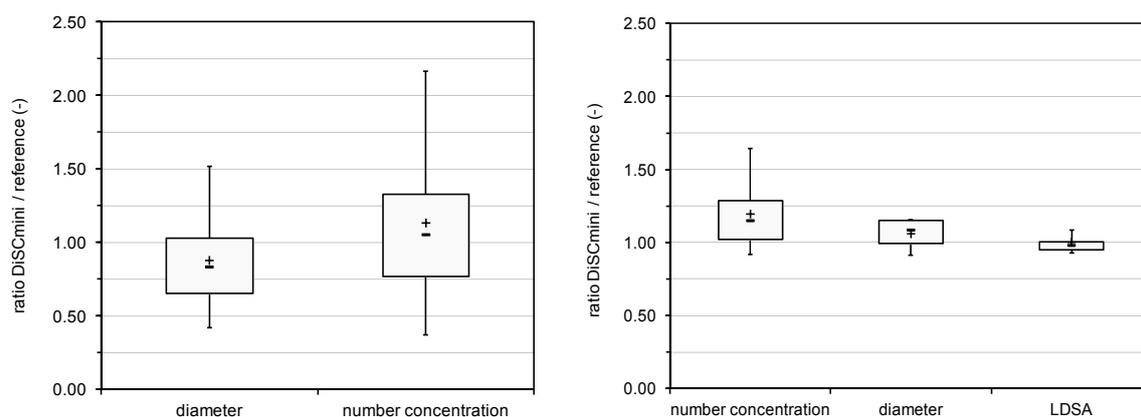


Figure 1. Comparison of DiSCmini diameter and number concentration with reference measurements for monodisperse aerosols (left) and polydisperse non-controlled aerosols (right).

The effect of particle surface coating on emission potential from calcium carbonate nanopowders

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INTRODUCTION: Increasing production and use of manufactured nanomaterials (MNM) driven by their novel properties is resulting in concern about human exposure and potential health effects. The dustiness is the propensity of a (nano) powder to become airborne and reflects the exposure potential for workers handling nanopowders. The dustiness of a MNM is influenced by the intrinsic physical-chemical properties of the powder including surface characteristics. MNM of which the particle surface is modified (coated) to enhance their use in a range of industrial applications are expected to have a higher dustiness index than their uncoated core material. As the methods used to estimate exposure to bulk materials are based on dustiness index of core materials, they may underestimate exposure for these functionalized MNM. The principal objective of this study was to assess whether particle surface coating affects the dustiness and therefore emission potential of a MNM. In addition, it was assessed whether this effect was influenced by differences in core material and whether the effect obtained by two European standard dustiness tests can be replicated in a simulated workplace situation.

MATERIAL AND METHOD: Calcium carbonate (CaCO₃) nanopowders were used to study the effect of particle surface coating on the potential emission from MNM. In order to assess whether differences in core material influences this effect, two coated powders obtained from two manufacturers were selected and compared to the uncoated powder from which they were made. These MNM were tested using two European standard dustiness tests, i.e. rotating drum and continuous drop. In addition, a workplace activity (dumping) was simulated in an experimental room with well-controlled environmental and ventilation conditions (19.5 m³). Concentrations were measured using several real-time size resolved particle counters in the size range 15 nm-20µm (SMPS, APS, ELPI). Online analysis was complemented with SEM/EDX analysis to characterize the morphology, composition and agglomeration state of the airborne particles.

RESULTS: Results from the two dustiness tests showed that the coated nanopowders were more likely to emit particles into the air than their equivalent uncoated powders, i.e. number concentrations were up to circa 40,000 times higher for the smaller particles <500 nm and up to 8 times higher for the coarser particles 0.5-20 µm. These results applied for powders from both producers. The size distributions showed modes for all powders between the 70 – 360 nm (SMPS) and 0.8 – 3.3 µm (APS). In general, the continuous drop tests showed lower modes than the rotating drum tests.

The results of the dustiness tests showed consequent higher particle number concentrations for uncoated powder of producer B compared to the uncoated powder of producer A ranging up to circa 2,000 times higher for the smaller particles and up to 8 times higher for the coarser particles. Overall, the uncoated powders of the two producers showed comparable modes.

Using the CaCO₃ nanopowders in a simulated dumping activity showed for producer B, comparable to the dustiness tests, that the coated nanopowders had a higher emission potential than the uncoated powder ranging up to 21 times higher. This result also applied for producer A for the particles in the coarser size range. However, against what was expected from the results of the dustiness tests, the uncoated nanopowder from producer A showed in the smaller size range higher total particle number concentrations (x9) than the coated powders.

CONCLUSION: The results from the dustiness tests and workplace simulation are not univocal. From the dustiness tests it can be concluded that emission of MNO can occur at comparatively higher levels during handling of coated CaCO₃ powders when compared to their equivalent uncoated powders. Workers might be exposed to higher levels influenced by the presence of surface coating but also influenced by difference between the production process of the core materials. However, the workplace simulations did not entirely corroborated the dustiness results. Future experiments should focus on the investigation of other MNM types and the effect of particle coating on the emission potential using dustiness tests as well as realistic workplace situations. Although the results were not univocal, it can be concluded that the European standard dustiness tests adapted for the use of nanopowders give useful information to estimate potential of exposure. This study can be seen as an exploratory study on the effect of particle surface coating as a determinant of emission potential.

Acknowledgement: This work is supported by NanoNextNL, a micro and nanotechnology consortium of the Government of the Netherlands and 130 partners.

**Laboratory and field evaluation of a personal sampler
for engineered nanoparticle exposures**

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Effective assessment of nanoparticle exposures requires accurate characterization of the aerosol. Of increasing concern is personal exposure to engineered nanoparticles that are specifically designed for use in the nanotechnology sector. This presentation will describe the design, operation, and performance of a personal sampler that utilizes thermophoretic force to collect nanoparticles onto a standard TEM (transmission electron microscope) grid. After collection, nanoparticles on the TEM grid are analyzed with an electron microscope, and the resultant data used to determine the characteristics of the nanoparticle aerosol sampled. Further analysis of the collected nanoparticles using energy dispersive spectroscopy allows discriminating engineered nanoparticles that may be of particular concern, from nanoparticles of natural or incidental sources. Thus, the TPS allows evaluation of the potential health risk due to exposure to specific, engineered nanoparticles independently of the potential risk posed by exposure to other aerosol particles that may be present at the same time.

Laboratory experiments were conducted to determine the inlet losses and collection efficiency of the thermophoretic sampler for particles between 20 and 600 nm in diameter. These results are used together with theory for thermophoretic velocity to form a transfer function that relates the properties of the collected particles to the properties of the sampled aerosol. The transfer function utilizes a normalization factor, $F(d)$, which is larger than unity for very small particles but approaches unity for particles larger than about 70 nm. We have also demonstrated TPS performance for sampling and discriminating engineered and non-engineered nanoparticles in the field.

Acknowledgement: This work was supported by grants from the National Institute for Occupational Safety and Health (R03OH009381), the Pennsylvania Nanomaterials Consortium, and the U.S. Environmental Protection Agency (EP-13-H-000188).

Airmon

15-19 June 2014

Marseille, France

Session 4:

Semi volatile organic compounds sampling and analysis

***Chair: Kevin Ashley- NIOSH, USA
Eddy Langlois, INRS, France***

Plenary lecture

NIOSH Manual of Analytical Methods 5th Edition and Harmonization of Occupational Exposure Monitoring

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Keywords: Air monitoring, Exposure assessment, Sampling and analysis, Voluntary consensus standards

The *NIOSH Manual of Analytical Methods* (NMAM: www.cdc.gov/niosh/nmam) is a collection of methods for sampling and analysis of contaminants in workplace air (or surfaces) and in the blood and urine of workers who are occupationally exposed. NIOSH methods are used worldwide for occupational exposure assessment to chemical and biological agents. These methods have been developed or adapted by NIOSH and/or its partners and have been evaluated according to established experimental protocols and performance criteria (Kennedy *et al.*, 1995). NMAM also includes associated chapters on quality assurance, sampling guidance, instrumentation, aerosol measurement, gas and vapor monitoring, portable monitoring devices, and so forth.

Often NIOSH methods are developed in coordination with voluntary consensus standards organizations such as ASTM International, the Comité Européen de Normalisation (CEN) and the International Organization for Standardization (ISO). Efforts to harmonize NIOSH methods with relevant consensus standards procedures are of particular interest and are highlighted (e.g., Ashley *et al.*, 2012; Oatts *et al.*, 2012). NIOSH also has a formal Memorandum of Understanding (MOU) with the Institute for Occupational Safety and Health of the German Social Accident Insurances (IFA), whereby NIOSH is adopting selected IFA methods and vice-versa.

An overview of recent research and technology transfer activities relating to NMAM methods will be provided, with selected examples in applications to exposure science, notably workplace air monitoring. Included in the discussion are newly approved methods and those under development, as well as needs for new methods and updates. Of particular interest are recent NIOSH recommendations (Ashley & Harper, 2013) and associated research (Harper & Ashley, 2013) on aerosol samplers used for sampling and analysis of airborne particles.

Ashley, K., Shulman, S. A., Brisson, M. J., & Howe, A. M. (2012), *J. Environ. Monit.* 14, 360-367.

Ashley, K., & Harper, M. (2013), *J. Occup. Environ. Hyg.* 10, D29-D33.

Harper, M., & Ashley, K. (2013), *J. Occup. Environ. Hyg.* 10, 297-306.

Kennedy, E. R., Fischbach, T. J., Song, R., Eller, P. M., & Shulman, S. A. (1995), *Guidelines for Air Sampling and Analytical Development and Evaluation*. Cincinnati: CDC/NIOSH; DHHS (NIOSH) Publ. No. 95-117.

Oatts, T. J., Hicks, C. E., Adams, A. R., Brisson, M. J., Youmans-McDonald, L. D., Hoover, M. D., & Ashley, K. (2012), *J. Environ. Monit.* 14, 391-401.

ECOS-PM: a nationwide survey of semi-volatile organic compounds in indoor air

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Semi-volatile organic compounds (SVOCs) are of concern due to their established or suspected health effects and due to the widespread exposure through different environmental media and pathways. The objective of this study is to assess the indoor SVOC concentrations on airborne particles (PM₁₀) collected at a nationwide scale. Sixty-six SVOCs, including phthalates, polybrominated diphenyl ethers (PBDEs), polychlorinated biphenyls (PCBs), polycyclic aromatic hydrocarbons (PAHs), pyrethroids, organochlorine and organophosphorous pesticides, alkylphenols, synthetic musks, tributylphosphate and triclosan, were selected after a health-based ranking and taking into account technical feasibility.

The samples (n = 300) were collected during a nationwide survey carried out by the French Observatory of indoor air quality (2003-2005) in a representative sample of the housing stock. The PM₁₀ were collected in the living-room on polytetrafluoroethylene (PTFE) filters during 7 days (sampled volume: 14 m³). The filters were stored at -18°C before analysis. SVOCs were analyzed by thermal desorption coupled with gas chromatography / tandem mass spectrometry (TD-GC/MS/MS).

Most of the PAHs, two phthalates (DiNP and DEHP), BDE-47 and BDE-99, and triclosan were quantified in more than 90% of the dwellings. Lindane, musks (galaxolide and tonalide), permethrin, bisphenol-A, and some PCBs were also commonly found. Pesticides such as atrazine, aldrin, endrin and chlordane were rarely detected. The use of sampling weights enables to extrapolate these results to the national housing stock.

This data, combined to other results from the ECOS-project, will be used to assess exposure to SVOCs in French homes and associated health effects. Relationships between concentrations, building characteristics and household activities will also be studied to identify SVOC determinants in indoor air.

Acknowledgement: This research was funded by the French Agency for Food, Environmental and Occupational Health and Safety (Anses, Grant n°EST-2011/1/128).

**Neurotoxic semi volatile organic compounds (SVOCs) in house settled dust:
contamination and determinants**

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People are exposed to multiple pollutants at home and especially children by dust ingestion due to hand to mouth contact. Among these contaminants, semi-volatile organic compounds (SVOCs) have been of growing interest over the past decade due to their possible health effects. Among SVOCs found in indoor dust, some of them are considered or suspected to be neurotoxicants: polybrominated diphenyl ethers (PBDEs), polychlorobiphenyls (PCBs), pyrethroids, organochlorine and organophosphorous pesticides. This study aims to measure numerous neurotoxic SVOCs in indoor dust of children's home and study their determinants including house characteristics (age of building, urban/rural location, renovation work, aeration, etc.) and people habits (type and frequency of floor cleaning, use of pesticides, etc.).

289 children's home from the PELAGIE mother-child cohort (France) were investigated (2009-2012) with collection of dust from domestic vacuum cleaners. Among them, 251 samples with a sufficient amount of dust were analysed after sieving to < 100 µm. Compounds were extracted from dust by pressurized liquid extraction with dichloromethane, followed by gas chromatography coupled to mass spectrometry. Statistical analyses were conducted for the 19 (out of 26) compounds detected in over 10% of the houses, using tobit or logistic multivariate models.

The major SVOCs in home dust were pyrethroids (permethrin and cypermethrin) and BDE209. Lindane, deltamethrin, tetramethrin, dieldrin, BDE85, BDE99, BDE100, PCB52, PCB101, PCB105, PCB118, PCB138, PCB153 and PCB180 were detected in 10-50% of dwellings. Before 1970's homes had statistically significantly higher concentrations of lindane, dieldrin and PCBs. Frequency of floor cleaning or window opening has been associated with reduced concentrations for lindane, dieldrin and some PCBs, especially for the oldest dwellings. Concentrations of pyrethroids increased with the reported household use of insecticides.

CONCLUSION: For the first time, relationships between concentrations, building characteristics and occupants' activities were studied in order to identify SVOCs' determinants. Some SVOCs' concentrations are related to building characteristics and occupants' activities including the frequency of floor cleaning for persistent pollutants.

Acknowledgement: This study was supported by the ANR 2009 (Projet ANR - PRSP 2009 - PEPSY)

Semi-volatile organic compounds in the air and dust of 30 French schools

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The development of new building materials, furnishings, and consumer products has resulted in a corresponding increase in new chemicals like Semi-Volatile Organic Compounds (SVOCs) in buildings (Weschler, 2009). People exposure to SVOCs in indoor environment and associated health risks are poorly investigated in France. Due to their physiology and their behaviour, children are considered as highly sensitive persons. In this context, the French Indoor Air Quality Observatory decided to include the measurements of SVOCs in its nationwide survey in schools. Prior to this campaign, a pilot study was carried out by EHESP/LERES to develop sampling and analytical methods to measure SVOCs in air and settled dust of schools. This study also provided the first data of SVOCs contamination levels in thirty schools in Rennes area (Brittany).

Fifty five compounds from seven families (pesticides, phosphoric esters, musks, polycyclic aromatic hydrocarbons (PAHs), polychlorobiphenyls (PCBs), phthalates and polybromodiphenylethers (PBDEs) were selected on the basis of their potential health effects (Bonvallet *et al.*, 2010) and analytical feasibility (Mercier *et al.*, 2010). Ninety classrooms were investigated in thirty voluntary pre-schools and primary schools between October 2009 and June 2010. Air samples were dynamically collected in glass cartridges fitted with quartz fiber filter and polyurethane foam (PUF). Settled dust was collected with a vacuum cleaner and with wipes to allow for the comparison between two sampling methods. Samples were analyzed by gas chromatography and tandem mass spectrometry (GC/MS/MS).

The measured SVOCs were classified into two groups. In air samples, PAHs (phenanthrene, fluorene), pesticides (lindane) and tributylphosphate were found in lower concentrations (1-10 ng/m³) than musks (galaxolide and tonalide) and phthalates (diisobutyl phthalate, dibutyl phthalate, diethyl phthalate) (10.800 ng/m³). For dust sample, PAHs (phenanthrene, pyrene, fluoranthene), musks (galaxolide and tonalide), pesticides (permethrin) and tributyl phosphate were found in lower concentrations (100-1000 ng/g; 3-20 µg/m²) than phthalates (di(2-ethylhexyl) phthalate, diisononyl phthalate, diisobutyl phthalate) (250-1400 µg/g; 20.1200 µg/m²). SVOC concentrations were higher in wiped dust than in vacuumed dust. However the mass of collected dust was more important with the vacuum cleaner, thus allowing the detection of more compounds.

Results showed that indoor air and dust in the investigated schools are contaminated by SVOCs in a large range of concentrations. Sampling and analytical methods developed in this pilot study are currently used in the national survey in order to provide representative data about SVOCs levels in the French building stock of schools.

Acknowledgement: This study was supported by the French Indoor Air Quality Observatory funded by the Ministries in charge of Housing, Environment and Health, the Environment and Energy Management Agency (ADEME) and the Scientific and Technical Building Centre (CSTB).

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Airmon

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Session 5:

Air sampling and air monitoring

Chair: Martin Harper - NIOSH, USA

Marco Mecchia – INAIL, Italy

Plenary lecture

Where occupational and environmental hygiene overlap

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Occupational hygiene was defined as a distinct discipline to deal with workplace health issues early in the 20th Century, whilst the equivalent response to environmental concerns arose rather later. Occupational hygiene is constrained by being considered an internal affair between workers and managers at specific locations. Environmental hygiene (or health) is more expansive, but for many practitioners the concerns are considered to end at the factory gates. Thus occupational exposures are not being included for people whose general health is being monitored for response to environmental pollutants and environmental contributions to ill-health are not being considered in traditional occupational hygiene. Recent interest in the concepts of the “exposome” and “total worker health” has spotlighted the drawbacks inherent in this division. It is easy to imagine exposures to substances such as diesel exhaust which may take place at home or on the way to work and continue at work. The latest concept of “Exposure Science” (Pleil et al., 2012) is important in allowing us to transcend boundaries. Closer collaboration between occupational and environmental Agencies will be necessary to resolve differences such as between particle penetration conventions. This was the subject of a mini-Symposium at the recent International Society for Exposure Science meeting in Seattle, WA. This talk is further illustrated by recent work involving exposures of Forest Service personnel at work to mineral fibers (asbestos and erionite) in their environment. Both NIOSH and the Environmental Protection Agency have an interest in evaluating risks from these exposures, which has led to a necessary comparison and harmonization of methods and techniques.

Disclaimer: The conclusions and opinions in this presentation are those of the Author and do not necessarily reflect the policy of the US Centers for Disease Control and Prevention.

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Application of respondent-based sampling approach in a national indoor air survey in Canada

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Inhalation is a major human exposure route to volatile organic compounds (VOCs). Both active and passive sampling techniques have been used to collect VOCs in air. Passive sampling often yields time-averaged exposure data as it collects VOCs over a period of several days or several weeks. In Canada, a national survey of indoor air VOCs was conducted between September 2009 and November 2011. 84 VOCs in about 4000 homes were measured in the survey.

The survey was population based with results representing 96% of the population in Canada. Geographic units (clusters) across the country were first created for constructing and selecting collection sites. 18 clusters were selected for the survey. In each selected cluster, a list frame of the dwellings was established for data collection. Different types of dwellings and dwellings in both urban and rural areas were covered in the survey.

A commercially available thermal desorption tube was used for the passive sampling of VOCs in indoor air for the survey. The tube was subsequently analysed using thermal desorption GC/MS. Because samples were collected across the country, it is financially prohibitive to send lab technicians to homes to collect air samples. Therefore, we adopted a respondent-based approach for the sample collection. In this approach, we explained and demonstrated the handling of the tube during respondent's visit to the mobile health examination centre that was set up for each collection site, and provided them afterwards a detailed instruction on how to use the tube at home.

Respondents were responsible to deploy the tube at home for a consecutive 7 days, terminate the tube exposure, seal the tube, and mail the tube to the testing laboratory in a pre-paid mailing envelop. Respondents were also asked to record the starting and ending time of tube exposure. At least two phone calls, one to remind them to deploy the tube and the other to terminate the tube, were made to ensure the proper execution of tube exposure at home.

This approach has been successfully used in the survey. Of the 4686 tubs given to the respondents, indoor air data from 3857 households (82.3%) were considered valid and included in the survey database. While the majority of tubes were handled and returned to the testing laboratory according to the protocol, some deviations from the protocol were observed that include missing exposure times when tubes were returned to the testing laboratory, mismatched tube identification on the tube and on the mailing envelop, too short (less than required minimal exposure time of 4 days) or too long exposure time (more than 10 days) of the tube at homes, tubes were exposed to air at the wrong tube end, and loss of tubes (tubes were not returned to the testing laboratory).

Lessons learned from this survey in using respondent-based sample collection can be used for other large survey of similar nature. In fact, the same approach is being used in the current Canadian national indoor air survey, which is from January 2012 to December 2015.

Acknowledgement: This work was supported by the Canadian Government's Chemicals Management Plan. Authors also thank Scott MacLean and Shirley Bryan and their staff at Statistics Canada for the field operation. Indoor air samples were analysed at CASSEN Testing Laboratories in Toronto, Canada.

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**Validation of control guidance sheets for filling of containers with organic solvents
Worker's exposure to solvent vapours during these activities and efficiency
of protective measures**

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Control banding is more and more used in occupational exposure assessment. The Easy-to-use workplace control scheme for hazardous substances (EMKG) is the BAuA tool for chemical control banding. The corresponding Control Guidance Sheets (CGS) describe the required safety measures for different tasks.

Filling and emptying of containers is one of the most frequent processes involving hazardous substances in workday life over a widespread range of enterprises. Therefore, we started our validation program in enterprises filling organic solvents into different containers such as tanks, IBCs, kegs and drums. For each of the tasks an exposure band is predicted under given protective measures which results, when different volumes of organic solvents with given physical and toxicological properties are filled into containers. The corresponding decision parameters are volatility and R-phrases/hazards, respectively.

The validation investigations have been performed in ten enterprises trading organic solvents. For this purpose a measurement strategy has been developed which includes stationary measurements direct at the exhaust ventilation and near the emission source in the working range. Furthermore, personal air sampling was performed at the worker filling the containers.

It was found that only a few enterprises fulfil the requirements postulated by CGSs. Therefore, we used the predicted exposure band to check if other technical solutions for filling of containers result in the same exposure band. The investigations have been focused on filling of 200 L drums. Sampling has been performed using thermal desorption tubes connected with personal air pumps. The collected samples were analysed in the laboratory using thermal desorption coupled with gas chromatography. Additional, the PIMEX system (PIcture Mixed EXposure) coupled with a direct reading photoionization detector has been used for visualisation of task related exposure and the efficiency of technical measures.

Especially, for filling of drums the measurements show that different technical solutions exhibit the same level of protection. As a consequence for this task some parallel CGSs may be derived. This leads to increasing acceptance of the CGSs in the enterprises.

The developed measurement strategy has been proven to be applicable for validation of Control Guidance Sheets. Therefore, this measurement strategy will be used for further validations of other tasks and their corresponding CGSs.

Development of ASTM international standards for occupational exposure monitoring

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Key words: Air monitoring, Exposure assessment, Sampling and analysis, Voluntary consensus standards

The health of workers in many industries is at risk through occupational exposure to toxic substances. In order to estimate workers' exposures, occupational contact with airborne hazardous materials at the job site is typically monitored by sampling and analyzing workplace atmospheres. This monitoring takes place because, in occupational settings, inhalation is ordinarily the most likely route of entry of hazardous substances into the body. Dermal contact and ingestion are other potential routes of occupational exposure to chemical agents. Hence in addition to methods for workplace air monitoring, procedures for measuring surface contaminants in the workplace are also desirable.

Within ASTM International Committee D22 on Air Quality (Ashley, 2004), Subcommittee D22.04 on Workplace Air Quality produces standards that describe methods of collecting and measuring chemical hazards in the workplace (Ashley & Harper, 2005). This subcommittee has been active for decades, and its members (presently numbering more than 90) have developed many needed standards consisting of test methods, practices, specifications and guides. These consensus standards are meant for use by industrial hygienists, chemists, engineers, health physicists, toxicologists, epidemiologists, and myriad other professionals. To date, Subcommittee D22.04 has promulgated more than 45 standards.

Consensus standards are considered by many to be the most technically sound and most credible documents for use in their particular fields of application. This was recognized in the U.S. through passage of the National Technology Transfer and Advancement Act of 1995, which directs federal agencies to (a) rely upon consensus standards in their guidelines and activities, and (b) participate in the consensus standards development process. Voluntary consensus standards are often used as a basis for commercial and regulatory action. For instance, in the United States, many ASTM standards having to do with the workplace and the environment have been cited in regulations promulgated by the U.S. Environmental Protection Agency and the Occupational Safety and Health Administration.

The manner in which ASTM International standards are developed differs markedly from that of the International Organization for Standardization (ISO). ASTM membership is open to any and all interested participants, while ISO membership is limited to representatives from member countries only. In ASTM, each individual member has one vote, while in ISO each member country has one vote. This presentation will discuss the development of ASTM standards, with emphasis on occupational exposure monitoring.

Key words: Air monitoring, Exposure assessment, Sampling and analysis, Voluntary consensus standards

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Detection and quantification of short-time chemical exposures in some military activities

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In real-life occupational environments military personnel, like other workers, could be exposed to chemical substances for times regarded as *short* in occupational hygiene, typically less than 5 minutes. An example of these conditions for military personnel is the exposure to smokes after firing rockets. Even if these exposures are not frequent they justify a careful risk assessment because gaseous and particulate substances could be present at high concentrations.

Unfortunately methods in occupational hygiene are often validated for sampling times in the range 15 minutes to 8 hours and could not be employed for shorter times without additional validation. Because our laboratory is implicated in the human risk assessment of military personnel in such conditions, we develop a specific program dedicated to the validation of sampling/measuring methods for short time chemical exposures. Another aspect of this work not detailed in this paper deals with the fixation of specific guidelines as companions of the measurements to allow the final conclusions about the related chemical exposures.

We will detail an example of the two options retained to deal with the evaluation of these short-time chemical exposures: direct reading methods (with rapidly equilibrating sensors) and traditional sampling methods validated – in laboratory conditions – for shorter times.

The capabilities of direct reading methods will be demonstrated with the response times obtained by a carbon monoxide (CO) electrochemical sensor exposed to a controlled gas, allowing the assessment of exposures as short as 1 or 2 minutes.

The capabilities of sampling methods will be demonstrated with the validation results obtained for hydrogen chloride (HCl) sampled on carbonate impregnated filters (adapted from INRS Metropol method) allowing the assessment of exposures as short as 1 minute.

Finally, examples of measurement results made in real-life (training) conditions will be presented and discussed.

Biological particules of the air and their health impact

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If plants are part of the natural landscape, some of them may have an adverse effect on health. While a large number of plant species use insects for pollination, a small number of them use wind to transfer pollen grains from the male flower to female flower. These pollens can have high allergy potency (which is specific to a taxa and its content of allergens) and be in very large quantities in the air. The allergy risk is the health impact due to the exposure of these types of pollen.

Allergenic pollens cause to 20% of the population troubles known as "hay fever" or "pollinosis". The symptoms observed are particularly seasonal: conjunctivitis, rhinitis, asthma but also eczema, tiredness... The symptoms cause significant disability and a sharp decline of intellectual or physical work.

To measure the exposure in France, a pollen trap network, located so as to cover a wide back-ground (urban areas, on the roof of buildings), representative of the air that people breathe, has been established by the RNSA (French Network of Aerobiology). The trap number is close to eighty, and these traps are distributed throughout the French territory. The traps, Hirst type, are inhaling weathervanes allowing the continuous impaction of pollen grains. The pollen grains are fixed on a coated transparent strip. Then, this sample is prepared on a slide with a stain. The readings and analysis are carried out by optical microscopy to record data with a bi-hourly time step. The reading and counting are controlled by computer programs.

To measure the health impact, the RNSA uses a network of sentinel clinicians who provide weekly information about the type of hay fever symptoms and their intensity during consultations. They send clinical information thanks to the clinical report available via internet. With this information, it is possible to determine a clinical index to evaluate the intensity of symptoms, representing the health impact of exposure to pollen (Thibaudon *et al*, 2008). The clinical index is calculated from gravity of symptoms (null, weak, mean or strong).

By using the clinical index, it is possible to make curves involving pollen index (exposure) and clinical index (health impact) for a city, a region or even the whole country and compare them over the years.

With a history of several years of data, the clinical index also allowed to establish a relation Health impact / exposure with a trigger point and a saturation rate, and this for the main allergenic taxa (ditto with the score-symptom data).

For the patient symptoms, R.N.S.A use the French version of Pollen Hayfever Diary website where the patients fill in a form to indicate the symptoms they feel and, from this information, a score-symptom is calculated, following the same kind of calculation as for the clinical index. Score-symptom has been recorded from the 8500 French patients registered till now.

By adding clinical and phenological information, pollen data and weather forecasts, weekly forecast about health impact of pollens (allergy risk) is broadcast to different partners, clinicians, patients and health authorities using several transmission media such as internet, mobile and mailing to warn allergy sufferers.

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Development of a miniature sensor network for studying the impact of ventilation on indoor air quality

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Indoor air quality is an issue of concern for, not only public health but also in the field of occupational health. Today, increasing numbers of workers are employed in the tertiary sector, and a large proportion of these work in offices. Along with the reduction of pollutant sources in indoor environments, ventilation is therefore a priority for limiting the chronic risk for this population of workers. Here, we present a network of sensors that has been developed to allow assessment of the impact of ventilation on indoor air quality (IAQ).

Preliminary tests, using formaldehyde as an indicator of pollution, have revealed that ventilation parameters, such as the rate of air exchange or the type and position of diffusers, have a significant impact on the spatial and temporal distribution of pollutants. Unfortunately, the reference systems that are used to estimate VOC or formaldehyde (DNPH cartridges and HPLC analysis) are associated with a long response time, preventing from linking aerologic perturbations to the concentration variation of contaminants.

A network of resistive miniature sensors was therefore developed in order to monitor the total VOC indicator present as a function of variations in ventilation parameters. In the presence of detectable gas, sensor conductivity increases depending on the gas concentration in the air. The type of sensor used was chosen on the basis of metrological aspects, such as sensitivity, response time or range of measurement, as well as practical issues such as cost, size and energy consumption. Five sensors were identified: models TGS 2600, TGS 2620, TGS 2602 TGS 2100 and TGS 800 (manufactured by Figaro). Experiments were performed in a sealed stainless-steel enclosure in order to first compare the response of each type of sensor when exposed to different building materials, e.g. wooden chipboard, carpet, or waxed flooring. This procedure will also enable us to identify the most sensitive sensor-material pairing for detecting changes in the ventilation system.

A network of eight sensors (TGS 2620) was developed with the objective of demonstrating the feasibility and usefulness of instrumented cabin. The experimental room was built to replicate the use of an office space and the ventilation system can be completely modified according to experimental requirements.

In parallel, and in order to better characterize the impact of ventilation on IAQ, a second type of experiment is currently being developed. A system of CO₂ gas tracers connected to a network of CO₂ sensors (TGS 4160 or 4161) will enable the evolution of local fresh air flow rate in the room to be monitored.

Filter capture efficiency testing for the biological glove box in the international space station

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In the Threshold Acceleration for Gravisensing-2 (Gravi-2) experiment lentil seedling roots will be used as a model to study the mechanisms by which the plant responds to a change in the direction of the gravity field. These tests are scheduled to be carried out in the International Space Station in 2014. This research project requires improvements of the biological glove box (BGB) unit to allow the safe use of hazardous chemicals for fixation of the tested plant roots. The solution needed for fixation of these samples contains formaldehyde (3.0 w%), glutaraldehyde (2.5 and 3.5 w%) and ethanol (70 w%). New filters were developed to capture these substances in the case of a spill. The objective of this project was to test the filter capture efficiency of these new BGB filters for aqueous solutions of formaldehyde, glutaraldehyde and ethanol in a simulated spill scenario.

The aqueous solution containing the chemical substance of interest was supplied to a M12 mini Cori Flow mass flow meter. The flow was controlled electronically and the total volume was determined with a precision of 0.2 w%. The liquid was then supplied to an air-spray nebulizer with an internal diameter of 1.5 μm . This nebula of finely dispersed aerosols was captured on the test filter at an air flow of 75 L/min. Downstream of the tested filter the real-time concentration was monitored using the multi-gas monitor type INNOVA 1312. For quantification of the filter capture efficiency two 150 mm diameter binder-free glass fibre membrane filters were impregnated with 3.0 g of 2,4-dinitrophenylhydrazine (DNPH) and placed in front and back-up position to be able to capture formaldehyde and glutaraldehyde. The respective hydrazine complexes were determined on HPCL-UV. For the off-line measurement of ethanol 0.2 L/min was sampled from the air flow and passed through activated coal. Ethanol was desorbed from the coal and analyzed by gas chromatography equipped with flame ionization detection (GC-FID).

The filters were tested using an aliquot volume defined in a dedicated spill scenario that is close to the conditions used during the Gravi-2 experiment. For formaldehyde and glutaraldehyde this aliquot was 10.0 mL and for ethanol this was 5.0 mL. In addition, the filters were challenged in a continued exposure involving a volume of tenfold the volume of the spill scenario. This second challenge caused a breakthrough representing a worst case scenario.

Table 1: Filter efficiency and downstream concentration as determined in experiment 1 (arithmetic mean \pm standard deviation based on observations in triplicate)

Aqueous solution	Aliquot of the spill (ml)	BGB-filter capture efficiency (w%)	Concentration in downstream air (mg/m^3)	Relative to SMAC (%)
3.0 w% formaldehyde	10.0 \pm 0.06	99.54 \pm 0.15	0.295 \pm 0.094	49.0 \pm 15.6
2.5 w% glutaraldehyde	10.0 \pm 0.02	99.93 \pm 0.07	0.05 \pm 0.04	51.3 \pm 51.2
3.5 w% glutaraldehyde	10.0 \pm 0.04	99.97 \pm 0.02	0.018 \pm 0.015	25.9 \pm 18.3
70 w% ethanol	5.63 \pm 0.08	97.54 \pm 1.01	19.4 \pm 7.8	0.19 \pm 0.08

^aNASA uses space maximum allowable concentrations (SMAC) as standards for the air quality in a space station. For formaldehyde, glutaraldehyde and ethanol these values are 0.6, 0.08 and 10,000 mg/m^3 , respectively.

The new design of the BGB filter unit loaded with 200 g of activated coal showed that a challenge with a small aliquot of test solution leads to downstream air concentrations not exceeding the SMAC (see Table 1). A continued test showed that breakthrough occurred only after a exposing the BGB filter unit to a volume of test solution corresponding to tenfold the volume in the original spill scenario.

Gravi-2 information on : http://www.nasa.gov/mission_pages/station/research/experiments/2.html

Supercritical CO₂ desorption for air sampling analysis

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For organic compounds, atmospheric pollution assessment is based on the adsorption of chemical substances on porous sorbent and later desorption and analysis. Desorption step often implies solvents which present a lot of drawbacks. The use of porous polymers as sorbent prevent from the solvent extraction, then other desorption means are enable like thermal desorption or microwave assisted desorption for example (Esteve & Langlois, 2012). But any alternative method is totally universal for any pollutants and any sorbents because of the diversity and the complexity of the interaction between them. Furthermore, thermal treatment induced by these methods prevents the online coupling with liquid chromatography and the analysis of thermolabile compounds.

In the study, we propose to develop an analytical device able to desorb any organic compounds from any sorbents without solvent and to perform the online analysis with gas or liquid chromatography. Extractions are performed with supercritical CO₂: at high pressure and high temperature, matter can be brought to the supercritical state, between the gas state and the liquid state. The supercritical state gives fluids penetration and solubility properties that are far superior to those of usual liquid solvents. Extraction by using supercritical fluids is thus an extremely high-performance technique (Chaudot *et al.* 1997). CO₂ was chosen because it has relatively low critical pressure and temperature: 73,8 bars and 31°C which are common conditions used in analytical laboratories for high performance liquid chromatography (HPLC) for example. Another advantage of this type of extraction is the ease of separation between the solvent and the solutes: a mere expansion suffices to bring a supercritical fluid back to its gas state and to keep only the solutes in the liquid state.

Activated charcoal is the sorbent of interest because it is the more commonly used for the air sampling as well for indoor atmospheres as for workplace atmospheres and the sorbent that cannot be efficiently desorbed with thermal techniques. Studied chemical substances are monocyclic aromatic compounds: benzene, toluene and m-xylene (BTX). Samples are prepared in controlled test atmospheres according to the ALASCA proficiency testing scheme protocol, with a reference concentration with an overall accuracy less than 4.5% (Langlois *et al.*, 2008).

Results presented in this work belong to the first part of the study and concern the extraction condition optimisation and the extraction reactor design. All the optimisation experiments were performed with off-line protocol: sample are desorbed on the extraction device, extracted fractions are collected in heptane prior to gas chromatography injection. Charcoal is subsequently extracted with CS₂ with conventional solvent extraction method, and overall extraction efficiency is calculated.

Pressure, temperature, CO₂ flowrate, and extraction time were determined in order to perform the extraction with efficiency over 99.5% for all compounds, as mentioned in table 1. Samplers designed in this study consist of either stainless steel or PEEK HPLC columns (50x4.6mm) filled with any sorbent and they are re usable and can be directly used as personal sampler both active and passive ways, just like thermal desorption samplers does.

Pressure (bars)		200			300			
Time (min)		20	40	60	40	60	80	100
Extraction efficiency (%)	Benzene	98.9	100	100	100	100	100	100
	Toluene	89.7	97.9	99.0	99.3	99.5	99.7	99.7
	m-xylene	65.5	87.6	92.0	96.1	99.0	99.4	99.6

Table1 : Effect of pressure and extraction time on the activated charcoal extraction efficiency (T=80°C)

This first step give the proof that supercritical CO₂ can be efficiently used to desorb organic compound that are strongly trapped on sorbent, we have now to develop the on line chromatography coupling to propose an totally automated free solvent universal desorption method. This will offer two advantages: firstly protecting laboratory handlers from chemical risks, and secondly simplifying the analytical process that constitutes major part of the cost in risk assessment.

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Dispersal of bioaerosols emitted on composting facility assessed using molecular techniques

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Bioaerosols generated at composting plants are released during processes that involve vigorous movement of material: fresh waste delivery, shredding, compost pile turning, screening. Bioaerosols are a cause of concern because of their potential impact on the health of workers and residents living close to such facilities due to the presence of thermophilic actinomycetes, molds, endotoxins and 1-3 β -glucans.

Using 16S rRNA and 18S rRNA molecular inventories, the microbial signature of composting aerosols was defined and gave us access to microbial indicators strongly associated with compost. Quantitative PCR systems were designed for two phylotypes : one targeting *Saccharopolyspora rectivirgula* and relatives and one targeting a phylotype belonging to the *Thermoactinomyces*. The indicators were validated by comparing their concentrations in impacted samples to their background levels in natural environments. Their concentration in compost during a whole process was monitored in two composting facilities treating different types of waste, as well as their levels in aerosols emitted during operational activities. Sampling campaigns were then performed (13 days of measurements) on both sites to analyze the dispersal of bioaerosol emitted during turning and screening activities by monitoring the indicators on-site and at increasing distances downwind. The impact of the concentration at the emission point and of meteorological conditions was analyzed. Finally, the particle-size distribution of airborne bacteria and of the indicator affiliated to *Saccharopolyspora rectivirgula* and relatives was determined by qPCR using samples from an Electrical Low Pressure Impactor. The results showed that single-bacterial cells are predominant in aerosols emitted by the composting facility investigated.

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Size-Segregated mass concentrations and elemental compositions of particle matter (PM) from different cooking components

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Key Words: PM, Cooking, Elemental Composition, Size-Segregated

Particles from cooking sources can cause high pollutant exposures with likely adverse health effects. Understanding the health effects of indoor cooking sources and how to reduce them will require the knowledge of the concentration and the composition of the pollutants. See and Balasubramanian, (Atm Env 2008,42, 8852-8862) found that during deep-frying, Cu, Fe, and Zn were the three major metals emitted. Zhang et al. (*Int. J. Environ. Res. Public Health* 2010, 7, 1744-1759) measured the black carbon concentrations emitted from cooking activities. Little is known about the chemical properties of particles emitted from cooking. Elemental compositions of emitted particles from different cooking activities have been poorly investigated in the literature. The aim of this study is to perform controlled measurements of the particle mass and elemental composition distributions to understand the contribution of each cooking components to overall PM concentrations. The cooking components include electric stove, cooking pan, cooking oil, additives, and meats.

The experiments are conducted using an electric stove in an on campus house at Middle East Technical University Northern Cyprus Campus in Güzelyurt, Northern Cyprus. Filter based mass measurements using an Eight Stage Non-Viable Impactor are performed to collect the generated particles from the range of PM_{0.4} to PM_{3.3}. The filters are analyzed using an inductively coupled plasma mass spectrometer (ICPMS) to estimate the elemental concentrations. An OC/EC analyzer is utilized to measure the elemental and organic carbon concentrations. The sampling instrument is located in the kitchen to perform sampling during cooking. Particles collected from different elements of cooking are analyzed for mass concentrations and elemental compositions. All filters are weighed before and after sampling to monitor the mass concentrations. Each sampled filter is considered for three types of analyses including OC/EC analysis, mass concentration and elemental composition. After weighing the sampled filter, a portion of the sampled filter is cut for OC/EC analysis and the rest of that is digested using a microwave oven. The digested filter in the acid solution will be shipped for analysis by ICPMS. All experiments are replicated at least three times. Preliminary results obtained by Amouei Torkmahalleh et al. (2013), and presented to “2013 Conference Environment and Health –Basel, Switzerland” found the presence of Fe, Zn, Mn and unexpected high level of Ba in total particle mass during heating of cooking oils (Figure 1). The distributions of different elements, organic and elemental carbon at different size fractions of PM are carefully investigated in this study. This study provides new information on the composition and size fractions of different metals generated from different cooking components. In particular, the generation of some potentially toxic metals such as chromium during toasting is explored.

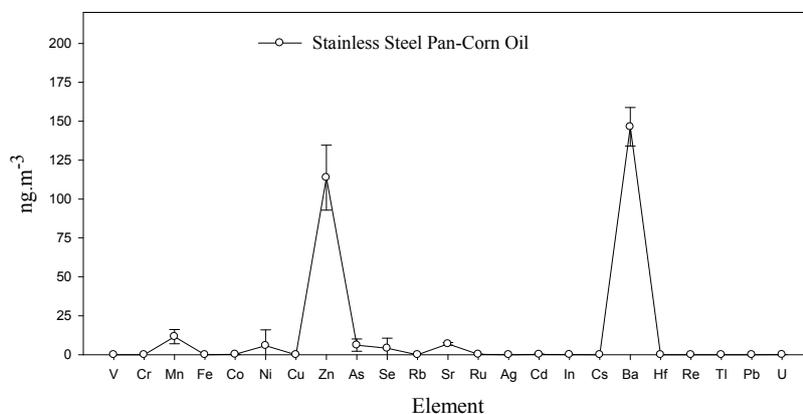


Figure 1. Elemental compositions of PM emitted during heating of corn oil in steel pan-

Amouei Torkmahalleh et al. 2013- presented to “2013 Conference Environment and Health –Basel, Switzerland”

Laboratory determinations of the penetration curve of respirable cyclones and workplace comparisons between different models of respirable cyclones

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A cyclone for the respirable fraction is usually characterized by determining its penetration as a function of particle size. Over the years many different respirable samplers have been characterized by a long array of institutions. A problem has always been the lack of what in analytical chemistry is termed “certified reference materials”. The only way to objectively approach this inherent problem in aerosol sampler characterization has been comparisons with penetration curves for the sampler published by other institutions. This leads potentially to a high variability among penetration curves determined at different institutions.

Respirable samplers are used to show compliance/non-compliance with national or other regulations on worker exposure, and therefore all uncertainties need to be reduced as far as reasonable. It is not uncommon that two respirable samplers which both have been shown to have penetration curves similar to the respirable sampling convention, actually show significant bias relative to each other when used in parallel sampling at workplaces. This presentation will discuss the limits of the accuracy of measured penetration curves and why two seemingly respirable cyclones may have a considerable bias in determined mass concentrations.

Cyclone penetration curves for three cyclone models (the Dorr-Oliver 10 mm nylon (US) cyclone, and the Higgins-Dewell (HD or British) cyclone and the SKC Aluminium cyclone), which have been extensively characterized by many investigators have been examined in detail. For example, of three investigations of the HD cyclone, two agree on both shape of the separation curve and the flow rate dependence of the cut size, whereas the third differs concerning the shape of the separation curve. Of five investigations of the nylon cyclone, three agree on both shape of the separation curve and the flow rate dependence of the cut size, whereas the other four differ concerning the flow rate dependence of the cut size.

A grand model was constructed based on almost all cyclone cut-size data found in the scientific literature, and from it was the inter-lab variability determined, as well as the effect of using non-spherical particles. The residual standard deviation of the cut-size was ~5%, with several laboratories having significant bias in the range 7–24%. Using non-spherical test particles (but assuming they were spherical) caused a negative bias of ~9%.

Large biases can be encountered when two cyclones of different models (whose cut-sizes previously were determined in laboratories) are compared in workplace parallel sampling. The many potential causes for this may be divided into explicitly and implicitly assumptions regarding what optimizations relative to the respirable sampling convention actually achieve. Among these are an optimization based on average bias for many particle size distributions versus the actual workplace particle size distribution; Difference in slope of the penetration curve between cyclone models; How well the tail is characterized; Using non-conducting cyclones when encountering a highly charged workplace aerosol; and Amount of non-respirable particles deposited in the cyclone. The effect of the assumptions will be discussed based on the published literature.

Several recommendations regarding both standardized laboratorial testing and workplace sampler comparisons are drawn. The most important are: The effect of dust loading in a cyclone must be determined when cyclones are characterized in laboratories, i.e. how is dust loading parameterized both regarding the cyclone geometry and the airborne particles; Determine how the cyclone penetration curve depends on the shape of non-spherical particles; Develop a reference sampler that almost perfectly follows the respirable sampling convention (with no loading effect) to be used in workplace parallel sampling comparisons.

Sampling, measurement and analysis of VOCs: what are the best tools for the job?

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Air pollution remains a global concern due to its damaging effect on human health and the ozone layer. Clean Air Acts have been implemented worldwide with the intention of reducing toxic air pollution in order to protect against further ozone depletion and health issues. Standard methods for measuring pollutants in urban air require the detection of bulk gases, e.g. carbon dioxide and methane, as well as more analytically challenging compounds like CFCs and HCFCs.

Many techniques are available for the sampling and measurement of VOCs in air/gas, but which is the best to use?

Canister samples are the current gold standard in the US and Asia for analysis of air toxics and other volatile organic compounds at various concentrations, but as the list of target compounds continues to grow, canisters are being pushed to their performance limit. Another option is the use of sorbent tubes. They are very versatile and depending on the sampling situation various techniques can be used to retain VOCs on the media; diffusive (passive) and pumped (active) sampling. There is no one correct method but rather the use of a range of sampling methods which will give the best overall picture.

These compounds may only be present at very low concentrations, nevertheless they have high 'global warming' potential. The US Environmental Protection Agency TO-15 and TO-17 methods currently list a number of air toxics or 'hazardous air pollutants' (HAPs) which must be monitored in urban or industrial. Due to their hazardous nature, it is vital to obtain comprehensive and sensitive data for an air sample in order to detect all compounds down to the lowest concentrations.

The paper will discuss the new advances for sampling a variety of VOCs in a range of sampling situations and the advantages of each technique, including the latest developments in analysis and detection of VOCs, and advanced data processing software.

Airmon

15-19 June 2014

Marseille, France

Session 6:

Air sampling and air monitoring

Chair: Dietmar Brueur - IFA, GERMANY

Owen Butler – HSL, United Kingdom

Plenary lecture

Development and field testing of a miniaturized sampling system for simultaneous sampling of gases and vapours

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Numerous substances used at workplaces fall into the group of semi volatile compounds. At the end of 2013 the standard EN 13936 was published by CEN¹. The standard defines the basic requirements for compounds that can occur as vapour and particle at the same time. Vapour and particles shall not be sampled separately and particles have to be sampled as inhalable fraction. These requirements were only hard to meet with the available sampling technologies. Samplers for the inhalable dust fraction usually apply clearly higher airflow rates than the collection of gases and vapours.

In Germany, the requirements of EN 13936 were already included in the regulations for occupational exposure limit values^{2,3}. In mid-2013 for semi volatile compounds the note „The substance can occur simultaneously as vapour and aerosol“ was added. Many of these compounds were currently sampled with classical vapour sampling systems as for example adsorption tubes.

EN 13936 defines sampler containing filter and pumped sorbent tube in series as one of the most suitable sampling trains. IFA has developed a miniaturized sampling head GGP (Figure) which is designed to sample the inhalable fraction at low flow rates as used for vapour sampling. The GGP-Mini can be easily combined with adsorption tubes. Particles will be sampled on a 13 mm filter. A basic set up with glass fiber filter (Ø 13 mm) and charcoal tube (coconut shell charcoal, 300/600 mg; OD 7 mm, ID 5 mm) was tested.

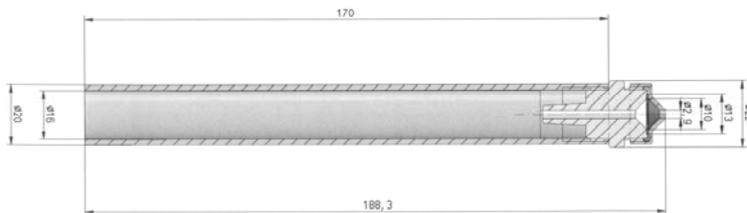


Figure. GGP-Mini vapour aerosol sampler

Laboratory tests were performed with propylene glycol (boiling point (b.p.) 188 °C), diethylene glycol monomethyl ether (b.p. 193 °C), ethylene glycol (b.p. 197 °C), diethylene glycol monoethyl ether (b.p. 202 °C), diethylene glycol monobutyl ether (b.p. 231 °C), diethylene glycol (b.p. 244 °C), n-hexadecane (b.p. 287 °C) and n-octadecane (b.p. 318 °C.). With a microliter syringe the substances were spiked directly on the filter and then 40 L of air sucked through. Substances having boiling points below 230 °C were almost completely evaporated. Substances with boiling points above 230 °C up to 300 °C, were found on both substrates, filter and charcoal tube. The low-volatile n-octadecane remained almost completely on the filter.

In a flow tube reactor⁴ aerosol/vapour mixtures of n-hexadecane, n-octadecane and diethylene glycol with droplet sizes between 1 µm and 3 µm were generated. The concentrations were analysed online with a particle counter (particle number and concentration) and a flame ionisation detector (overall concentration). In parallel samples were taken with the GGP Mini (0,33 L/min; 2 h). As example for n-hexadecane with a droplet size of 2 µm (4440 particles/cm³) the online measurements gives a result of 13 mg/m³ for the aerosol and 24,2 mg/m³ for the overall concentration (sum of vapour and aerosol). The offline results with the GGP-Mini showed a different distribution between droplets (8,5 mg/m³) and vapour (16,7 mg/m³), nevertheless the results for the sum of vapour (25,2 mg/m³) were in good agreement to the online measurement.

¹ EN 13936, Workplace exposure - Procedures for measuring a chemical agent present as a mixture of airborne particles and vapour - Requirements and test methods" (21013)

² Technical Rule for Hazardous Substances TRGS 900: Arbeitsplatzgrenzwerte, Version: January 2006, last amended and supplemented GMBI 2013 S. 943-947 v. 19.9.2013

³ List of MAK and BAT Values 2013: Maximum Concentrations and Biological Tolerance Values at the Workplace, Editor(s): Deutsche Forschungsgemeinschaft (DFG), Published Online: 15 AUG 2013, <http://onlinelibrary.wiley.com/book/10.1002/9783527675128>

⁴ G.C. Dragan, E. Karg, H. Nordsieck, J. Schnelle-Kreis and R. Zimmermann, Design of a simulation facility for workplace relevant aerosols of semi-volatile organic hydrocarbons: Set-up and first results European Aerosol Conference, Granada, 2.-7. September 2012.

Real-time ambient air monitoring using selected ion flow tube-mass spectrometry (SIFT-MS)

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Introduction: Selected Ion Flow Tube Mass Spectrometry (SIFT-MS) (Smith & Spanel, 2005) is a real-time analytical technique that detects volatile organic compounds (VOCs) and certain inorganic gases down to part-per-trillion levels without sample preparation or preconcentration (Prince *et al.*, 2010). These characteristics mean that SIFT-MS can easily be applied to real-time detection of volatile organic air pollutants and analytical results have been shown to compare well with those obtained by regulatory methods at accredited laboratory (Langford *et al.*, 2014).

This paper presents real-time air monitoring undertaken at Shu-Lin Primary School in Taoyuan County, near Taipei, Taiwan R.O.C. Full scan SIFT-MS data were acquired and subsequently processed using Syft's proprietary software package to give analyte concentrations.

Method: Continuous monitoring of outdoor air over a two-day period was undertaken. Air was drawn through approximately five meters of 1/4" o.d. Teflon tubing by the Voice200 instrument at a flow rate of 25 mL per minute. This equates to a residence time in the Teflon tubing of about three minutes.

SIFT-MS uses chemical ionization reactions coupled with mass spectrometric detection to rapidly quantify targeted VOCs (). VOCs are identified and quantified in real time from whole-gas samples based on the known rate coefficients for reaction of the chemically ionizing species (so-called reagent ions) with the target analytes. The soft chemical ionization used in SIFT-MS yields a smaller range of product ions than is common in electron impact mass spectrometry (as used by gas chromatography mass spectrometry (GC-MS), for example). Hence the need for gas chromatographic separation of the sample is circumvented, speeding sample throughput and providing instantaneous quantification of VOCs. Use of several rapidly switchable reagent ions (10 ms) to independently quantify target analytes also greatly reduces interferences, markedly increasing the specificity of SIFT-MS versus other whole-gas analysis technologies.

The Syft Technologies Voice200 SIFT-MS instrument can be operated in both full scan mode and selected ion mode (SIM). Because of the preliminary nature of this study, we employed a full scan approach that allowed subsequent, rapid reprocessing to obtain concentrations for target compounds. Full mass scans were acquired over the range m/z 10 to 200 Daltons for each of the three standard SIFT-MS reagent ions H_3O^+ , NO^+ and O_2^+ . Each reagent ion – product ion pair was sampled for approximately 0.5 seconds per five minute measurement cycle. Concentrations are reported in parts-per-billion by volume (ppb).

Results: The high-speed analysis provided by SIFT-MS allows the instrument to provide continuous monitoring. Concentration data were extracted from the full scan data for 48 compounds, many of which had been previously identified at the site using GC-MS. A number of these compounds exhibited interesting trends over the sampling period, including toluene, C₃-alkylbenzenes (e.g. mesitylene), methanol, isopropyl alcohol, acetone and N,N-dimethylmethanamide. Measured concentrations range from sub-ppb to peak levels for methanol of nearly 250 ppb.

Conclusion: The SIFT-MS technique has the capability to undertake sensitive, quantitative real-time monitoring of a diverse range of VOCs. This makes the technology useful for routine ambient air monitoring as well as a wide range of other environmental and occupational safety and health applications. In this study, we used the instrument in full scan mode to allow data to be subsequently and easily reanalyzed if and when other pollutants are identified.

Acknowledgement: We thank Mr Eddie Lin, Integrated Scientific Services Group, Taiwan, Professor Yang-Chien Ling and his research group, National Tsing Hua University, Taiwan, and Shu-Lin Primary School, Taoyuan County, Taiwan for the opportunity to undertake this study.

Langford, V.S., Graves, I., & McEwan, M.J. (2014) *Rapid Commun. Mass Spectrom.*, 28, 10–18.

Prince, B.J., Milligan, D.B., & McEwan, M.J. (2010). *Rapid Commun. Mass Spectrom.*, 24, 1763-1769.

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Indoor aerosolized bacterial population characterization by culture and pyrosequencing.

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For several years an increase in respiratory diseases was observed in the population, including asthma and chronic obstructive pulmonary disease. Pollution and increased individual allergic susceptibility are clearly involved. But, in recent years, many studies have also shown the role of indoor environment in these conditions, and in particular certain chemical compounds and microbial agents. In addition, improving the energy performance of homes has also increased the confinement and thus exposure to indoor contaminants. This exposure is over all the more important as we spend about 90% of our time indoors (housing, workplaces, transport...). The role of molds has been clearly established in the occurrence of respiratory disorders and in particular in the exacerbation of asthma. But, since a few years, the international scientific community has also been interested in environmental bacteria. Some bacterial components like endotoxins, present in large quantities in farming environments, are causing breathing problems via pro-inflammatory pathways.

Little is known on the influence of exposure to bacteria at home. To explore the population of bacteria indoor, we developed an indoor air sampling test based on cyclonic liquid impaction. The Coriolis® cyclone collector (Bertin Technologies, France) was used at a flow rate of 300 L/min to sample 3 m³ of air in the living room. Fifteen dwellings were selected for their characteristics (house or apartment, rural or urban, old or new, presence of children or not, presence of pets or not). During a dwelling visit, indoor air samplings were done, some environmental parameters (temperature, humidity) were measured and a questionnaire was administered to inhabitants. Analysis of bacterial populations was done using culture on agar plates – trypticase soy (TCS) – and a quantification of endotoxins was assayed by chromogenic LAL method concurrently. Furthermore, DNA was extracted from the samples and sequenced on 16S gene by pyrosequencing on 454 Roche system.

Geometric means were established at 2,900 CFU/m³ with the cyclonic biocollector. Moreover, bacterial cultures highlighted a large variability of contamination between dwellings: from 700 to 9,200 CFU/m³. The same result was observed for endotoxin indoor concentrations: from 0.178 to 3.618 EU/m³, with a geometric mean of 0.806 EU/m³.

No correlation has been evidenced between counted CFU/m³ and measured endotoxin concentrations. This could be explained by the high prevalence of Gram-positive cocci bacteria on agar plate cultures while endotoxins are membranous components of Gram-negative bacteria.

Pyrosequencing analysis showed on genera level the high frequency of *Burkholderia* (almost 50% for 7 dwellings), and to a lesser extent *Pseudomonas*, *Micrococcus*, *Staphylococcus* and *Ralstonia* (which is close to *Burkholderia*). *Stenotrophomonas* that are associated with health disease in hospital (as an important nosocomial pathogen) has also been detected in 10 dwellings and *Acinetobacter baumannii* in 3 dwellings.

Analysis of dwellings characteristics showed that bacteria load and endotoxin concentrations seem to be higher in rural dwellings, in the presence of children and pets.

This study characterizes the bacterial flora in indoor air samples of dwellings from Western France. Results evidenced high amounts of endotoxins and microorganisms, notably some pathogenic that could be at risk for immunocompromised patients returning home after hospitalization.

Kettleson E, Kumar S, Reponen T, Vesper S, Méheust D, Grinshpun SA, Adhikari A. *Stenotrophomonas*, *Mycobacterium*, and *Streptomyces* in home dust and air: associations with moldiness and other home/family characteristics. *Indoor Air*. 2013 Oct;23(5):387-96.

Aerosol fungi in dwellings: evaluation of an air ERMI and comparison with NGS sequencing

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Exposure to homes with high Environmental Relative Moldiness Index (ERMI) values have been shown to be associated with the development of childhood asthma (Reponen et al., 2011). ERMI is based on the quantification of 36 fungi in dust samples collected by vacuum (Vesper *et al.*, 2007). Here, we investigated the correlation between aerosol-based measures of fungal contamination and ERMI values in Brittany, France dwellings. Furthermore, we compared the ERMI results to a next generation sequencing analysis of fungi in air samples.

Dust and air samples were obtained from 40 dwellings (20 with visible mold and 20 without visible mold) and analyzed by quantitative PCR (QPCR). Dust samples were collected by vacuuming two m² in the living room and two m² in a bedroom for five min each with a MitestTM sampler-fitted vacuum. The Coriolis[®] cyclone collector (Bertin Technologies, France) was used at a flow rate of 300 L/min to sample 3 m³ of air in the living room and also in the bedroom. Airborne microorganisms were sampled in collection liquid with an initial volume of 15 mL. DNA was extracted and amplified by PCR and sequencing was realized on 18S gene by pyrosequencing with Roche 454 system on 20 samples (10 moldy and 10 non moldy) out of 40.

Higher ERMI values in dust samples were correlated (significant Kendall's tau values) with higher fungal concentrations in air samples in the living room and bedroom analyzed by QPCR. 22 species were found in significantly greater concentrations in French homes relative to those in US homes: *Aspergillus restrictus*, *Aspergillus fumigatus*, *Aspergillus versicolor*, *Aureobasidium pullulans* *Penicillium crustosum*, *Wallemia sebi*. Even outdoor species of fungi were found in greater concentrations: *Cladosporium cladosporoides*, *Cladosporium herbarum*. This might be due to windows being more commonly open for ventilation in French homes compare to US which rely more on air-conditioning (Vandentorren *et al.*, 2006). Analyses of sequences by pyrosequencing showed a same trend of contamination than observed by "air" ERMI. The most frequent genera in homes are *Aspergillus*, *Penicillium* and *Cladosporium* but in some samples different genera can be detected in significant amount suggesting that the genera used in ERMI has to be adapted to France. Furthermore some genera described to be involved in clinical cases have been detected like *Cryptococcus*.

ERMI-based analysis can be completed in 24 to 48 h. This is one of the main advantages of this methodology in comparison with the traditional culture analysis that can take days to weeks. Aerosol samples obtained with the Coriolis[®] cyclone collector and analyzed by QPCR and next generation sequencing may provide an useful additional information in understanding indoor fungal contamination.

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Vesper, S.J., McKinstry, C., Haugland, R.A., Wymer, L., Ashley, P., Cox, D., DeWalt, G., Friedman, W., 2007. *J. Occup. Environ. Med.* 49, 829–833.

Airmon

15-19 June 2014

Marseille, France

Session 7:

Air sampling and air monitoring

Chair:

Wolfgang Rosenberger - HMS, Germany

Xavier Simon - INRS, France

Plenary lecture

Air quality in aircraft cabins – in-flight measurements of organophosphates and other hazardous substances in different types of aero planes

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Keywords: aircraft, cabin air quality, aerotoxic syndrome, organophosphates, volatile organic compounds

Since the 1960s most commercial aircrafts are supplied with bleed air from the engines for pressurisation and air conditioning of the cabin and the flight deck. One exception is the Boeing 787 “Dreamliner” (maiden flight on December 15th, 2009) which uses ram air for cabin pressurisation.

In recent years, crew members and passengers of bleed air technology aircrafts reported neurotoxic and other, mostly non-specific symptoms after so-called “fume events”. These symptoms are sometimes referred to as an “aerotoxic syndrome”. It has been repeatedly suspected that the release of hazardous neurotoxic substances from the engines or the auxiliary power unit (APU), respectively, through the environmental control system (ECS) into the cabin and flight deck might be responsible for the reported health effects. Also, in some isolated cases a forced landing of aircrafts was necessary due to acute illness of the pilot crew after fume events.

In addition to the assumed bleed air contaminants there is still a significant set of other possible sources for chemical air pollution in aircrafts, for example fuel and exhaust gas entry during taxi manoeuvres on the ground as well as air contamination by hydraulic oils, de-icing liquids, pesticides from disinfection spraying, ozone from atmospheric air, emission from furnish surfaces, and temporary emission of various compounds after maintenance. Not at least, offensive smells from passengers may add to odour nuisance in an aircraft.

Given that aircraft cabin quality is a sensitive issue for passengers and crew members alike, it seems advisable to gain further knowledge about potentially hazardous compounds in cabin air. Continuous and discontinuous methods are available to detect and quantify a wide range of air contaminants in aircrafts. Also, the analysis of construction materials and wipe samples may be useful to identify sources of contamination.

This keynote will provide a summary and discussion of the current research and results on aircraft cabin air quality, and also on the results of human biomonitoring studies. In particular, the rationale and outcome of our own in-flight measurements in four different types of aircrafts (Boeing 757-300, BAE 146, Airbus A320 and Airbus A 380), including reported “smell events”, de-icing-procedures and normal operation conditions, will be presented.

Advances in air quality monitoring in aircraft cabins

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Providing clean air supply without nuisances is one of the top priorities of aircraft manufacturers and operators likewise. Contaminants introduced inadvertently during manufacturing of the aircraft but also during operation as well as technical malfunctions can sometimes lead to temporary smell occurrences in the aircraft cabin. There is a growing interest to assess airborne contaminants during such smell events in order to ensure that these occurrences are safe and do not imply a health risk. Beside this, based on the contamination pattern and its chronological sequence, approaches are being made to elucidate the origin of such short-time odour nuisances in order to quickly rectify the root cause and avoid future nuisances. However, 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.

Environmental monitoring in aircraft cabins compared to ground based measurements imply additional challenges with respect to methodology and requirements for equipment related to their impact on flight safety. Operational loads and vibrations make it difficult to use highly sensitive laboratory instrumentation. Differently to ground based environments specific requirements exist regarding fastening and containment of measurement equipment even during loads accounted for during an aircraft emergency landing scenario. Likewise it needs to be ensured that no electromagnetic interference with electrical aircraft systems and radio transmission exists. Furthermore electrical power supply characteristics on an aircraft are significantly different to those of ground based sources and may include short-time interrupts. Often the operation of self-sustained equipment seems to be the best solution but the use of batteries is subject to limitations in terms of space provisions, weight and additional safety aspects.

Further challenges arise from operational constraints. Due to the dynamic change of both outside conditions and operational state of the complex air supply system, measurements during short-time intervals may be desired, for example it would be ideal if a sampling interval could be started upon a sudden occurrence of odour perception. On the other hand, on-board aircraft operation or supervision of applied measurement techniques by dedicated personnel is often not possible or extremely costly. Consequently for such monitoring missions sampling and measurement systems are needed, which are automated to a large extent in order to minimize operating tasks during flight

A sophisticated sampling and measurement system was developed and applied in cooperation between Airbus, Fraunhofer IBP and Ionicon in order to identify and trace airborne contaminants during production flight tests. Monitoring of inorganic gases, thermodynamic parameters and sampling for later laboratory analysis with established analytical methods with a high degree of automation was performed in parallel to online mass spectrometry combined with proton transfer reaction ionisation [1].

Based on the results, a source for short-time contamination during production flight tests was identified and corrective actions were implemented. Experiences made during these measurements were incorporated in the evolution of measurement equipment that will be used within further measurement campaigns.

[1] Bezold, A.. (2012). *Cabin air quality – The Key to a comfortable flight*, FAST Magazine, 50, 22-29.

Environmental and cultural heritage: development of an analytical protocol for sampling and analysis of air pollutants by solid phase micro extraction

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Keywords: cultural heritage, solid phase micro extraction, air pollutants, gas chromatography, air sampling

Monuments registered on UNESCO's list of the world heritage require special monitoring. The Historic Centre of Florence, was inscribed in the World Heritage List in 1982 during the sixth session of the UNESCO World Heritage Committee. Every year, all around the world, old and new cultural heritage and health harmful pollutants are characterized, thanks to innovative methodologies and instruments. As a consequence of the premises, Volatile Organic Compounds concentrations have to be constantly characterized and monitored, since they can affect cultural heritage (Dalva *et al.*, 2010; de la Fuente *et al.*, 2011; Fenech *et al.*, 2010; Gibson *et al.*, 1997). The objective of this work is to assess the potential critical relationships between environmental factors and damage of the artifacts and other cultural heritage and public health into the historic centre of Florence by studying: *i*) the direct outdoor/ indirect indoor unconventional pollutants concentration; *ii*) the distribution and circulation of the unconventional pollutants; *iii*) the chemical interactions between the unconventional pollutants in the gas phase leading to removal and/or formation of secondary pollutants; *iv*) the potential final interaction of the unconventional pollutants with the surfaces of artistic interests and possibly the potential effects on public health.

The sampling of the air pollutants (aldehydes, fatty acids, total oxidants, oxone and phenols) is performed by Solid Phase Micro Extraction (SPME) fibers derivatized before sampling and accommodated on electric cars in different environmental situations. The SPME fibers, after the sampling, were thermally desorbed in the Fast Gas Chromatography and the Mass Spectrometry analysis were conducted by narrow bore 10 meter column with a 0,10 mm internal diameter and 0,10 µm film thickness.

The overall data were crosschecked with the scientific literature by means of specific data base so to assess the potential impact on cultural heritage and public health. The collected data also show the great difference, from a chemical point of view, between the city centre and the boulevards where the concentrations are 1-2 order of magnitude higher than the former. Relevant concentrations of formic and acetic acids were found everywhere; these acids erodes artifact also causing efflorescence formation and can be very aggressive towards metals and stones. The analysis revealed the presence of aldehydes too, especially formaldehyde and acetaldehyde that represent a danger for metals.

An important output of the performed analytical activities was the development of a specific methodology to sample, analyze and monitor the selected unconventional molecules. As a result an analytical standard protocol was produced so to be used for future monitoring campaign.

Acknowledgement: This work was supported by the POR FESR 2007-2013 REGIONE TOSCANA (Italy), Project n. 436948, eleCtric mobiLity to analyse tourist bEhaviour in urBAN areas (CLEAN).

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ECOS-PER: semi-volatile organic compounds in indoor air and settled dust in 30 French dwellings

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Semi-volatile organic compounds (SVOCs) are ubiquitous contaminants in the indoor environments, emanating from different sources and partitioning among several compartments, including the gas phase, airborne particles and settled dust. The aim of this study was to measure concentrations in indoor air and settled dust in French dwellings for a wide range of SVOCs. The target compounds were phthalates, polybrominated diphenyl ethers, bisphenols, polychlorinated biphenyls, polycyclic aromatic hydrocarbons, synthetic musks and pesticides.

30 dwellings were investigated in Brittany, France, between December 2010 and April 2011. Airborne particles and gas phase were sampled using a URG personal sampler (University Research Glassware, Chapel Hill, NC) with a size-selective impactor inlet that had an average particle size cut point of 10µm. Dust samples were collected using a commercial vacuum cleaner, modified to collect dust in a Whatman cellulose extraction thimble inserted between the crevice tool and the vacuum tube extender. Dust was sieved to <100µm before extraction. Dust and air samples (only PUF) were extracted by pressurized liquid extraction with dichloromethane. Dust and air extracts (PUF) were analysed by gas chromatography coupled with mass spectrometry (GC/MS). Airborne particles collected on quartz fiber filters were analysed by thermal desorption coupled with gas chromatography / mass spectrometry (TD-GC/MS).

A total of 40 out of 57 target compounds were detected in settled dust and 34 compounds in gas phase and airborne particles. Phthalates were the most abundant compounds in all three compartments. In dust, diethyl hexyl phthalate (DEHP) and di-iso-nonyl phthalate (DiNP) were present at the highest concentrations, respectively 289 and 130 µg/g (median values). In air, di-iso-butyl phthalate (DiBP) and diethyl phthalate (DEP) were detected at the highest concentrations, respectively 377 and 157 ng/m³ (median values in gas phase + airborne particles). These two compounds were more abundant in the gas phase. Significant concentrations of bisphenol-A (BPA) and synthetic musks in settled dust and indoor air were also observed. The median concentrations of BPA were 4.7 µg/g in dust and 0.64 ng/m³ in airborne particles. Concentrations in the 3 compartments showed that partitioning of SVOCs mostly depends on their volatility.

The originality of this study was to take into account the concentrations of SVOCs simultaneously in three separate compartments: gas phase, airborne particles and settled dust. These data will be used to test a partitioning model of SVOCs between these three indoor compartments, within the ECOS project.

Acknowledgement: This research was funded by the French Agency for Food, environmental and Occupational Health and Safety (Anses).

Airmon

15-19 June 2014

Marseille, France

Session 8:

Exposure assessment-strategies, peak exposures, multi-exposures

Chair:

Yngvar Thomassen - STAMI, Norway

Gerd Sallsten – Univ. of Gothenburg, Sweden

Plenary lecture

Studies of the solubility and bioaccessibility of work-room aerosols

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Most compounds of the elements present as particulate matter in workroom air can occur in different physical states, namely gas, vapour or liquid and solid particles. Each of these states can influence or determine the nature of exposure, deposition, uptake or absorption, clearance and toxicological consequences. In general, particle toxicity is determined by many parameters including particle type, deposited amounts, size distribution, solubility, chemical reactivity, surface characteristics as well as frequency and duration of exposure. Many workplace and ambient particulate matter are composed of complex mixtures of elemental compounds ranging from e.g. pure elements, alloys, oxides and salts. The particle dissolution in the human body is important both for potential local or systemic adverse health effects. For example, it has been suggested that the soluble transition metals in welding particles might be a primer inducer of lung oxidative stress and inflammation¹. For a better understanding of the uptake and biological effects of elemental compounds it is also important to find the relationship between airborne exposure and concentrations in biological fluids. Elemental bioavailability can be defined as the extent of systemic absorption of elemental species. The amount of ion binding the target would ideally represent its true bioavailability and thus the toxic dose. Assessing elemental bioavailability in humans requires, however, bio-monitoring strategies. Alternatively, the potential bioavailability, the *bioaccessibility*, of elemental compounds or species can be investigated by measuring their solubility in artificial human tissue fluids or in samples of natural tissue fluids. Different fluids may be applied for such solubility studies: e.g. deionised water, lung epithelial lining fluid stimulant (Gamble's solution), artificial lung lining fluid stimulant (Hatch's solution) or gastric juice. Gamble's solution has been used for decades for determining the solubility of nucleotides and man-made fibres. It represents the interstitial fluid deep within the lung. Citrate is used in the place of proteins and acetate to represent organic acids. Hatch's solution contains some proteins and enzymes in addition.

Since a number of factors are involved in determining toxicological responses to the chemical exposure, the aim of this presentation will focus on the solubility/bioaccessibility of air particulate matter present in the workroom air in aluminium smelter potrooms and during different welding operations.

¹ J.M. Antonini, M.D. Taylor, A.T. Zimmer and J.R. Roberts, Pulmonary responses to welding fumes: role of metal constituents. *J. Toxicol. Environ. Health, A:67(3), 233-249.*

Cumulative indoor exposures to semi-volatile organic compounds (SVOCs) in France: progression of the ECOS project

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Introduction: Semivolatile organic compounds (SVOCs) are widely used indoors as plasticizers, flame retardants, or pesticides. The objective of the ECOS project is to assess cumulative exposure to these substances and associated health risks.

Methods: the framework of the project is presented in figure 1.

The project comprises:

- Health based SVOC ranking and selection
- Exposure assessment
 - Multi-residue analytical developments (GC/MS)
 - Nationwide representative measurements in settled dust and particulate matter (PM)
 - Gas phase modelling
 - Exposure assessment
- Toxicity assessment
 - Clustering of chemicals according to mode of action
 - cumulative reference values derivation

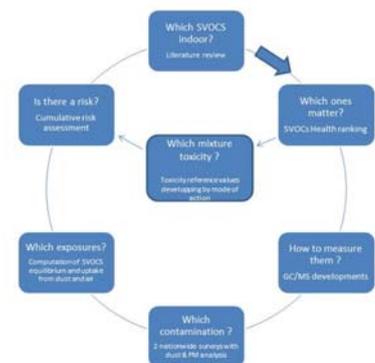


Fig. 1. The ECOS project framework.

Results: SVOCs have been ranked (Bonvallot et al. Indoor Air. 2010;20:458-472), measurements methods developed and tested (Mercier et al. J. Chrom. A 2012; 1254:107-14, Blanchard et al. Indoor air 10.1111/ina.12066), and implemented to measure 50 SVOCs in settled dust (n=145) and PM (n=296) (results presented at this conference).

In parallel, the toxicity of target SVOCs was reviewed to identify SVOCs with common modes of action, in order to develop cumulative toxicity indexes for reprotoxic (decrease of testosterone synthesis) and neurotoxic effects (neuronal cells impairment) (ongoing work).

First results indicate that several of the frequently detected compounds in house dust have common mode of action (ex: decreased of testosterone synthesis for some phthalates, polybromodiphenylethers, bisphenols, pyrethroids...). Cumulative risk assessment seems therefore relevant and possible.

Conclusions: Originality of this project is 1) inclusion of SVOCs from different chemical families on the basis of health concern, 2) corresponding specific analytical developments, 3) nationwide representative samples, and 4) cumulative assessment. Limit is difficulties in assessing the dermal pathway. Assessing risks due to SVOCs will help targeting prevention measures through the identification of compounds and media of exposure that lead to a greater risk.

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Occupational exposure to particulate matter in two Portuguese waste sorting units

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In waste sorting units workers are exposed to diverse risk factors and particulate matter seems to be an important risk factor due to not only to the mass, number and chemical characteristics but also because particles may act as a carrier and a source of nutrients for fungi (Seedorf *et al.*, 1998) and bacteria (Becker *et al.*, 2002; Halstensen *et al.*, 2013)

This study intended to characterize the occupational exposure to particles in two waste sorting plants located in Lisbon city, Portugal.

Particulate matter contamination was measured in different workplaces by portable direct-reading equipment (Lighthouse, model 3016 IAQ) in the two units. Besides mass concentration in 5 different sizes (PM_{0.5}; PM₁; PM_{2.5}; PM₅; PM₁₀) also data related with particles counts (number) by each diameter size was obtained. Measurements were taken in the workplaces where the workers spend more time.

Both sorting units showed the same distribution concerning mass concentration exposure metric: PM₅ and PM₁₀ were responsible for the highest levels of contamination. In both units, the particle fraction with higher number of particle concentration through all workplaces was the 0.3 µm. The waste sorting plant B showed significantly ($p < 0.05$) higher levels of mass concentration in all particles' sizes and in number of particles concentration.

Workers from both waste sorting plants were exposed to particles and the differences obtained between units' highlights the influence of ventilation systems that weren't available in unit B. Moreover, although health effects related with exposure have mainly been investigated with mass-measuring instruments or gravimetric analysis, there are studies that support that particle count may have advantages over particle mass concentration for assessing the health effects of airborne particles (Wichmann *et al.*, 2000; Weijers *et al.*, 2004). It can be an alternative metric that give more detail information regarding the amount of particles that can reach and deposited onto the walls of the respiratory tract (Schmid *et al.*, 2009). Particles can be also rich in endotoxins and mycotoxins and these facts promote concern regarding exposure to mixtures and possible additive and synergistic health effects (Zock *et al.*, 1995).

Acknowledgement: This work was supported by Lisbon School of Health Technology/Institute Polytechnic of Lisbon.

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Tiered exposure assessment approach for human risk assessment

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In the last years various approaches have been developed for exposure assessment of engineered nanomaterials (ENMs). These assessments are usually based on a tiered approach with increasing integration of quantitative data from measurement campaigns. However, the criteria for moving to a higher tier in these approaches are not based on an assessment of risk, but rather on the likelihood that exposure occurs, irrespective of the nature of the exposure. However, for human risk assessment, before moving to a higher tier it is necessary to have a better understanding of the overall risk (i.e. the combination of the exposure and the hazard) and the criteria used or proposed to move to a higher tier assessment.

As part of the EU FP7 project MARINA (Managing the Risk of Nanomaterials) a tiered exposure assessment approach for workers and consumers is being developed to be included in a human health risk assessment methodology focusing on exposure to ENMs. In each tier the uncertainty in the exposure estimates is reduced using data and tools (e.g. exposure scenario library, control banding tools, exposure models).

The Tier 1 assessment will provide qualitative or semi-quantitative estimates of release, based on information on the physico-chemical characterisation of the ENMs and the process / activities carried out in the scenario. The aim of Tier 2 in exposure assessment is to obtain a basic understanding of the likelihood and level of exposure. The aim of Tier 3 is to obtain a thorough characterization and quantification of the personal exposure to ENMs using an array of exposure metrics. Depending on the needs to further reduce uncertainty, it may be necessary to provide quantitative estimates of exposure

This is flexible approach where different methodologies and tools may be applied as long as it provides estimates at the right level of precision and quantification required for the human risk assessment.

Exposure to ultrafine particles and carbon monoxide in norwegian manganese and silicon smelters

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Exposure to ambient particulate matter has been well documented as a risk factor for cardiovascular disease (CVD) (Chen *et al.*, 2008; Næss *et al.*, 2007). Increasing experimental evidence suggests that particle size is of importance, with increased toxicity related to the fine particulate matter. Workers in different occupational settings are exposed to ultrafine aerosols as incidental products of combustion processes. The reported relatively high risks of CVD deaths related to ambient air pollution have, however, not convincingly been confirmed in the occupational setting, where the exposure levels are substantially higher (Fang *et al.*, 2010). The relationship between occupational exposure to ultrafine particles (UFP) and CVD needs therefore to be further explored.

As a part of this approach workers' exposure to ultrafine and respirable particulate matter and carbon monoxide (CO) was assessed in one Norwegian silicon metal and two manganese alloy smelters. The silicon smelter was producing silicon metal and collecting the incidentally formed amorphous silica fume, while the two alloy smelters were producing ferromanganese and silicomanganese alloys. Full-shift (8 hours) personal air samples were collected by 37-mm respirable cyclones (Cyclone 1). Shorter term (1 – 8 hours) personal air samples were collected by Sioutas cascade impactors which were operated in parallel with 37-mm respirable cyclones (Cyclone 2). Because of the relatively high fume concentrations in the smelters, the 8-hour operation of the impactors was challenging. Dräger Pac 7000 personal single gas monitors were applied for the full-shift measurement of the CO concentrations in the workers' breathing zone. The Sioutas cascade impactor equipped with 25-mm PTFE filters operates at 9 L/min and at this flow rate the 50% cut-points are 2.5, 1.0, 0.50 and 0.25 µm. Particles below the 0.25 µm cut-point of the last stage are collected on a 37-mm PTFE filter. The respirable sampling cassettes were equipped with 37-mm Millipore PVC membrane filters. Collected aerosol particulate masses on different impactor stages and PVC filters were determined gravimetrically by a Sartorius Micro model MC5 balance in a weighing room dedicated to low filter mass measurements.

More details of the aerosol sampling, concentrations of the different aerosol size fractions, time variations of the CO concentrations, methods for the estimation of the full time UFP exposures and the 8-hour exposure data will be presented at the conference.

Acknowledgement: This work was supported by the Norwegian Research Council Programme on Sickness Absence, Work and Health.

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Formaldehyde exposures in 5 major industrial sectors in France and Germany from 2002 to 2011

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Performing atmospheric measurements is one aspect to assess the work-related health risk at the workplaces subsequent from hazardous substances. In France and Germany exposure databases have been developed, where the results of these measurements are documented together with comprehensive exposure-related and workplace-related information. In France, this is the COLCHIC database (Vincent & Jeandel, 2001), provided by INRS² and the MEGA database (Gabriel, Koppisch, & Range, 2010), provided by the German IFA¹. In the present work, formaldehyde exposure levels of 5 major industrial sectors from France and Germany are compared. This substance is currently increasing in an EU-wide focus of discussion owing to its carcinogenic effects.

Between 2002 and 2011, together in both databases the results of more than 15 000 exposure measurements were documented. Grouping the data according to the European Union's NACE classification, the industrial sectors by country, in which formaldehyde is most often measured, were identified. These are: human health activities; manufacture of wood, furniture and related; manufacture of basic metals; manufacture of rubber and plastic products and manufacture of textiles. As basis for comparison selected measurement data issue from static and personal samples, with sampling durations of between 30 minutes and 240 minutes. Figure 1 provides an overview of the selected exposure data from COLCHIC (C) and MEGA (M), static and personal, differentiated according to the selected industrial sectors. The line (n) gives the numbers of results (n) and the bars give 50th, 75th, 90th and 95th percentiles.

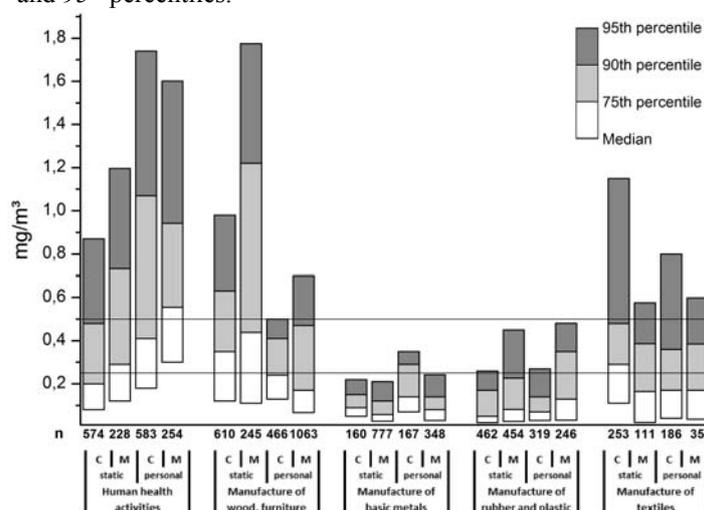


Figure 1. Formaldehyde exposures of 5 major industrial sectors; n = number of measurements, C = COLCHIC data, M = MEGA data; horizontal line: SCOEL 8 hour TWA of 0.25 mg/m³ and STEL (15 min.) of 0.5 mg/m³

Taken the SCOEL limit values for formaldehyde (SCOEL, 2008) as a rough estimate for risk assessment, it has to be stated, that 20% of the selected data exceed the 8 hour TWA (time weighted average) and even 10% the STEL for 15 min. (short-term exposure limit). MEGA data give the impression that exposure to formaldehyde in Germany is largely stable over the data period. French COLCHIC data show a peak in the years 2004-2005 and then a decrease to reach levels similar to Germany.

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Peak exposure measurements for task analysis and toxicity studies

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Keywords: peak exposure, real-time measurement, video exposure monitoring

Real-time measurements of exposure to gases/dusts with direct-reading instruments provide information on exposure and the effectiveness of control measures which is either unobtainable or different from time-weighted average (TWA) measurements. TWA exposure can be predominantly influenced by the peaks associated with specific work tasks/activities (Meijster *et al*, 2008). Furthermore, high peak exposures can produce an elevated dose rate at target tissues and organs, and short-term, high exposure levels can influence chronic occupational diseases (Preller *et al*, 2004 and refs. therein).

The data used for our peak exposure studies were derived from in-house video and real-time exposure monitoring data using the Video Exposure Monitoring (VEM) technique (Rosén *et al*, 2005). A web-based database (VEMDB) was created, searchable by industry, hazard and activity, with data from around 150 visits, collected over a period of 20 years from a wide range of industries (~25) and substances (~15). Analysis of exposure data was performed using scrollable, auto-scaling, labelled charts, capable of managing very large datasets, which are linked to multiple still images, derived from the video, showing worker activity (Figure 1).

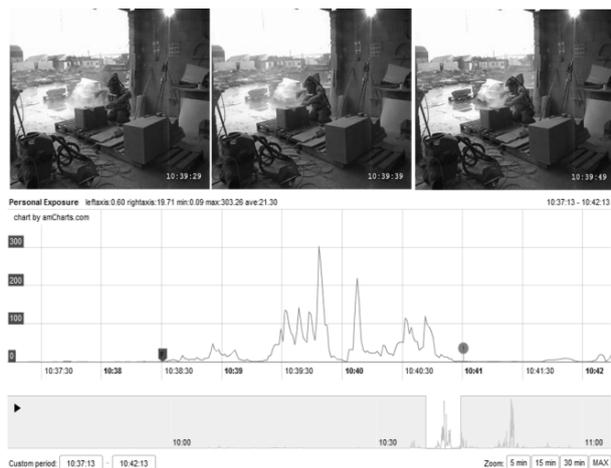


Figure 1 VEMDB output showing images (stonemason disk cutting stone block) with labelled, scrollable exposure chart (respirable silica).

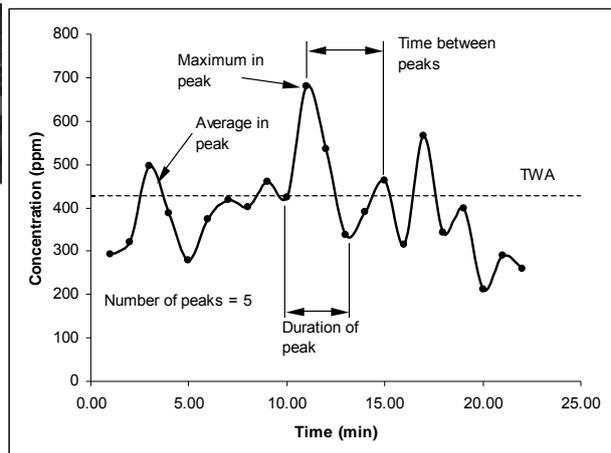


Figure 2 Styrene exposure profile (applying glass reinforced plastic with roller to boat hull) with peak metrics

Data from construction (exposure to respirable silica particulate) and boat building (styrene) industries were used to classify exposure peaks by means of suitable metrics. These were then compared across activities. Two types of metric were computed: standard statistical parameters and peak characteristics (e.g. in Preller *et al*, 2004). Examples of some of the 21 calculated metrics are shown in Figure 2 from a sample of our styrene data. Furthermore, a methodology was developed to compute metrics which accommodated measurements containing values below a detection limit.

Work is also underway to input peak exposure profiles, characterised by the above metrics, into suitably validated Physiologically-Based Toxicokinetic (PBTK) risk assessment models for these substances to compare body burdens with their constant, equivalent TWA exposures.

Acknowledgement: We thank Susan Hambling (HSE) for support and stimulating discussions.

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Indoor exposure to chemical and biological contaminants: results from the Asthm'child study on risk factors for childhood upper and lower airways inflammation

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Prevalence of childhood asthma has dramatically increased worldwide over the last decades (Asher *et al.*, 2006). Because of the time spent in enclosed spaces, indoor air pollutants may play a role in this incidence (Heinrich, 2011). The Asthm'Child project aims to measure and model the levels of these contaminants in order to assess childhood exposure.

150 homes from the mother-child PELAGIE cohort (Brittany, Western France) were visited between September 2012 and October 2013. In each dwelling, a questionnaire was completed in order to describe housing characteristics, habits and daily activities of residents during the sampling period. Moreover, a 5-day air sampling was conducted in order to assess the concentration of 45 volatile organic compounds (VOCs) among which 4 chlorinated trihalomethanes and 9 aldehydes, 10 semi-volatile organic compounds (SVOCs) among which 8 phthalates and 2 synthetic musks and culturable moulds. Active sampling methods were used to assess air concentration of trihalomethanes, SVOCs and culturable moulds. Other volatiles compounds, including aldehydes, were measured passively. Furthermore, moulds and 4 allergens (Der p1, Der f1, Fel d1 and Can f1) were measured in settled dust in the child's bedroom. Classical statistical methods were used to describe the distribution of contaminants.

Many molecules were detected and quantified in most dwellings. Among VOCs, formaldehyde was highly present and above 30 $\mu\text{g}/\text{m}^3$ in 40% of the homes with a median value of 28.6 $\mu\text{g}/\text{m}^3$ in the child's bedroom. Hexanal showed a median value of 25.1 $\mu\text{g}/\text{m}^3$. The sum of the 4 chlorinated trihalomethanes, measured in the shower cabin during a simulated shower, had a median value of 39.2 $\mu\text{g}/\text{m}^3$. Among SVOCs, both synthetic musks were quantified in all dwellings, showing median values of 90.1 ng/m^3 for galaxolide and 14.7 ng/m^3 for tonalide in the living room. Diisobutyl phthalate (median value of 361.6 ng/m^3) and dimethyl phthalate (median value of 22.5 ng/m^3) were also always quantified. Among the 6 other measured phthalates, four were present in more than 70% of the housings. Mould levels in the child's bedroom and in the living room were above 500 cfu/m^3 in more than 55% of dwellings.

This study provides an important dataset (150 dwellings) of indoor concentrations of various chemical and biological contaminants known or suspected to contribute to respiratory conditions and highlights the high level of indoor contamination. Collected data (measurements and questionnaires) will be processed using various statistical methods to derive a predictive model linking the characteristics of dwellings and their occupants' activities with pollutant concentrations. This model will then be used to estimate the association between exposure to indoor air pollution and upper and lower airways inflammatory conditions among the cohort participants aged 6-8 years.

Acknowledgement: This work was supported by the French Environment and Energy Management Agency (ADEME) and by a grant from Anses, the national agency for health security.

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Exposure assessment of military personnel to smokes and dust

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Military personnel is exposed to various aerosols related to their work including some that are rarely or not encountered in other professions. These aerosols include for example signalling and obscurant smokes and dust caused by firing and impacting of ballistic projectiles. Due to the special nature of the work it is often difficult to monitor exposure in the field.

The Dutch MoD funds several projects aimed at establishing the exposure of military personnel by performing tests in a controlled environment and extrapolating the results to real-life situations. In addition a project aimed at monitoring exposure during military operations is in progress. Here we report the results of tests with different types of orange, red and green signalling smokes inside a bunker.

Aerosol concentrations as a function of time and particle size distribution were measured with 4 instruments : a TSI 3321 APS (Aerodynamic Particle Sizer) for particles between 0.5 and 20 μm , a TSI 3081 SMPS (Scanning Mobility Sizer) for particles below 0.5 μm , an Andersen 8-stage impactor and an ELPI (Electrical Low Pressure Impactor) from Dekati. Air samples were taken and applied to an air-liquid interface system with cultured A549 human lung cells, to establish acute toxicity using various biomarkers: metabolic activity, oxidative stress, membrane integrity, and inflammatory processes.

Figure 1 shows the mass concentration during a test with orange smoke as a function of time measured with the APS of three experiments from the same batch of smoke grenades . The ELPI and Andersen impactor give similar results. AO3, the test with the lowest concentration resulted in no increase in toxicological markers compared to reference samples (negative control) exposed to clean medicinal air. AO2 showed a statistically significant effect on cell viability and marginally significant for oxidative stress. AO1, the test with the highest smoke concentration, showed clear a toxicological effect on all of measured biomarkers. The tests with other smokes did not show these dose-dependent results; some showed a clear toxic response, however most of them did not.

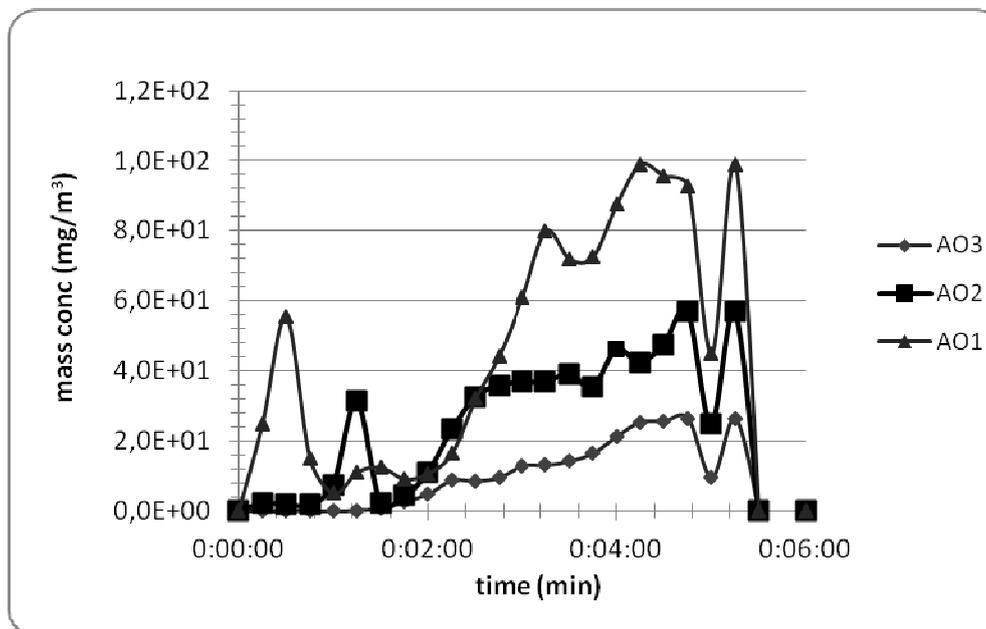


Figure 1. Concentration-time measurements during experiments with orange smoke (experiment in triplicate). The difference is due to varying burning efficiency within a batch and environmental differences, notably temperature, as the test bunker was not heated and had an open door to the outside world.

Analysis with electron microscopy showed varying amounts of short fiber-like structures on the ELPI samples. These probably result from a (chemical) reaction after sampling and may cause possible adverse effects on a longer time scale than the lung cell tests performed here. However this was not investigated in this project.

Acknowledgement: This work was funded by the Dutch MOD.

Safe use of nitrous oxide in delivery suites

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Introduction and objectives. Based on occupational hygienic surveys (FIOH 1996 – 2008) 40% of the midwives' exposure assessments in delivery rooms exceeded the OEL_{8h} (Occupational Exposure Level; eight hour, 100 ppm) and 84% of the OEL limit for pregnant workers ($0,1 \times \text{OEL}_{8h}$) for nitrous oxide (N₂O). These exposure levels have caused uncertainty among staff, hospital safety personnel and occupational health professionals and authorities.

Excessive exposure may cause headache, drowsiness and decrease in psychomotor functions. Due to Finnish regulation (Council of State 1334/2004) the anesthetic gases constitute a health risk to pregnant workers and to fetuses. Self-administered nitrous oxide is used in ca. 50% of deliveries in Finland for pain relief. During last years new equipment for dosing and scavenging N₂O has been widely adopted but verified knowledge of its effects on exposure levels is lacking. Thus, we studied exposure parameters, influence of work methods, equipment and ventilation to exposure levels in delivery suites at maternity hospitals. Aim was to generate guidelines to midwives for safe use of nitrous oxide.

Material and methods. The factors affecting exposure levels were studied: ventilation in the delivery rooms, concentrations of N₂O/O₂ in use, duration of use, impact of work method, quality of technical apparatus and comparison of "right", "common" and "wrong" way of equipment use. Six Finnish maternity hospitals were studied. In four of the hospitals a number of the suites were equipped with Aga Ventyo N₂O/O₂ –blenders with built-in scavenging and the rest of the delivery rooms with Bird Low Flow or Juno Mark Blenders, all without scavenging system. In one of the hospitals every room was equipped with Aga Ventyo system and in one hospital Anevac F apparatus was in use with a double mask and a Medicvent fan system for evacuating waste gas. Midwives' eight hour time weighted exposure (n=48) and stationary sampling in delivery suites (n=41) was assessed. Sampling of nitrous oxide was performed with ATD-molecular sieve tubes and the analyzing with a thermodesorption-GC/EC method. Stationary real time measuring was done with Gasmeter portable FTIR multi-gas analyzer. Air flows were measured with SwemaFlow 125 and Swema 3000 apparatus.

Results. The air measurements in breathing zone during 2009 – 2011 showed that exposure levels were significantly lower than during previous years, in 4% of the assessments OEL_{8h} was exceeded, and for pregnant workers it was exceeded in 58% of the assessments. Under testing conditions the change of N₂O ratio from 30% to 70% increased fivefold the concentration of N₂O near the breathing zone. Also, the optimal use of the technical equipment for administering and scavenging N₂O, resulted in very low room concentrations, while a "common" and a "wrong" use raised air concentrations to high levels. The position of midwife in relation to the breathing zone of the delivering mother had a great impact on the exposure level. A tenfold difference in air concentrations was measured 0,5 m in front of the breathing zone of the source, compared to 0,5 m beside the source.

All of the studied hospitals had a mixing ventilation system. Air flows were often lower than recommended values (8 dm³/sm²). Our measurements showed deviations from designed values of supply air between -18 ... - 36 [%] and in exhaust air between - 5 ... - 49 [%].

Discussion Midwives' exposure levels depend on many factors such as the quality and use of technical equipment, duration of N₂O analgesy, dosing ratio of N₂O/O₂ and time spent in the suite. Scheduled maintenance of scavenging equipment as well as daily check of their proper use and leak check of equipment enable to keep N₂O concentrations at a low level. The air concentration of waste gas is highest near the breathing zone of the woman in labour. Thus, good hygienic midwife practices include avoiding leaning over the patient, preferring staying on the backside and an adequate understanding of the function of the blending and scavenging equipment. Also, to ensure non-excessive self-administration of N₂O a good collaboration with the delivering mother and her accompanying person is essential. As an output of the study we produced a guide (www.ttl.fi) for midwives for safe use of nitrous oxide in delivery suites.

Acknowledgement: This work was supported by The Finnish Work Environment Fund grant 108323/2011.

Reported in Finnish language at www.ttl.fi/.../typpioksiduulin_turvallinen_kaytto_sairaloissa_tsr_Loppuraportti.pdf

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Microbial species and enzymes in aerosols from grass seeds causing organic dust toxic syndrome versus from reference grass seeds

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An outbreak of organic dust toxic syndrome (ODTS) in workers at a Danish grass seed plant after exposure to a particularly dusty lot of grass seeds has been described (Madsen et al., 2012). The seeds causing ODTS are in the following called problematic seeds. Several workers working with the problematic seeds had symptoms consistent with ODTS. The association between development of ODTS and the handling of grass seeds causing exposure was assessed in a four-step model: (i) identification of exposure source, (ii) characterization of the emission of bioaerosols from the problematic and reference seeds, (iii) personal and stationary exposure measurement at the plant and (iv) repeated health examinations. In this study we have further characterise the aerosols from step ii and iii in the model.

In moisture damaged schools a significantly higher fungal diversity and occurrence of airway symptoms amongst school children has been found compared to in schools with no known moisture problems (Meklin *et al.*, 2005). In this study we want to get further knowledge on the microbial diversity and microbial enzymes in aerosols from problematic seeds causing ODTS and reference seed.

In aerosols from problematic and reference seeds we are measuring microbial diversity using sequencing. In addition we have quantified the numbers of microorganisms and identified microbial species using MALDI-TOF (El-Bouri *et al.* 2012). Serine protease, chitinase, β -xylosidase, α -amylase, β -glucosidase, endotoxin and β -glucan have been quantified in aerosol samples.

Significantly more serine protease, chitinase, β -xylosidase, α -amylase, β -glucan, fungi, bacteria and endotoxin were released per kg handled problematic seeds than per kg reference seed. The exposures to serine protease and chitinase were highest in the working area with the seed silo. The highest exposures to α -amylase, β -xylosidase and β -glucosidase were found for a person working with reception of problematic seeds and packaging of seeds. In general a high exposure to enzymes was related to a high exposure to microorganisms.

A significant higher emission of enzymes, endotoxin and microorganism from seeds causing ODTS than from reference seeds was found. The exposure assessment and health examination showed that it may be the simultaneous exposure to high levels of many different bioaerosol components that caused the development of ODTS. If we had measured only one component as e.g. an enzyme or endotoxin we could have been misled to conclude that it was this one component which caused the ODTS. But we cannot know, whether it is the combination of different bioaerosol components or a single component which is responsible for the development of ODTS. We are now studying the microbial diversity in aerosols from the problematic and the reference seeds to see whether there is a different species composition in the problematic seeds than in the reference seeds. We want to know whether there is a larger or smaller microbial diversity in problematic seeds than in reference seeds.

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Relationships between air and urinary concentrations of beryllium in Cu-foundry, Al foundry and Al-smelter workers

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Beryllium occurrence in occupational areas is a major concern as low-level exposure could lead to development of beryllium sensitization (BeS) and of a chronic beryllium disease (CBD), a long latency granulomatous disorder that primarily affects lungs. To efficiently protect workers exposed to beryllium, a diminution of workplace exposure threshold limit values was recommended from 2 to 0.05 $\mu\text{g}\cdot\text{m}^{-3}$ by the American Conference of Governmental Industrial Hygienists (ACGIH) and to 0.01 $\mu\text{g}\cdot\text{m}^{-3}$ by the French Agency for Food, Environmental and Occupational Health & Safety (ANSES). This implies use of reliable and sensitive analytical methods for beryllium exposure assessment.

In this study, urinary concentrations of beryllium were investigated as a potential tool for exposure monitoring in three factories: a copper-beryllium (CuBe) alloy foundry, an aluminium-beryllium (AlBe) alloy foundry, and an aluminium smelter. Personal air samples were collected each working day for several days. All urine specimens (all the mictions at the workplace and home) were collected during the same period, resting days included. In addition particle size distribution and solubility of beryllium were determined for specific activities. Skin sampling was also performed occasionally before and after working day.

Ranges of beryllium urinary (BeU) and atmospheric (BeA) concentrations were different between workplaces. Although a statistically significant relationship at the level of confidence of 95.0 % between BeU and BeA (ln-ln scale, $R^2 = 0.43$) was found, the model after logarithmic transformation was not adequate to describe the observed data (Figure 1). No alternative model could explain the data. In first approach, it is thus obvious that the dosage of the urinary beryllium cannot be used as marker of beryllium exposure. In details, some variations in urinary levels could be explained by others parameter, such as skin exposures, beryllium solubility, as well as individual factors such as hygiene and smoking habit.

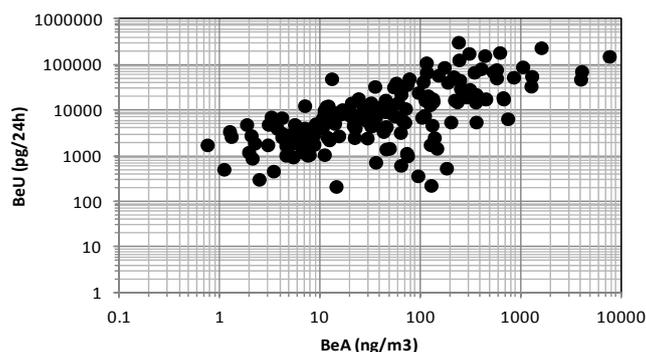


Figure 1. Relationship between beryllium urinary (BeU) and atmospheric (BeA) concentrations in three workplaces.

**Reference Material developments at the UK Health
and Safety Laboratory**

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The health of workers in many industries is at risk through exposure to chemicals, dusts and fibres and occupational hygienists need to determine the effectiveness of measures taken to control such exposure. This is generally achieved by making personal exposure measurements, the trueness of which relies heavily upon either the use of calibrated real-time instrumentation for *in-situ* measurements or the use of validated measurement methods when samples are returned to the laboratory for analysis. Hence, in the laboratory, reference materials are required to assess the extent of bias in analytical results.

This presentation will present an overview of the current status of reference materials in this occupational hygiene measurement field and will then detail current HSL reference material initiatives to fill gaps in this arena. In particular, the preparation and certification of asbestos, welding fume, silica and VOCs on sorbent tubes reference materials will be presented.

Acknowledgement: Aspects of this work have been funded by the HSL Investment Research Programme

Airmon

15-19 June 2014

Marseille, France

Session 9:

Active and passive sampling of organic and inorganic substances

Chair:

George-Constantin Dragan- HZM, Germany

Bo Strandberg, Univ. of Gothenburg, Sweden

Plenary lecture

Semi-volatile aerosols and evaluation of their impact on various workplace aerosol samplers in connection with air monitoring and human health.

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Aerosols of Semi-Volatile Organic Compound (SVOC) origin represent a big challenge to industrial hygienists due to toxicological as well as sampling issues. Especially problematic is the sampling of harmful semi-volatiles that are occurring fractionated particulate and gaseous phases in the workplace. More attention has to be given to these dynamic aerosol systems as the particle-vapor distribution is considerably depending on the sampling conditions.

The accurate distinguishability between particulate and vapor phases is of high importance mainly due to the different toxicity that each phase carries. Previous studies have showed that particles have a greater harmful effect even though present in lower concentrations. Particulate matter can penetrate and deposit deeper into the lungs while vapors are more likely to be exhaled. Health risks could be underestimated if the chosen sampling method does not differentiate between phases.

A study was carried out to address the issue of semi-volatile aerosol evaporation theoretically and experimentally as well as to provide experimental data that show the extent of evaporation losses that might bias the workplace risk assessment.

This talk provides a general overview on semi-volatile aerosols with focus on the dynamics of particle-vapor mixtures and related artefacts that can influence the risk assessment. The results presented address the properties of semi-volatile aerosols from a theoretical as well as experimental point of view. Experiments conducted in a temperature-controlled laboratory show the influence that parameters like vapor pressure, particle diameter, number concentration, temperature and vapor saturation have on the fractionation and dynamic between particulate and vapor phases. In addition, comparisons between measurement techniques will be presented and discussed. Outcomes will be discussed in the context of air monitoring and health relevance.

Comparison of French and German methods for bitumen fumes sampling and analysis

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Keywords: bitumen fumes, semi-volatile aerosol, samplers, quantification methods

Several sampling and analysis methods for bitumen fumes are reported in the literature. But these methods often produce incomparable results which constitute a problem for interpretation of exposure studies.

The Institute for Occupational Safety and Health of the German Social Accident Insurance (IFA) and the Institut National de Recherche et Sécurité (INRS) carried a comparative study on the sensibility, reliability and conversion between their methods for sampling and analysing bitumen fumes.

A bitumen fume generation device was developed to produce controlled polluted atmospheres in laboratory from different bitumen. Bitumen fume concentration and humidity are regulated over time to the desired level ranging from 0.5 to 80 mg.m⁻³ and 5 to 90 % RH respectively.

Two sampling methods were compared : IFA method n°6305 using the German GGP sampler for vapours and aerosols of bitumen (Breuer, 2008) and the INRS sampler designed for bitumen fumes. For each sampling test, six German GGP and six INRS samplers were placed in the exposition chamber and were exposed simultaneously to the same fume atmosphere. The results are averages of the six similar samplers. The collection substrates of GGPs samplers (Glass fibre filters and XAD-2 beds) were tetrachloroethylene extracted prior to infrared spectroscopy analysis (FT-IR) according to the IFA method while the collection substrates of INRS samplers (Teflon membrane filters and XAD-2 tubes) were extracted with n-heptane and analysed by gas chromatography equipped with a flame ionisation detector (GC-FID) and high pressure liquid chromatography with a fluorescence detection (HPLC-FLUO). Each analytical method was calibrated on a bitumen fume condensate produced by the INRS from the same bitumen used for the sampler exposure tests.

Results showed a good agreement between FT-IR and GC-FID methods for high bitumen fumes concentrations, over 1 mg.m⁻³ (Table 1). But quantifications from HPLC-FLUO are significantly different from GC-FID and FT-IR even if calibrations were made on the same standards.

Table 1. Bitumen fumes quantifications by the three analytical methods for two different bitumen and three concentrations

Bitumen fumes concentrations (mg.m ⁻³)	INRS sampler		GGP sampler
	HPLC-FLUO	GC-FID	FT-IR
Bitumen 1	0.49 ± 0.02	1.92 ± 0.19	1.86 ± 0.05
	0.89 ± 0.03	3.72 ± 0.20	4.19 ± 0.17
	2.00 ± 0.06	11.68 ± 0.56	10.45 ± 0.21
Bitumen 2	0.70 ± 0.03	2.71 ± 0.29	3.05 ± 0.19
	0.85 ± 0.05	5.90 ± 0.41	7.46 ± 0.13
	1.46 ± 0.28	10.44 ± 0.88	10.07 ± 0.30

These results confirmed that GC-FID and FT-IR analytical methods give very similar results and the highest quantifications, independently of the sampler used. Consequently, no conversion factor is needed between these methods. The reason of the significant gap between GC-FID or FT-IR techniques and HPLC-FLUO has to be found out.

Acknowledgement: Bitumens used for this study were gently provided by the French professional association of bitumen producers called *Groupement Professionnel des Bitumes (GPB)*.

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Adsorbent media for workplace nitrous oxide sampling

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Nitrous oxide (N₂O) is used as an anesthetic agent in medical, dental, and veterinary operatories. This gas is also used as a foaming agent for whipped cream, an oxidant for organic compounds, a nitrating agent for alkali metals, and a component of certain rocket fuels. Several toxicological studies have shown that occupational exposure to N₂O causes adverse effects such as reduced fertility, spontaneous abortions, and neurologic, renal, and liver disease (Rowland *et al.* 1992). The American Conference of Governmental Industrial Hygienists (ACGIH) threshold limit value (TLV) for N₂O is 50 ppm as an 8-hour TWA (ACGIH 1993). In France, the circular DGS/3A/667 set the threshold limit value to 25 ppm during the maintenance of anesthesia.

The actual method developed by INRS is based on the passive sampling of N₂O on a thermal desorption tube filled with 750 mg of molecular sieve 5Å. This method has strong limitation due to the relative low affinity between the adsorbent, 5Å, and the adsorbate, N₂O molecules, and therefore to the retrodiffusion phenomena as the concentration of N₂O decreases during the sampling. Literature reports numerous studies on the adsorption of N₂O onto inorganic and organic media (Godbout *et al.*, 2006; Zhang *et al.*, 2011; Saha & Deng, 2010; Centi *et al.*, 2000).

Among those media, molecular sieve 4Å and ion-exchanged ZSM5 zeolites have been tested in order to improve the actual sampling method. The performance of each material was tested by active sampling at several concentrations and sampling time. Each adsorbent was followed by a tube of 5Å in order to evaluate the adsorption efficiency. Results obtained are presented on table 1.

Zeolites	Microporous Volume cm ³ (STP)/g	Theoretical weight of N ₂ O (µg)	Weight measured on zeolites	Weight measured on 5Å	Percentage of total weight recovered on zeolites	Percentage of total weight recovered on 5Å
		6.328	1.772	4.904	28.01	71.99
4 Å	/	12.656	1.123	11.744	8.87	91.13
		19.248	0.746	18.832	3.88	96.12
AgZSM5	0.16	11.98	9.81	0.02	81.86	0.15
		18.91	17.07	0.46	90.25	2.44
		23.78	17.92	0.05	75.34	0.21
CuZSM5	0.14	11.54	6.27	0.01	54.36	0.07
		18.91	13.48	0.02	71.26	0.08
		23.92	13.41	0.01	56.07	0.03
BaZSM5	0.14	11.50	12.59	0.07	99.36	0.64
		23.48	17.99	0.18	76.63	0.75

Table 1: Weight and percentage of N₂O adsorb on tested zeolites as a function of theoretical loading

Most of the N₂O break through 4Å and is collected by the tube of 5Å. The higher the concentration of N₂O or the sampling time, the lower is the efficiency rate. The three ion-exchanged ZSM5 zeolites exhibit good adsorption properties as almost no nitrous oxide is present on 5Å. However, not all N₂O loaded is recovered during analysis, especially for CuZSM5. This can be explained by the desorption temperature, 350°C, which can induce the catalytic decomposition of N₂O. BaZSM5 appears as the most suitable zeolite for the sampling of nitrous oxide and its analysis by thermal desorption. Further investigation will be performed such as the adsorption capacities as a function of flow concentration, influence of humidity.

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Radiello diffusive sampler® for measurement of VOC emission from landfill biogas: influence of meteorological conditions

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Landfill sites have been identified as one of the major anthropogenic sources of biogas emissions. The main part of this emission is collected through pipe network for energy production; nevertheless a fraction of the biogas is emitted to the atmosphere through the waste cover due to leakage. Mainly composed with CH₄ and CO₂, biogas contains various VOCs which can entail health issues or olfactory nuisances for landfill surrounding populations. VOC sampling strategies implemented during field campaigns are mainly based on SPME fibres or various carbon sorbents gas sampling, and subsequent thermal desorption coupled with GC-MS analysis (Dincer et al., 2006; Rodriguez-Navas et al., 2012). Nevertheless these techniques are disputed since samplings have been taken in short periods (at most 1h) and may be unrepresentative of the average. The radial passive sampler (Radiello®) was used by Gallego et al. (2011), allowing to average 3 to 14 days of VOC samplings. However, the author highlights substantial concentration differences compared to active sampling methods, but also a high influence of the sampling time over the concentration. Besides, various authors have studied the Radiello® sampler behaviour in different environmental conditions. The environmental factors are highlighted as the cause of the main concentration uncertainty by Plaisance et al. (2008). A weak temperature effect on sampling rates has been shown whereas the humidity and the wind speed are supposed to be insignificant factors due to the hydrophobicity of the sorbent and the use of a thick porous membrane allowing to confine the sampler from airflow.

This work aims to investigate the suitability of the Radiello® passive flux sampler for the identification of specific biogas VOC levels in landfills on short sampling times (8h). Sixteen compounds including 3 alkanes, 3 halogenated, 1 ketone, 1 alcohol, 1 ester, 2 sulfured, 2 terpenes and 3 aromatics were selected in biogas composition as targeted species. Firstly, the retention capacity of the sampler constitutive sorbent and the analytical reproducibility were simultaneously evaluated by 7 successive spiking procedures (about 500ng on cartridge). Secondly, 4 samplers were exposed to controlled VOC mixtures at typical landfill concentrations in an atmospheric chamber simulating various meteorological conditions (3 different temperatures, 2 humidity rates, 5 wind speeds have been tested); sampling rates have been calculated and compared to those provided by the manufacturer. The preliminary results show that only 6 of the 16 analytes (isopentane, THF, cyclohexane, toluene, p-xylene and decane) can be measured with a variation coefficient inferior to 10%. Sulfur compounds and some halogenated are not adsorbed by the sorbent while the others compounds although adsorbed exhibit non reproducible loads. The non-influence of humidity rate and the weak influence of temperature have been confirmed. Temperature influence has only been observed for decane. However the strong influence of wind velocity has been noticed, especially from 4m.s⁻¹. For toluene, wind velocity variation from 2 and 7m.s⁻¹ has resulted to a 125% sampling rate increase. Apart from the lower rates exhibited by decane and xylene for 8h sampling, analytes reveal equivalent sampling rates as those provided by the producer on 14 days.

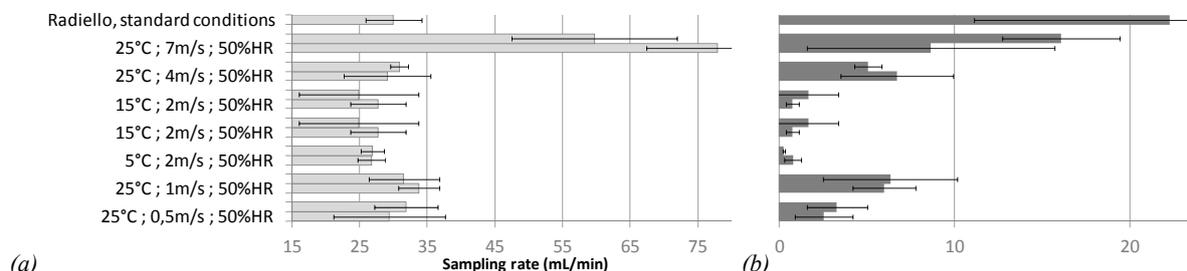


Figure 1. Sampling rates determines for toluene (a) and decane (b) for various meteorological conditions

This work tempt to prove that the passive diffusive sampler should be used in short sampling periods for the 6 above mentioned analytes, but with limitations in windy areas.

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Airmon

15-19 June 2014

Marseille, France

Session 10:

Biological monitoring - biomarkers of exposure

Chair:

Jaroslav Mraz - SZU, Czech Republic

Alain Robert – INRS, France

Plenary lecture

Globin adducts as in vivo dosimeters of cumulative exposure to chemicals

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Biological monitoring together with the analysis of workplace air constitute two complementary approaches to assess exposure to chemicals in occupational settings. A typical biomarker of exposure is the parent chemical or its metabolic product whereas biomarkers of biochemical effect are endogenous compounds (small molecules, biochemical intermediates, enzymes) which have altered their physiological levels due to interfering action of a chemical. The commonly used biomarkers are mostly determined in the urine or blood, and their levels reflect exposures occurring during last few hours or days.

A specific class of biomarkers are the adducts of electrophilic chemicals with biological macromolecules. Historically, the initial interest was focused on the adduct formation with DNA, a target molecule associated with chemical mutagenesis and carcinogenesis. Specific DNA adducts have been determined in leukocytes or directly in target tissues mainly by ³²P-postlabeling method, which is extremely sensitive but laborious and tricky. Numerous electrophilic chemicals capable of binding to the DNA also form covalent adducts with proteins. The adducts with globin (in erythrocytes) and serum albumin have been used increasingly as in vivo dosimeters in the assessment of occupational and environmental exposures to several groups of toxicologically relevant chemicals such as alkylating agents, arylamines or isocyanates. The major sites for covalent binding of chemicals to blood proteins are cysteine (Cys), histidine (His) and lysine (Lys) residues in both globin and albumin, and N-terminal valine (Val) in globin. The great advantage of biomonitoring based on blood protein adducts is their long-term persistence in the body. Life span of globin adducts reflects the life span of erythrocytes, which is ca. 126 days in humans. Half-life of human albumin is 20 days. Thus, a single determination of a protein adduct allows to assess cumulative exposure to a parent chemical over a period of several weeks to months. Another advantage of globin and serum albumin is their accessibility in sufficient amounts (approx. 140 and 30 mg/ml blood, respectively). For determination of principal adduct types, reliable analytical procedures have been developed. Globin adducts of some industrial chemicals were assigned biological limit values to facilitate more effective occupational exposure control.

Whereas formation, properties, methods of analysis and application of various types of globin adducts have been described extensively, their subsequent fate following physiological removal of erythrocytes from the circulation has been, to our knowledge, totally unexplored. Therefore, we addressed the issue of globin adduct removal in our current project. We hypothesize that the adducted globin undergoes proteolytic degradation to free amino acids and amino acid adducts, the latter being excreted in urine. If so, the amino acid adducts in urine would constitute a novel category of biomarkers of exposure, combining three major features: specificity for the parent compound, potential for monitoring of long-term cumulative exposure, and accessibility by a non-invasive sampling.

In our investigations, amino acid adducts with industrial chemicals N,N-dimethylformamide (DMF), ethylene oxide (EO), acrylamide, and styrene were chosen as model compounds. Synthesis and in vitro preparation of the DMF adducts were carried out using a reactive intermediate, methylisocyanate (MIC). In the Stage I studies, synthetic standards of amino acid adducts Val-MIC, Lys-MIC, Val-EO and Cys-EO were administered to rats. All compounds were eliminated rapidly and in high yields, either unchanged (Val-MIC and Val-EO) or in the form of simple metabolic products (Lys-MIC and Cys-EO). In the Stage II studies, rats were dosed intraperitoneally with DMF and EO, or intravenously with rat erythrocytes that had been treated with MIC and EO (a new toxicological model to study the fate of globin adducts). Following both types of administration, subsequent decay in the globin adduct levels was found to be closely related to the kinetics of rat erythrocytes' removal. Analysis of urine samples from both experiments confirmed presence of the amino acid adducts or their metabolites, as identified in the Stage I study. Moreover, adducted dipeptide EO-Val-Leu was identified as a new metabolic product and a potential biomarker of EO. Kinetics of the globin adducts in blood and of adduct degradation products in urine were closely associated. Thus, the concept of degradation products of globin adducts in urine as a new category of biomarkers appears to be realistic.

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Dermal absorption of cyclic siloxanes (D4/D5): Implications for human risk assessment

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Consumer exposure to personal care products (PCPs) may be studied through the analysis of cyclosiloxanes or other components of PCPs in end-exhaled air. The aim of this study was the quantitative determination of octamethylcyclotetrasiloxane (D4) and decamethylcyclopentasiloxane (D5) in end-exhaled air in order to investigate dermal absorption of PCPs.

We exposed the forearm of healthy volunteers for 60 minutes to pure D4 or D5 and to commercial products containing D4 and D5 (such as a cream, a deodorant and a combination of cream and deodorant). Inhalation was minimized by keeping the forearm in a flow cabinet during dermal exposure and by supplying filtered air to the breathing zone of the volunteer during the post-exposure period. End-exhaled air was collected using a breath sampler (Bio-VOC), transferred to carbograph multi-bed adsorbent tubes and analyzed by thermal desorption gas chromatography mass spectrometry (TD-GC-MS).

In the end-exhaled air of non-exposed volunteers (also refraining from use of PCPs for 24 h prior to visiting the laboratory), background levels of D4 (0.8-3.5 ng/L) and D5 (0.8-4.0 ng/L) were observed. When the volunteers were exposed to one of the aforementioned products, D4 and D5 concentrations in end-exhaled air did not or only barely exceed background levels. However, we observed a sharp peak in the D4/D5 concentrations in end-exhaled air at t=90 min. We attributed this peak to inhalation of these substances during a planned toilet visit for collection of urine samples. After removing this visit from the protocol, the peak disappeared indicating a negligible contribution of dermal absorption to end-exhaled air concentrations of D4/D5. This is in contrast to earlier findings by Plotzke *et al.* (2000, 2002), who reported peak levels at 15 to 60 minutes after application of ¹³C-labeled D4/D5 ranging from 30 to 111 ng/L (D4) and from 347 to 2315 ng/L (D5). We suspect that the dermal absorption levels reported by Plotzke *et al.* (2000, 2002) are an artifact due to inhalation of evaporated D4/D5. Therefore, the PBPK model for D4 (Reddy *et al.* 2007) that is based on these experiments may overestimate dermal absorption.

Overall, the results of our experimental work using D4 and D5 as a pure substance or as a component of cream and deodorant indicate that dermal absorption of D4 and D5 contributes only marginally to the internal exposure. Inhalation is the primary route of entry, and risk assessment for consumer products should focus on this route. Analysis of end-exhaled air represents a new and promising non-invasive approach to exposure assessment in studies on the use of PCPs in residential settings.

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Variance components of short-term biomarkers of manganese exposure in an inception cohort of welder trainees

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Elevated manganese (Mn) exposures have long been an occupational health concern, as chronic elevated exposures have been implicated in the development of “manganism” a Parkinson’s-like syndrome (Lucchini et al. 2009) Various biomarkers of exposure have been explored as a way to quantitatively estimate an internal dose of Mn, but given the tight regulation of Mn in the body, inter-individual variability in baseline Mn levels, and variability in timing between exposure and uptake into various biological tissues, identification of a valuable and useful biomarker for Mn exposure has been elusive. Thus, we investigated the factors associated with variability in Mn measured in plasma, urine, and whole blood in a group of nine newly-exposed apprentice welders, on whom baseline and subsequent longitudinal samples were taken over a three month exposure period. After analysis for elemental Mn, all blood ($n=64$) and plasma ($n=63$) samples were above the LOD, but 18 of the 63 urine samples (28.5%) fell below the LOD of 0.038 $\mu\text{g/L}$. For analysis of variance components, urine samples below the LOD were handled two ways: 1) replaced with the $\text{LOD}/\sqrt{2}$ (Hornung and Reed 1990) prior to being creatinine corrected, and 2) imputed using multiple imputation interval regression prior to being creatinine corrected. A mixed model estimating variance components using REML was used to assess the within- and between-variance components in blood (MnB), plasma (MnP), and urine (MnU) both replaced and imputed, including subject as a random effect, and time of the sample and use of respiratory protection as fixed effects. Table 1 shows the within-individual and between-individual variance component from the mixed model.

In MnU (both replaced and imputed), nearly all of the variance is within the individual, though there is greater total variance in the imputed sample (2.14 vs. 1.34). Like MnU, MnP also exhibits more variability within the individual (78.79%) than between individuals (21.21%); however not as starkly contrasted as in urine. Considering MnB, nearly all of the variability (93.69%) is between individual, with only 6.31% being within individual. Overall, this study represents the first time that variance components in MnU, MnP, and MnB have been explored. With the majority of variance being within-subject in MnU and MnP, a single sample would not be adequate to establish a mean value for a subject, and it would be difficult to determine if a change in MnP or MnU is due to exposure or just due to within-subject variation. Moreover, with the majority of variance being between-subject in MnB a single sample is likely to approximate a subject’s mean value, but it is difficult know if differences between individuals are due to exposure or between-subject variation. Future research looking at biomarkers of Mn, whether in relation to a health outcome or external exposure, require repeated measures so variance components can be assessed in relation to the outcome of interest.

Variance Components	In MnB		In MnP		In MnU*		In MnU**	
	Coefficient (SE)	%						
Within-subject variance	0.007 (0.001)	6.31%	0.052 (0.010)	78.79%	1.34 (0.248)	>99.9%	2.13 (0.888)	99.53%
Between-subject variance	0.105 (0.053)	93.69%	0.014 (0.011)	21.21%	<0.001 (<0.001)	<0.01%	0.011 (0.170)	0.47%
Total variance	0.111 (0.053)	--	0.111 (0.053)	--	1.34 (0.248)	--	2.14 (0.904)	--

*values under the LOD replaced with $0.038/\sqrt{2}$, then corrected for creatinine

**values under the LOD creatinine-corrected, then imputed using interval regression multiple imputation

Table 1: Variance components from mixed models using REML to estimate variances

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Photonic portable detection system to evaluate the oxidative potential of airborne nanoparticles and related oxidative stress in exhaled air

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Of the unintentional routes of human exposure to particulates, inhalation is considered the most significant (Afsset, 2010). The lungs are an efficient entry portal for a variety of gaseous and aerosol-transported molecules, providing a large surface area and thin epithelial barrier, in addition to extensive vasculature. Inhalation of nanoparticles has already been documented to induce oxidative stress associated with the development of a plethora of pulmonary and cardiovascular diseases. Recent studies have shown that oxidative potential of nanoparticles are a key parameter able to induce oxidative stress in exposed cells (Burello, 2011). Among the different (bio)markers of oxidative stress processes within the lungs, hydrogen peroxide (H_2O_2) is a main reactive oxygen species (ROS) target but efforts to standardize its detection in the exhaled air/EBC are needed.

In that context, we have developed a novel photonic system for the sensitive detection of H_2O_2 able to quantify both the oxidative potential of airborne nanoparticles and the H_2O_2 content in exhaled air. The core of the system relies on the following physical principle: multiple scattering occurring into porous material enables optical path elongation and thus absorbance enhancement (Suárez et al. PCT/IB2011/0558192011). Therefore, the functionalisation of a scattering random medium (e.g. glass fiber membrane or microbeads aggregates) with H_2O_2 -sensitive (bio)molecules such as cytochrome *c* or Fe(II)/orange xylenol (FOX) gives rise to detection devices with enhanced sensitivity (40-folds) and particularly low limit-of-detection at the nano-/sub-nanoMolar range (Suárez, 2013; Suárez, 2014). With the present system (Figure 1) the reactivity of a series of aerosolized nanoparticles can be determined (in H_2O_2 equivalents) leading to their classification. In another version, the aerosol is eluted into any solution of choice (e.g. different pH) and the assay reagents are added in-line between the elution chamber and the photonic sensor. Concerning the exhaled air analysis, the detection system is currently being validated in lab with the final objective of on-site sensitive measurements on exposed workers.

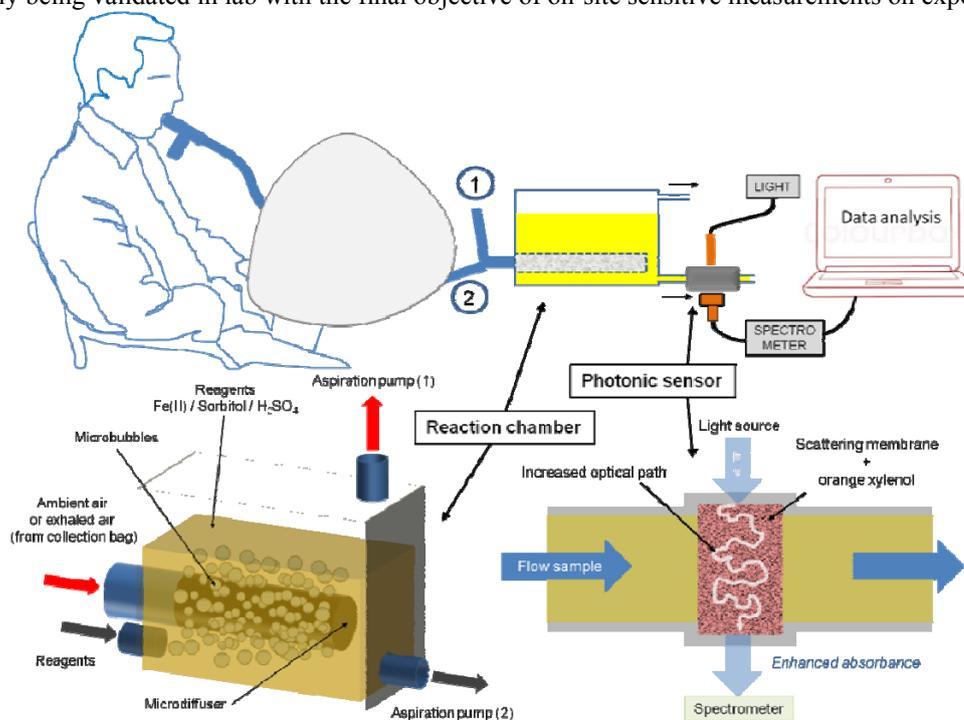


Figure 1. Schematics of the photonic portable detection system for on-line determination of either the oxidative potential of airborne nanoparticles (1) or oxidative stress in lung cells via the ROS present in exhaled air (2).

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Aniline exposure, methemoglobinemia and hemoglobin adducts

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The association between airborne exposure to aniline with the formation of methemoglobin (Met-Hb) and hemoglobin adducts (Hb adducts) in blood and the excretion of aniline in urine was studied in order to protect workers' health and contribute to exposure and risk assessment.

An 6-hr exposure of 2 ppm aniline (maximum exposure limit at the workplace in Germany) in 19 non-smoking volunteers (10 males, 9 females, 15 slow and 4 fast acetylators) resulted in a time-dependent increase of Met-Hb in blood up to 2.07%, total aniline in urine up to 418.3 µg/L and Hb-adduct levels of aniline in blood up to 18.04 ng/L. Maximum Met-Hb saturation was reached at the end of exposure with a mean saturation of $1.21 \pm 0.29\%$ (range 0.80-2.07%). Maximum aniline elimination was also observed at the end of exposure after 6 h with a mean level of 168.0 ± 51.8 µg/L (range: 79.5-418.3 µg/L). Maximum Hb adduct formation of aniline again was observed post-shift with 5.59 ± 4.02 µg/L (range: 0.74-18.04 µg/L).

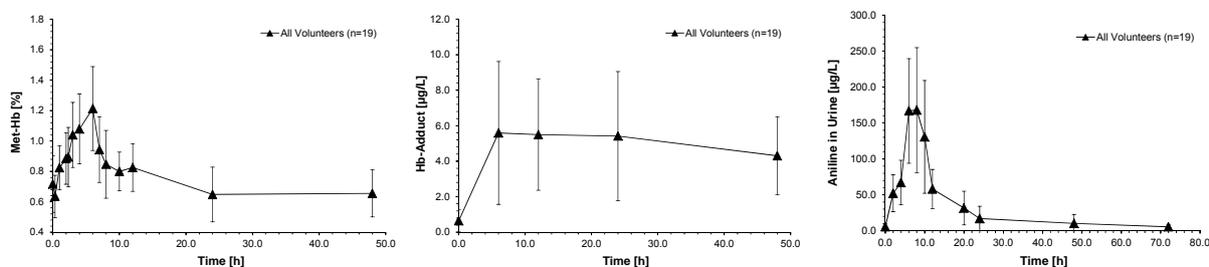


Figure 1. Time-dependent formation of Met-Hb (left) and Hb adduct (middle) in blood and aniline excretion in urine (right) in 19 volunteers at a constant full-body exposure of 2 ppm aniline for 6 h.

All biomarkers of exposure (Met-Hb saturation in blood, aniline in urine, Hb adduct of aniline in blood) were well below the corresponding current threshold limits for of aniline in Germany (Aniline in urine: 1,000 µg/L; Hb-Adduct of aniline: 100 µg/L; BMAS, 2013) or guidance levels by the MAK-commission of the Deutsche Forschungsgesellschaft (Met-Hb: 5%; DFG, 2007). In addition, Met-Hb saturation in blood and aniline in urine rapidly decreased after the end of exposure and ~24 h post exposure the levels were in the range of those observed prior exposure or non-exposed individuals. In line with the prolonged half-life of Hb adducts and the life span of erythrocytes in humans (120 d) the Hb adduct levels of aniline decreased more slowly. Overall, the results indicated no differences between males and females as well as between slow and fast acetylators for any of the biomarkers with the exception of a minor difference in Hb adduct levels of aniline between slow and fast acetylators with ~30% higher levels in slow acetylators in post-shift blood samples.

The results obtained after exposure of 6 h were also comparable to those observed in four non-smoking volunteers (all slow acetylators and non-smokers) after exposure of 8 h. There, maximum levels of Met-Hb and aniline in urine were 1.57% and 305.6 µg/L. Overall, our results contribute to risk assessment of aniline and protecting workers from aniline-derived adverse health effects at the workplace.

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Phthalate exposure in school children and their parents

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Keywords: chemical exposure; urine; phthalate metabolite; glucuronic acid; children

Phthalates, the diesters of phthalic acid, industrial chemicals widely used in commercial products, mainly plastics, but also cosmetics and pharmaceuticals, are classified as endocrine interferents and have been also associated with oxidative stress, cognitive disorders and obesity,; for these reasons the use of phthalates is regulated in the UE, but only for what concerns the content of six phthalate diesters in toys and other children products, according to the reception of 79/769/EEC.

Being phthalates ubiquitous pollutants, the sources of exposure are not only the mentioned commercial products but also food, water and air. School children (age 3–15) are especially susceptible to these toxicants as they are in the phase of both sexual and cognitive development.

The present study determined the urinary levels of 5 metabolites of phthalates, with and without the hydrolysis of the glucuronidated forms, in a group of 20 school children and to compare them to the urinary levels found in the urine of their parents in order to explore the possible differences both in the metabolic pattern and in the exposure sources.

Phthalate metabolites are excreted in the urine conjugated with glucuronic acid, and therefore an enzymatic hydrolysis is carried out before analysis to determine the total amount; the free fraction is determined without hydrolysis. The quantitative determination was carried out by HPLC-MS/MS with isotopic dilution for the following metabolites: the monoethylphthalate (MEP) for the diethyl phthalate (DEP), the mono (2-ethylhexyl) phthalate (MEHP) and mono (2-ethyl-5-hydroxyethyl) phthalate (MEHHP) for the diethylsilphthalate (DEHP), the mono butyl phthalate (MnBP) for the n-butyl phthalate (DNBP) and the mono benzylphthalate (MBzP) for the butyl-benzylphthalate (BBzP).

Table 1 and 2 show that children have urinary levels of MEP higher than their parents; they also present a higher free fraction of MEHP, indicating a lower rate of conjugation with glucuronic acid, and therefore a longer half life and a higher susceptibility to the effects of DEHP, one of the phthalates considered by 76/769/EEC.

Results stress the importance of performing phthalate exposure assessment studies in the school environments; it would be also desirable to limit the concentration of phthalates in products for schoolchildren.

Table 1: Parents

	MnBP	MEP	MBzP	MEHP	MEHHP
median	28.94	29.57	2.43	3.17	7.80
min	15.46	3.39	0.60	0.82	3.67
max	44.49	177.41	5.62	4.80	14.30
%free	7.68	75.66	N.D.	26.23	0.98

Table 2: Children

	MnBP	MEP	MBzP	MEHP	MEHHP
median	26.80	37.15	1.19	1.68	6.52
min	11.34	5.68	0.62	0.53	2.58
max	123.50	315.42	7.15	8.06	18.79
%free	9.75	73.86	N.D.	43.40	1.20

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Product emissions into indoor air: important factors for interlaboratory studies with emission test chambers

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Quality and trueness of results received from measurements are very important for all involved parties, producers and consumers as well; particularly if the results are used for acceptance of a product within a labelling or certification procedure. Over the last years BAM conducted several inter-laboratory studies with many German, European and further international laboratories. A focus was set on emission test chamber experiments and the connected analytical procedure for quantifying volatile organic compounds (VOC) in air. VOC have a dominating influence when applying the German AgBB scheme for health evaluation of building products. Therefore it is necessary to ensure that the results between the testing laboratories are comparable. The successful participation in round robin tests is often essential for the acceptance of results given by a laboratory.

Figure 1 demonstrates that many parameters can influence the results of emission chamber tests and of course the results of inter-laboratory studies. One of the main problems in these studies is the lack of a reference material. Therefore the organising institution of such an inter-laboratory study must select a suited material. This must be homogeneous which has to be stated with many complete chamber tests in advance. Within these tests several chambers, analytical equipment and operators should be included to get knowledge of the possible variation of the results. Some results of such a round robin test preparation will be given.

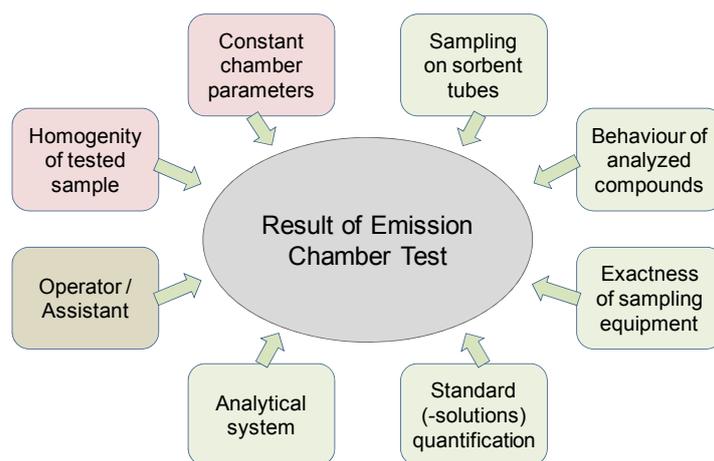


Figure 1. Parameters influencing emission test chamber results and the comparability of interlaboratory studies.

To overcome these problems we developed a candidate reference material within the EMRP-project MACPoll based on a lacquer which contains indoor air contaminants with a wide range of volatility. As analytes the five VOCs styrene, 2-ethylhexanol, N-methylpyrrolidone, dimethyl phthalate, n-hexadecane and also the two SVOCs dibutyl phthalate and lindane were selected.

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Identification of work-related exposure to carcinogenic substances in Germany

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Keywords: carcinogenic substances, tolerance concentration, acceptance concentration, database MEGA

Occupational exposures to carcinogenic substances like benzo[a]pyrene, ethylenoxide, trichlorethene or butadiene occur in variety fields of industry. The risk strategy for carcinogenic substances in Germany entails a system for assessing hazards due to exposure at the workplace.

Substance-specific concentration values were determined to which a certain risk of contracting work-related cancer as a result of exposure on a day-to-day basis at work is assigned. Below an acceptance concentration, exposure is deemed acceptable; above a tolerance concentration, it is no longer deemed tolerable. Ranges of low, medium and high risk can thus be distinguished and subsequently linked to measures for minimization of the exposure which are not specific to a particular substance.

Under the German Code of Social Law (SGB) and in the framework of prevention IFA organises the measurement system for exposure assessment – MGU. It provides and documents valid and quantifiable measurement data and associated company data on inhalative exposure. The data recorded in the MGU are documented in the MEGA exposure database.

By comparing the substance-specific acceptance or tolerance concentrations with data from the MEGA exposure database it is possible to identify workplaces at which employees are exposed to a higher than the accepted risk of contracting occupationally induced cancer.

For these four substances the table shows the distribution of the measured values in percent in the low (light grey), medium (medium grey) and high (dark grey) risk ranges.

	Benzo[a]pyrene	Ethylenoxide	Trichlorethene	1,3-Butadiene
Number of measured data, total	2.193	223	624	257
Number of measured data with high risk (measurement value > tolerance concentrations in %)	20.0	21.5	40.5	0
Number of measured data with average risk (tolerance concentrations \geq measurement value > acceptance concentration in %)	11.8	35.0	9.9	0.4
Number of measured data with low risk (measurement value \leq acceptance concentrations in %)	6.2	25.6	45.7	0
Not allocated measurement values in %	62.0	17.9	3.9	99.6

For benzo[a]pyrene 662 measured values lie above the analytical limit of detection, 246 of these in the medium-risk range, 414 in the high-risk range. Only 132 measured values can be clearly assigned to low-risk exposure. In contrast, for 1,3-butadiene all measured values with just one exception lie below the analytical limit of detection. The performance of measurements in the range of the acceptable concentration presents problems.

Further selections and evaluations according the sector of industry and the working area (with and without local exhaust ventilation) show that over 50 % of the values measured in each case for ethylene oxide and trichlorethene are above the respective acceptance concentration. In many cases, the tolerance concentration is exceeded by the 75th or even the 50th percentiles of sectoral groups or groups of working areas.

Airmon

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Session 11:

Exposure modeling

Chair:

Raymond Vincent - INRS, France

Peter Görner – INRS, France

Plenary lecture

Measurement of occupational exposure to airborne chemical agents: which type of strategy?

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The development of methods of sampling and analysis of chemical agents in the air of workplaces boomed after World War II. Advances in electronics and miniaturisation have enabled the design of portable, reliable and robust sampling devices such as controlled flow sampling pumps which are essential tools for measuring exposure to chemical agents in the workplace (Cherrie, 2003). At the same time, analysis techniques have improved in terms of quantification limits, precision and selectivity. Many works and studies have improved methods for measuring particles, gases and vapours taking into account the parameters that can influence the measurement results such as air conditions, humidity and the simultaneous presence of several chemical agents in the workplace air. Many organisations worldwide have developed validated sampling and analytical methods to measure the concentrations of agents to which workers are exposed when they breathe the air in their workplaces. Standardisation work carried out by working groups at national level, at European level in CEN and internationally within the ISO gives rise to a wide range of techniques and methodologies for assessing exposure related to the use of chemicals during work activities. The primary objective of these exposure measurements is to protect workers from irreversible damage to their health (Harper, 2004).

The occupational exposure limit values (OELs), whether regulatory or indicative, exist for that purpose and to prevent the outbreak or occurrence of occupational diseases and injuries among exposed workers. These threshold limit values (TLV) are defined as the time-weighted average concentrations (TWA) not to be exceeded over a period of time, also called reference period, which is 8 hours (TLV-TWA-8h) for the effects on long-term health and 15 minutes for acute effects (TLV-STEL: TLV Short-term exposure limit). For long-term effects such as carcinogenic effects, this means that the exposure of each worker, for each working day (210 days / year) and throughout his working life (40 years) must not exceed the TLV-TWA-8h for a given chemical agent. While for some hazards such as ionising radiation, it is possible to measure the exposure of each worker for each day worked, in the case of chemical agents this approach is not applicable mainly for technical and economic reasons. When the objective of the measurements is to ensure that worker exposure does not exceed the OEL, it is necessary to establish a sampling strategy that will define the number and duration of measurements, the number of workers to be monitored, etc. The first document describing this sampling approach was published by NIOSH in the late 70s (Leidel *et al.*, 1977). This comprehensive document stressed the need to make measurements representative of worker exposure, taking individual samples during the entire duration of the shift from several workers randomly selected from a homogeneous exposure group (HEG). It also underlined the need to prepare each intervention and to collect during the survey all the information needed to interpret the results of the exposure measurements. Due to the variability of workers' exposure, compliance with OELs is estimated by assuming a log-normal distribution of the exposure measurements.

Since that time, many studies have investigated the sources of variability of occupational exposure and the methods for obtaining reliable and representative measurements of worker exposure for a HEG (Rappaport, 1991; Kromhout *et al.*, 1993). This work was the basis for the development of sampling strategy standards such as EN 689 in 1995, guides such as the 2011 BOHS guide to report writing, and regulation that was adopted in France in 2009.

The assessment of occupational exposure to chemical agents based on expert judgment can never be a substitute for measurements by sampling and analysis of workplace air: how to estimate compliance with an OEL of a few micrograms per cubic meter of air? The development of reliable and accurate methods of sampling and analysis is a long and expensive process. These methods for measuring workers' exposure to chemicals must be used in an equally rigorous framework to obtain representative measurements. The margin for progress in this area is still significant and the application of the sampling strategy, and in particular the quality of the measurement tools, must be taken into account. The sampling strategy should not be the Achilles heel of the measurement of occupational exposure to chemical agents.

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Emission profiles characterization for hand-held wood working machines

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There is a clear need of characterizing and evaluating wood dust emission profiles from wood working machines in order to predict potential exposure peaks and to ensure the safety of workers. Indeed, wood dust is classified as a well known carcinogen [1]. Moreover, in the occupational population of the 25 member states of the European Union, around 3.6 million workers were exposed to inhalable wood dust [2]. In order to limit the exposure of workers to excessive dust, the European directive 98/24/CE has fixed the Occupational Exposure Level (OEL) to $5\text{mg}\cdot\text{m}^{-3}$. This directive has been transcribed into French law in 2003 declaring that the OEL would be lowered down to $1\text{mg}\cdot\text{m}^{-3}$. Among the common wood dust emission sources, the most emissive are by far hand-held electrical wood working tools, such as sanders, routers and circular saw. In the majority of cases, the dust collecting systems are not dimensioned properly; therefore, the wood dust is not well collected [3-4]. Accordingly, we are currently developing a method that should allow characterizing the emission profiles from wood working machines, so as to classify the machines with respect to their emission potential.

The evaluation procedure of wood dust emission is based on the use of a mathematical algorithm called "inversion algorithm" which allows reconstructing the emission rate by means of measurements taken at different working environment points. This procedure includes two distinct steps. The first phase consists in determining the parameters of the inversion model by using a known source of dust and corresponding concentration measurements. In the second phase, the unknown source is reconstructed by inverting the model, with corresponding concentration measurement.

After presenting the source-estimation method, this paper discusses two important approaches related to its development. The first one deals with the automatic determination of optimal positions for the sensors. The second one concerns the experimental validation of the method and the investigation of the robustness of the inversion algorithm.

[1] Poussières de bois - Prévenir les risques – INRS, ED 974.

[2] Occupational Exposure to Inhalable Wood Dust in the Member States of European Union – Kauppinen et al (2006)

[3] Focus on BIA's work - N°0047 - Hand-held motor-operated electric woodworking tools 11/2003.

[4] Evaluation des performances de captage de trois types de machines à bois portatives – INRS, ND2321 - 218-10.

Modeling of exposure of welders to welding fumes: comparison of predicted concentrations with field measured concentrations.

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A predictive model for assessing the exposure of welders to welding fumes has been developed as a mutual project of employers in the metal product industry and unions. Statistical analysis of a large database of welding measurements from the period 1983–2003 identified significant determinants of exposure; welding technique, local exhaust ventilation, respiratory protective equipment, enclosure of work, additional grinding work, welding on a clean metal surface, instructions for safe welding and the personal aspect: hygienic behaviour of the welder. The algorithm of the initial predictive model (name: VBC lasrook) was build on these determinants. Pre-requisite for valid prediction was a certain minimum of general ventilation of the workroom (< 800 m³/h per welder).

In order to assess the accuracy of the predicted exposure of the model measurements were performed in 24 companies (ship building and metal construction) in the period 2011 - 2013. Personal air samples of inhalable welding dust in the helmet of the welder were taken and the working conditions, welding techniques and protective measures of welders were recorded on a standardized list/questionnaire. The average measured level of exposure was 2.9 mg/m³ (as AM) and 1.6 mg/m³ (as GM)

In total measurements of 170 welders were available of which all contextual information was present that was needed for the prediction of the exposure level (resulting in 170 pairs of measured and simultaneously modelled concentrations. The measured average concentration was AM = 3.2 mg/m³ and GM = 1.9 mg/m³ and the predicted average concentration with the initial model was AM = 0.9 mg/m³ and GM = 0.7 mg/m³.

Figure 1. Frequency distribution of measured concentrations of welding fume (= PAS lasrook), predicted concentration with the initial model (VBC lasrook) and predicted concentration with the adjusted model (VBC 2014 variant 2). The log-normal fit is added to each of the three distributions.

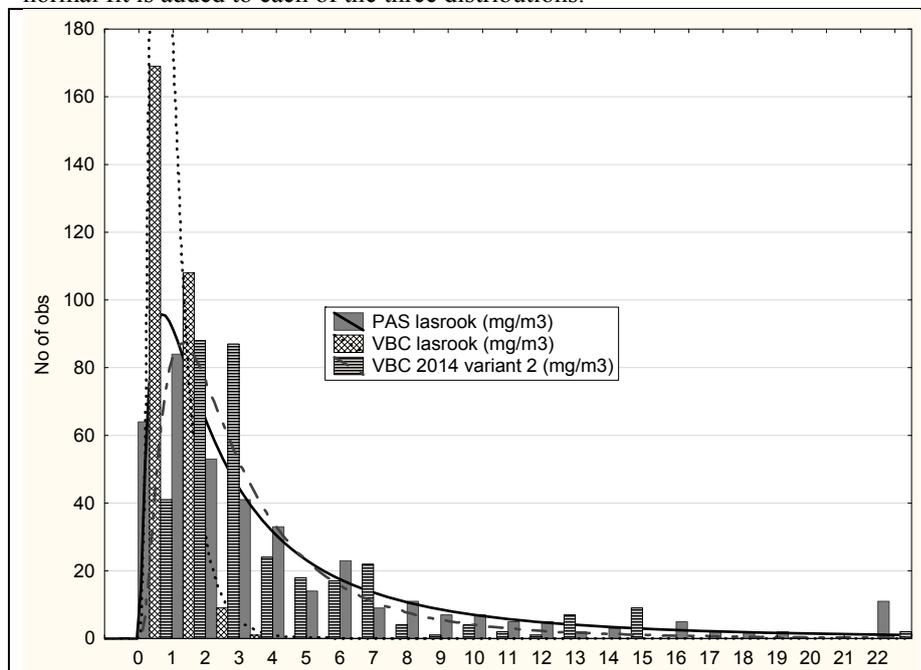


Figure 1 shows the frequency distribution of measured and the predicted concentration welding fume. It shows that the average predicted concentration is lower than the measured concentration. Also, that the variation of measured concentration is much larger than the predicted concentration. It appeared that the initial model was not yet sufficient accurate to predict the level of exposure of a welder.

Statistical re-analysis of determinants of exposure was done with the measurements of 2011-2013. It showed that local exhaust ventilation (i), confined space (ii) and high quality RPE (iii) such as welding helmets, class TH2 and TH3, were

factors that significantly determine the exposure to welding fume. Based on these results, the algorithm of the predictive model was adjusted. The predicted average concentration with the adapted model (name: VBC 2014 - variant 2) was AM = 2.3 mg/m³ and GM = 1.9 mg/m³. The frequency distribution of the adjusted-model-predicted concentrations is added to figure 1 (= VBC 2014 - variant 2). This predicted distribution fits quite well to the measured distribution (= PAS lasrook). The performance of the adjusted model VBC 2014 – variant 2 allow the use as a screening tool for welder exposure assessment.

Modeling patterns of occupational exposure to formaldehyde for chronic health risk assessment

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Keywords : formaldehyde, risk assessment, inhalation exposure, modeling

Introduction and aims: formaldehyde (FA) is an irritative and carcinogenic pollutant frequently encountered within workplaces such as laboratories or sanitary structures. Its irritative properties can contribute to both short-term effects but also to chronic nasopharyngeal cancer due to a specific threshold mechanism of action. It is thus of high importance to monitor both short-term and long-term exposures in order to correctly assess chronic health risks, which wouldn't be necessary for many other pollutants. The large variability of working conditions observed within workplaces often preclude a systematic monitoring of all exposures. Our aim was to develop an approach based on individual trajectories of exposure (i.e., using workers activity / location data and exposure patterns) to formaldehyde to model health risk for laboratory workers.

Materials and Methods: 12 workers from a pathology lab were observed over a 1-year period in order to characterize the frequency / duration of all tasks and the associated locations of the workers during these tasks, as illustrated in Fig 1. Simultaneously, 4 to 8 individual as well as few ambient air monitorings were performed during each pollutant task in order to determine both near-field (NF) and far-field (FF) exposure profiles to formaldehyde in the lab. Daily and monthly patterns of polluting tasks per job were constructed and a two-zone model was used to model chronic inhalation exposures to formaldehyde and associated hazard quotients (HQ) using 0.2 ppm as threshold value (TLV).

Results: 7 polluting and 6 non-polluting tasks were identified as relevant for the health risk assessment. Tasks durations ranged from 5 minutes to several hours and their frequency ranged from once a month to several times a day. Air monitoring revealed frequent high short-term exposures (up to 5 ppm) to formaldehyde but much lower 8-hr averaged exposures in the majority. A one-month period was identified as relevant for modelling chronic risks to formaldehyde in this lab, based on observed activities per job. Distribution of the modeled risk is illustrated in Fig 2 for two jobs. We found 3 jobs (pathologists and residents) associated with higher risks (median HQ: 0.3, mean TLV exceedance probability = 16%) whereas the 6 other jobs were with lower risks (median HQ: 0.02 to 0.14, mean TLV exceedance probability from <0.1% to 3.5%).

Conclusion: We have developed a risk assessment approach based on individual trajectories of exposure integrating the combined use of detailed description of working conditions and patterns of inhalation exposures in a probabilistic exposure model. This method has turned out useful for assessing long-term risk to formaldehyde resulting from repeated short-term exposures in complex environments where systematic air monitoring is impossible or not fully representative.

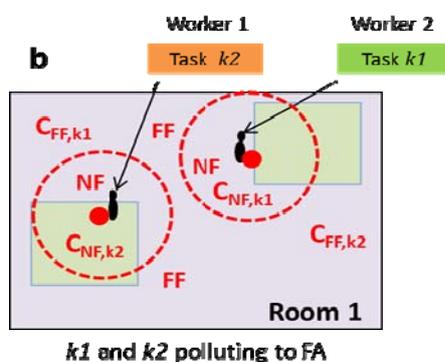


Fig.1. Illustration of simultaneous polluting tasks.

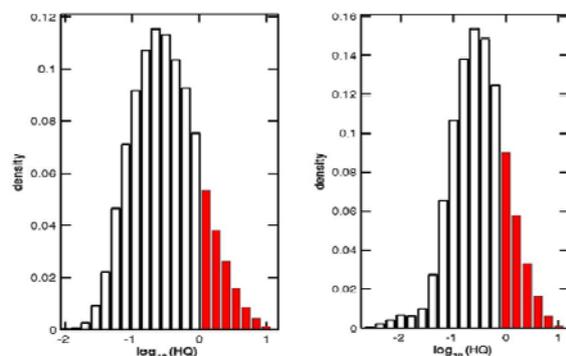


Fig.2. Distribution of HQ modelled for two jobs.

Use of the MEGA database for the validation of determinants of exposure to welding fume derived from the WELDOX study

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Welding joins metal pieces by intense heat. The exploration of potential determinants of the wide range of welding-fume concentrations is an important step towards prevention of welders from the health hazards of welding fumes. WELDOX was conducted as a cross-sectional study in welders from different German industries. Concentrations of respirable and inhalable welding fume were measured in the breathing zone of 241 welders. A statistical model has been developed to assess potential determinants of exposure to respirable welding fume (Lehnert *et al.*, 2012). Welding process, welded material, working in confined space, and local exhaust ventilation (LEV) were significant predictors. In this presentation we want to present a validation of the “WELDOX model” with data from the German exposure database MEGA.

Concentrations of welding fume from personal measurements were retrieved from the MEGA database with auxiliary data on potential predictors according to WELDOX. Variables for the welded material and the quality of local exhaust ventilation had to be derived by extracting textual information and categorization according to the WELDOX formats with expert judgment. We compared the geometric means of measured values for combinations of determinants with the predicted concentration using the WELDOX parameter estimates for these determinants.

We compiled 1,710 personal measurements of respirable welding fume from the MEGA database. Information on welding in confined space was frequently missing. Tungsten inert gas welding (TIG) was confirmed as associated with lower exposure levels than gas metal arc welding (GMAW). The predicted values derived from the WELDOX model were only slightly lower than the geometric means from MEGA data. For the scenario ‘GMAW, mild steel, no confined space, no LEV’ (n=93) the MEGA average was 12% higher than estimated with the WELDOX model, for another typical scenario ‘TIG, stainless steel, no confined space, no LEV’ (n=38) the MEGA average was 17.5% higher.

The MEGA database is a valuable resource for exposure modeling. We could demonstrate a good performance of the WELDOX model derived in 241 welders when compared with measurement data from MEGA on respirable welding fume. The slightly lower concentrations of welding fume of the predicted values with the WELDOX might be explained by a better assessment of confined space and efficient LEV. MEGA has information on the existence of LEV but not its efficiency. Further, confined space was not systematically documented. Statistical modeling offers the possibility to quantitatively assess determinants of exposure to welding fume for purposes of prevention. Substitution of high-emission techniques and efficient LEV can reduce exposure to welding fumes where applicable.

Lehnert *et al.* Ann Occup Hyg. 2012 Jul;56(5):557-67.

Short courses

Tuesday, 17 June

18:40 to 20:00	<i>SC1 - Short courses in parallel</i>
	Molecular methods to characterize airborne microorganisms <i>Anne Oppliger-Goudet, IST (CH) - Philippe Duquenne, INRS (F)</i>
	Generating, filtering and sampling semi-volatile aerosols <i>Benjamin Sutter INRS (F)</i>
	NIOSH aerosol sampling methods <i>Martin Harper, NIOSH, (US)</i>

Wednesday 18 June

14:50 to 16:10	<i>SC2 - Short courses in parallel</i>
	Sampling and analytical method validation <i>Kevin Ashley, NIOSH, (US)</i>
	Solvent-free desorption and extraction. <i>Eddy Langlois, INRS, (F)</i>
	Biomonitoring of organic compounds <i>Jaroslav Mraz, SZU, (CZ)</i>

Short courses in parallel: Tuesday, 17 June, 18:40-20:00

Molecular methods to characterize airborne microorganisms

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Numerous analytical methods are available for studying microbial aerosols. During the past decades, a strong interest toward the development of methods involving the use of microbial DNA (RNA) has emerged. These molecular tools identify and quantify microbial populations in bioaerosol samples. The aim of this short course is to provide an overview of these currently used techniques, mainly focusing on PCR (Polymerase Chain Reaction) and quantitative PCR. After a brief methods description, discussions on the advantages and drawbacks and points on some critical aspects will follow. For instance, the DNA extraction efficiency (or RNA for some viruses), the inclusion of an internal positive control and the choice of standard curve are important steps to consider when setting up robust PCR protocols. The presentations include concrete examples illustrating the utility of main available methods. The suitability of sampling methods and strategies for DNA analysis will be tackled. This interactive course is dedicated to current or future users and is expected to be a forum for sharing experiences and opinions.

Generating, filtering and sampling semi-volatile aerosols

Benjamin Sutter

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Semi-volatile aerosols are defined differently for different specialities. In occupational hygiene, examples of organic compound families considered as semi-volatile include pesticides, cutting fluids, bitumen fumes, and nitrosamines. This short course will be developed in four parts to review the specific problems related to semi-volatile compounds. We will present the bases of evaporation theory applied to the case of semi-volatile compounds. Building on this theoretical background, discussion will lead to a proposed definition. The second part will explore the ways in which this type of aerosol is generated in the workplace atmosphere based on real-life examples. Then, filtration of semi-volatile aerosols will be theoretically and experimentally addressed, comparing expected and experimental behaviour. Finally, sampling strategies and samplers appropriate for use with semi-volatile aerosols will be discussed.

NIOSH Aerosol Sampling Methods

Martin Harper

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The US National Institute for Occupational Safety and Health (NIOSH) publishes a Manual of Analytical Methods to support quantitative exposure assessments in occupational hygiene. Many of these Methods are for the assessment of aerosols. Sampling for aerosols is fundamentally different from sampling gases and vapors as there is a size-selection component in the health-related assessment of aerosols. Much additional information, which qualifies the individual methods, is available in the Chapters of the manual, particularly Chapter O: Factors Affecting Aerosol Sampling, but also Chapter R: Determination of Airborne Crystalline Silica, Chapter L: Measurement of Fibers, and so on, and failures to appreciate these Chapters have led to misunderstandings of the individual Methods. In particular, there has been considerable confusion with respect to the NIOSH paradigms regarding inhalable, thoracic and respirable size-fraction sampling. Guidance will be provided on appropriate procedures, which are consistent with the Methods. In particular, issues of aerosol deposition within the sampler and on the filter will be discussed. One way to achieve lower detection limits for respirable crystalline silica in air samples is to increase the volume of air sampled, which, for a fixed time-period, means higher flow-rates. However, the performance of size-selective samplers is a function of the flow-rate, so an appropriate sampler must be selected. Several samplers have been tested for collecting respirable fractions at higher flow-rates. These will be described, together with the factors that must be considered in selection. Work on a novel nanoparticle airways deposition sampler will also be presented.

Short courses in parallel: Wednesday, 18 June, 14:50-16:10

Sampling and analytical method validation

Kevin Ashley, Ph.D.

NIOSH - National Institute for Occupational Safety and Health, US Department of Health and Human Services, Centers for Disease Control and Prevention, Cincinnati, Ohio 45226-1998, USA

Sampling and analytical methods that are used globally for conducting occupational exposure assessment to hazardous substances include those promulgated by governmental agencies and voluntary consensus standards organizations. In the United States, the National Institute for Occupational Safety and Health (NIOSH) has the responsibility to carry out research on suitable sampling and analytical methods which, when fully validated, are published in the NIOSH Manual of Analytical Methods (NMAM). The methods published in the NMAM are developed, evaluated and validated in order to provide standardized, harmonized protocols for making valid occupational exposure measurements for a wide variety of hazardous substances. NIOSH has published guidelines that describe the experiments necessary to validate occupational exposure assessment methods (Kennedy et al., 1995). These guidelines form the basis for NIOSH sampling and analytical methods and have been applied to myriad chemical agents. The NIOSH guidelines are consistent with applicable validation protocols established by voluntary consensus standards organizations such as ASTM International, the Comité Européen de Normalisation (CEN) and the International Organization for Standardization (ISO). New NIOSH guidance on the evaluation of direct-reading monitors is also available (NIOSH, 2012).

This short course will provide an overview of the procedures used by NIOSH to estimate the precision, bias and accuracy of a candidate sampling and analysis method. For a particular analyte of interest, considerations must be given to a number of factors that can affect overall method accuracy, which is a measure of the method uncertainty. Main factors to consider include: (a) selection of appropriate sampling media; (b) investigation of analytical methods that are fit-for-purpose; (c) assessment of sampler capacity; (d) evaluation of sample stability; (e) studies of sample preparation methods; (f) investigation of environmental effects and experimental conditions, and (g) ruggedness assessment of the overall sampling and analytical method. Besides in-house experimental protocols, interlaboratory evaluations and field investigations are also addressed as key parts of thorough validations. Application of the NIOSH guidelines protocol to newly-promulgated methods evaluated and published recently will be illustrated.

Solvent-free desorption and extraction.

Eddy Langlois

INRS, Institut National de Recherche et de Sécurité, 54519 Vandoeuvre lès Nancy, France

Air pollution with volatile organic compounds is assessed by conventional sampling methods based on trapping the compounds on porous sorbent and desorption prior to analysis. In the most basic methods, non-polar compounds are trapped on activated charcoal and desorbed with solvents.

This course will review alternative, solvent-free, desorption methods. The first of these to be investigated in recent decades was thermal desorption. As thermal desorption is almost completely inefficient with charcoal, porous polymers and resins must be used for trapping. These supports are incompatible with solvent desorption because they are soluble in some solvents. Thermal desorption with these resins is especially efficient for polar compounds. Today, thermal desorption offers good results when qualitatively and quantitatively assessing pollution, but this analytical method presents some limitations that prevent its use in all situations.

Microwave-assisted thermal desorption will also be discussed. With this technique, microwaves are focused on the sample to provide the sorbent with sufficient energy to allow complete desorption. In this way, poorly volatile substances can be efficiently desorbed from charcoal. The main drawback with this technique is that it requires the use of ceramic tubes and small quantities of sorbent due to the size of the spot of microwave energy focused on the sample.

Finally, supercritical CO₂ (scCO₂) for desorption of any pollutant on any sorbent will be discussed. ScCO₂ is particularly efficient, but we must now tackle how the extraction and analytical devices can be coupled.

Biomonitoring of occupational exposure to organic compounds

Jaroslav Mráz

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Analysis of ambient air and biomonitoring are two complementary approaches to assess human exposure to chemicals in the workplace. Whereas the most critical and carefully controlled step in the analysis of airborne chemicals is sampling, uptake of a chemical by the organism followed by its distribution, metabolism and excretion are natural processes subject to significant biological variability. Then, the science and art of biomonitoring focus mainly on the selection of a suitable biomarker, sample work-up procedure, and results interpretation. These three aspects of biomonitoring will be dealt with in the short course, with an attention to organic compounds.

Depending on physico-chemical properties resulting from their structure, various organic chemicals may circulate in the body, be deposited in some tissues, be rapidly eliminated unchanged, undergo metabolic conversion to a single predominant metabolite or a range of products. Elimination half-times of various forms of a chemical in the body may differ from minutes to months. Thus, criteria underlying the choice of the biomarker and sampling time will be discussed.

Modern analytical methods based on gas or liquid chromatographic-mass spectrometric instrumentation are in most cases sufficiently sensitive and selective to detect biomarkers of interest in body fluids or tissues. However, the sample work-up is still critical to protect instruments from contamination by the matrix components, reduce matrix effects, enable or enhance detectability of the analytes by chemical derivatization, etc. In this short course, current approaches to sample analysis in biomonitoring will be demonstrated.

An important part of biomonitoring is interpretation of measured values in the terms of health risk. Biomarker levels depend not only on the magnitude of the exposure but may be affected by other factors such as individual metabolic capacity or co-exposure to other chemicals. Increased levels of a biomarker of exposure or that of biochemical effect do not necessary mean any damage to the individuals' health, but a possible association with health on a group basis has to be considered. In this context, the existing concepts of biological exposure limits as health protection tools will be presented.

POSTERS

<i>Session A - Sampling and measurement of aerosols and bioaerosols</i>	
A01	The Respicon aerosol sampler/monitor: improvements for the second version <i>C. Möhlmann, J. Haus, W. Dunkhorst, H. Lödding, W. Koch</i>
A02	Endotoxin deposits on the inner surfaces of closed-face cassettes during bioaerosol sampling: a field investigation at composting facilities <i>P. Duquenne, X. Simon, V. Demange, M. Harper, P. Wild</i>
A03	Sampling efficiency comparison of four bioaerosol samplers and two particle counters <i>A. McDonagh, C.J. Noakes</i>
A04	A method for sampling and analysis of wood dust <i>M. Harper, M.M. Chirila</i>
A05	Sampling bacteria in metal working fluids <i>A. Dahlman-Höglund, Å. Lindgren, M. Andersson, I. Mattsby-Baltzer</i>
A06	Particulate air pollution in six cities in Indonesia <i>M. Santoso, D.D. Lestiani, S. Kurniawati, E. Hamonangan, M. Rita, Hari Wahyudi, Tamrin, Sukadi, Nurkholik, V. Nurul, Triyambodo, Rully Fatwani</i>
A07	Use of a passive badge for sampling asbestos among building finishing workers <i>C. Eypert-Blaison, A. Roméro-Hariot, S. Veissière, L. Fréville, M.C. Starck, F. Clerc, P. Wild</i>
A08	Complementary use of conventional and molecular methods to assess fungal contamination in occupational settings <i>C. Viegas, A. Q. Gomes, J. Malta-Vacas, R. Sabino</i>
A09	Measurement of electrical charges on airborne bacteria generated using a single-pass bubbling aerosolizer <i>X. Simon, S. Bau, P. Duquenne</i>
A10	Efficiency of cleaning procedures in reducing fungal contamination in one waste-sorting plant <i>C. Viegas, E. Carolino, R. Dias, T. Faria, M. Menezes, S. Viegas</i>
A11	Testing of a new sampling procedure for airborne allergens in the workplace atmosphere <i>A. Kolk, A. Riethmüller, H. Holbach, G. Schneider, M. Raulf, H. J. Hillen, I. Sander, U. Stephan, E. Zahradnik</i>
A12	Influence of operating conditions on composition of particulate matter emissions from residential combustion <i>E.D. Vicente, M.A. Duarte, A.I. Calvo, T.F. Nunes, C.A. Alves</i>
A13	Development of a respirable miniCyclone for use with the headset mounting arrangement <i>G. Lidén, A. Gudmundsson, P. Berg</i>
A14	Aerosol physical properties from tire wear <i>C.A. Alves, D. Baumgardner, A. Calvo, A. Vicente, M. Gustafsson</i>
A15	Sources of particulate matter in OPORTO during 1 year of measurements: local versus distant sources of black carbon <i>M. Tomé, C.A. Alves, M. Duarte, T. Nunes, C. Pio, P. Fialho</i>
A16	Characterization of soot particles in aluminium smelters by transmission electron microscopy <i>N. Benker, K. Kandler, A. Skogstad, D.G. Ellingsen, B. Berlinger, Y. Thomassen, S. Weinbruch</i>
A17	Bioaerosol monitoring at subtropical locations <i>G. Engling, S. Jiang, P. Lin</i>
A18	Measurements of organic and elemental carbon in downtown Rome and background area: physical behavior and chemical speciation <i>P. Avino, M. Manigrasso, A. Rosada, A. Dodaro</i>
A19	Environmentally controlled chamber for bioaerosol modeling and aging studies <i>D. Verreault, C. Duchaine, M. Marcoux-Voiselle, N. Turgeon, C.J. Roy</i>

Session B - Nano-aerosol sampling and measurements

B01	Ultrafine particles emitted by thermal spraying of metals <i>V. Matera, D. Bémer, Y. Morele, J.M. Elcabache</i>
B02	Evaluation of the emission of ultra-fine particles from laser printers in office environments - a pilot study <i>G. Castellet Y Ballarà, E. Incocciati, M. Mecchia</i>
B03	A new methodology for determination of airborne nanoparticle effective density with the tandem DMA-ELPI based on multiple charging correction <i>S. Bau, D. Bémer, F. Gripari, J.C. Appert-Collin, D. Thomas</i>
B04	Determining the count median diameter of nanoaerosols from their number and lung-deposited surface area concentrations <i>S. Bau, O. Witschger, F. Gensdarmes, D. Thomas</i>
B05	Passive sampling of particle-bound PAH and O-PAH: linking detectability and high sample throughput with ATD-GC-MS <i>K. Arnoldsson, L. Häggglund, R. Magnusson, C. Lejon, K. Svensson, H. Wingfors</i>

Session C - Chemical speciation and Semi volatile organic compounds sampling and analysis

C01	ECOS-POUSS: a nationwide survey of semi-volatile organic compounds in home settled dust <i>C. Mandin, F. Mercier, J-P. Lucas, O. Ramalho, O. Blanchard, N. Bonvallot, G. Raffy, E. Gilles, P. Glorennec, B. Le Bot</i>
C02	ECOS-PM: a nationwide survey of semi-volatile organic compounds in indoor air <i>C. Mandin, F. Mercier, J-P. Lucas, O. Ramalho, O. Blanchard, N. Bonvallot, P. Glorennec, B. Le Bot</i>
C03	Organic components in particulate matter from cooking <i>C.A. Alves, S. Rocha, R. Moreira, A. Vicente, M. Duarte, T. Nunes</i>
C04	Emission factors for road traffic from a tunnel study <i>C.A. Alves, J. Gomes, T. Nunes, M. Duarte, A. Calvo, D. Custódio, C. Pio, A. Karanasiou, X. Querol</i>
C05	Structural characteristics of ambient aerosols in an indoor university gymnasium <i>C.A. Alves, R. Fraile, A. Castro, A. Isabel Calvo, B. Artíñano, E. Coz</i>
C06	Particles from the interaction between pavement and tyres <i>C.A. Alves, A. Vicente, A. Calvo, C. Monteiro, S. Rocha, M. Gustafsson</i>
C07	Determination of manganese valence states in some typical welding fumes by synchrotron-based XANES spectroscopy <i>G. Lidén, L. Lundgren</i>
C08	Chemical characterisation of exhaust particles emitted by light-duty vehicles <i>C.A. Alves, S. Rocha, C. Barbosa, A. Calvo, T. Nunes, M. Cerqueira, A. Karanasiou, X. Querol</i>
C09	A multi-residue method for the simultaneous analysis of several classes of semi-volatile organic compounds in airborne particles <i>F. Mercier, E. Gilles, G. Raffy, P. Glorennec, C. Mandin, B. Le Bot</i>

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D15	Measurement strategy of atmospheric particulate matter in operational conditions <i>A. Gollion-Evrard, G. Crehange, J-U. Mullot</i>
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Airmon

15-19 June 2014

Marseille, France

***Session A - Sampling and measurement of
aerosols and bioaerosols***

The respicon aerosol sampler/monitor: improvements for the second version

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The Respicon aerosol sampler and monitor is a well-known instrument to determine workplace aerosol concentrations of the inhalable, thoracic and respirable dust fractions. Because of the current decrease of dust limit values, an improvement in personal air monitors was seen necessary in order to be able to determine dust concentrations well below 1 mg/m³. The Respicon was chosen because of its unique characteristics.

The improvements of the Respicon were on the one hand realised by doubling the air flow to 6.2 l/min and on the other hand by integrating more sensitive light scattering photometers. With help of a powerful personal air pump (SG 10-2 from GSA, Neuss, Germany) a new set of virtual impactors and critical orifices was developed to allow air flows of 5.32 l/min for the respirable fraction, 0.66 for the middle stage and 0.22 for the third stage collecting the larger particles. Performing only weighing of the dust loads on the filters, the limit of detection for the respirable fraction will be 0.47 mg/m³ for 2 h sampling and 0.11 for 8 h, using a minimum weight difference of 0.3 mg.

A new data logger will support electrical energy and display and store measurement data (Fig. 1). The photometers were changed by integrating more powerful laser diodes together with high sensitive photo diodes. They were tested for parallel performance, temperature drift, long term performance and dependency on kind of dust. The sensitivity of the photometer of the old Respicon with 3.1 l/min ranges between 5 and 34 mV/mg/m³ for the respirable fraction, depending on the kind of dust (Koch et al. 1999). The sensitivity was increased up to 140 to 430 mV/mg/m³ depending on particle size and refractive index, with mean values between 200 and 350 mV/mg/m³ for the five dusts tested (Fig. 2). The temperature drift mainly determines the limit of detection which is seen well below 10 µg/m³.

Further tests are ongoing to reach all desired characteristics and a launch on the market in near future.



Figure 1. Respicon with 6.2 l/min and new data logger

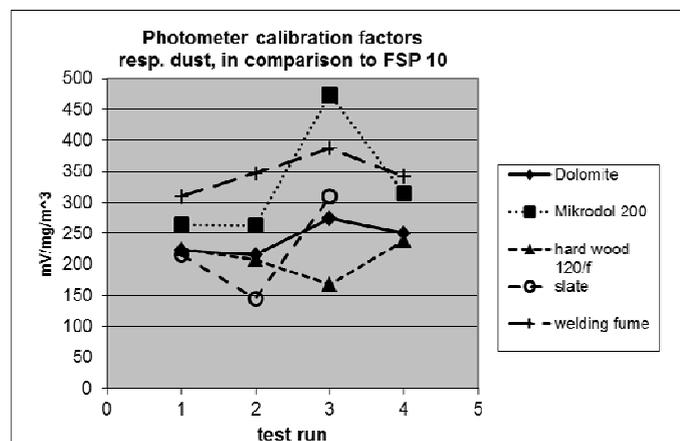


Figure 2. Photometer calibration factors for different dusts

Koch, W., Dunkhorst, W. & Lödding, H. (1999): Design and Performance of a new personal Aerosol Monitor, *Aerosol Science and Technology*, 31:231-246.

Endotoxin deposits on the inner surfaces of closed-face cassettes during bioaerosol sampling: a field investigation at composting facilities

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Sampling on filters is the most widely used method in the literature for airborne endotoxins measurements (Duquenne *et al.*, 2013). The protocols used involve the analysis of endotoxins collected only on the filters following elution. However, several studies have reported the presence of particle deposits on the inner surfaces of filter holders when sampling aerosols to perform gravimetric analyses of dust, analyses of organic compounds, metals and non-metals as well as silica (Harper and Demange, 2007). The deposits on the inner surfaces of samplers could account for a large fraction of the aerosol sampled and measurement protocols have been modified to include these deposits in the analysis of samples. The occurrence of endotoxin deposits on the inner surfaces of the closed-face filter cassette (CFC) has not been explored up to now and very few data are available on this issue. The objective was to measure the quantity of endotoxin deposits on the inner surfaces of the cassettes (sometimes referred to as “inner surfaces deposits”).

A set of 270 bioaerosol samples was taken from 15 composting facilities using polypropylene CFCs. The amount of endotoxins collected on the filter and deposited on inner surfaces of CFCs was quantified using the LAL method. The results show that endotoxins are deposited on the inner surfaces of the CFCs through sampling and/or handling of samples. The quantity of endotoxins measured on inner surfaces range between the limit of detection of the method and 3100 Endotoxin Units per cassette. The deposits can represent a large and variable percentage of the total amount of endotoxins sampled (figure 1).

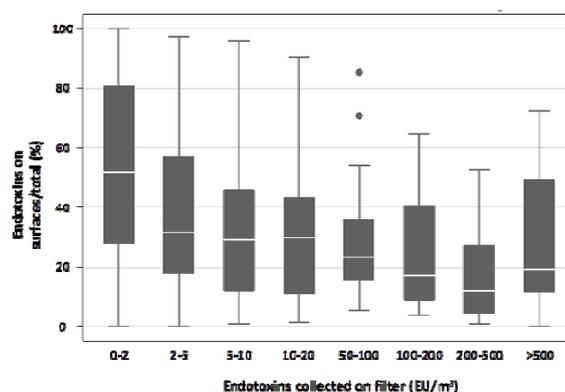


Figure 1. Proportions of endotoxins deposited on the inner surfaces of cassettes in comparison to the total endotoxins collected (filter+inner surfaces).

More than a third of the samples presented a percentage of inner surface deposits higher than 40% of the total quantity of endotoxins collected (filter+inner surfaces). Omitting these inner surfaces deposits in the analytical process leads to measurement errors, resulting in underestimated exposures, and may affect the decision whether or not a result is acceptable in comparison to airborne concentration limits. The results of this study suggest including the endotoxins deposited on the inner surfaces of CFCs during analysis. However, additional research is needed in order to investigate the phenomenon in other occupational environments and to determine whether or not to consider the deposits for endotoxin exposure. The communication presents possible alternative technical solutions.

Harper M, Demange M. (2007). *J Occup Environ Hyg*; 4: 81-86.

Duquenne P, Marchand G, Duchaine C. (2013). *Ann Occup Hyg*; 57: 137-72.

Sampling efficiency comparison of four bioaerosol samplers and two particle counters

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The bioaerosol sampler chosen by researchers for an experiment is often based on familiarity and availability. However, amongst the most popular general purpose samplers, is one more appropriate than the others for different sampling conditions? This project aims to examine 6 common samplers, in terms of their efficiency for detecting the total concentration and size distribution of airborne bacterium.

All experiments were carried out in a mechanically ventilated, class 2 aerobiological test chamber. The chamber has a volume of 32 m³ (4.20 m x 3.36 m x 2.26 m) with a 7.6 m³ ante-room between the chamber and the laboratory. The temperature, humidity, ventilation rate and ventilation regime within the chamber were externally controlled. Background samples were taken with each sampler. Then a known concentration of either *Staphylococcus aureus* or *Bacillus Subtilis* was continually introduced into the centre of the chamber via a six-jet Collision Nebuliser (CN 25, BGI Inc, USA) at a flow rate of 8 L m⁻¹ and a pressure of 12 psi. Once steady state conditions were achieved within the chamber, a second set of samples were taken with each sampler. The particle counters used included an Aerodynamic Particle Sizer (APS) Spectrometer and a Geo- α Handheld Laser Particle Counter. The biosamplers used include: a single- and a six-stage Andersen Cascade Impactor, an SKC BioSampler® Impinger and an All Glass Impinger (AGI 30).

	Aerodynamic Particle Sizer Spectrometer (Model 3321)	Geo-α Handheld Laser Particle Counter (Model 3886)	Single Stage Viable (Microbial) Impactor	Six Stage Viable Cascade Impactor	BioSampler® Swirling Aerosol Collector (SKC Impinger)	All Glass Impinger (AGI 30)
Manufacturer	TSI Inc.	Kanomax Japan Inc.	Various	Various	SKC Inc.	Ace Glass Co.
Operating Principle	Particle spectrometer	Particle spectrometer	Inertial impaction	Inertial impaction	Liquid impingement	Liquid impingement
Size Range	0.5 - 20 μm	0.3- 5.0 μm	0.65 - 1 μm	0.65 - 7.0+ μm	D ₅₀ : 0.30 μm	D ₅₀ : 0.30 μm
Size Resolution	52 channels	5 channels	1 stage	6 stages	n/a	n/a
Time Resolution	1 s - 18 hrs	1 s - 99 mins	Typically a few - 30 mins	Typically a few - 30 mins	Typically 0.5 - 4 hrs	Typically 10 - 30 mins
Flow Rate	1.0 \pm 0.2 L/min	2.83 L/min	28.3 L/min	28.3 L/min	12.5 L/min	12.5 L/min

Table 1. Summary of sampler specifications

The particle counters were located within the chamber near the ventilation extract and connected to a laptop in the ante-room to facilitate continuous monitoring of the chamber air. They were continuously counting and sizing the airborne particles within the chamber before, during and after the nebulisation of the bacterium. The bioaerosol samplers were located in the ante-room and sequentially sampled the chamber air through a tube located at the ventilation extract. Each piece of equipment was operated according the manufacturer's instructions.

The results for this study are yet to be analysed but comparisons will be made between each piece of sampling equipment, in terms of the total concentrations and the size distributions of airborne bioaerosols detected (as appropriate). The impact of sampler operating principle will be deliberated. The influences of ventilation rate and airborne bioaerosol concentration on the collection efficiency of each sampler will also be discussed. Finally, sampler repeatability and reliability will be examined.

Based on the results obtained in these experiments, recommendations will be made on the appropriate choice of bioaerosol sampler, for a range of sampling conditions. Furthermore, the experimental and environmental conditions which are necessary to achieve repeatable and reliable results will be determined. This will facilitate researchers in making informed decisions on their choice of biological sampler, hence generating more accurate studies in the field of aerosol science.

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A method for sampling and analysis of wood dust

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Recent studies on wood dust suggest that most samplers intended for collection of the inhalable fraction collect a similar fraction from real workplace atmospheres⁽¹⁾, although some samplers overestimate dosage as a result of sampling very large particles with efficiency greater than expected from consideration of human inhalability.⁽²⁾ The Button sampler (SKC, Inc.) likely collects an aerosol more reflective of that which would be inhaled by a worker in practice. It has additional advantages, including a relatively homogeneous deposit on the filter and minimal deposition other than on the filter. Glass fiber filters allow the use of pumps of reasonable size and weight to pull 4 LPM through a 25 mm diameter filter and still allow gravimetric determination within required accuracy. Should results from gravimetric analysis of Button sampler filters indicate a concentration around limit values of concern, it is also possible to submit the filter for additional analysis by diffuse reflectance Fourier-transform infra-red spectroscopy (DRIFTS).⁽³⁻⁵⁾ Samples are pre-treated with ethyl acetate to remove interfering soluble organic material and then the cellulose and lignin contents can be quantified directly on filter using DRIFTS. The selected wavelengths are compared to the equivalent wavelengths on standard wood dust samples treated similarly. The DRIFTS method has been refined through several iterations and a recent version has been used in two different laboratories, using different spectrometers with different software packages on the same standards and 181 samples from six different woodworking facilities. Limits of Detection for DRIFTS are approximately 35 µg per sample for hard wood and 70 µg for soft wood, while the Limits of Quantitation are approximately 110 µg and 230 µg, respectively. Standard statistical tests for equivalence confirm the two sets of results can be considered equivalent. Between the two laboratories, 62% of samples measured within 25%, with a mean difference of 18.5%. Since the samples and standards are not destroyed by this method, other laboratories are welcome to contribute to the evaluation of this method using the samples. Further scrutiny of the data suggests a procedure for distinguishing hard wood from soft wood and determining their relative proportion of mixed dusts in order to optimize the calibration according to the sample.

Disclaimer: The conclusions and opinions in this presentation are those of the Author and do not necessarily reflect the policy of the US Centers for Disease Control and Prevention.

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4. Chirila M, Lee T, Flemmer M, Slaven JE, Harper M [2011]. Quantitative mid-infrared diffuse reflection of occupational wood dust exposures. *Appl. Spectr.*, 65: 243-249.
5. Kwon C-W, Chirila MM, Lee T, Harper M, Rando RJ [2013]. Determination of airborne wood in Button samples by diffuse reflectance infra-red Fourier transform spectroscopy (DRIFTS). *Int. J. Environ. Anal. Chem.* 93: 1356-1366.
6. Chirila MM, Harper M, Sarkisian K, Andrew ME, Kwon C-W, Rando RJ [In Preparation]. Reproducibility of occupational wood dust exposure assessment using button sampler and diffuse reflection infra-red Fourier transform spectroscopy (DRIFTS).

Sampling bacteria in metal working fluids

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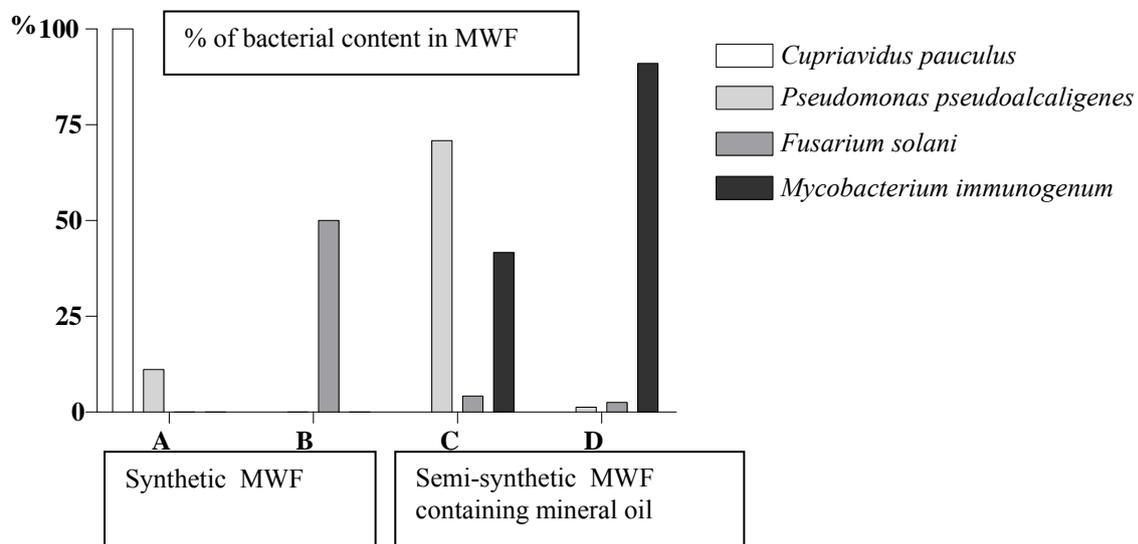
²Department of Microbiology, University of Gothenburg, Sweden.

Recent outbreaks of respiratory symptoms such as dry cough, asthma symptoms and pneumonitis among workers exposed to MWF (metal working fluids) in a big machine shop, has initiated a cohort-study of 200 workers exposed to MWF. The aim of this study is to identify and describe the exposure of bacteria in inhalable MWF aerosols among machine shop workers.

Methods: Personal full-shift air samples of inhalable aerosol sampled on PAS-6 and endotoxin sampled on Sioutas Cascade Impactor (5 fractions, 2.5-0.25 µm) were collected on operators in different machine shops. The PAS-6 filters were analysed gravimetrically for MWF aerosol and for endotoxin. Filters from the impactor were analysed for endotoxin. Quantification of bacteria was done in MWF by viable counts, estimating both total bacterial counts and bacterial species. Bacterial spp were identified by MALDI-TOF.

Results: 81 measurements of inhalable MWF aerosols on 52 persons were conducted in machine shops a big company. The average exposure to inhalable aerosol ranged from 0.03 to 1.08 mg/m³ with geometric mean 0.15 mg/m³ air and geometric standard deviation 2.07. Endotoxin levels on PAS-6 filter varied from 0.30 to 76.7 EU/m³ air with geometric mean 0.20 mg/m³ air and geometric standard deviation 3.92. Most of the endotoxins were found on fraction 2.5 µm, filter A from the impactor. There was a correlation between endotoxin on PAS-6 and fraction 2.5 µm estimated to be 0.67. The highest concentration of endotoxin was found in a machine with synthetic MWF where *Cupriavidus pauculus* dominated. *Mycobacterium immunogenum* was found in machines using semi-synthetic MWF containing mineral (figure).

Conclusions: The study showed a low mean exposure of MWF aerosol compared to the Swedish exposure limit value for MWF aerosols (oil mist) of 1 mg/m³. We found big difference between different MWF in contents of endotoxins, bacteria and new identified bacterial species as *Cupriavidus pauculus*. *Mycobacterium immunogenum* was only found in MWF containing mineral oils.



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Particulate air pollution in six cities in Indonesia

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Keywords: phasing out leaded Gasoline; lead concentration; Bandung, Indonesia

In Indonesia, air pollution control programs have been conducted through several actions. But, the increased air pollutions in several cities are still occurring and need a serious attention, in order to avoid the health impact and greater financial losses. National Nuclear Energy Agency of Indonesia, BATAN has contributed in solving air pollution problems through the application of nuclear analytical techniques for characterization of air particulate samples. As implementation of BATAN's agreement with Center of Environmental Management, Minister of Environment and local environmental protection agencies, in 2012 we have started the monitoring and evaluation of PM_{2.5} covering 6 cities in Indonesia, i.e. Jakarta, Serpong, Bandung, Yogyakarta, Semarang, and Surabaya. Sampling of PM_{2.5} was conducted once a week for 24 hours using Gent stacked filter unit sampler. Sample was analysed for mass concentration, black carbon as well as the elemental concentrations. Elemental determination was done using X-ray fluorescence (XRF) that advance and suitable for characterization of PM_{2.5} which has a small mass ~ 200 µg. The results showed the annual average of PM_{2.5} concentration in Jakarta, Serpong, Bandung, Yogyakarta, Semarang and Surabaya were 18.83, 12.85, 17.84, 10.33, 8.91 and 19.66 µg/m³. The results showed that annual average concentration of PM_{2.5} in Jakarta, Bandung and Surabaya has violated the national ambient air quality standard (15 µg/m³). Black carbon concentrations in these locations were also higher than other three cities (Figure 1). Besides that, in Surabaya the heavy metals pollution such as Pb, Fe and Zn were identified high which ten to thousand times higher than other cities, while in Serpong also showed the lead pollution detected from 1996 and monitored in previous study is still occurring in 2012 (Figure 2). These results will be used as a key in identification and estimation of pollutant sources to design the appropriate and right policies.

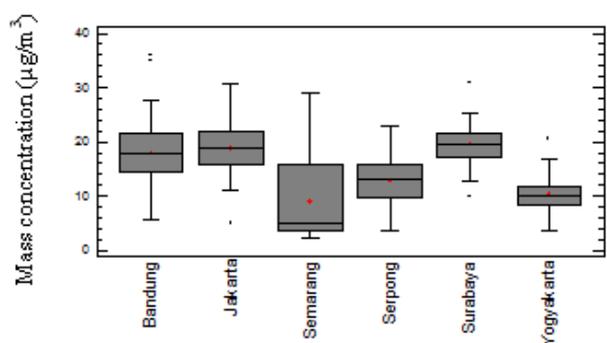


Figure 1. Time series of box and whisker plots for mass concentrations

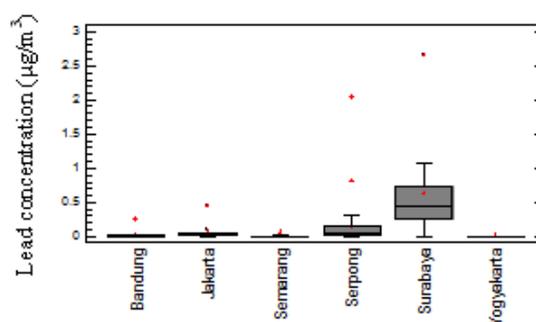


Figure 2. Time series of box and whisker plots for lead concentrations in six cities in Indonesia

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Use of a passive badge for sampling asbestos among building finishing workers

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In the French construction sector, almost one million workers are potentially exposed to the risk of inhaling asbestos fibres. However, knowledge of the exposures and follow-up of these populations remain poor considering the small size of the majority of enterprises and logistical constraints linked to conventional sampling, as tasks dealing with asbestos-containing materials often lead to both random and short-term exposures. The aims of this study were to assess the performance of a passive sampler allowing asbestos fibres to be sampled and to apply it to a selected population of employees who are potentially exposed, namely plumbers-heating engineers.

The first part, undertaken in the laboratory, completed the work carried out in the United Kingdom by the Health and Safety Laboratory (Burdett, 2007) by estimating the equivalent flow rate of the badge as a function of the physical parameters likely to influence it and compatible with the occupational ambient conditions. This sampler was then used to evaluate the asbestos fibre concentration to which plumbers-heating engineers were exposed over a week's activity. This second phase was undertaken with the contribution of the Confederation of Self-Employed Builders and Small Building Enterprises (CAPEB), which was responsible for recruiting volunteers.

Combining the wearing of the sampler for a week, an individual questionnaire and intervention sheets, these experiments identified asbestos exposure in 35% of cases. Almost half of the operators were unaware of this risk.

The results of this study will serve to raise the awareness of professionals carrying out finishing work in the building industry. This work should lead to a review of the practices of the plumber heating engineer profession intended to improve their training, their knowledge of asbestos risk and, in particular, of collective and individual means of protection.

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Complementary use of conventional and molecular methods to assess fungal contamination in occupational settings

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It is known that the exclusive use of conventional cultural methods for fungal quantification may underestimate the results (Zorman & Jersek, 2008). The use of complementary molecular methods allows the suppression of some limitations of the cultural methods, detecting the presence of non-viable particles and identifying potential mycotoxin producing strains.

Therefore, our study aims at confirming the complementarity of both methodologies (conventional and molecular) when assessing fungal contamination. Different settings were studied, namely seven poultries, two waste-sorting plants and one incineration plant. Air samples from those settings were collected through impaction method, surface sampling, and also litter sampling (in poultries). After laboratory processing and incubation of the collected samples, quantitative and qualitative data were obtained, with the identification of the isolated fungal species. For molecular methods, air samples of 250L were collected using the impinger method. Molecular detection of *Aspergillus fumigatus* complex, *Stachybotrys chartarum* and toxigenic strains from *Aspergillus flavus* complex was achieved by Real Time PCR (RT-PCR).

Regarding poultries, we were able to detect, through molecular biology the presence of aflatoxigenic strains in pavilions in which *A. flavus* did not grow in culture. *Aspergillus fumigatus* was only found in one indoor air sample by conventional methods. Using molecular methodologies, however, *A. fumigatus* complex was detected in seven indoor samples from three different poultry units. Concerning the waste sorting plants, RT-PCR has succeeded in amplifying DNA from *A. fumigatus* complex in one additional site of one plant when compared with the ones detected by conventional methods. In the other plant, *A. fumigatus* was detected in two samples and *S. chartarum* was detected in one sample, neither of which were detected by conventional methodologies. In the incineration plant, RT-PCR was able to detect isolates belonging to *A. fumigatus* complex in one more sampling site when compared to conventional methods. Despite the fact that molecular methods are more sensitive, cultural methods have the advantage of enabling identification and quantification of viable microorganisms only and, therefore, the ones that probably represent higher health risks (when compared to non-viable organisms).

It is important the continuous use of both methodologies in order to better evaluate fungal contamination in occupational settings, and consequently, the potential health risks of exposed workers (Viegas et al., 2013).

Acknowledgement: This work was supported by Portuguese Authority for Work Conditions and by Lisbon School of Health Technology/Institute Polytechnic of Lisbon.

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Measurement of electrical charges on airborne bacteria Generated using a single-pass bubbling aerosolizer

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Laboratory-generators are likely to produce electrostatically charged particles. The amount of electrical charges carried by airborne particles, including microorganisms and other biological airborne entities, can greatly influence their behaviour (deposition, filtration, etc.). Microorganisms are more complex in their composition than inert particles and naturally contain electrical charges. Mainelis *et al.* (2001) suggested that electrical charges carried by laboratory-generated bacteria consist of two components: their own natural charge, which can be high, and the charge imparted by the aerosolization process. Inert non-biological particles, in contrast, carry only the charges induced by the dispersion process.

We previously developed and characterized the performances of a ‘Liquid Sparging Aerosolizer’-type bioaerosol generator (Simon *et al.*, 2010) where microorganisms are dispersed by bubbling compressed air through a film of microbial suspension. The selection of this liquid-based generator was mainly guided by its gentle bubbling aerosolization, which minimizes stress and damage to airborne microorganisms. We also assumed that the generated microorganisms will carry few electrical charges; such a scenario would imply that a neutralization step, with expected additional negative effect on the viability of sensitive microorganisms, is not necessary. The objectives of this study were to measure the fraction of neutral particles and the number of elementary charges per particle as a function of the aerodynamic diameter of the airborne gram-negative sensitive bacteria (*Escherichia coli* and *Enterococcus hirae*), for different operating conditions.

The experimental setup (Fig. 1) includes the tested bioaerosol generator, an electrostatic precipitator (ESP), a custom-built sampling volume with 6 parallel probes and real-time devices to characterize the airborne particles (Aerosol Electrometer IONER EL-5030, Ramem S.A - Aerodynamic Particle Sizer APS, TSI model 3321 - Electrical Low Pressure Impactor ELPI, Dekati).

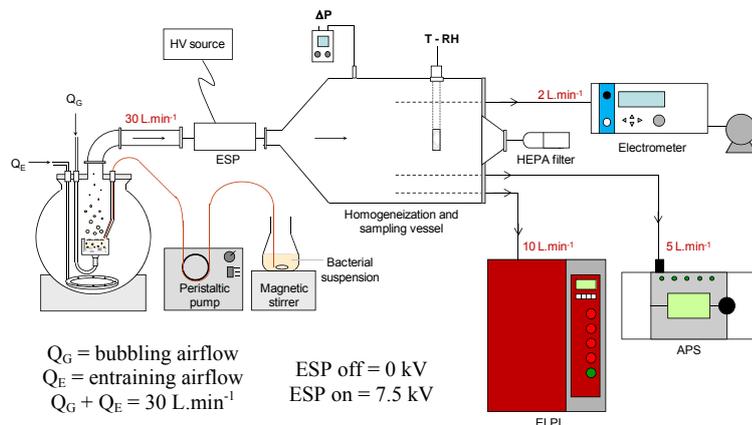


Figure 1. Schematic of the experimental setup.

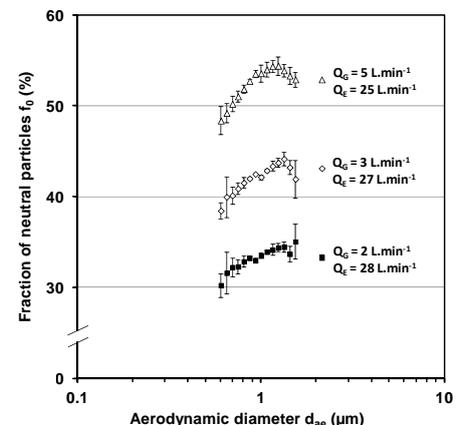


Figure 2: Fraction of neutral particles (*E. coli*).

The populations of vegetative cells of *E. coli* or *E. hirae* present aerodynamic diameters between 0.6 and around 2 μm . The fractions of neutral particles ranged from around 30% to 50%, depending on the operating conditions. As it can be seen in Fig. 2, the higher the bubbling airflow, the greater the fraction of neutral particles in the generated bioaerosol. Whatever the species or the operating condition considered, the net electrical charge carried by the aerosolized bacteria is negative, what is consistent with previous published works. The average number of elementary charges carried per particle varied from around -10 to -50 elementary units. The higher the bubbling airflow or the aerodynamic diameter, the greater (absolute value) the number of elementary charges carried by bacteria. In such wet dispersion method, different physical factors and charging mechanisms are responsible for the electrical charges carried by airborne microorganisms: liquid disrupting forces, contact charging effect, initial size of the droplets, initial electrical charges carried by these droplets and by microbial particles, etc. Given the number of elementary charges carried by the generated bacteria, a neutralization step seems not to be necessary. Nevertheless, if an equilibrium state of charge is required, our results also suggest that the use of the neutral fraction downstream an ESP may be advantageous instead of using neutralizers.

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Efficiency of cleaning procedures in reducing fungal contamination in one waste-sorting plant

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High loads of fungi are reported in different types of waste management plants (Wouters et al., 2006), being airborne fungal contaminants increasingly gaining importance in view of health hazards caused by the spores themselves or by microbial metabolites (Fisher and Dott, 2003), such as microbial volatile organic compounds (MVOC's) (Korpi et al., 2009). However, the relevance of fungal metabolites in working environments has not been sufficiently studied (Fischer et al. 1999).

This study aims to assess fungal contamination and volatile organic compounds (VOC's) concentration in one waste-sorting plant, more precisely in one presorting cabinet, before and after cleaning procedures, to analyze effectiveness of this procedure. Air samples of 50L were collected through an impaction method with a flow rate of 140 L/min onto malt extract agar (MEA) supplemented with chloramphenicol (0.05%), using the Millipore air Tester (Millipore), during a work day. All the collected samples were incubated at 27°C for 5 to 7 days. After laboratory processing and incubation of the collected samples, quantitative (colony-forming units - CFU/m³) results were obtained. Measurements of VOCs were also performed before and after cleaning procedures using a portable direct-reading equipment (Wolfsense IQ-610- Graywolf Sensing Solutions; range: 0–10,000 ppm; accuracy: 3%). Measurements were taken where the workers spend more time and the mean, maximum and minimum values obtained were considered. All measurements were performed at a height of about 1.5 m and during routine work. Regarding total fungal contamination, fungal load was higher before cleaning procedures (10060 CFU/m³) than after (5520 CFU/m³), being found, in all sampling moments, higher load before than after cleaning. However, VOC's showed different results: mean values before cleaning (0.72 ± 0.35 ppm) lower than after cleaning (1.17 ± 0.36 ppm). In this study, was not possible to identify the specific VOC's present making difficult to recognize the specific emission sources. However, the positive correlation found between CFU/m³ and VOC's before cleaning procedures, although not statistically significant ($r=0.595$, $p=0.289$), is probably related with the fact that MVOC's are more likely to be produce when high levels of contamination occur (Korpi et al., 2009). Additionally, is important to consider that not only fungal load can contribute to MVOC's, but also other environmental parameters, such as nutrients availability, pH, humidity and temperature (Korpi et al. 2009), and that can explain the VOC's higher results after cleaning.

Considering obtained data from this preliminary studied, we can conclude that cleaning procedures are being efficient to reduce fungal load in this specific setting, but other risk factors must be consider, since workers are exposed, simultaneously, to fungi and their metabolites (MVOC's), and also to VOC's from others emission sources. The risk assessment process must consider possible synergetic effects of this multiple exposure, being important to developed more research work about this matter.

Acknowledgement: This work was supported by Lisbon School of Health Technology/Institute Polytechnic of Lisbon.

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Testing of a new sampling procedure for airborne allergens in the workplace atmosphere

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Airborne allergens have become an increasing importance in different environments such as indoor and occupational settings in recent years. Measuring methods are few and not all of them are suitable for every task. The standard procedure for sampling of airborne allergens at workplaces is the filtration method. Samples were taken using sampling devices like the IFA whole-dust-sampling-system (GSP) with a sampling volume of 10 L per hour in combination with Teflon-filters (PFTE) for at least four hours. Filters are extracted in the laboratory and the allergen-concentration from the air sample is determined within the extracts by the use of specific and sensitive enzyme linked immunosorbent assays (ELISA) commonly practiced as sandwich-ELISA.

Regarding health problems which might be connected to the presence of moulds in indoor environments, the occurrence of allergens is also a frequently asked question. For the sampling of allergens in indoor air, a new device has been developed (AS 100, Holbach Umweltanalytik, Wadern, Germany). The principle of this method is direct sampling of the airborne particles and antigenic/ allergenic proteins with high sampling rate (100 L per minute) into the test receptacle, which is used for the ELISA.

Reduction of the sampling time because of the higher sampling volume may be advantageous to describe the allergen concentration at indoor-workplaces or for short-time measurements. Furthermore it was the idea to save the extraction step by direct sampling of the air into the test receptacle for the ELISA. This might be an advantage in quantitative sample analysis, especially for the proof of small allergen concentrations. For this reason, the AS 100 is operated with single stripes of microtiter plates containing eight wells as sampling units.

In 2013 IFA initiated a research project focused on the testing of the new sampling procedure, regarding its suitability for the sampling of airborne allergens at workplaces. First investigations using both sampling systems in parallel were done in cattle farms, looking for one of the major cow hair and dander allergens, Bos d 2. This allergen had been chosen for sampling experiments, because the analytical test kit for Bos d 2 is purchasable and sampling in workplace atmosphere with high or low allergen concentrations might be possible in different areas of the farms (stable, office, changing room etc.).

Within three measurements in different areas of the stables accompanying activities like feeding or dividing of straw material at three different farms, Bos d 2 was detectable with both measuring systems which had been used in parallel. Single results varied within a wide range: 57.0 to 1,700 ng Bos d 2 · m⁻³ for filter samples (n=28) and 0.38 to 429 ng Bos d 2 · m⁻³ for samples taken with the AS 100 (n=30). Most data received with the AS 100 were lower than results measured by standard filtration. This might partially be owed to the fact, that Bos d 2 analysis of the sampling units of AS 100 was carried out as direct ELISA. Recovering of Bos d 2 was 51 % in direct ELISA compared to sandwich ELISA. Recovery-experiment was carried out in five dilutions (n=3 replicates each) of an extract of a material sample containing silage and stable dust. Furthermore it has to be investigated, to what extent the antigen/allergen containing airborne particle fraction is precipitated in sample units of the AS 100 compared to their collection on filters.

Influence of operating conditions on composition of particulate matter emissions from residential combustion

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Currently, most developed countries suffer from a heavy dependence on fossil fuels. In this context, there have been environmental policies that encourage the use of biomass as a renewable energy source (Khan *et al.*, 2009; Saidur *et al.*, 2011). Despite the recognised advantages of the use of biomass, residential wood combustion for heat production has been pointed out as a major source of fine particle emissions (Borrego *et al.*, 2010; Gonçalves *et al.*, 2012), especially during winter-time. The airborne particles arising from residential combustion have harmful effects on public health (Nevalainen & Pekkanen, 1998) and cause disturbances in atmospheric chemistry and climate (Calvo *et al.*, 2013; Pöschl, 2005). Taking into account the impact of these emissions and the need for compliance with legal norms, a rigorous quantification and characterisation of emissions from this sector is necessary. Several studies have shown that emissions from the residential wood combustion are highly variable (Alves *et al.*, 2011; Gonçalves *et al.*, 2010; Tissari *et al.*, 2008; Johansson *et al.*, 2004). The types of appliances, wood fuel and operational practices have a great influence on emissions from this sector.

The aim of this study was to experimentally quantify and characterise the emissions of particulate matter (PM₁₀) resulting from combustion in a typical Portuguese woodstove with variations in fuel (pine and beech), and operational conditions. The variables evaluated were ignition technique (upside down and bottom up lighting), fuel load and, in the case of high load, split and non-split logs.

The highest PM₁₀ emission factor was observed for the operation with reduced load for both woods. The top-down method of lighting can decrease the PM₁₀ emission factor to less than half when compared with the traditional technique. Quantitative analysis of the carbonaceous material showed that the mass of particles emitted was mainly composed of organic carbon (OC), while elemental carbon (EC) represented a minor mass fraction. The OC content of PM₁₀ was higher when loading a lower amount of wood (59%), in the case of beech, or when increasing wood loads (58%), in the case of pine. The top-down method of lighting contributed to substantial mass fractions of EC in PM₁₀, corresponding to 25 and 33% for pine and beech, respectively.

The major organic components of smoke particles from biomass burning are monosaccharide derivatives from the breakdown of cellulose and hemicelluloses, such as levoglucosan, a specific marker for wood combustion in ambient PM samples, which is usually the most abundant organic compound. Average mass concentrations in PM₁₀ ranged from 1.8 to 11.2% for beech and from 1.5 to 10.9% for pine wood smoke, which are in general agreement with levoglucosan contents of 0.2 to 17% found for Portuguese woods (Gonçalves *et al.*, 2010) and 0.1 to 15.1% obtained for Alpine species (Schmidl *et al.*, 2008). The highest mass concentrations in PM₁₀ have been recorded for the operation with the reduced load for both woods.

Acknowledgement: This work was supported by EC through the "Testing and development of air quality mitigation measures in Southern Europe" (AIRUSE), 11/ENV/ES/000584 LIFE project.

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Development of a respirable miniCyclone for use with the headset mounting arrangement

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Introduction In a research project with the aim of sampling manganese in welding fume it was decided to develop a small cyclone (a miniCyclone) for the SKC *Face Level Sampling Headset* (SKC, 2014). Currently, only one small aerosol sampler exists for this system, an open-face cassette for 13 mm filters originally intended for manganese (Lidén and Surakka, 2011). As the intention was to additionally determine respirable iron and dust in the samples it was decided to sample the respirable fraction, even though manganese in welding is overwhelmingly respirable.

The GK cyclone family has a shallow penetration curve (Kenny and Gussman, 2001), and it was scaled theoretically to a cut-size of 4.0 μm at 0.75 LPM. A small GK cyclone was manufactured and the penetration curves were determined for two flow rates with a TSI APS 3320 using glass beads as test aerosols. Based on these experiments an optimal cyclone body size was determined. Twelve cyclone specimens were manufactured in brass. Downstream the outlet of the miniCyclone, the sample is collected in the 13 mm welding fume miniSampler.

Methods In the workplace sampling, the cyclones were used as personal samplers mounted close to the welder's nose or mouth (behind the visor when in place). In total, samples were collected from 77 welders at eight factories using a wide variety of welding methods. Additionally, a static sampler parallel comparison was carried out with the SKC aluminium cyclone for respirable dust at 2.5 LPM. At each work shift per visited factory, two pairs of parallel samples were collected. The comparison is based on the respirable dust (gravimetric) samples, as there is very little non-respirable manganese in welding fume.

The used version of the miniCyclone will be tested according to the foreseen new European standard (CEN 2014) this spring using an APS and glass beads as test aerosol. [These data will be presented at AirMon.]

Results The respirable concentrations measured with the static miniCyclone and the SKC Al cyclone are presented in Figure 2. A linear regression through the origin with constant residual standard deviation gave a slope of 1.12, an $r^2=0.957$ and $s_{\text{res}}=0.27 \text{ mg/m}^3$. Restriction to the range below 1 mg/m^3 gives almost identical results.

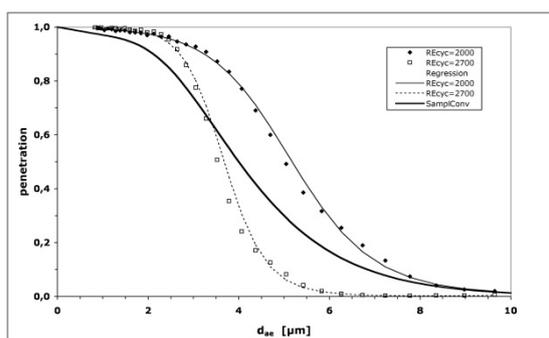


Figure 1. Penetration curves measured for a small GK cyclone at two Reynolds numbers (flow rates) and Sampling convention for respirable dust

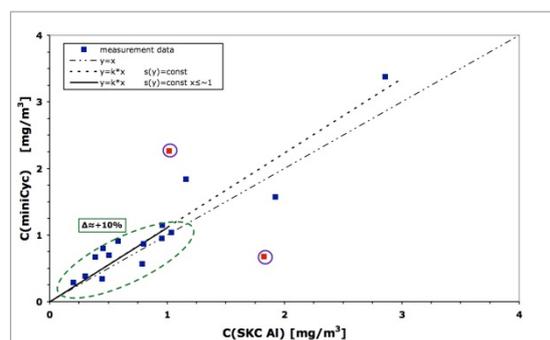


Figure 2. Parallel sampling between miniCyclone and SKC Al cyclone – respirable gravimetric welding dust. Encircled data are considered outliers.

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Aerosol physical properties from tire wear

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Road traffic constitutes an important source of atmospheric particulate matter, mainly in urban areas. It has been estimated that exhaust and non-exhaust sources contributed approximately equal amounts to total traffic-related emissions [1]. Among the non-exhaust emissions from road vehicles, tire wear has been identified as an important contributor of PM₁₀ emissions, with annual losses of rubber from tires in Europe estimated to be several thousands of tons [2]. Improved information about these emissions is important to implement source-oriented mitigation measures, health effects studies and to model source contributions.

At the Swedish National Road and Transport Research Institute (VTI) a circular road simulator was used to generate wear particles [3]. The road simulator runs four wheels around a circular track at a speed of 70 km h⁻¹ and was equipped with several types of pavements. Two different types of tires were tested: i) Michelin Energy Saver and ii) Bridgestone Turanza ER300. The particle size distributions were monitored using a scanning mobility particle sizer (SMPS) and an aerosol particle sizer (APS), for particle sizes between 14 and 660 nm, and 0.54 and 18 μm in diameter, respectively. Additional measurements were made of particle mass concentration with a TEOM and a DustTrack.

Measurements were made over a period of 5 days with total kilometers per test ranging from 250 to 500. Emission factors were calculated using the simple box model of Dahl et al. [4], which assumes that the concentration in the test chamber reaches an equilibrium value when emissions are balanced by sedimentation. The mass emission rate, Q, is determined by fitting the equation $M(t) = M_0 e^{-kt} + (Q/k)(1 - e^{-kt})$ to the measurements, as shown in Fig. 1, where $\tau = 1/k$ is the response time. In this example, the mass emission rate was 1.9 mg/km/vehicle.

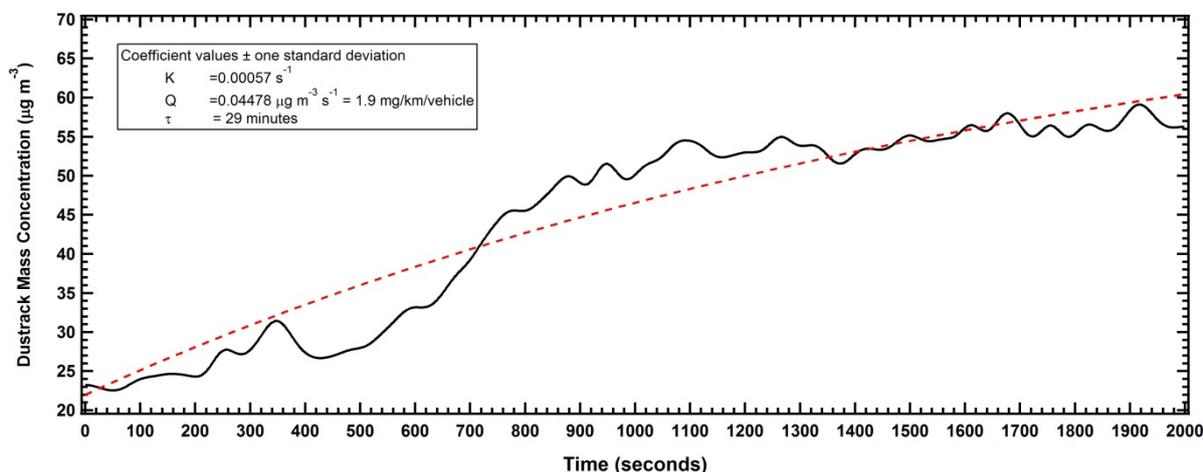


Figure 1. An example of the mass concentration measured by the DustTrak (0.1 – 10 μm) at the beginning of the road test. The dashed line is the best fit of the box model equation, where K and Q are the dependent variables.

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Sources of particulate matter in OPORTO during 1 year of measurements: local versus distant sources of black carbon

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Black carbon (BC) influences the climate directly through radiative forcing and thereby induces a warming in the earth atmosphere system (Panicker *et al.*, 2013). Hence it is necessary to observe the spatial and temporal changes in BC concentrations. In the present study, continuous BC measurements were carried out in the city of Oporto (Portugal) between January 2013 and January 2014. A Magee Scientific aethalometer (AE-30) with 7 channels (370, 470, 520, 590, 660, 880, and 950 nm) was used with averaging periods of five minutes. For the winter period, assuming that BC originates mainly by traffic and wood smoke, one can apply the three component model proposed by Favez *et al.* (2010) to estimate the carbonaceous material: $CM_{total} = CM_{traffic} + CM_{wood\ smoke} + CM_{other} = C_1 \cdot b_{abs}(950\text{ nm}) + C_2 \cdot b_{abs}(470\text{ nm}) + C_3$. In this model, b_{abs} represents the absorption coefficient, C_1 and C_2 relate the light absorption to the particulate mass of both sources, and C_3 corresponds to the amount of non-combustion organic aerosol. Obviously, $CM_{total} = BC + OM$, where OM stands for organic matter. The application of this source apportionment model to the dataset corroborate the findings of other studies stressing the influence of domestic biomass burning on BC concentrations (Healy *et al.*, 2012; Mohr *et al.*, 2013; Wang *et al.*, 2011). Further, since the spatial distribution of BC aerosols in the atmosphere is significantly influenced by the prevailing winds, the HYSPLIT model was applied to cluster 72h backward trajectories. Other atmospheric pollutants and meteorological data continuously monitored were also used to interpret different episodic cases.

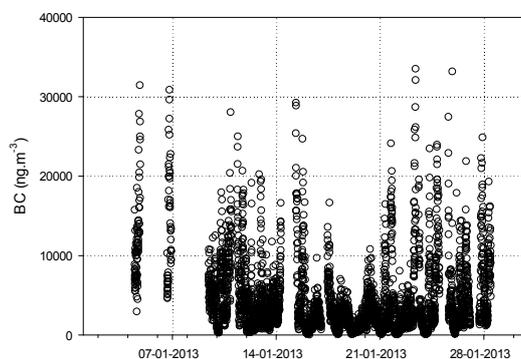


Figure 1. Black carbon concentration computed by the 880 nm light record in January 2013 assuming a mass extinction coefficient of $16.6\text{ m}^2\text{ g}^{-1}$ (Harrison *et al.*, 2013).

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Characterization of soot particles in aluminium smelters by transmission electron microscopy

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Soot originates from incomplete combustion and is an important component of many workplace aerosols. Diesel engines are the most prominent source of soot in urban areas as well as at many workplaces. In this contribution, we report the first results of a study that aims to differentiate between different soot sources on the scale of individual agglomerates. Aerosol particles were collected on TEM Cu-grids with an electrostatic precipitator. Air samples were obtained from the workroom atmospheres in different departments of two aluminium smelters in Norway. Size, morphology, nanostructure and chemical composition of carbon rich agglomerates found among the collected aerosol particles were investigated by high-resolution transmission electron microscopy (HRTEM) and energy-dispersive X-ray microanalysis (EDX).

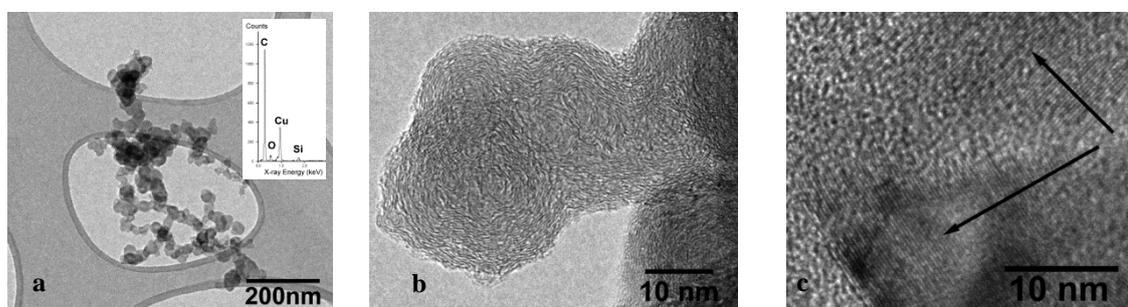


Figure 1. (a) Bright field TEM image and EDX spectrum of a soot agglomerate; (b) HRTEM image of a soot primary particle; (c) HRTEM image of a carbon nanotube particle (arrows).

Most carbon-dominated particles encountered at workplaces in the two aluminum smelters appear to be soot from diesel engines. They occur as agglomerates (Figure 1a) of primary particles with a typical diameter between 20 and 30 nm. In the EDX spectrum (Figure 1a, insert), silicon and oxygen peaks are observed beside the dominating carbon peak (the Cu signal is an artefact from the sample holder). The microstructure of primary particles was investigated by high-resolution imaging. The nanocrystalline primary particles (Figure 1b) exhibit the typical onion-shell structure consisting of (002) graphite lattice planes with a lattice plane distance of 0.38 nm. The classification as particles from diesel engines is based on results of previous TEM studies of vehicular emissions (e.g., Wentzel et al., 2003) and from comparison with particles collected directly at the exhaust pipe of diesel engines. Some diesel soot agglomerates may be internally mixed with other particles, e.g. iron-rich particles, cryolite, or fly ash particles (Figure 2). In addition to the dominating diesel soot agglomerates, a few carbon nanotube and a few soot particles that contain sulphur were observed (Figure 2). The example of a carbon nanotube particle is shown in Figure 1c.

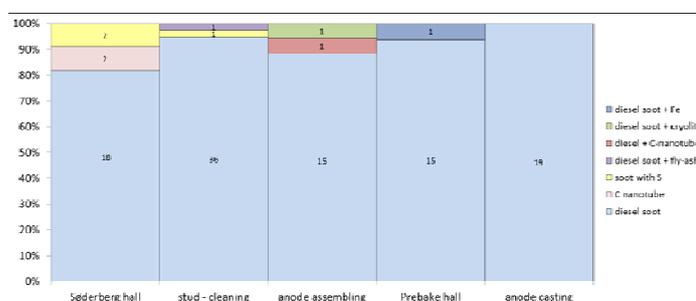


Figure 2. Relative number abundance of different types of carbon-dominated particles encountered at workplaces in aluminium smelters (number of agglomerates investigated is shown within the columns).

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Bioaerosol monitoring at subtropical locations

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The chemical composition of aerosol particles strongly affects the extent to which atmospheric particulate matter interacts with the natural and manmade environment, including human health and climate. Recently, the importance of suspended biological material in the atmosphere (a.k.a. bioaerosol) has been subject to increased scientific attention based on new insights regarding the influence of such particles on various environmental processes, including cloud and ice nucleation, thus exerting indirect climate effects. Specifically, fungal spores have been identified as a major type of bioaerosol, with significant contributions to the total aerosol burden especially in subtropical and tropical environments (Despres *et al.*, 2012). Aside from traditional, i.e., biological, techniques, alternative methods for bioaerosol characterization have recently emerged. For instance, certain organic compounds, such as sugar alcohols, have been proposed and applied as molecular tracers for the quantification of fungal spores (Bauer *et al.*, 2008), while DNA analysis has been demonstrated as a powerful method for detailed characterization of various microbial species (Despres *et al.*, 2007).

The main goal of this study was to gain insights into the abundance and characteristics of bioaerosol, and specifically fungal spores, in a subtropical environment, based on a multi-method approach, using both traditional and advanced measurement techniques. Several sample collection methods were utilized, including common aerosol filter sampling and special bioaerosol samplers, such as impingers for collection of microorganisms into liquid media. In addition, an on-line fluorescence based bioaerosol monitor was employed. The sampling was conducted at several locations throughout the Taiwan island, including coastal sites, high-altitude locations and a forest, in order to investigate spatial and temporal variations in the bioaerosol characteristics. Organic compounds derived from biological/biogenic sources, such as fungal activities, were measured by various analytical techniques, including high-performance anion exchange chromatography (HPAEC, Iinuma *et al.*, 2009), while selected biological techniques, such as flow cytometry, were tested as well.

The study results revealed clear seasonal and spatial patterns in the molecular tracers for biogenic sources, including fungal spores and secondary organic aerosol (SOA) from isoprene oxidation. The total amount of fungal spores was determined by flow cytometry and correlated with the molecular tracer concentrations. The initial results from HPAEC analysis show rather high levels of the fungal tracers (arabitol, mannitol) and isoprene-derived SOA tracers (2-methyltetrols), indicating important influence of these biogenic sources to ambient subtropical aerosol mass. A strong particle size dependence was observed, with the majority (up to 90%) of the fungal tracers present in the coarse mode. Additional measurements were conducted in fog water samples and correlated with ambient aerosol composition, showing a large abundance of fungal material in the aqueous phase, which confirms the potential of certain bioaerosol species to act as cloud condensation nuclei (CCN) and thus exert indirect climate effects.

Acknowledgement: This study was financially supported by the National Science Council of Taiwan under grant 101-2113-M-007-003-MY2.

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Measurements of organic and elemental carbon in downtown Rome and background area: physical behavior and chemical speciation

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Carbonaceous particles (or Total Carbon, TC) are composed of two main fractions, Elemental Carbon (EC) and Organic Carbon (OC). The EC (or black carbon or soot) has a graphitic-like structure with several adsorption sites which are capable of enhancing catalytic processes (Avino et al., 2000). The OC represents a large variety of organic compounds, e.g. aliphatic, aromatic compounds, alcohols, acids, etc.

While EC is essentially a primary pollutant emitted directly from the incomplete combustion of fuels, OC has both primary and secondary origins. Primary particulate organic carbon is formed during combustion and emitted mainly as submicron particles. Secondary particulate organic carbon has origin from gas-to-particle conversion of volatile organic compounds in the atmosphere either as result of the condensation of low vapor pressure volatile organics or from physical or chemical adsorption of gaseous species on aerosol particles surface. The measurements of TC and the distinction between EC and OC were performed by means an Ambient Carbon Particulate Monitor equipped with a NDIR detector (Avino et al., 2001). The OC/EC separation is carried out on the same filter: OC is oxidized to CO₂ during the pre-combustion step at 350 °C, instead EC is calculated by the difference between the TC, determined after combustion at 750 °C, and the OC.

In this paper TC, EC and OC concentrations determined in Rome urban area for 10 year-long are discussed considering the influence of the meteorological conditions on the temporal-spatial distributions of the aerosol concentrations; simultaneously, they have been compared with similar measures performed in a semi-rural monitoring station located at ENEA R.C.-Casaccia. The EC and OC concentrations trends are compared with the CO trends, a specific indicator of autovehicular traffic, for identifying the primary and secondary formation of TC.

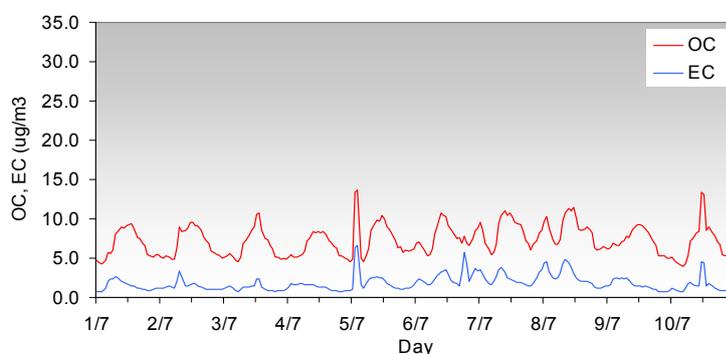


Figure 1. OC and EC trends during hot period in downtown Rome.

Finally, a chemical investigation is reported for investigating how the main species such as PolyAromatic Hydrocarbons, ion fractions and heavy metals, varied their levels during this period in relationship to new regulations and/or technological innovations.

Acknowledgement: This work was supported by INAIL under grant P20L09 and P20L01.

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Environmentally controlled chamber for bioaerosol modeling and aging studies

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In order to study the long-term effects of environmental stresses on the integrity of bioaerosols, a chamber was designed and built. A 55.5 liter cylindrical chamber which can rotate at variable speeds on its horizontal axis and contained within an insulated enclosure was developed. Piezoelectric units are used to heat and cool the chamber. A ultraviolet light located at the center of rotation of the chamber was added as well as access ports, located on the stationary sections on both ends of the chamber. Various lengths of meshed tubes surrounded by desiccation materials are used to control the relative humidity in the chamber. Temperature inside the rotating chamber is stable with less than 0.5°C in variation when set between 18 and 30°C with the UV light having no effect of temperature when operated for five minutes. Relative humidity levels set at 20%, 50% and 80% varied by 2.2%, 3.3% and 3.3% respectively over a 14 hour period. The remaining fraction of particles after 18 hours of suspension was 9% at one rotation per minute (rpm) and 3% at zero rpm with the mass median aerodynamic diameter (MMAD) changing from $1.21 \pm 0.04 \mu\text{m}$ to $1.30 \pm 0.02 \mu\text{m}$ at one rpm and from $1.21 \pm 0.04 \mu\text{m}$ to $0.91 \pm 0.01 \mu\text{m}$ at zero rpm within the same time period. The newly designed this rotating chamber can be used to increase the time of particle suspension in an aerosol cloud and control the temperature, relative humidity and UV exposure and can be used to study the aging of bioaerosols.

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Airmon

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Marseille, France

***Session B - Nano-aerosol sampling and
measurements***

Ultrafine particles emitted by thermal spraying of metals

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Many industrial processes may generate ultrafine particles (UFP) which are characterised by particle diameter less than 100 nm and refer to nanosized particles not intentionally produced. These UFP are mainly considered as the byproduct of processes involving combustion or vaporization/condensation phenomena.

Thermal spraying (TS) is a surface treatment process, which enables different types of material (metals, metal alloys, ceramics and even plastics) to be deposited on various substrates. The coating product, in wire or powder form, is melted by a heat source and then sprayed onto a surface previously prepared by sandblasting.

Bémer et al. (2013) have shown that one specific thermal spraying process (electric arc) was particularly high emissive of UFP. In this study, emissions characterisation of TS was extended to the five main TS processes (wire flame, electric arc, powder flame, plasma and High Velocity Oxy-Fuel), and for two different metallic (or alloys) coating materials for each process. The metals most commonly used for treatments are zinc and zinc/aluminium alloys (for wire flame, electric arc spraying) and special alloys sometimes containing highly toxic metals such as chromium, cobalt, nickel, etc. for others processes.

Aerosol emitted during the metal-coating process is collected through a semi-circular suction panel connected to a 35 cm diameter and 2 m long duct, from which the aerosol is sampled.

The experimental set-up for generated aerosol characterisation was based on methods for nanoparticles sampling and measurements. This set-up was the same for all experiments and is composed of real time monitoring instruments and membrane based sampling systems allowing to access to: (i) mass concentration (ii) number concentration (iii) particle size distribution and (iv) chemical composition of particles.

Considering all the configuration tested, Electrical Low Pressure Impactor (ELPI) measurements confirm a significant exposure to UFP with an average of 90% of emitted particles in number classified as UFP, whatever the TS process or the sprayed material tested. In order to illustrate some results, Table 1 shows some aerosols characteristics of selected experiments : the measured mass emission rate (TEOM data) are ranging from 3 to 175 mg/s (depending of process and coating material) and the mean number concentration reached (CNC counter) is especially high (close to 10^{14} particles/s).

Table 1. Some aerosol characteristics depending of thermal spraying process and coating material

Thermal spraying process	Coating material main composition	% part < 100 nm (in number) using ELPI data	Emission rate (in mg/s) using TEOM data	Emission rate (in part./s) using CNC data
Electric arc	Zn	80	175	$2.7 \cdot 10^{14}$
Wire flame	Zn	95	121	$2.0 \cdot 10^{14}$
Powder flame	Ni/Cr/Si/Fe/B/C/O	99	3	$0.5 \cdot 10^{14}$
Plasma	CrO	99	108	$1.0 \cdot 10^{14}$
HVOF	WC/Co/Cr	89	101	$2.7 \cdot 10^{14}$

All the results, added with the recent studies on nanotoxicology, support the fact that safety of the workers and particle rejections into atmosphere must be considered carefully regarding to TS activities.

Acknowledgement: This work was carried out in close collaboration with D. Billières and C. Mateus (Saint Gobain Coating Solutions, Avignon, France).

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**Evaluation of the emission of ultra-fine particles from laser printers
in office environments – a pilot study**

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Studies focused on potential sources of indoor unintentionally formed ultra-fine particles have evidenced that, during the heating in printing processes, laser printers release substances representing a human health hazard. The evidence for health risks of ultra-fine particles after inhalation has been increasing over the last decade and it has been proved that ultra-fine particles are of concern relating to the diseases associated to exposure to pollutants related to sick-building syndrome. Despite the apparent simplicity of testing the emissions from laser printers, the persistent challenge is in interpreting the results, which stem from several potential contributors to the emissions such as paper, toner powder, fuser roller, lubrication oil as well as a number of possible physicochemical pathways for particle formation.

The present paper describes the results from a set of measurements carried out in office environments with the aim to investigate both workers exposure to ultra-fine particles from laser printer operation and methods for characterizing airborne ultra-fine particles in general. Different kinds of laser printers have been tested regarding emission of sub-micrometer particles. Total concentration of ultra-fine particles as well as particle size distributions have been measured. Toner coverage, paper type, and the number of pages printed were varied in printing processes. The dependence of the particle emission on the page coverage and the number of printed pages has been investigated. Collected data have been compared to the outcomes of the research studies conducted to date on the same topic in order to provide guidance on methods available to minimize exposure to such emissions.

A new methodology for determination of airborne nanoparticle effective density with the tandem DMA-ELPI based on multiple charging correction

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Nanoparticles are increasingly used in a wide variety of industries and are also a by-product of numerous industrial processes such as arc welding, thermal metal spraying, metal arc cutting and combustion. However, their health effects have not yet been fully characterized. Effective density is considered a key characteristic of airborne nanoparticles due to its role in particle deposition in the human respiratory tract (ICRP, 1994) and in the conversion of number distributions to mass distributions (Mc Murry *et al.*, 2002). Because it cannot be measured directly, different methods have been developed to determine this parameter.

The approach chosen in this study is based on the simultaneous measurement of airborne nanoparticle electrical mobility and aerodynamic equivalent diameters. More precisely, particles of a given size are selected on the basis of their electrical mobility diameter as determined using a Differential Mobility Analyzer (DMA) and are subsequently classified according to their aerodynamic diameter by means of an Electrical Low Pressure Impactor (ELPI) (e.g. Van Gulijk *et al.*, 2005).

Test aerosols consisted of spherical nanoparticles of Di-Ethyl-Hexyl-Sebacate (DEHS) produced by nebulization (PALAS AGK 2000). Particles brought to Boltzmann equilibrium with a radioactive neutralizer were selected with the DMA (Grimm Vienna Type L-DMA) and then directed to the ELPI. The current and number size distributions measured by the ELPI were then used to determine the aerodynamic modal diameters and thus the corresponding particle effective density (approaches 'A' & 'B', respectively, in Figure 1).

To take into account the presence of particles carrying multiple elementary charges at the DMA outlet, a theoretical model was developed in which the successive mechanisms undergone by particles are accounted for. More precisely, the calculations incorporate aerosol neutralization, selection within the DMA, charging in the ELPI charger, and finally impaction within the cascade impactor. Computations allow the proportion of each population exiting the DMA ($n = 1, 2, \dots, 5$ elementary charges) in each channel of the overall ELPI signal to be extracted. Particle effective density can therefore be estimated for each population (approaches 'C1' to 'C5' in Figure 1). As can be seen in Figure 1, approaches based on multiple charging correction result in better estimation of effective density. Application of this methodology to thermal spraying fumes will be discussed.

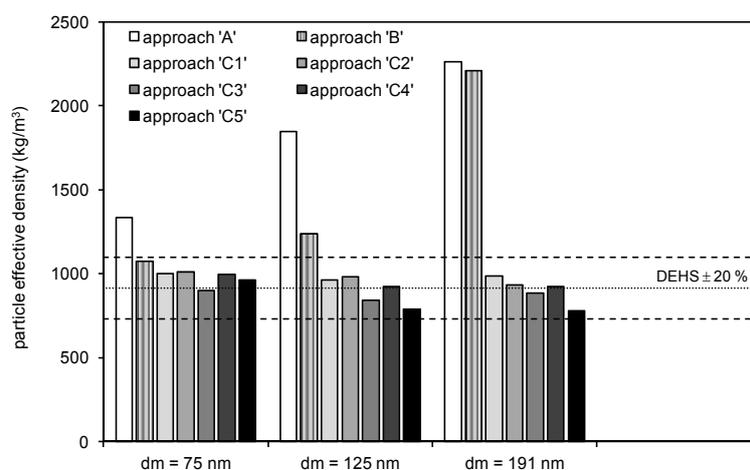


Figure 1. Comparison of the effective density of spherical DEHS particles determined using different approaches for three sizes selected using a DMA.

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Determining the count median diameter of nanoaerosols from their number and lung-deposited surface area concentrations

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Although nanomaterials are increasingly used in a variety of fields including energy, health, cosmetics and materials, uncertainties remain regarding their potential health effects. In parallel, the number of occupational inhalation exposure situations is probably rising, leading to recent proposals of generic strategies for assessing workplace exposure to airborne nanomaterials (e.g. Methner *et al.*, 2010; Witschger *et al.*, 2012). Such strategies indicate that, in addition to chemical composition, a variety of parameters must be assessed in order to characterize exposure to airborne nanomaterials. Among them, particle concentration and size play an important role, since they provide information on the quantities of nanoparticles inhaled and the regions of the respiratory tract where particles are deposited and may potentially interact.

In this work, we propose a method based on simultaneous size-integrated measurements of two particle concentrations (number and lung-deposited surface area, CNC/NSAM), and on the estimation of the average size of potentially inhaled particles obtained by combining these measurements (Bau *et al.*, 2013). The proposed method could form part of a practical measurement strategy, as it would use field-portable, commercially available aerosol instruments. In the absence of instruments that provide real-time size-resolved measurements, this original approach can be carried out because the ratio of the particle concentrations is a monotonous function of particle size, a function which depends only on the geometric standard deviation of airborne particle number size distribution, assumed to be lognormal. Although different authors (e.g. Woo *et al.*, 2001; Maynard, 2003) have applied such methods for determining the surface area concentration of airborne nanoparticles, none of the studies considered the possibility of estimating the aerosol count median diameter.

Compared to SMPS data for polydisperse aerosols characterized by three chemical compositions and count median diameters ranging from 64 nm to 177 nm, experimental results were obtained with acceptable relative discrepancies of $\pm 30\%$. Even though the method proposed is less accurate than one that employs traditional instruments such as SMPS, it might nevertheless be used for workplace air monitoring or as a screening tool for detecting the presence of airborne nanoparticles.

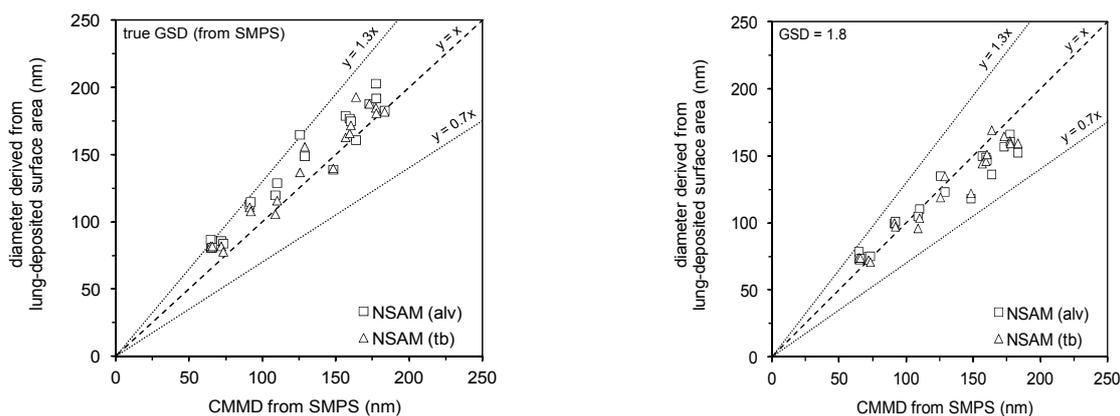


Figure 1. Comparison of count median diameters derived from lung-deposited surface-area determinations and count median mobility diameters obtained from SMPS measurements. Calculations were made using the true GSD (left), or with a GSD set at 1.8 (right). Each data series includes the results obtained for all substances.

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Passive sampling of particle-bound pah and o-pah: linking detectability and high sample throughput with ATD-GC-MS

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Risk assessment of chemical exposure in the occupational environment for deployed military personnel is challenging. Remote areas, high threat levels, and variable working tasks are factors that complicate standard occupational investigations. Monitoring systems based on passive sampling is an attractive alternative for gaseous compounds. However, recent hazard assessments (Magnusson *et al.*, 2012) from deployed areas demonstrate that exposure to particulate matter (PM) pose the greatest risk of exceeding applicable exposure guidelines, especially related to combustion sources. Hence, accurate health assessments of PM measurements must consider chemical composition and source. To address these issues we are developing a robust axial passive sampler, designed to sample gaseous compounds and PM, in combination with a fast and sensitive method for analysis of a broad range of polyaromatic hydrocarbons (PAH) and oxygenated PAHs (O-PAH).

The sampler was evaluated under controlled conditions in an exposure chamber using diesel exhaust (PM_{10} , $550 \mu\text{g}/\text{m}^3$), with a sampling period of 7.5h. The sampler consists of a holder with a baseplate for a substrate, an adjustable spacer, and a mesh net to protect the substrate from wind effects, leaving diffusion and gravitation as the main driving sampling forces. The substrates evaluated were glass fiber filter (GFF, 25 mm diameter) coated with or without Tenax TA™ polymer (2,6-diphenylene oxide). The effect of the length of the diffusion path was evaluated using different spacers. Simultaneous active sampling enabled calculation of passive sampling rates. Chemical analysis of substrates was performed with ATD-GC-MS according to Wingfors *et al.* (2014). The study focused on compounds associated to both the gaseous and particulate phase.

Detectable amounts of most PAHs and O-PAHs were found on filters both with and without Tenax TA™. The addition of polymer to the filter substrate increased the total amount collected, and hence the sampling rate, for most PAH. However, the addition of polymer did not substantially increase the amount of several O-PAH, which were found to exist predominantly in the particulate phase. This contrasts the active sampling as ~50/50 partitioning between gas and particles was found for these O-PAH. The association of O-PAH with particles could be explained by the findings of Lee and Lane (2010), where O-PAH formed in the reaction with OH-radicals and phenantrene were quickly associated with particles. The diffusion path length affected the collected mass of O-PAH, but only to a lesser extent.

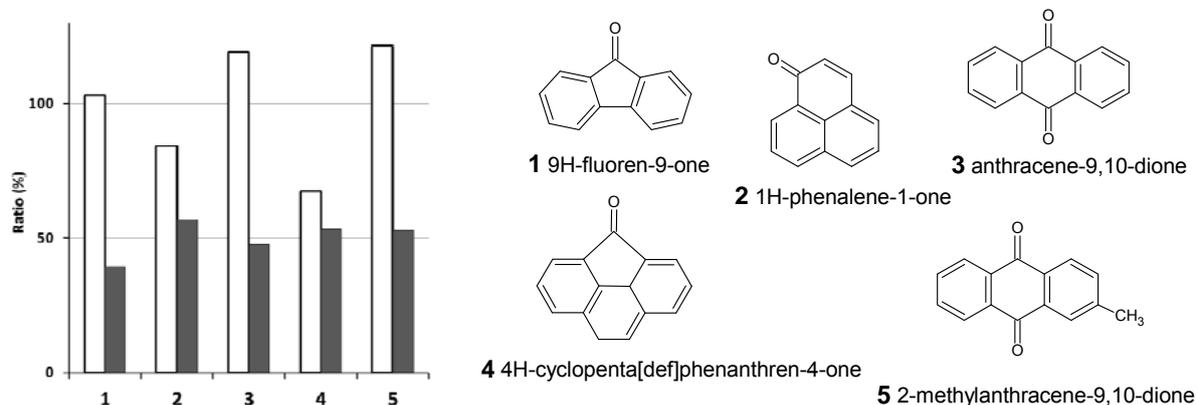


Figure 1. The ratio of particle associated O-PAH compared to the sum of particle and gas phase. White = passive sampling, black = active sampling. Numbers refer to respective O-PAH, see structures.

Acknowledgement: This work was undertaken as part of a FOI research project funded by Swedish Ministry of Defense.

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***Session C - Chemical speciation and Semi
volatile organic compounds sampling
and analysis***

ECOS-POUSS: a nationwide survey of semi-volatile organic compounds in home settled dust

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Semi-volatile organic compounds (SVOCs) are of concern due to their established or suspected health effects and due to the widespread exposure through different environmental media and pathways. The objective of this study is to assess the indoor SVOC concentrations in home settled dust at a nationwide scale. Forty-eight SVOCs including phthalates, polybrominated diphenyl ethers (PBDEs), polychlorinated biphenyls (PCBs), polycyclic aromatic hydrocarbons (PAHs), pyrethroids, organochlorine and organophosphorous pesticides, synthetic musks, bisphenol-A and tributylphosphate, were selected after a health-based ranking and taking into account technical feasibility.

Vacuum cleaner bags were collected during a nationwide survey carried out in dwellings where at least one child aged 6 months to 6 years lives (2008-2009). Bags containing dust from outside the dwelling, or not containing enough dust after sieving to <100 µm, or not properly stored during transport, were discarded. 145 dust samples were finally analyzed. SVOCs were extracted by pressurized liquid extraction with dichloromethane, and analyzed by gas chromatography / mass spectrometry (GC/MS) or tandem mass spectrometry (GC/MS/MS). The use of sampling weights enables to extrapolate the results to the national housing stock inhabited by children aged 6 months to 6 years.

Ten compounds were quantified in nearly (> 98%) all the dwellings (in brackets: median nationwide concentration in µg per g of dust): DEHP (341), DiNP (144), DiBP (17.1), BBP (10.8), DBP (10.3), bisphenol-A (4.29), DEP (3.27), permethrin (2.64), galaxolide (1.08), and BDE-209 (0.761). The highest concentrations (> 1 mg/g) were measured for DEHP, DiNP, DiBP, BBP, and permethrin.

The estimated nationwide home settled dust concentrations will enable an exposure assessment including also the indoor air contribution. In parallel, common modes of action are considered to derive toxicological indexes and to conduct a cumulative health risk assessment of indoor SVOC mixtures.

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ECOS-PM: a nationwide survey of semi-volatile organic compounds in indoor air

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Semi-volatile organic compounds (SVOCs) are of concern due to their established or suspected health effects and due to the widespread exposure through different environmental media and pathways. The objective of this study is to assess the indoor SVOC concentrations on airborne particles (PM₁₀) collected at a nationwide scale. Sixty-six SVOCs, including phthalates, polybrominated diphenyl ethers (PBDEs), polychlorinated biphenyls (PCBs), polycyclic aromatic hydrocarbons (PAHs), pyrethroids, organochlorine and organophosphorous pesticides, alkylphenols, synthetic musks, tributylphosphate and triclosan, were selected after a health-based ranking and taking into account technical feasibility.

The samples (n = 300) were collected during a nationwide survey carried out by the French Observatory of indoor air quality (2003-2005) in a representative sample of the housing stock. The PM₁₀ were collected in the living-room on polytetrafluoroethylene (PTFE) filters during 7 days (sampled volume: 14 m³). The filters were stored at -18°C before analysis. SVOCs were analyzed by thermal desorption coupled with gas chromatography / tandem mass spectrometry (TD-GC/MS/MS).

Most of the PAHs, two phthalates (DiNP and DEHP), BDE-47 and BDE-99, and triclosan were quantified in more than 90% of the dwellings. Lindane, musks (galaxolide and tonalide), permethrin, bisphenol-A, and some PCBs were also commonly found. Pesticides such as atrazine, aldrin, endrin and chlordane were rarely detected. The use of sampling weights enables to extrapolate these results to the national housing stock.

This data, combined to other results from the ECOS-project, will be used to assess exposure to SVOCs in French homes and associated health effects. Relationships between concentrations, building characteristics and household activities will also be studied to identify SVOC determinants in indoor air.

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Organic components in particulate matter from cooking

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The threshold values stipulated for PM_{2.5} are frequently exceeded in many urban areas. Source apportionment studies performed in the USA indicated that, along with vehicle and biomass burning emissions, cooking activities represent one of the major sources of PM_{2.5} (McDonald et al., 2003). Improved information about the chemical characteristics of these emissions is essential to model source contributions and to implement either source-oriented mitigation measures or health protection programmes. Some emission profiles have been obtained for USA (McDonald et al., 2003; Schauer et al., 1999) and Chinese (He et al., 2004; Zhao et al., 2007) cooking styles. However, emissions depend strongly on the cooking method and food ingredients, and nothing is known about the speciation of particle emissions from the preparation of European dishes.

In this study, low-volume PM_{2.5} samples were collected from the exhaust stacks on the roofs of an university canteen, a charcoal-grilled chicken restaurant and a wood-oven roasted piglet restaurant, during the preparation of lunches and/or dinners. Samples were solvent-extracted and analysed by gas chromatography-mass spectrometry. The use of thick exhaust hood filters and of gas and electricity as cooking fuels in the kitchen of the university canteen contributed to the emission of much lower PM_{2.5} levels compared to the restaurants. The PM_{2.5} samples from the canteen exhausts presented concentrations between 24 and 525 µg m⁻³. The charcoal-grilled chicken restaurant emitted particles at concentrations from 26 to 127 mg m⁻³ (avg=72 mg m⁻³). A similar average concentration (73 mg m⁻³) was obtained for the wood-oven roasted piglet restaurant. In the exhaust of this establishment, PM_{2.5} ranged from 445 mg m⁻³, when vine cuttings were used to fire up the brick ovens in which piglets were roasted, to 203 µg m⁻³, at the final stage of roasting. Aliphatics, one of the dominant organic classes, represented, on average, 66.6 and 2.4 µg mg⁻¹ PM_{2.5} emitted by the stacks of the canteen and charcoal-grilled chicken restaurant, respectively. This group of compounds accounted for 634 ng mg⁻¹ PM_{2.5} when vine cuttings were used to heat the ovens of the piglet restaurant, whilst at the final stage of roasting the mean mass fraction was 2.4 µg mg⁻¹ PM_{2.5}. The carbon preference index (CPI) of the homologous series of *n*-alkanes in samples from the canteen and piglet restaurant were ≤ 1. The very high abundances of tritriacontane and pentatriacontane in PM_{2.5} emitted by the chicken restaurant contributed to CPI values (3-93) in a range generally pointed out as typical of biomass burning. However, the emission signature of this latter source presents C_{max} at C₂₇ and C₂₉. The mass fractions of polycyclic aromatic hydrocarbons (PAH) were, on average, 120 ng mg⁻¹ PM_{2.5} for the canteen and 215 ng mg⁻¹ for the chicken restaurant. Nevertheless, values of 22 µg PAH mg⁻¹ PM_{2.5} were reached during the heating phase of the ovens, decreasing to 4.1 µg PAH mg⁻¹ PM_{2.5} during the roasting of piglets. Naphthalene (4.02-406 ng mg⁻¹ PM_{2.5}) was the most abundant polyaromatic in particle emissions from the canteen, while fluoranthene (21.6-5348 ng mg⁻¹ PM_{2.5}) and pyrene (20.2-5410 ng mg⁻¹ PM_{2.5}) were the dominant PAH in samples from the other establishments. Ratios between PAH overlap those of biomass burning and vehicle exhausts, making questionable their use as source assignment tool. Cholesterol (3.77-13093 ng mg⁻¹ PM_{2.5}) was always the prevailing sterol. It represented 38% of the mass fractions of compounds with functional groups -OH in particles emitted by the canteen. Excepting the heating phase of the ovens of the piglet restaurant, percentages of 91-98% were obtained in emissions from the other commercial establishments. Cholesterol may be pointed out as a good tracer for cooking emissions.

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Emission factors for road traffic from a tunnel study

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In urban areas, road traffic is recognised as an important source of both particles and certain metals [1, 2]. Road traffic involves either exhaust or non-exhaust emissions. In order to address these emissions, studies need to be performed under realistic driving conditions in environments where the input from other sources is minimised. Measurements in traffic tunnels have been used successfully for quantifying emissions [e.g. 3, 5], but so far no study has established emission factors for Portugal. To fill this gap, a sampling campaign was carried out over one week in the Avenida da Liberdade Tunnel (Braga, Portugal). The campaign included the monitoring of gases (CO₂, CO, NO_x) and particles at two sites, one in the tunnel and another at an urban background location. Particulate matter collected with a high volume sampler was segregated into four size ranges (PM_{0.5}; PM_{0.5-1}; PM_{1-2.5} and PM_{2.5-10}). Its carbonaceous content (organic and elemental carbon, OC and EC) was determined by a thermal optical transmittance system, whereas elements were analysed by ICP-MS and ICP-AES.

The finest particulate matter (PM_{0.5}) accounted for 56% of the total aerosol mass, whilst the coarse fraction (PM_{2.5-10}) represented only 12%. The carbonaceous fraction was largely concentrated in the smallest size range, encompassing 88% of the EC and 67% of the OC present in PM₁₀. The dominant elements could be divided into two groups. Fe, Ba, Mo, Cu and Zn were more abundant in particles sized between 1 and 2 µm and have been associated with tyre and break wear. Ca, Al, K, Sr and Ti were present in particles with average diameter larger than 2 µm and have been pointed out as characteristic elements of soil resuspension. In this study, emission factors of particulate matter, carbonaceous constituents, elements and vehicle exhaust gases (CO, CO₂ and NO_x) were also calculated (Table 1). The obtained values were slightly lower than those found for other tunnels, but within the ranges presented by the EMEP/EEA inventory.

Table 1. Average emission factors determined by the carbon balance method [6]

CO ₂	CO	NO _x	PM ₁₀	OC in PM ₁₀	EC in PM ₁₀	PM _{2.5}	OC in PM _{2.5}	EC in PM _{2.5}
g.v ⁻¹ .km ⁻¹			mg.v ⁻¹ .km ⁻¹					
212	4.02	1.22	152	39	39	133	34	38

Acknowledgement: This work was funded by the Portuguese Science Foundation through the project “Source apportionment of URBan Emissions of primary particulate matter”, PTDC/AAC-AMB/117956/2010 (URBE).

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Structural characteristics of ambient aerosols in an indoor university gymnasium

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Particulate air pollution, specifically the fine particle fraction ($PM_{2.5}$), has been associated with increased cardiopulmonary morbidity and mortality. Occupational exposure to fine particulate matter is needed to assess the health risks of the population. The present study focuses on the structural properties of ambient particles in an indoor sport facility –a gymnasium– belonging to the University of León, Spain. The gymnasium is 15 m wide, 27 m long and has a height of 10.6 m. It has no windows and a half-cylinder skylight (5 m diameter and 20.3 m length) centered on the roof. The vinyl flooring is practically coated with gym mats and safety mattresses. The sports equipment included asymmetric bars/high bar, rings, parallel bars, beams, pommel horse, tumble track, trampolines, wall bars, and dug pit with foam cubes. Due to the high temperatures reached after the late morning hours, a side gate was frequently open when the gymnasium was busy. The gym does not have any mechanical ventilation system. During the sampling campaign, a set of specific samplings was conducted for subsequent analysis by electron microscopy. PM_{10} particles were collected on polycarbonate filters from approximately 9:00h to 18:00h, covering the period of maximum activity. The filters were inspected with a Field Emission Scanning Electron Microscope (Jeol JSM 6335F) equipped with an Energy-Dispersive X-ray Spectrometer. Size, morphology and elemental composition from the individual particles were characterized.

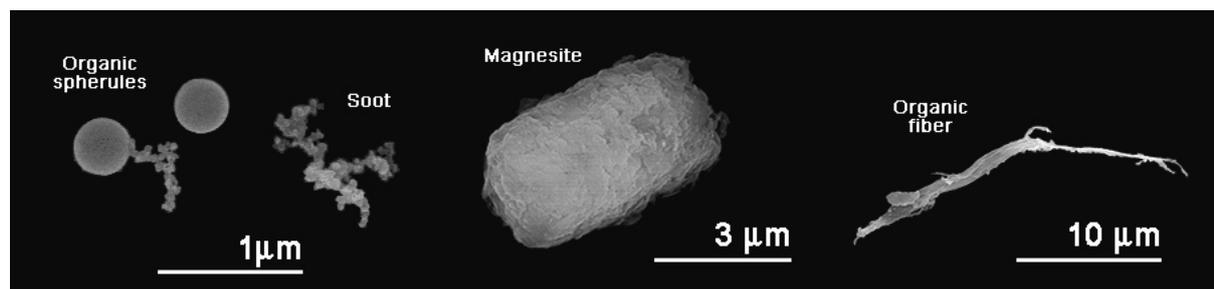


Figure 1. Images of some of the most abundant particles in the samples.

Two main phases were found on the samples investigated: (1) mineral dust, linked to the coarse fraction and (2) carbonaceous matter, on the submicrometric range (Figure 1). The mineral fraction was mainly comprised of magnesium oxides and carbonates, aluminosilicates, and halides (KCl and NaCl) that tend to form micro-crystals in the surface onto the magnesite and clay minerals. Organic fibres were also abundant in the coarse range. Soot aggregates and organic, organic particles, sulphates and some of the previous mentioned halides in the form of micro-crystals composed the submicrometric range.

The particles in the coarse range are probably consequence of the gymnasium activities as consequence of the disintegration of material. The magnesite is used to as a drying agent for hands and the fibers are probably from the disintegration of the gym mats. The submicrometric particles are typical from anthropogenic emissions (i.e. vehicles, heating...) that might have enter into the facility from the exterior.

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Particles from the interaction between pavement and tyres

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It has become more evident that wear particles from road pavements and tyres may contribute to very high levels of inhalable particles in outdoor air (Hosiokangas *et al.*, 2004; Swietlicki *et al.*, 2004). In many countries, non-exhaust particles are seen as an important research field due to the lack of knowledge and the complex formation and emission processes (Denier van der Gon *et al.*, 2013). Moreover, while control technologies have led to substantial reductions in exhaust emissions, vehicle non-exhaust emissions are still unabated.

A road simulator was used to generate wear particles with very low contamination from ambient particles and no contamination from exhaust pipes, since the system is electrically actuated (Dahl *et al.*, 2006; Gustafsson *et al.*, 2008). Two types of tyres were tested in the simulator (Michelin Energy Saver and Bridgestone Turanza ER300 Ecopia). To be able to detect short time variations, mass concentration of PM₁₀ was monitored with both a DustTrak instrument (TSI) and a TEOM (Series 1400a, Thermo). High-volume quartz filter PM₁₀ samples (EcoTech HiVol 3000) were collected during several hours of running the road simulator at 70 km/h. After sampling, these filters were analysed for organic and elemental carbon (OC and EC) by a thermal-optical technique and for organic constituents by GC-MS. Rubber tyre fragments were also solvent-extracted and analysed by GC-MS.

Once the experiments have started, the PM₁₀ concentration increased from about 20 µg/m³ to 60-80 µg/m³, approximately 20 min later. Afterwards, the concentrations stabilised due to the equilibrium between generation and deposition of particles. Regardless the type of tyre, total carbon represented around 4.2% of the PM₁₀ mass, whilst EC accounted for 1%. The PAHs/OC mass fractions in particles resulting from the wear of one type of tyre were 2 to 7 times higher than those measured for the other type. The dominant PAH was naphthalene, followed by fluoranthene, chrysene, pyrene and phenanthrene. Benzothiazole, previously pointed out as a good tracer for tyre wear particles (Wik & Dave, 2009), was detected at levels slightly above the detection limit, either in PM₁₀ or in the tyre samples. The major hydroxyl compounds in both PM₁₀ and tyre samples were *n*-alkanols > C₂₂ and sterols. In the PM₁₀ samples, they were present at individual mass concentrations ranging from about 50 to 400 µg/g OC. The mass fractions of these constituents were up to 3 times higher in PM₁₀ resulting from the interaction between the pavement and one of the tyre types. Depending on the PM₁₀ sample, the major aliphatic compounds were tetratriacontane (34 mg/g OC) or tritriacontane (56 mg/g OC). However, while the first *n*-alkane was present in both tyre samples, the second was only detected in one of the rubbers. Hopanes, generally referred to as markers of primary particle emissions from gasoline and diesel engines (Alves, 2008), were detected at mass concentrations of 3.9-5.4 mg/g OC and 166-220 ng/g in PM₁₀ and tyre samples, respectively. Significant unresolved complex mixtures (UCM), composed of a myriad of branched and cyclic hydrocarbons, were observed in all samples.

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Determination of manganese valence states in some typical welding fumes by synchrotron-based XANES spectroscopy

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Introduction Welders constitute the largest group of workers exposed to manganese (Mn). Welding methods differ in which chemical compounds (and hence valence states) Mn occurs in the fume. The critical health effect of Mn is pre-clinical impairment of psychomotor performance, e.g. motor activity, speed, memory and cognition. This is influenced by accumulation of Mn in the basal ganglia in the brain - the main entrance for Mn into the brain is via the blood circulation (the blood brain barrier). In order for Mn deposited in the alveoli to be transported into the blood circulation it must first be dissolved (Taube, 2013). Welding fume Mn consisting of a lower valence state (II) is expected to be more easily dissolved than higher valence states (III or IV). The aim was to study the Mn valence states using XANES spectroscopy for welding fumes sampled on membrane filters.

Methods 10 typical airborne Mn-containing welding fumes were sampled on membrane filters (Millipore AAWP 37mm) at the outlet of a welding exposure chamber (chamber described in ISO 15011-1:2009). Model compounds were powders of Mn(II)O, Mn(III)₂O₃, Mn(IV)O₂ and Mn(II,III)₃O₄. Additional XANES reference data available free from IFEFFIT (<http://cars9.uchicago.edu/ifeffit/Ifeffit>) were also used (Manceau, 2012). Mn K-edge XANES spectra were collected at the wiggler beam-line I811 at the MAXLab synchrotron facility at Lund University, Sweden, equipped with a Si[111] double-crystal monochromator. Data collection was performed in transmission mode (model compounds) using ionization chambers and in fluorescence mode (welding fume on membrane filters) with either a Lytle or a solid state (PIPS) detector. A Mn metal foil was used for energy calibration and was run simultaneously with the samples. The scans were evaluated with the free software Athena iXAFS (an interactive web-based programme for XAFS analysis – available from IFEFFIT) for valence states fingerprints (determined as described by Ressler, 1999). The linear combination fit (principal component analysis using normalized $\mu(E)$ fitting space) was performed with the same software.

Results In Figure 1, the K-edge spectra of Mn for four of the 10 studied welding fumes are shown together with the spectra of the model compounds MnO, Mn₂O₃ and MnO₂. The valence states and the principal component analysis are shown in the inserted table in the figure.

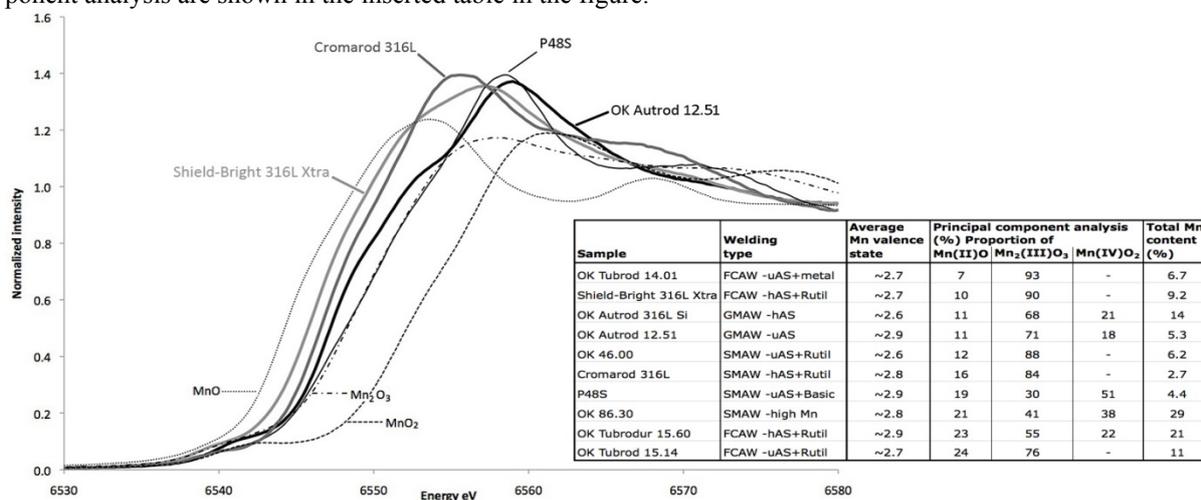


Figure 1. XANES spectra of four different manganese containing welding fumes samples – inset table show additional data for all 10 samples.

Conclusions XANES spectroscopy can be a useful scientific tool for the investigation of valence states of welding fume components. The tested welding methods mainly generated mixtures of Mn(III)₂O₃ and Mn(IV)O₂.

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Chemical characterisation of exhaust particles emitted by light-duty vehicles

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Motor vehicle emissions are the dominant sources of particulate matter (PM) in urban environments. Numerous studies have linked vehicular exhaust particles to adverse health effects, including premature deaths [1, 2], respiratory and cardiovascular problems [3-7], and neurodegenerative disorders [8]. Primary PM emitted by vehicles contains a variety of chemical constituents, such as polycyclic aromatic hydrocarbons (PAHs) and trace elements that are usually of environmental and health interest. Its composition varies depending on the vehicle age and type, fuel, and after-treatment technology. The main purpose of this work was to evaluate the chemical composition of PM emitted by 8 different vehicles representing the Portuguese fleet. Exhaust samples from petrol and diesel cars (Euro 3 to Euro 5) were collected in a chassis dynamometer facility. To simulate the real-world driving conditions, three ARTEMIS cycles were followed: road, to simulate a fluid traffic flow, and urban with hot and cold starts, to simulate driving conditions in cities. Samples were analysed for the water soluble ions, for the elemental composition, and for PAHs, respectively, by ion chromatography, Inductively Coupled Plasma Atomic Emission Spectroscopy (ICP-AES) and Inductively Coupled Plasma Mass Spectrometry (ICP-MS), and Gas-Chromatography-Mass Spectrometry (GC-MS).

Nitrate and phosphate were the major water soluble ions in the exhaust particles emitted from diesel and petrol vehicles, respectively. The amount of material emitted is affected by the vehicle age. For vehicles \geq Euro 4, most elements were below the detection limits. Sodium, with emission factors in the ranges 23.5-62.4 $\mu\text{g.km}^{-1}$ and 78.2-227 $\mu\text{g.km}^{-1}$, for petrol and diesel Euro 3 vehicles, respectively, was the major element. The emission factors of metallic elements indicated that diesel vehicles release three to five times more than petrol automobiles. By comparing different cycles it was observed that emissions under driving conditions in urban areas are higher than those found for on-road driving, being three or four times higher, for petrol vehicles, and two or three times, for diesel vehicles. This difference between cycles is mainly due to the high emissions for the urban cycle with hot start-up. As registered for elements, most of the PAH emissions for vehicles \geq Euro 4 were also below the detection limits. Naphthalene, with emission factors up to around 140 mg.km^{-1} , was always the dominant PAH. The highest emission factors were noticed for a petrol-powered vehicle belonging to the Euro 3 class under the road driving cycle. The individual emission factors for 3 to 6 ring PAHs emitted by this vehicle ranged from 22 to 1207 $\mu\text{g.km}^{-1}$. The corresponding emission factors for the Euro 3 diesel-fuelled vehicle under the same driving cycle varied between 0.05 and 6.7 $\mu\text{g.km}^{-1}$.

Acknowledgement: This work was funded by the Portuguese Science Foundation through the project "Source apportionment of URBan Emissions of primary particulate matter", PTDC/AAC-AMB/117956/2010 (URBE).

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A multi-residue method for the simultaneous analysis of several classes of semi-volatile organic compounds in airborne particles

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People are exposed to multiple pollutants, especially indoors. In the perspective of a cumulative risk assessment, a multi-residue method was developed for the simultaneous analysis in airborne particles of several classes of semi-volatile organic compounds (SVOCs), from trace to highly concentrated compounds. These include alkylphenols, polycyclic musks, organochlorines (OCs), organophosphates (OPs), polycyclic aromatic hydrocarbons (PAHs), polybromodiphenylethers (PBDEs), polychlorobiphenyls (PCBs), phthalates and pyrethroids. The method was based on thermal desorption (TD) and gas chromatography/tandem mass spectrometry (GC/MS/MS). TD is a suitable on-line alternative to traditional off-line extraction techniques that require larger amounts of sample and organic solvent, and generally involve tedious and time-consuming multi-step procedures.

Investigated SVOCs (n = 66) were selected according to their health interest and their compatibility with a GC analysis. The accuracy and precision of the method were assessed via replicate analysis of the National Institute of Standards and Technology (NIST) standard reference materials SRM 1649b (urban dust) and 2585 (house dust). Its applicability was tested for 25 indoor PM₁₀ samples collected in the living-room of French dwellings on polytetrafluoroethylene (PTFE) membranes.

The results obtained on SRMs demonstrated excellent agreement with the indicative, reference or certified values with RSD < 20%, indicating good accuracy and precision of the method. The results obtained on real samples confirmed the presence of a wide range of SVOCs in French indoor PM₁₀: 59 SVOCs were detected above the limit of detection (LOD) at least once, 38 in more than 50% of the samples, and 23 (some alkylphenols, musks, OCs, PAHs, PBDEs and phthalates) in all the samples.

This TD-GC/MS/MS method is simple and efficient. It provides many advantages over traditional methods including organic solvent-free, reduced analysis time and cost, and high sample throughput, making it appropriate for environmental monitoring programs or large-scale studies. Moreover, the results obtained on real PM₁₀ samples illustrate its ability to quantify a wide range of SVOCs in a single analysis. It was afterwards applied to 300 indoor PM₁₀ samples collected during a nationwide survey carried out by the French observatory of indoor air quality (2003-2005) in a representative sample of French dwellings (ECOS-PM project).

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***Session D - Air sampling and air
monitoring***

Sampling and analysis of 2,6-diisopropylphenyl isocyanate (DIPPI) as a thermal degradation product of polycarbodiimide

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Isocyanates are skin and respiratory tract irritants and also strong sensitizers. They are well known for their preponderant role in occupational asthma. They are widely used in many applications and industrial processes such as the application of coatings, glues, insulation and upholstery fabrication. Thermal degradation of polyurethane-based products has been found to be an occupational source of exposure to isocyanates (Boutin *et al.* 2006, Karlsson *et al.* 2002). An additive containing polycarbodiimide is used to produce thermoplastic products and has been suspected, when heated, of emitting isocyanates uncommonly found in workplaces. The goal of this study was to measure the concentration of 2,6-diisopropylphenyl isocyanate (DIPPI, CAS# 28178-42-9) in workplace atmospheres by adapting the existing high sensitivity method developed at the IRSST for isocyanate sampling and analysis (Gagné *et al.* 2013).

The high sensitivity method for isocyanates, IRSST #366, uses a closed-face 37-mm cassette which has two glass fibre filters coated with 9-(N-methylaminomethyl)anthracene (MAMA). This method is designed to measure very low concentrations of vapour-phase monomeric isocyanate. The sampling is done at 1 L min⁻¹. The analysis is performed using a liquid chromatograph mass spectrometer (Roberge *et al.* 2013). The quantification limit was evaluated to be 1 ng per sample.

The industrial process involves a thermoplastic resin and two additives, which are melted and extruded at approximately 270°C to form a sheath around a metal wire. One of the additives contains polycarbodiimide which is originally formed by isocyanates reacting with a catalyst.

The results (n = 6) for DIPPI ranged from 4.6 to 150 µg.m⁻³ for a sampling duration from 128 to 185 minutes. The highest concentrations, 130 and 150 µg.m⁻³, were measured at the emission source (ambient sampling), i.e., next to the zone where the additives and resin are injected. The highest concentrations measured in personal sampling, 13 and 24 µg/m³, were obtained for the production line worker. Despite the fact that these results do not represent time-weighted exposure values, the concentrations were in the same order of magnitude as the Swedish OELs (8h: 40 µg.m⁻³ (5 ppb), 5min: 80 µg.m⁻³ (10 ppb)) (SWEA 2005). These results are most likely an underestimation of the real isocyanate concentrations for the two following reasons: 1) only one of the two expected isocyanates was analyzed; and 2) particle-phase DIPPI (from recondensation) was poorly derivatized on the impregnated filter (sampler limitation).

In conclusion, this adapted version of IRSST method #366 was able to measure significant concentrations of 2,6-diisopropylphenyl isocyanate in a workplace atmosphere. Moreover, it emphasizes the fact that the thermal degradation of polycarbodiimide-based polymer could produce isocyanate exposures close to or above the typical OEL for isocyanates (5 ppb).

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Monitoring volatile BTX (benzene, toluene and xylenes) molecules in workplaces: towards a real-time portable analyzer

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Benzene, Toluene and Xylenes (BTX) are known for their toxicity. They can be found in the atmosphere of outdoor and indoor environments. Long exposure to these volatile compounds may have dangerous impacts on human health (Mögel et al. 2011).

The aim of this work is to develop real-time detecting device based on the pre-concentration of airborne BTX molecules on a material and their simultaneous detecting by ultra-violet spectroscopy in order to monitor the exposition towards BTX in workplace environments.

The developed material should have a large specific area and an adapted functionalization to target the BTX molecules in a very complex matrix such as the air.

Much research conducted on silica materials has shown the advantages of these materials for monitoring volatile organic compounds (Parida et al. 2006). In this view, we have synthesized mesoporous silica nanoparticles material using a modified Stöber process, the templating agent used was cetyltrimethylammonium chloride (CTACl). We added phenyl functions (up to 10% molar ratio) in order to enhance the selectivity toward BTX molecules (Yuliarto et al. 2009; Kim et al. 2008).

The nanoparticles were assembled on a quartz substrate using drop-coating technique. A 4µm thickness film was obtained and tested in a dedicated laboratory experimental set-up. Interesting results were obtained, reversible adsorption – regeneration cycles were observed on the film (Fig.1). The presentation will summarize the different aspects of the present work and some results obtained with the developed film.

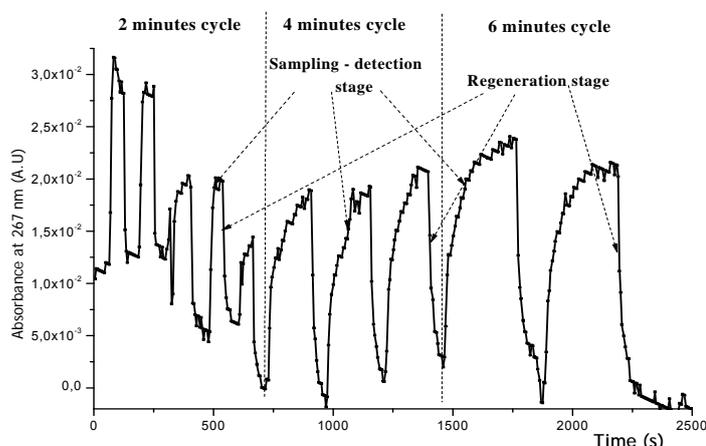


Fig 1. Cycles of adsorption-regeneration of toluene (20 ppm_v) on a 4µm nanoparticles film

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Determination of tricresyl phosphate air contamination in aircraft type BAe 146/AVRO RJ

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For many years, the exposition to tricresyl phosphates (TCP) and tri-*o*-cresyl phosphate (ToCP) in particular of cabin crews in commercial aircrafts is described as a cause of occupational diseases. The Aircraft BAe 146/Avro RJ was identified as a particularly striking. This small short-haul aircraft with four jet engines was reported more frequently than other aircrafts by so-called fume events. Tricresyl phosphates are components of aircraft engine oils, such as those used for many years. The *o*-cresyl phosphates (*o*CPs) are known neurotoxins. From studies of engine oils it is known that the critical *o*CPs are minor contaminants with less than 0.1 % of ToCP in total.

In 2012, the BG Verkehr and the IFA had the opportunity to perform extensive measurements in five aircrafts of type BAe 146/Avro RJ. In addition to the samples on organo phosphates, samples were also drawn to other volatile organic compounds in the air on the plane. The samples were analysed in two independent laboratories.

The investigations showed that the main target compound ToCP was not present in the air of the aircraft cabins. However, other phosphates such as tri-*n*-butyl phosphate and tri-phenyl phosphate are detected which could have their origin in the hydraulic oil. The load of volatile organic compounds (VOC) in the aircraft was in a range, such as occurs in offices. Only on a flight where the plane had to be de-iced before take-off significant some components of de-icing fluid could be detected. However, these substances were no longer detectable after about 30 minutes of flight time.

In another study, a moisture trap from the ventilation system of a retired BAe 146 aircraft was examined for deposits. The inside surface was extracted with methyl tertiary-butyl ether (MtBE) and analysed for organophosphates. The inside surfaces of the filter are reflecting several years of operation and non-volatile organophosphates such as TCP can be accumulated. Also here, the critical ToCP is detectable only in traces, while the other phosphates were very well detectable (Figure 1).

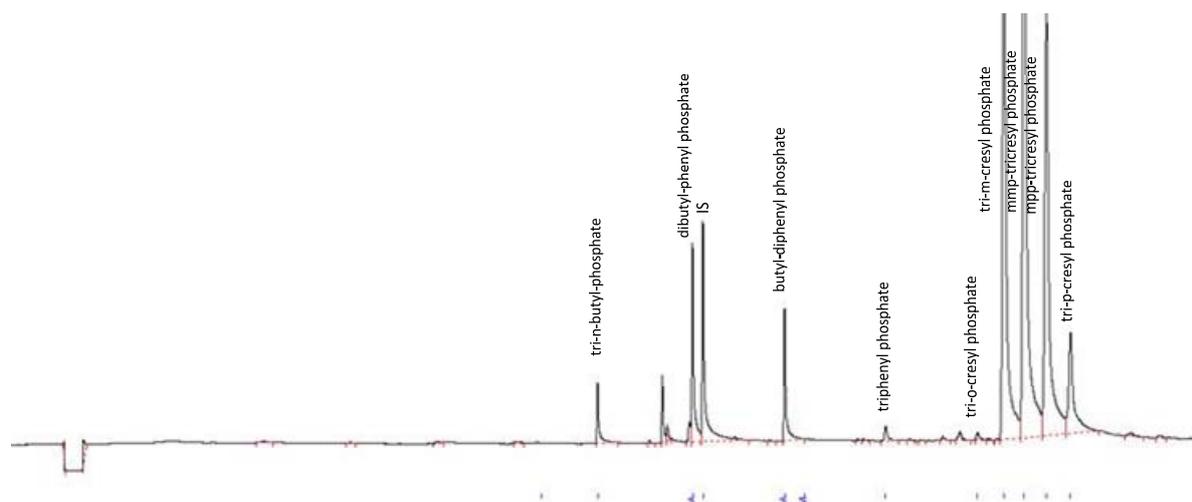


Figure 1: Chromatogram of an MtBE extract from a moisture trap of an BAe 146 aircraft

Chloroanisoles represent a common indoor air quality problem in Sweden

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Between 1961 and 1975 more than 476000 houses were built in Sweden with faulty regulations that caused many moisture damages. For example, wood impregnation with pentachlorophenol (PCP) was recommended as an alternative to traditional constructive methods to prevent moisture and subsequent microbial growth.

The recommended use of PCP was unfortunate because dampness favors microbial growth and some microorganisms can metabolize PCP into malodorous chloroanisoles that have extremely low odor thresholds and therefore often lead to indoor environment problems. Chloroanisoles are, therefore, interesting malodors to monitor in problem buildings and methods for measuring chloroanisoles in air and wood were introduced on the Swedish market in 1999. A subsequent academic study from Germany concluded that 'Chloroanisoles are good indicators of possible PCP-treatment of wood in frame houses and their detection should initiate investigation on PCP contamination' (Gunschera et al., 2004).

On this background, one might expect that the problems with wood preservatives and chloroanisoles should be well known and described in Sweden, especially considering that Swedish legislation states that malodors are unacceptable in public buildings and at non-industrial workplaces. Indeed, the problem with chloroanisoles is well known among building investigators and remediation practitioners but Swedish authorities, institutions and academia provide little if any information. Unfortunately, this leads to situations where residents become aware of the chemical origin of the malodors but then experience difficulties finding public information from authorities concerning e.g. the potential health effects of exposure.

From a health perspective, the scarce data point to indoor air levels of chloroanisoles in a very low range where no health risk for occupants is expected (Gunschera et al., 2004). Still, the malodors often cause concern and maybe even adverse health effects in people perceiving them as a health hazard. It is likely that information regarding the problem with wood preservatives and chloroanisoles would be appreciated and beneficial to those exposed and it could be argued that occupants should be given such information following the ethical principle of 'Right to know', including the fact that, to our knowledge, toxicological evaluations are lacking and therefore warranted.

In Sweden, we have begun to inform about this major indoor air problem, starting in a newsletter from the Swedish Chapter of International Society of Indoor Air Quality and Climate (Lorentzen et al., 2012a, 2012b). As indoor malodorous chloroanisoles occur also in other countries, we here use an international forum to highlight and review the developments and experiences that have accumulated in Sweden, since 1955 when PCP was first introduced and then used instead of moisture barriers on a large scale until it was banned in 1978. Most of the reviewed text was retrieved from Swedish documents, including a remarkable observation by the Swedish Wood Preservation Institute that the odor is often 'characterized as moldy and the houses in analogy as mold houses' (Nyman, 2004). Still today, this institute informs the public that that the odor is likely due to terpenes, which are natural components of wood.

We believe that the problem with chloroanisoles is of interest in many areas - including air monitoring in relation to problems with malodors, indoor environment and health.

Acknowledgement: This work was supported by a grant from The Swedish Research Council FORMAS for the project 'Occurrence and health effects of malodorous chloroanisoles from wood preservatives'.

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A new tool to compare respirable dust sampling techniques in the workplace atmosphere: the workplace atmosphere multisampler - WAM

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Uniting historical dust measurements from workplace atmospheres, performed with obsolete sampling methods such as konimeters and standard thermal precipitators and the analyses with semi quantitative techniques, to modern sampling and analyses methods, creates an overload of incomparable data. Some scientists proposed implementing conversion factors for the recovery of historical data. However, an increasing number of occupational hygienists agree on the influence of the different workplace atmospheres onto the dust sampling process and analysis.

Studying the effects that create differences between contemporary dust samplers (e.g. design, flow rate and sampling efficiency) is usually done by means of personal measurements or by comparing samplers in a standard atmosphere, thus ignoring workplace variability and congruent sampling. Previous comparison studies used unequal sampling methods (e.g. hanging samplers next to one another), and consequentially produced biased results.

The development of the WAM, Workplace Atmosphere Multisampler, makes it possible to determine the reproducibility of sampling data and to compare several samplers (up to 12) in 1 run.

In this study, sampling was performed in 3 distinct industries (foundry industry, enamel industry and brickworks industry) using 3 different respirable dust samplers. In this study, the Dorr Oliver 10 mm cyclone, Casella SIMPEDS plastic cyclone and the CIP10-R sampler were used to validate this device.

Single runs with identical samplers only, were used to validate the WAM for providing homogeneous dust aerosols to the samplers. Mixed runs, with different samplers in one run, were performed to confirm these results.

The gravimetric analyses for the SIMPEDS cyclone show reproducible results. All 6 runs show an average deviation below 10% (flow and analysis error included in these figures). The analyses of the Dorr Oliver cyclone produced varying results, which may be an indicator of the non-reproducibility of the results obtained out of the gravimetric analysis of this sampler. The results for the CIP10-R show deviations below 10%. These data prove the capability of the WAM to equally expose the samplers to respirable dust. This enables the comparison of dust samplers in the very unique atmospheres of divergent workplaces.

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Measurement and evaluation of formaldehyde levels in a modern university hospital anatomy department

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A recent update resulted in confirmation of formaldehyde as a Group-1 human carcinogen based on sufficient evidence for nasopharyngeal cancer, limited evidence for cancer of the nasal cavity and paranasal sinuses. The working group was not in full agreement concerning formaldehyde as a risk factor in leukaemia. This was based on a recent study by Hauptmann and co-workers (2009) conducted in anatomy workers and suggesting a dose-response for peak exposures in embalming.

The objective of this study was to evaluate the current exposure of anatomy workers in the training center of the anatomy department of the Radboud university medical centre.

Air concentrations of formaldehyde were measured using silicagel adsorbent tubes impregnated with 2,4-dinitrophenylhydrazine (DNPH-method). Three different types of measurements were conducted: monitoring of overall background air levels at fixed locations in different rooms before and during anatomy lessons, personal air sampling during 6-10 h to characterize the shift-average concentration in the breathing zone and personal air sampling in the breathing zone during 15 minutes when peak exposures were expected. The samples were analysed on a HPLC equipped with an Agilent Eclipse XDB-C18, 150 x 4,6 mm column and formaldehyde was detected at 360 nm. Calibration gave excellent results and a BCR reference material was used to verify accuracy.

Table 1: Air concentrations of formaldehyde at fixed sampling locations before the renovation.

Room	Air exchange rate	Sampling duration (h)	N	Number of observations overstepping occupational air standard (0.15 mg/m ³)	Geometric mean (mg/m ³)	Range (mg/m ³)
Background ^a	14.2	7-9	2	0	0.024	0.015-0.038
Training room A	14.2	7-9	8	3	0.080	0.0041-0.62
Training room B	23.4	6-9	6	1	0.011	0.0022-0.67
Storage	6.3	7-10	10	6	0.29	0.09-1.5
Preparation	23.7	7-10	10	2	0.075	0.04-0.17
Office	- ^b	8	1	0	0.012	-

^a In training room A when there was no activity; ^b not determined

Air sampling at fixed locations showed that formaldehyde concentrations in rooms with an air exchange rate of less than 10 h⁻¹ did not comply with the Dutch workplace standard defined as a time-weighted average over 8 h of 0.15 mg/m³. Of a total of 37 measurements of general background levels during preparation of anatomy classes 32 % were non-compliant, with a geometric mean (GM) of 0.096 mg/m³ (see Table 1). In the breathing zone 8 out of 14 samples overstepped the same workplace standard. The GM was 0.17 mg/m³. For peak exposures the Dutch workplace standard based on a 15 min time-weighted average of 0.5 mg/m³ was overstepped on 3 occasions out of 7 task-based measurement with a GM of 37 mg/m³. Several tasks in the storage room and preparation room resulted in unacceptable high peak exposures.

In a modern anatomy facility workers were exposed to levels of formaldehyde exceeding current workplace standards in the Netherlands. Air exchange rate in one room needs to be increased. Working procedures involving storage and preparation need to be reconsidered. Workers should be made aware of the health concerns of peak exposures. After introduction of technical solutions and improved work procedures the exposure needs to be re-evaluated.

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Evaluation of the influence of a combined dust reducing carpet and air filtration intervention on the indoor air quality in a primary school

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Schools in neighbourhoods with poor ambient air quality and/or high noise levels cannot rely on natural ventilation to improve indoor air quality (IAQ). Since 40 % of primary schools in The Netherlands do not have a ventilation and filtration system, there is interest in alternative solutions. Laboratory tests show promising results for dust reducing carpets and compact air filtration systems but there is no information on the performance of such interventions from in situ tests.

The objective of this study was to evaluate the combined effect of a dust reducing carpet and a compact air filtration system on the IAQ in a classroom in a real life setting.

IAQ measurements were performed in two classrooms, each occupied by 27 children (Figure 1). Measurements of PM-10 and PM-2.5 were performed by filter sampling and aerosol spectrometry. Other parameters included black smoke (BS), volatile organic compounds (VOC), NO₂ and formaldehyde (Scheepers et al., 2011). Both interventions were introduced in one classroom during one week, using the other classroom as a reference. In a second week the interventions were moved to the other classroom. In three additional weeks the class rooms were compared without interventions. An evaluation of the interventions in an unoccupied classroom was conducted over the weekend.

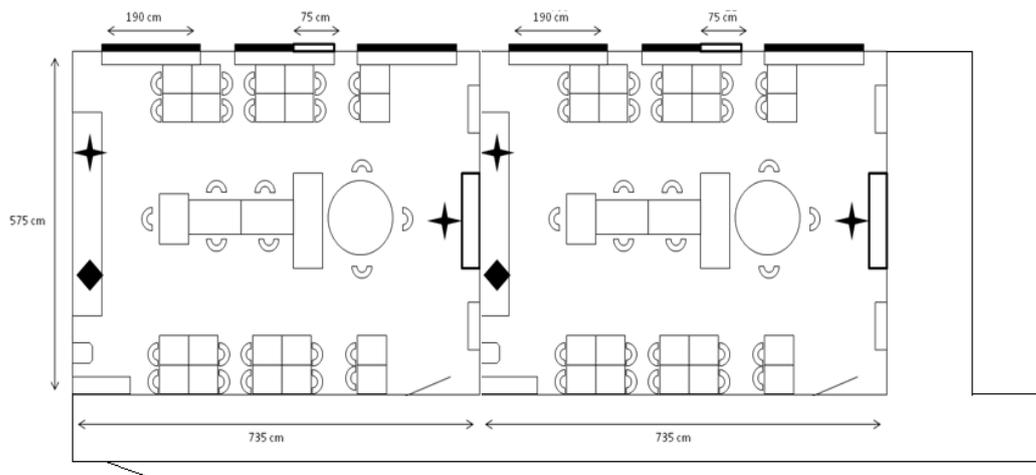


Figure 1. Lay-out of the two classrooms that were compared in a cross-over design. ◆ Air sampling equipment; ★ Compact air filtration system; ■ Closed window with ventilation grid; □ Opened window.

In the weekends the interventions resulted in reductions of PM-10 and PM-2.5 and their derived respective BS values, ranging from 60 % to > 90 %. During the lessons these reductions were 30-50 %. Levels of VOC, NO₂ and formaldehyde were rather low and showed much variability within and between the classrooms. A contribution of the interventions to the improvement of the IAQ was inconclusive.

A field test of a dust reducing carpet and a compact air filtration system yielded a consistent reduction of all PM-parameters in both filter measurements and aerosol spectrometry. Much higher reductions were observed over the weekend, suggesting an interaction of occupancy with the effectiveness of the interventions. A contribution to the reduction of gas-phase compounds remained inconclusive.

Acknowledgement: This work was supported by the Province of Gelderland, The Netherlands.

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A study of emissions from metal industries using “MOSS-BAGS”

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Deposition of heavy metals all over Norway has been regularly investigated by analysis of the naturally growing moss *Hylocomium splendens* since 1977 (Steinnes *et al.*, 2011a). Recently this approach has also been used to study metal deposition at sites where major industries are located (Steinnes *et al.*, 2011b) such as Mo i Rana. In this case there is no naturally growing moss inside the area and sampling sites were restricted outside the industrial area.

The use of “moss-bags” opens a possibility to extend moss biomonitoring to areas and territories where the moss does not grow naturally, such as inside the Mo Industrial Park in the present study. Dried moss samples (500 mg) from a background area were placed in hair nets, cleaned with 0.2 M HCl and dried, and then hung up in trees for a two months period at around 30 sites within the studied site. The exposed moss samples were decomposed with concentrated HNO₃ in an UltraClave unit and analyzed for 46 elements by sector-field ICP-MS.

Celsa Armeringsstål AS, FESIL Rana Metall AS, and Glencore Manganese Norway AS are the main relevant industrial plants at the site, and the deployment of the moss bags was aiming at distinguishing between emissions from these sources. Celsa receives scrap metals for re-melting, FESIL produces ferrosilicon, and Glencore produces ferromanganese alloys. In addition some moss-bags were placed in positions to evaluate contributions from other potential sources inside the park such as waste disposal sites, scrap yard, and mass transportation.

The metals showing the highest ratio relative to unexposed “moss-bags” were Cd, Cr, Mn, Mo, Pb and W. Peak values for these elements showed an increase by a factor of 200 or more. In addition the “priority metals” Zn, Hg and As showed relatively high values. These elements are essentially the same that had shown high values in previous moss surveys at Mo i Rana (Steinnes *et al.*, 2011b). Precise identification of sources of individual metals however was difficult because the plants were situated close to each other, FESIL and Glencore even stationed in different ends of the same building. The fact that most of the metals may be emitted from more than one plant makes the task even more complicated.

Some patterns are still evident. The values for Mn are highest near Glencore, as expected for this ferromanganese plant. Al, Ca, Cr, Fe, Hg, Mg, Mo and W show peak values around Celsa. Concentrations of As are highest in the area nearby FESIL and Glencore, probably with FESIL as the main contributor. Cd, Pb and Zn show the highest levels next to the Celsa scrap yard, which is also affected by mass transportation. Pb and Zn also show high concentrations nearby Celsa, whereas Cd shows no clear pattern. The Celsa emissions depend on the quality of the scrap iron received. The meltdown of scrap metal with varying constituents may be the reason for a broad range of metals (including Mo, Nb, W and Zr) released from this plant. Fesil and Glencore may also contribute some of the same metals showing peak values at Celsa, but to a smaller extent.

Even though the geographical distribution of some metals monitored in this study showed good accordance with emissions reported by the three plants, it proved difficult to distinguish contributions from sources located close to each other, especially when some of the components are released from more than one source. An attempt to use multivariate statistics for further source apportionment is under way.

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Application and comparison of two new measurement methods for the determination of indoor VOCs and formaldehyde during the construction phases of a wood frame house.

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Indoor air quality is now recognized as an important challenge for public health. The pollutant levels, especially those of VOCs and formaldehyde, are significantly higher than outdoor ones due to numerous indoor sources and the development of airtight low energy buildings. Hence, the environmental performance, and particularly indoor air quality, should be more systematically integrated in the building approach, from the construction phases to the final use. The objective of this study was therefore to monitor the indoor air quality during the construction phases of three low energy wood frame houses. Expectations are to identify the pollution sources and the concentration levels to which workers could be exposed. The test house was one of the three low energy demonstration building of the BOIS^{PE} technological platform, implemented in Egletons (France) for R&D studies and workers formation. The selected VOCs were formaldehyde, which is carcinogenic and regulated in France, acetaldehyde, hexanal, terpenes (such as α -pinene and d-limonene), and aromatics (benzene, toluene, styrene, xylenes). Two new measurement methods were applied and compared: one consists in a direct measurement of formaldehyde for a rapid diagnostic (Profil'Air, ETHERA). It involves an active air sampling during at least one hour. The formaldehyde is thus sorbed on a nanoporous sensor loaded with Fluoral-P as selective trapping media. Formaldehyde reacts with Fluoral P to produce a colored compound 3,5-diacetyl-1,4-dihydrolutidine (DDL), quantified by an absorbance measure at 420nm using a portable spectrophotometer. The second method, developed in our laboratory, is indirect. Air sampling is performed in vacuum glass vials equipped with a specially developed interface, the SPME-adapter. On site, vials are filled with air in few seconds. Then, an SPME fibre, loaded with O-(2,3,4,5,6-pentafluorobenzyl)hydroxylamine hydrochloride (PFBHA) was introduced into the vial during 30 minutes prior to its thermal desorption. This modified fiber allows analyzing formaldehyde and the other target VOC in one single GC run. The bedroom was chosen as room for sampling. Two successive Profil'Air measurements were carried out. In parallel, six vacuum samplings (SPME method) were performed. This methodology will be repeated for five construction phases. The results of the first campaign showed that the two methods are in good agreement for the formaldehyde: $9.9 \pm 2.0 \mu\text{g}/\text{m}^3$ and $10.9 \pm 1.7 \mu\text{g}/\text{m}^3$ for Profil'Air and SPME methods respectively. The SPME method also allowed to identify and quantify other target VOCs, such as hexanal and terpenes in relatively high levels (above $100 \mu\text{g}/\text{m}^3$). If these first results are encouraging, the other ongoing sampling campaigns will be decisive to complete the knowledge on the VOC profiles in these new wood frame houses and to assess the performance and the correlation of the two new methods tested.

Relational analysis of daily data between an automatic particle counter and a traditional pollen trap: preliminary study

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In 2013, the reliability of a new device to measure in real time the amounts of (biological?) particles in the air was assessed. The aim of this equipment, already used for this purpose in Japan (S.Kawashima *and al.* 2007), is to warn the population about the allergy risks on a daily basis. To carry out this study, an automatic particle meter (YAMATRONICS KH-3000-01) was used in parallel to a conventional Hirst type pollen trap. Data from automatic particle counter were collected every hour and grouped in an Excel file. These data were compared with pollen data from Lyon. The comparison was constructed with curves and statistical correlation analysis.

The curves obtained enabled to make a table of matching and mismatching days between the two types of comparative data from this study. What was defined as mismatching corresponds to the days when the two curves do not follow the same trend (increase or decrease of the amount of particles in the air relative to the previous day) and the two points appear quite apart. Statistical analysis resulted in a determination coefficient R^2 allowing to define the percentage of the variance of data that can be explained by other data (and vice versa).

The results for the period tend to show a correlation between the two types of data. From these results, it appears that the automatic particle counter takes into account the pollens in great majority.

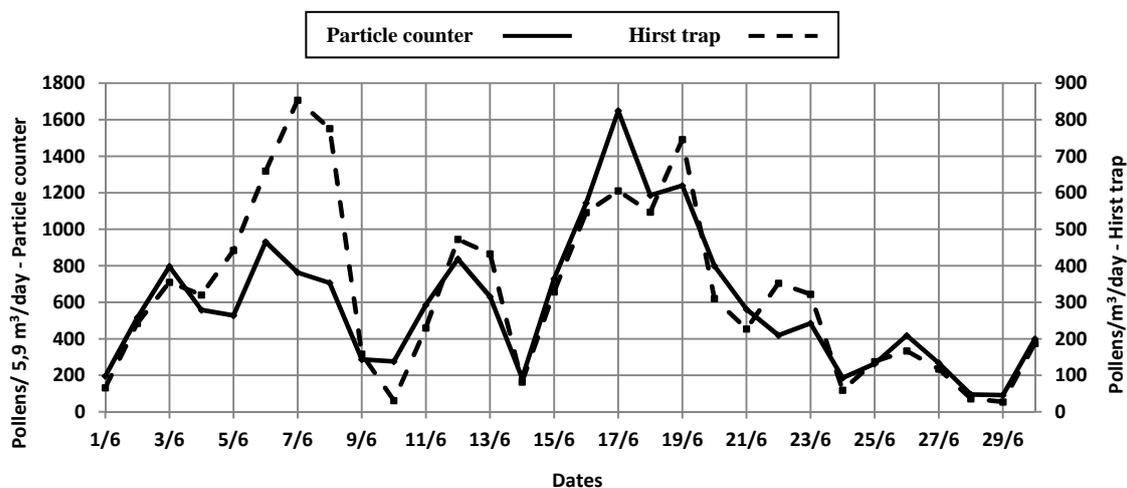


Figure 1. Comparison of the daily pollen amounts obtained with particle counter and with a Hirst pollen trap (June 2013, Lyon)

The results of this preliminary study should be continued to provide “on line” information to allergic and their referring physicians.

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Sampling for respirable silica

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Several recent studies on respirable dust sampling have shown that, with a few exceptions, most cyclones in common use have the performance characteristics necessary to be used to demonstrate compliance with International Standards on sampling the respirable fraction of dust.⁽¹⁻⁴⁾ Thus, they can be used for the determination of respirable crystalline silica (RCS). However, national and international limit values for the concentration of RCS that should be applied to maintain a healthy workplace are in flux. Eight-hour time-weighted average concentrations of 0.05 mg.m⁻³ and even 0.025 mg.m⁻³ are under consideration. The Limit of Quantitation (LOQ) of current analytical methods put constraints on the minimum sample that can be analyzed accurately. Typically, a LOQ of 10 µg per sample is achievable by the use of either infra-red or x-ray diffraction in laboratories maintaining a high standard of quality assurance with care. More commonly, commercial laboratories report higher values than 10 µg in practice. Ten µg of RCS is thus the bare minimum necessary for quantitative analysis of a sample. The RCS content of a sample at a specified exposure limit value depends on the sampling time and the flow-rate specific to the operation of a particular sampler. The current sampler most commonly used in the USA operates at 1.7 LPM and can be used to give a sample containing 10 µg at either concentration given above for 8-hour and even 4-hour samples. However, it cannot be used to quantify below 0.025 mgm⁻³ in half-shift samples, and it is typically preferred that the method be able to assure the user that the sample is below the limit value. The FSP-10 (GSA, GmbH) has been calibrated to provide a respirable sample at 11.2 LPM, which would provide adequate sensitivity for most purposes, even shorter task-based sampling at these concentrations. However, the cyclone is bulky and heavy and so are the personal pumps necessary for its operation. Workers, who are not used to such encumbrance, have resisted wearing them.⁽⁵⁾ Moderate flow-rate cyclones, such as the GK 2.69 (BGI, Inc.) offers a compromise between higher flow-rate and excessive burden. This cyclone will provide a respirable sample at 4.2 or 4.4 LPM, and therefore provide a sample loading of 12 or 13 µg RCS at a concentration one-half of 0.025 mg.m⁻³ over a 4-hour sample. Since it uses a 37 mm filter, the pressure-drop is within the range of the higher-end personal sampling pumps already in common use, so an 8-hour sample is also possible. The sample matrix affects the analysis and limits the determination of silica in samples containing less than 1%. A limit value of 0.025 mg.m⁻³ has a consequence of imposing a limit for the respirable fraction of Particles Not Otherwise Specified (or Regulated) of 2.5 mg.m⁻³.

Disclaimer: The conclusions and opinions in this presentation are those of the Author and do not necessarily reflect the policy of the US Centers for Disease Control and Prevention.

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A sensitive method using SPME pre-concentration for the quantification of aromatic amines in indoor air

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Aromatic amines like aniline, phenylethylamine, chloroanilines, naphthylamines, aminophenols, toluenediamines and 4-aminobiphenyl are biologically active compounds, well known as environmental pollutants because of their toxicity and carcinogenicity. They are widely used in industry to make dyes, cosmetics, medicines, rubber, textiles, agrochemicals and as reagents intermediates in many chemical syntheses.

It is also known that tobacco smoke contains aromatic amines in conjunction with other carcinogenic compounds like PAHs.

Therefore, the monitoring of levels of aliphatic and aromatic amines in indoor air is important to protect human health because of human exposure to these compounds through diet and inhalation.

Aromatic amines are sampled in indoor atmosphere by pumping of air through a filter followed by an adsorbant in order to collect simultaneously the particle and gas phases. After sampling, traps are solvent extracted and analysed by gas chromatography (GC) coupled with different detectors after a potential derivatisation step.

A sampling and analytical method using XAD-2 cartridges and gas chromatography coupled to mass spectrometry was used for assessing 25 aromatic amines in different smoking and on smoking indoor environment. After sampling of air (6 – 8 h sampling) delivering to 1 m³ of air, adsorbent was ultrasonically extracted with acetonitrile, concentrated and then injected in the GC/MS system (2 µL in splitless mode). Most of samples present amines concentrations below quantification limits (table 1). In order to increase the sensitivity of detection, a pre-concentration step by using SPME was developed. For this purpose, acetonitrile extract was diluted in 25 mL of water (pH=9; 5% NaCl) and then extracted for 40 minutes at 80°C using a DVB/CAR/PDMS fiber. With this method 21 on the 25 aromatic amines can be analyzed with detection limits up to 100-200 times lower than classic liquid injection. 4-Aminophenol, 3-Aminophenol, 3-Chloroaniline and 4-Chloroaniline were not detected with the SPME method. It can be assumed that aminophenols required a derivatisation step for their analysis by GC as these molecules were not detected whatever the injection mode used. Results of the sampling campaign are presented in table 1 and shows that with SPME pre-concentration, more aromatic amines can be detected. The level of contamination by aromatic amines is strongly correlated by the influence of smoking emissions.

Table 1. Comparison of indoor air concentrations of aromatic amines with and without SPME enrichment (in ng m⁻³).

Compounds	non-smoking		Smoking influence		Smoking area	
	Liq	SPME	Liq	SPME	Liq	SPME
N-Methylaniline	nd	1.93 – 4.50	nd – 0.01	4.10 – 11.6	nd - <LQ	8.08 – 8.41
N,N-Dimethylaniline	nd	2.44 – 8.31	nd	4.10 – 5.39	nd	7.97 – 10.1
m-Toluidine	nd	nd	nd	91.7 – 175	nd	220 – 513
2-Chloroaniline	nd	nd – 1.41	nd	1.23 – 7.27	nd	nd – 3.68
2-Aminophenol	nd	nd – <LQ	nd	nd	nd - <LQ	90.2 – 277
2,6-Dichloroaniline	nd	nd	nd	nd – 5.50	nd	5.31 – 9.60
4-Methyl-o-phénylenediamine	nd	nd	nd	nd – 7167	nd	nd – 3576
2,4-Dichloroaniline	nd	<LQ	nd	<LQ – 2.02	nd	1.70 – 6.17
2,5-Dichloroaniline	nd	1.10 – 1.82	nd	<LQ – 2.67	nd	1.64 – 1.82
(-)-Nicotine	nd	nd	nd	nd – 652.6	<LQ– 11.3	553 – 840
2,3-Dichloroaniline	nd	1.53 – 2.18	nd	1.90 – 3.28	nd	0.71 – 10.9
3,5-Dichloroaniline	nd	1.55 – 2.96	nd	<LQ – 9.03	nd - <LQ	5.67 – 14.9
2-Nitroaniline	nd	nd – <LQ	nd	nd – 442.9	nd	461 – 488
Diphenylamine	nd	7.64 – 14.9	nd	9.23 – 25.2	nd	19.3 – 19.8

nd : not detected ; <LQ : below quantification limit

The development and the advantages of the SPME pre-concentration step before GC/MS analysis will be presented in details during the communication.

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Long term airborne lead pollution monitoring in Bandung, Indonesia

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Keywords: phasing out leaded Gasoline; lead concentration; Bandung, Indonesia

Leaded gasoline was completely phased out in Indonesia since July 2006. As part of an air pollution study, the Pb monitoring was carried out from 2005-2012 in Bandung to assess the impact of the use unleaded gasoline in the ambient air in Indonesia. The airborne particulate samples were taken using a Gent stacked filter unit sampler in two size fractions of $< 2.5 \mu\text{m}$ (fine) and 2.5 to $10 \mu\text{m}$ (coarse) and total 528 pairs of samples were collected. Samples were analyzed for mass concentrations using gravimetric, black carbon (BC) using reflectance and elemental analysis were performed using particle induced X-ray emission (PIXE) and X-ray fluorescence. Elemental concentrations of S, Si, K, Pb, Fe and Zn were monitored, but only Pb concentrations in 2006 decreased significantly. Time variation of airborne lead concentrations plot in Figure 1 showed a decline trend over the years after implementation of government policy in phasing out of leaded gasoline. The decrease in airborne lead concentrations during monitoring period was approximately over 70%. The average of PM mass and black carbon concentrations are also presented and discussed. The phasing out of leaded gasoline in Indonesia showed encouraging results and decrease significantly over the six years. The significant decrease of Pb concentration in ambient air of Bandung is a result of an effectiveness and impact of the phase-out of leaded gasoline in Indonesia.

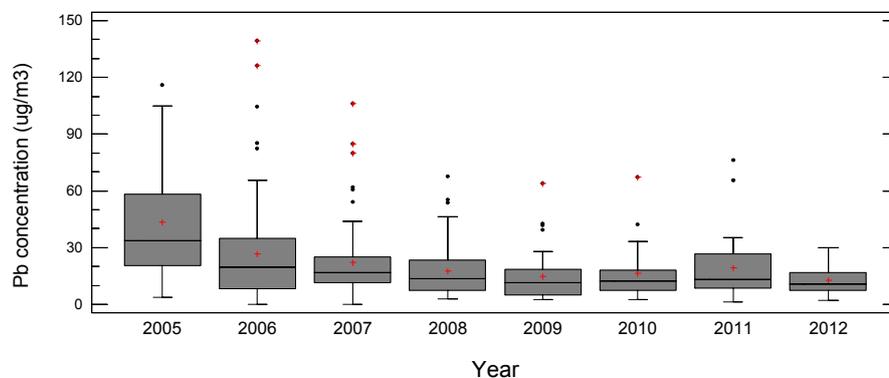


Figure 1. Time series of box and whisker plots for lead concentrations in $\text{PM}_{2.5}$ in Bandung, Indonesia

Acknowledgement: This work was supported by International Atomic Energy Agency and National Nuclear Energy Agency of Indonesia.

One-year high spatial resolution monitoring of air quality in Cremona urban area (Italy)

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Keywords: phasing out leaded Gasoline; lead concentration; Bandung, Indonesia

The Environmental Research Centre of Salvatore Maugeri Foundation launched a project named “Municipalities”, aimed at helping municipal governments in air quality monitoring and at collecting scientific data on the evolution of urban atmospheric pollution levels, as well as on citizens’ exposure to air pollutants.

Four air quality monitoring campaigns were carried out in Cremona urban area, from spring 2011 to spring 2012. Also, during winter and summer campaigns, the levels of exposure to air pollutants of a group of 20 local police officers were measured.

The air quality measurements were carried out by means of Radiello diffusive samplers (Cocheo *et al.* 1996), which were exposed for 7 days during each of the four seasons of the period april 2011 – march 2012. 128 sampling sites were distributed over a grid, covering the whole urban area, so as to obtain a high-resolution map of pollutants’ concentrations. The monitoring grid was built following the representativeness criteria defined by LIFE project “Resolution” (Cocheo *et al.* 2008).

In each sampling site VOCs (benzene, toluene, ethylbenzene, xylenes, methyl-*tert*-butylether, ethyl-*tert*-butylether), nitrogen dioxide, sulfur dioxide and ozone were measured. 44 high resolution isoconcentration maps were obtained. For the local police officers, the exposure to VOCs was measured in both winter and summer campaign; in addition, we measured the exposure to ozone in summer campaign and the exposure to nitrogen dioxide in winter.

The results showed very low concentration levels for BTEX (benzene, toluene, ethylbenzene, xylenes) and sulfur dioxide, while nitrogen dioxide and ozone showed higher values and remarkable seasonal trends. Nitrogen dioxide concentrations overcome the ambient air quality limit value in winter; the same was observed for ozone in summer.

As an outcome of the project “Municipalities”, a health protection program will be launched: it will involve the local police officers of the city of Pavia, who will undergo both environmental monitoring and clinical examinations (respiratory function, biomarkers, allergy testing).

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Measurement strategy of atmospheric particulate matter in operational conditions

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In response to rumors of fecal pollution of atmosphere on afghan territory, French Army Headquarter charges the Navy Expert Laboratory of Toulon (France) to conduct a chemical evaluation campaign of air quality in the city of Kabul (Afghanistan).

Hierarchization of environmental chemical risks in Kabul (Breton *et al.*, 2012) shows that airborne particulate matter (PM) concentration is the most preoccupying point. These particles have a double origin:

- Telluric origin in a desertic environment;
- Anthropogenic origin with traffic contribution, low-controlled industrial processes using combustion (brickworks, cement plants).

Materials and methods

Air quality measurement campaign was conducted from 12 to 20 september 2012. Measurements were realized in the waiting room of the military hospital of the KAIA International Airport (KAIA) and outdoor the hospital.

A real-time particles analyser (Thermo Scientific PDR-1500) was used. This analyzer performs simultaneously a selection of particle size (cyclone), an optical counting expressed as a mass, and impaction of a filter collecting the particles in order to make possible a mass correction and appropriate chemical analysis.

On external samples, it was decided to assess air quality in a single point, qualitatively considered representative of the average quality of air in the camp of KAIA and more generally in this part of the city of Kabul. This point was identified and selected far of punctual pollutants sources, compatible with practical and safety constraints.

Quality assurance precautions have been taken on site during the sampling:

- Blanks were made every day to overcome effects of transport and weather conditions. Blanks are stored at room temperature in same conditions that the sample,
- Daily inspection of flow rate.

Results and discussion

Concentrations of fine particulate matter (PM_{2.5} and PM₁₀) measured outdoor are important, regularly exceeding values proposed for exposure of military for 24 hours and systematically proposed values for annual exposure. For PM_{2.5}, the threshold limit value for 24 hours exposure is exceeded every day. For PM₁₀, threshold limit values are systematically exceeded. Health effects associated with these exceedances can be of two types:

- Immediate (acute) effects such as irritation of respiratory tract, throat and eyes, exacerbation of symptoms in sensitive persons, asthma or cardiovascular disease carriers.
- Delayed (chronic) effects after several days or weeks of exposure, mainly increased cardiovascular (atherosclerosis, myocardial infarction, angina) and respiratory asthma, chronic bronchitis, respiratory failure) morbidity and mortality. These effects are statistically associated with exposure to fine particles on the basis of epidemiological studies measuring the external particles (with exposed persons inside and outside), which means they will not occur automatically above thresholds but their probability of occurrence is increased, which may justify a particular epidemiological surveillance. Military personnel with respiratory or cardiovascular disease before deployment are among susceptible populations for which the risk is higher.

Breton D, Cazoulat A, Bohand S, Laroche P, Mullot J-U (2012). *Hiérarchisation des risques militaires d'origine environnementale lors d'opérations militaires extérieures. Environnement Risques & Santé, 111 (6), 502-510.*

Natural occurring asbestos occupational exposure assessment: protocol of sampling and analysis

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Keywords: natural occurring asbestos, occupational exposure, air monitoring

The term “natural occurring asbestos” (NOA) refers to asbestos fibers as a natural component of soils or rocks, with asbestos fibers content variable and not predictable quantitatively. In Italy the problem of NOA is present in various situations over the national territory, among these the “Serpentino della Valmalenco” (“massive” and schistose commercial varieties), derived from the Malenco massif (Central Alps, Sondrio), is a well-known serpentinitic stone.

The morphological characteristics of the natural asbestos fibers released in quarries and in processing laboratories of the Valmalenco serpentinitic stone and the experiences acquired during previous monitoring campaigns highlighted that this situation are not within application field of well-known international methods and the necessity to develop a new protocol for the evaluation of occupational exposure to NOA.

The protocol has been developed taking into account critical factors as: the correct dust amount on the filters, the sampling representativeness, fibers counting rules and possible interferences (mineralogical and morphological). The protocol describes the following phases: sampling preparation, air sampling, filter preparation for the analysis, analysis, measurement uncertainty and report and is applicable both in quarry that in processing laboratories.

Differences between laboratories in sweden and finland offering analysis of VOCs in indoor air

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The etiology of unspecific building related symptoms (or sick building syndrome, SBS) remains unclear despite numerous attempts to identify its causes. One known factor influencing the risk of having symptoms is ventilation (Fisk et al. 2009) which indicate that substances in the air are involved. Several risk factors, like dampness and mould, are known. When visible signs of damages are present it may be fairly easy to remedy causes to illness among people staying in a building, but sometimes there are no signs of damages and people still have symptoms. In that case some investigators use to take air samples of Volatile Organic Compounds, VOCs, to find chemical indicators of damages. The total amount of VOC, TVOC, as a risk index for health is questioned (Andersson et al. 1997) but it is used as an indicator in investigations of suspected indoor air problems. Other indicators for water damages or mould are also used. Based on results from VOC measurements some companies give interpretations and suggestions of possible causes of problems.

Fourteen companies in Sweden and Finland offering VOC analyses were contacted, and all of them answered a questionnaire regarding used methods for sampling and chemical analysis and nine of the laboratories were willing to participate in a comparison where they were to analyse samples taken from the same place.

A specific date was set for sampling and all participating laboratories sent samplers and instructions for sampling. The sampling started at the same time and samples were taken according to the instructions from each laboratory. One sample was taken from a room in a building with known indoor air problems and the person working in the room suffered for symptoms corresponding to unspecific building related symptoms. The other sample was taken from a residence that had been renovated during the preceding five months. No symptoms were reported from the inhabitants. Supelcos "Indoor Air Standard, 50 Component" was purchased from Sigma-Aldrich and an additional sample with 50 different compounds corresponding to $4 \mu\text{g}/\text{m}^3$ was prepared. Laboratories were asked to handle and report results according to their normal routines.

It took between 7 and 131 days to get the reports from the laboratories. Some did just report levels of found chemical and TVOCs without further comments, while others reported chromatograms, reference values, uncertainties in analysis, possible sources of chemicals and interpretations.

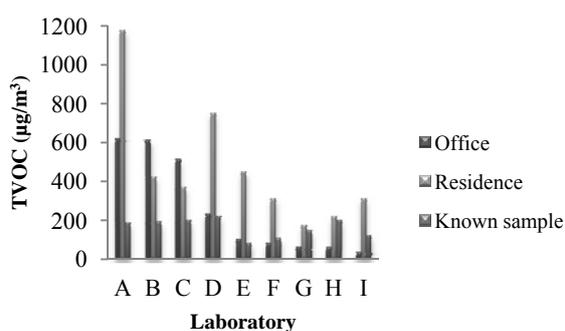


Figure 1. Reported concentrations in samples taken from an office, a residence and in a known sample.

The value of reported TVOCs varied between 30 and $620 \mu\text{g}/\text{m}^3$ for the sample from the office and

The results indicate that it is not possible to compare results from different companies and it can also be questionable to use VOC measurements as an argument for or against remediation actions to handle suspected with indoor air problems

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Andersson, K., Bakke, J. V., Bjorseth, O., Bornehag, C.-G., Clausen, G., Hongso, J. K., Kjellman, M., Kjaergaard, S., Levy, F., Molhave, L., Skerfving, S. & Sundell, J. 1997. *Indoor Air* **7**, 78-91.

Fisk, W. J., Mirer, A. G. & Mendell, M. J. 2009. *Indoor Air* **19**, 159-165.

between $170\text{-}1200 \mu\text{g}/\text{m}^3$ for the sample from the residence. TVOC for the known sample varied between $80\text{-}220 \mu\text{g}/\text{m}^3$ and reported levels of individual compounds varied at most between $1.20 \mu\text{g}/\text{m}^3$.

There was a significant difference between samples from the office taken with diffusive (laboratory A-C) and pumped sampling (laboratory D-I), where diffusive sampling yielded higher values. A likely explanation is that there was reduced ventilation during night in the office resulting in higher

Main atmospheric gaseous pollutants and relative seasonal VOC variations in Rome

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In urban area the air quality valuation is an important task performed by means of monitoring station equipped with different instrumentations. The determinations are usually performed at ground level. These measurements are important for understanding the pollutant behaviour because no influence of buildings and automotive traffic can affect the measurements. These data will be useful for policy decision because the measurements are obtained in absence of pollution sources.

In this communication the preliminary measurements related to a hot/cold period will be shown and discussed. The gaseous pollutants are ozone, SO₂, NO and NO₂, CO whereas few data are available for Particulate Matter. The station is equipped with automatic analyzers (Rupprecht & Patashnick Co. Inc, East Greenbush, NY, USA) able to investigate the above reported compounds. On the other hand, continuous concentration data of VOCs were measured in the urban air of Rome during 2011. Seasonal variations of different compounds were also analysed.

Figure 1 shows the trends of ozone and dioxide nitrogen in the same period (July 1-19) of two different years: the dot lines show the trends determined in 2012 at ground level whereas the lines report the behavior measured in 2013. Of course, the measurements are not simultaneously but these preliminary information can be index of important scientific consideration. Firstly, the levels in 2013 are significantly lower because determined in altitude even if the trend is quite similar. In fact, these two pollutants are secondary pollutants and their trends do not sensibly vary for a same period, as discussed in a previous paper.

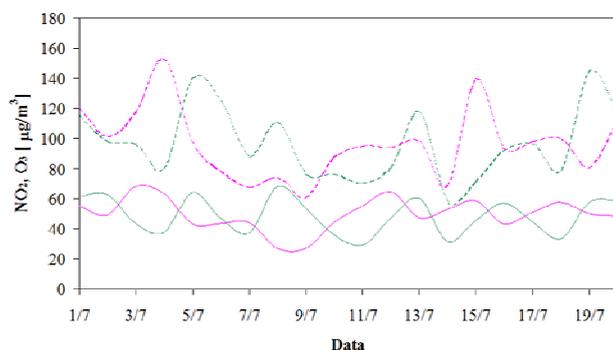


Figure 1. Ozone and NO₂ trends in altitude (1-19 July 2013) (line) and at ground level (1-19 July 2012) (dot).

For the VOC measurements, one-way ANOVA results showed significantly ($p < 0.05$) higher concentrations in winter respect to summer period for all the VOCs, except for ethane. Ethane low variability could be derived by its accumulation in the air due to relatively long atmospheric life.

Seasonal mean concentrations of VOCs varied from 78 $\mu\text{g m}^{-3}$ in the winter period to 37 $\mu\text{g m}^{-3}$ in the summer: total concentration of aromatics is reduced of 59 %, alkanes of 39 % and alkenes of 71 %. Similar data have been detected also in studies conducted in different world cities, i.e. Seoul, Lille, Tokyo, and reflect the different VOC photochemical removal rates from the atmosphere due to different OH radical concentrations during the year, minimum in cold period and maximum in hot period. Moreover lower heights of the boundary layer, characteristic of cold periods, promote the increase of trace gas concentrations contributing to reveal wintertime peak.

The results also indicate that the most abundant species among VOCs were i-pentane, toluene, ethene and propene. Similar to other urban areas in the world, alkanes were found to be a dominant component with about 50 % of all quantified VOCs.

Acknowledgement: This work was supported by INAIL under grants P20L01, P20L04 and P20L09.

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Occupational hygiene survey of exposure to diisocyanates and their corresponding diamines in a variety of exposure scenarios.

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Diisocyanates are widely used in a range of processes, some of which may lead to the generation of the corresponding diamine. Biological monitoring, which is used increasingly to determine whether exposure to isocyanates has occurred, is based on the measurement of the corresponding diamine in urine. As such there may be issues in determining whether raised diamine urine levels are due to diisocyanate exposure or direct exposure to process generated atmospheric diamine exposure. Knowledge of the extent of diamine formation during different processes would be beneficial due to the different health risks associated with these chemicals (sensitisation versus carcinogenicity) and to help interpret the level of isocyanate exposure itself for biological monitoring purposes, irrespective of the health end-point. Seven site visits were conducted at sites using diisocyanates in casting, spray painting, foam blowing and floor screeding. Air monitoring and glove analysis was conducted for both the relevant diisocyanate and its corresponding amine. Urine samples were measured for the corresponding amine in pre- and post-shift samples over a number of days following the site visit. The results show that no process related diamine generation was associated with casting or floor screeding (diisocyanate air levels for these processes were also very low but significant amounts were detected on gloves). Spray-painting, as expected, generated higher atmospheric levels of diisocyanates than the other processes investigated, with some diamine generation (<15% of the diisocyanate levels). Foam-blowing generated lower atmospheric levels of diisocyanates than spraying but showed a similar ratio of diamine generation (~15% of the diisocyanate levels). Biological monitoring results indicated potential skin absorption of diisocyanates during casting and floor screeding. Spray painting, foam-blowing and floor screeding were all associated with significant diamine levels in urine. The contribution to these urine levels from diisocyanates and diamines varies with the process and the implications will be discussed.

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A new method for the simultaneous determination of peracetic acid and hydrogen peroxide in the ambient air

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Keywords: Air Monitoring Method, Peracetic acid, Hydrogen peroxide, aseptic packaging, manual disinfection, irritation

Introduction

For the aseptic packaging of beverages and food and for the manual disinfection of tanks, instruments and plants peracetic acid and hydrogen peroxide are widely used. Due to the volatility of these substances and the excess pressure inside the filling machines the peroxides can be released to the ambient air as gas or aerosol.

Workers exposed to high peroxide concentrations have symptoms of irritation, like teary, sore, slight, red eyes, throat irritation, nasal secretion, headaches and sometimes even bleached hair.

To assess the risk for the employees we developed an air monitoring method for the simultaneous determination of both peroxides.

Air Monitoring Method

For sampling a suitable pump draws ambient air through an impinger filled with water. The flowrate is adjusted to 1.38L/min. Immediately after sampling two reagents are added to an aliquot of the absorption solution. According to a method of Kaarst et al.(1997) the absorbed peroxides lead to an oxidation to stable compounds. These two compounds are separated by means of high performance liquid chromatography and detected with a diode array detector. The quantitative determination could be performed by calibration curves based on defined weighed masses of the oxides of the reagents.

The impinger device must be leakproof. Personal as well as stationary measurements are possible. The sampling duration is either one hour or 15 minutes. The limit of quantification for each peroxide is 0.1 mg/L, equivalent to 0.05 mg/m³ based on an air sample volume of 83 L (Schuh, 2013).

Results

The measuring division of "Berufsgenossenschaft Nahrungsmittel und Gastgewerbe" has performed a lot of exposure measurements in the beverage and dairy industry. It was shown that the effect of irritation depends on the peroxide concentration within the working place atmosphere. The developed measuring method is a useful tool to locate the sources of emission in the surrounding of the packaging machines and confirm the effectiveness of measures.

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- 2 Schuh C., Peroxide Air Monitoring Methods in German Language, *MAK-Collection for Occupational Health and Safety*, published online: 15.04.2013, <http://onlinelibrary.wiley.com/doi/10.1002/3527600418.am7291d0017>.

Survival of airborne gastrointestinal pathogen norovirus

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Nosocomial infections are a major concern in health care facilities. Other than extending the stay of patient, they are the fourth cause of mortality in Canada and can also be an occupational problem for workers. Airborne transmission of microorganism is often related to respiratory pathogens but aerosols can sediment and then be transferred via fomites or be inhaled and ingested by swallowing. Norovirus gastroenteritis is an important nosocomial infection and can be rapidly transmitted to workers and patients during an outbreak. Human Norovirus cannot be cultured, thus, it is very difficult to assess its presence in the environment, hence the need to use molecular approaches.

In the current study, we looked at the presence and potential infectivity (using a model) in the air of a the human Norovirus, a gastrointestinal pathogen. The air of 8 health care facilities occupied by actively-infected Norovirus patients was sampled during a 2011 outbreak. Air samples were taken in patients rooms (n=27), 1 meter outside the room (n=16) and at the nurse's station (n=8). Surface samples were also taken on 3 different areas (floor, sink tap and bedrails). Samples Norovirus load was estimated by qPCR. In order to better understand the potential infectivity of human norovirus in the airborne state, we used a previously described murine Norovirus model to study the *in vitro* virus resistance to aerosolization. Murine Norovirus was nebulized in a SCL Medtech aerosol chamber and sampled using two the NIOSH 251® and the SKC Biosampler®. Viral load was estimated by qPCR and infectivity by cellular culture using Raw 264.7 monkey macrophages.

Airborne Noroviruses were detected in 7 of 27 samples (26%) with a median copy number of 1154/m³ (ranging from 80 to 5433 RNA copies/m³). Directly outside the rooms of patients with active gastroenteritis, 4 of 16 samples (25%) were positive with a median of 260 RNA copies/m³ (ranging from 57 to 1383 RNA copies/m³). Of the 8 samples taken from nursing stations, 1 (13%) was positive for Noroviruses. From the 40 surface samples from 27 different rooms of symptomatic patients were sampled, 4/40 (10%) were positive. Experiments in the environmental air chamber showed that both air samplers can recover infectious virus particles with culturable virus ratio ranging from 1.71% to 18.5% (mean ratios: 2.57% for Biosamplers and 12.10% for NIOSH 251).

These data's shows that the Norovirus can be found in the air of health care facilities and can support to be aerosolized and still remain infectious even after additional sampling stress.

Comparison of aerosol optical thickness and particle size distribution at Oujda (Morocco) and Avignon (France) for 2011

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Keywords: particle size distribution, aerosol optical thickness, sun photometer

The AERONET is a federation of ground-based remote sensing aerosol networks established by NASA and PHOTONS (Univ. of Lille 1, CNES, and CNRS-INSU) and is greatly expanded by scientists' partners. The program provides a long-term, continuous and readily accessible public domain database of aerosol optical, microphysical and radiative properties for aerosol research and characterization.

The present study focuses on aerosol optical thickness (AOT) and particle size distribution (PSD) variation relative to Avignon (43.93275° N, 4.87807 E, 32.0 m) in France and Oujda (34.65317° N, 1.89850° W, 620.0 m) in Morocco for 2011. The AOT varies from 0.008 to 1.17 with a significant growths observed in September for Avignon and August for Oujda.

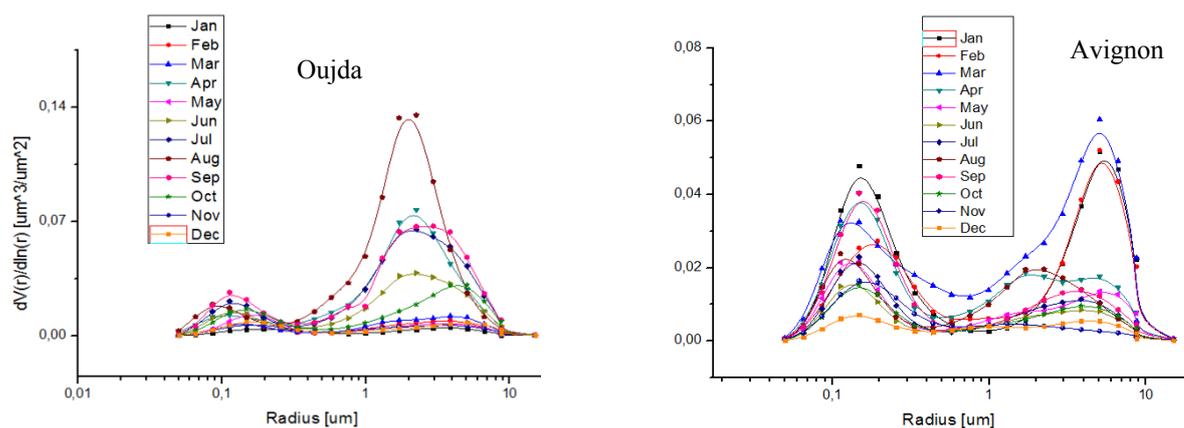


Figure: Mean monthly of distributions of aerosol particles (2011).

The monthly average volumetric PSD relative to the atmospheric column (Figure) shows the presence of two modes: the fine around 0.1 μm for Oujda and 0.15 μm for Avignon, the second mode relative to big particles is near 2 μm for Oujda and 5 μm for Avignon. We observe a clear significance of the big particle mode for Oujda which is explained by the desert air mass advection occurred on summer. For Avignon we record an important growth relative to the two modes for January, February and March explained by the effect of combustion happened during this period.

Acknowledgement: The used sun-photometer is a gift of the laboratory LOA, Lille1 University, France.

Occupational exposure to air contaminants at military shooting ranges

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Military personnel are exposed to air contaminants originating from firing of weapons. These exposures occur predominantly at shooting ranges, where during practise, multiple shots are fired within limited time frames. Exposures to Pb during military shooting practise and contamination of the environment have been addressed, enforcing management of these issues, by use of lead-free ammunition and sheltered outdoor shooting ranges with ventilation systems.

During each firing considerable amounts of “gun smoke” is emitted into the breathing zone of the soldiers. In addition, the general atmosphere at shooting ranges is contaminated resulting in co-exposure among instructors. “Gun smoke” consists of a complex mixture of organic and inorganic components in gaseous, vaporous and particulate phases.

The aims of this study were to characterise “gun smoke” with respect to particle size mass distributions and chemical composition as well as assessing air breathing zone concentrations of major contaminants during shooting practises when using rifles/machine guns and different type of ammunition.

Air contaminants at two different shooting ranges were measured, one outdoor and one sheltered outdoor.

Air contaminants characterized and assessed were inhalable, thoracic and respirable masses of Cu, Pb, Bi, Sb and Zn, elemental and organic carbon, aldehydes, amines, volatile organic compounds (VOC) and isocyanates using stationary air sampling equipment mounted in the breathing zone of the soldiers during firing. Direct reading instruments were used to assess the air concentrations of carbon monoxide, nitrogen dioxide and particle mass size distributions.

The results showed that “gun smoke” was dominated by fine particulate matter (PM₁). Higher respirable air concentrations of Bi, Cu and Zn when shooting with lead-free ammunition compared to lead-containing ammunition were found. The variability in air concentrations for both gases and particulate matter showed short-term peak events associated with each firing exercise. A major concern was high short-term peak concentrations of carbon monoxide shown for both the outdoor shooting range (980 ppm) and sheltered shooting range (78 ppm).

Field measurement of volatile organic compounds in the atmosphere using dynamic solid-phase microextraction and portable gas chromatography-mass spectrometry

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Keywords: VOCs, aerosol particles, SPME sampling, portable GC-MS, PTR-MS.

Volatile organic compounds (VOCs) participate in many physicochemical processes in the atmosphere (Ning & Sioutas, 2010). Studies indicate that these reactive compounds contribute significantly to the particle formation by e.g. photo-oxidation to non-volatile species that lead to the formation and growth of secondary organic aerosols (Riipinen *et al.*, 2012).

In this study, measurement of VOCs were performed in mid-summer 2013 during one week at the Station for Measuring Ecosystem-Atmosphere Relations, SMEAR II in Hyytiälä, Finland, to test the applicability of the developed methodology for the determination of atmospheric VOCs and their oxidation products. The compounds were efficiently sampled on PDMS/DVB coated solid-phase microextraction (SPME) fibers, and on-field analysis was performed by a portable gas chromatograph-mass spectrometer (GC-MS). Numerous chemical classes of compounds were identified and semi-quantified, including monoterpenes and their oxidation products, aldehydes, acids, ketones, organosulfates and amines.

In the interpretation of the results meteorological conditions during the sampling were exploited, and the results achieved were compared to the total amount of monoterpenes obtained by proton-transfer-reaction mass spectrometry (PTR-MS). The study demonstrated the successful applicability of the method with reduced number of analytical steps, for the rapid *in situ* determination of organic gaseous compounds in the atmosphere.

Acknowledgement: Financial support was provided by the Academy of Finland Centre of Excellence program (project no 1118615) and Emil Aaltonen Foundation (JP).

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Assessment of welding fume concentration in workplace air for welders and locksmiths in small and medium size workshops

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Employee who performs welding and metal working is subjected to series of harmful factors. Welding fume consisting of various metal salts and oxides is released in work environment air; and potentially can impact human health. In small and medium size workshops welders and locksmiths are working very close to each other. As from laboratory experience, many of assessed welders' and locksmiths work places have no appropriate ventilation systems, employees use respirators which do not prevent inhaling the welding fume therefore it is possible for various occupational diseases to develop.

According to general conception of occupational risk assessment in Latvia, welding fume is not the risk factor for locksmiths. The aim of the study was to test the validity of this assumption.

Air samples of welding fumes were gathered from the breathing zone of the workers during the active work periods. Cellulose acetate membrane filters (Millipore, 0.8 μm) with a 37-mm open-face cassette were used as collection media. The flow rate was 2 L/min (Buck and GilAir sampling equipment were used), and the sample time varied from 45 to 90 minutes according to work phase. The inhalable dust concentration was then calculated from the weight difference (method of gravimetry) of the filters before and after sampling, and the corresponding of air volume was done, too.

The metal arc welding fume samples in the breathing zones of 27 welders (concentration range from 0.44 to 141.35 mg/m^3), concentration median 7.00 mg/m^3 were collected, of them 15 or 55.6% exceeded the occupational exposure limit (4 mg/m^3). The concentration range of welding fume in the twenty locksmiths breathing zone varied from 0.28 to 16.22 mg/m^3 , concentration median 2.60 mg/m^3 . This results show that more than in 50% of assessed workplaces exposure index of welding fumes is greater than 0.65, according to national legislation this risk factor should be taken in to account in risk assessment procedure.

According to literature data metal arc welding fume consists predominately of particle agglomerates smaller than 1 μm . This means that most of the fume is respirable (Jenkins *et al.*, 2005). Lehnert *et al.* (2012) indicate that the welding process is the major determinant of the exposure to particles in different size fractions, however in welding processes can be observed large numbers of small - sized particles including also ultra fine particles.

The concentrations of welding fumes in workplace air from small and medium size workshops in Latvia show high probability of health effects not only for welders but also for locksmiths. This risk factor should be taken in account in risk assessment procedure not only for welders but also for locksmiths.

Acknowledgement: This work was supported by project "The development of up-to-date diagnostic and research methods for the risks caused by nanoparticles and ergonomic factors at workplaces", Agreement No. 2013/0050/1DP/1.1.1.2.0/13/APIA/VIAA/025

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Airmon

15-19 June 2014

Marseille, France

***Session E - Exposure assessment-
strategies, peak exposures,
multi-exposures***

Occupational exposure to aflatoxine B1 and ochratoxin A: co-exposure in swine production

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Although the existence of extensive literature on the ingestion of food contaminated with aflatoxin B₁ (AFB₁) and Ochratoxin A (OTA), only a small number of studies explore the exposure in occupational settings (Halstensen, 2008). In the same mode, a smaller number of studies have paid attention to the cases of co-exposure to both mycotoxins in the same occupational setting.

Taking this into consideration, our study was developed aiming to elucidate if there is occupational exposure to AFB₁ and OTA in Portuguese swine production facilities. With this purpose, specific biomarkers were used to assess exposure to both mycotoxins. Measurement of AFB₁ and OTA in serum was performed by enzyme-linked immunosorbent assay (ELISA). A total of 28 workers participated in this study and a control group (n=30) composed by subjects without any type of contact with agricultural activity was also considered. This control group allowed to have an idea of the background level of these two mycotoxins in the Portuguese population since there wasn't no information available (Viegas *et al.*, 2013).

Twenty one workers (75%) showed detectable levels of AFB₁ with values ranging from <1 ng/ml to 8.94 ng/ml and with mean value of 1.91 ± 1.68 ng/ml. In the control group, the AFB₁ values were all below 1 ng/ml. In the case of OTA results there wasn't found a statistical difference between workers (1.16 ± 0.45 ng/ml) and controls (1.40 ± 0.15 ng/ml).

In this study a biomarker of internal dose was used providing information regarding recent exposure to both mycotoxins, the exposure intensity and also absorption rates (Zhang *et al.*, 2003; Viegas *et al.*, 2012). The obtained results suggest that occupational exposure to AFB₁ occurs and can be related with different causes and contamination sources present in this occupational setting (Viegas *et al.*, 2013a,b). Regarding OTA, probably food ingestion plays an important role regarding exposure of workers and controls. It must be consider the additive effect reported in experimental studies regarding the interaction between these two mycotoxins and the significant risk that represents to human health (Speijers & Speijers, 2004; Šegvić, 2012).

Acknowledgement: This work was supported by Lisbon School of Health Technology/Institute Polytechnic of Lisbon.

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Chronic exposure to hydrogen sulfide in wastewater treatment plant

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Acute or accidental exposure to hydrogen sulfide (H₂S) is well documented and regulated in occupational situations. By contrast, chronic exposure to H₂S and impacts on human health remain today still badly known.

In this context, our study aimed to measure chronic exposure of workers in wastewater treatment plant's (WWTP) in France. Four objectives were pursued: 1) to test a sensor able to measure continuously (real-time) low concentrations of H₂S in specific conditions of strong humidity; 2) to assess the level and the distribution of chronic exposure to H₂S in different categories of workers in WWTP; 3) to explore factors influencing individual chronic exposure and 4) to identify homogenous groups of exposure among workers.

Five plants in south of France with different technical characteristics were selected (confined or opened, coastal or inland, etc.). Personal and fixed H₂S measurements (in different locations into the plant) were conducted simultaneously with the same devices. Measurements took place from 2011 in summer (may-june) to 2012 in winter (january-february) to test the influence of the season. Real-time measurements (one measure each minute) were realized with miniature sensors (weight = 55 g ; dimension : diameter = 32 mm, length = 62 mm) developed by the society Cairpol. Sensors are completely autonomous and able to detect ppb pollution levels (0.20 000 ppb ; LD = 8 ppb). Sensors were tested and validated in laboratory and then in occupational situations with specific conditions of strong humidity. Each participant was equipped with personal samplers for 8 hours of daily work during 5 successive days (from Monday to Friday). Simultaneously fixed measurements were carried out in different locations in the plant for 24h during the 5 days. A specific software allowed to transfer and store all the daily collected data with a simple connection. Furthermore, individual measurements were supplemented by a questionnaire related to time activity patterns (15 minutes time step).

A total of 56 volunteers participated in the study, representing 372 days of measurements (summer and winter), 11 220 hourly quarter data. Levels of chronic exposure (8h) from individual sampling vary between about 10 and 600 ppb, with an average concentration of 63 ppb (median = 14 ppb). Results show a difference between plants, depending on their characteristics (confined > opened ; coastal > inland), but no clear difference between winter and summer. In plants with low H₂S chronic levels, no difference between categories of workers appears. By contrast, in plants with higher chronic exposure, results tend to show a gradient of exposure depending on the category of job exercised.

This study indicates for the first time the level of chronic exposure to H₂S among workers in WWTP. It constitutes an important data-base, with more than 182 000 measurements of one minute. Results show a difference in chronic exposure to H₂S among workers of WWTP, depending more on characteristics of the plants than on exercised jobs.

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Assessment of occupational exposure to trihalomethanes in swimming pool workers through biological monitoring and PBPK modeling

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The presence of disinfection by-products (DBPs) in water and air of swimming pools, such as trichloramine (CAM) and trihalomethanes [THMs: chloroform (TCM), dichlorobromomethane (DCBM), dibromochloromethane (CDBM), and bromoform (TBM)] results from the reaction between chlorine and organic matter. This could result in exposure to potentially high levels of DBPs of swimming pool workers (SPWorkers) and presumably health impacts since several adverse effects have been associated/related to these contaminants (e.g., asthma, irritation, carcinogenicity, genotoxicity). The objective of this study was to assess occupational exposure to DBPs in SPWorkers through environmental (water, air) and biological (alveolar air, urine) sampling during their working hours. A total of 35 SPWorkers from 8 pools (5 from Montreal, 3 from Quebec City) were recruited for this study. They were asked to provide urine and alveolar air samples before and after variable time durations during their working shift for the analysis of THMs. THMs, and other DBPs, were also measured in air (pool and workers office) and in water of each pool during exposure. The potential daily exposure dose of TCM ($\mu\text{g}/\text{kg}/\text{day}$) the most abundant THM, was estimated by physiologically-based pharmacokinetic (PBPK) modeling of exposure to average levels of TCM measured in ambient air of each pool.

Levels of THMs varied importantly between pools. In 7 pools TCM showed the highest concentrations in air (~88%) and in water (~90%) (Table 1). In one pool TCM was lower than DCBM and CDBM. Similarly, TCM was the predominating THM in alveolar air and urine of SPWorkers (Table 2).

Table 1. Mean levels and ranges of individual and total THMs measured in 8 swimming pools

	Air (office)					Air (pool)					Water (pool)				
	$(\mu\text{g}/\text{m}^3)$					$(\mu\text{g}/\text{m}^3)$					$(\mu\text{g}/\text{L})$				
	TCM	DCBM	CDBM	TBM	TOTAL	TCM	DCBM	CDBM	TBM	TOTAL	TCM	DCBM	CDBM	TBM	TOTAL
Mean	55.6	5.4	2.2	1.2	63.3	145.2	24.6	16.2	9.6	192.0	63.5	9.9	21.1	13.0	84.6
SD	52.4	5.7	1.9	0.5	55.5	67.7	29.3	33.0	15.2	81.5	28.8	12.9	30.0	16.4	36.2
Min	2.7	0.1	nd	nd	---	53.7	2.7	0.2	nd	---	21.9	1.1	nd	nd	---
Max	134.2	16.2	4.8	1.8	---	241.3	86.3	95.4	36.1	---	100.1	37.6	55.6	24.6	---

Table 2. Levels of TCM measured in alveolar air and urine collected at the end of exposure

	Alveolar air $(\mu\text{g}/\text{m}^3)$	Urine (ng/L)
Min	4.8	34.7
Max	72.7	306.2
Mean	32	151.8
SD	20.5	78.2
n	35	32

The potential daily dose of TCM was estimated for a typical worker (70 kg) by PBPK modeling according to a scenario involving exposure exclusively by inhalation (at rest) during 2 periods of 3.5 h at the average air TCM level measured in each pool, separated by 1 hr exposure at the level measured in each corresponding pool office (total of 7 hr). The TCM doses estimated for such a 7 hr-exposure ranged from 2 to 8 $\mu\text{g}/\text{kg}/\text{day}$. This is to be compared with the Acceptable Daily Dose of 6.2 $\mu\text{g}/\text{kg}/\text{day}$ that was used by Health Canada (2006) to calculate the Maximal Acceptable Concentration for TCM (80 $\mu\text{g}/\text{L}$) in drinking water that is based on water ingestion (1.5 L) and a 30-min shower (inhalation and dermal exposures).

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DNELs for workplaces observations from an inspection of the GESTIS DNEL database

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Derived No-Effect Levels (DNELs) are established by manufacturers and importers in the context of the EU REACH chemical programme and provide new assessment benchmarks for health protection at work. The reported DNEL values are published by the European Chemicals Agency (ECHA), in the first instance without review.

For exposure assessment the GESTIS DNEL database provides parties involved in OSH a readily accessible collection of workplace-related DNELs. It currently contains DNELs for workers (local and/or systemic effects in the event of inhalative long-term exposure) for about 1,400 substances. Key data for each substance are also listed for its identification (synonyms, index numbers, formulae) together with a link to further substance data in the GESTIS Substance database. Where applicable, also a comparison to other exposure limit values can be found and an indication if the substance is classified as carcinogenic. Besides the DNEL database, these data are also available in the form of an Excel file, which additionally also includes further DNEL values for substance groups, mixtures, resins, fats, reaction mixtures, and other items that are not precisely defined.

An initial review of the DNEL database has revealed a number of discrepancies and shortcomings (Nies *et al.*, 2013). The database contains for example over 40 DNEL values for carcinogenic substances. Also for substances without a known toxicological effect threshold very low DNELs are found.

Table 1: Substances with very low DNELs not classified as harmful.

Substance	CAS number	DNEL [mg/m ³]
Benzoin	119-53-9	0,1
Aluminium fluoride	7784-18-1	0,047
Dodecane-12-lactam	947-04-6	0,88

A comparison of the DNELs with German workplace limit values (AGWs), MAK values (maximum workplace concentrations) of the German Research Foundation (DFG) and European Indicative Occupational Exposure Limit Values (IOELs) revealed also deviations of DNELs from other existing occupational limit values.

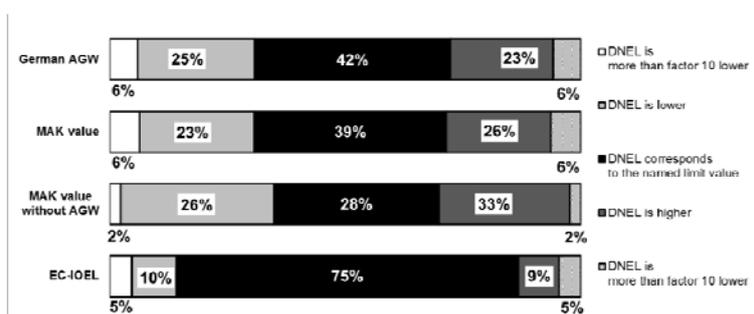


Figure 1: Degree of match between DNELs and German AGW or MAK values of the DFG (for all MAK substances or MAK substances that have no AGW) or the IOELs of the European Commission.

Acknowledgement: The GESTIS DNEL database has been established at the initiative and with the support of the German Social Accident Insurance Institutions and the representatives of the German regional governments, the Federal Institute for Occupational Safety and Health (BAuA), the association of the German chemical industry (VCI) and the Austrian Workers' Compensation Board (AUVA).

GESTIS DNEL database:

<http://www.dguv.de/ifa/Gefahrstoffdatenbanken/GESTIS-DNEL-Datenbank>

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The MiXiE software: assess risks related with a mixture of chemical substances

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MiXiE is a web based software created by the University of Montreal and the Institut de recherche Robert-Sauvé en Santé et en sécurité du Travail (IRSST, 2014). It is aimed at helping the industrial hygienist in assessing the risks associated with the exposure to a mixture of airborne chemical substances at the workplace. The toxicological effects of around 700 substances have been listed and categorized into 32 toxicological classes, such as carcinogenic effects or liver disorders. For example, toluene can cause central nervous system disorders, eye disorders, upper respiratory tract irritations and embryonic or fetal disorders. The effects of the substances in a toxicological class are considered additive. Given a mixture, to each toxicological class an exposure index defined as the sum of the ratios C/OEL is assigned, where C is the airborne concentration of a substance and OEL , its occupational exposure limit. The exposure index R_m of the mixture is then the maximum of all the combinations of the mixture. On the basis of R_m , the industrial hygienist gets an insight of the risks related with the mixture of substances.

This algorithm has been applied to the mixtures from the COLCHIC database (Vincent & Jeandel, 2001). This database contains more than 900.000 records of air sample analysis realized in French enterprises. COLCHIC uses more than 700 different substances and reports around 48.000 work situations. A work situation is a set of measurements of one or more substances, realized in the same enterprise, for the same task and during the same month. In this study, the most recent data (years 2003-2012) from COLCHIC were analyzed using the MiXiE algorithm. For each work situation, the toxicological classes were identified and the R_m was computed and compared to a threshold of 1. A work situation for which the $R_m > 1$ is considered to represent a high risk to the workers health.

For the considered period, of the 13.452 work situations reported in COLCHIC, only 5.339 were useable by MiXiE because the chemical substances of MiXiE do not match exactly those of COLCHIC. According to MiXiE's results, among these 5.339 work situations, 1.042 presents one or more toxicological class with $R_m > 1$. Among these 1.042 situations, 188 do not present any measurement value with a ratio $C/OEL > 1$ it means that the risk is directly due to the mixture. Moreover, in these 188 situations, some high risk toxicological classes are investigated in order to identify work scenarios. It appears that the activity sectors related to waste treatment and composite materials are associated with toxicological classes with $R_m > 1$.

In this study, the use of Mixie -- on historic COLCHIC data -- shows empirically the need to take into account exposure to mixtures as opposed to exposure to single chemicals. It gives a way to identify the work situations that pose more risks for the worker's health and thus where the prevention messages should be reinforced.

IRSST (2014), MiXiE - Institut de recherche Robert-Sauvé en Santé et en sécurité du Travail, http://www.irsst.qc.ca/media/outils/intertox/jsndx_en.htm

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Lapachol, 2-methylantraquinone and deoxylapachol as chemical markers in teak dust exposure assessment

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The American Conference of Governmental Industrial Hygienists (ACGIH) has classified teak, together with birch, mahogany, and walnut, as suspected (and oak and beech as confirmed) human carcinogens. The aim of this study was to study the field reliability of Lapachol (LP), 2-methylantraquinone (2-MEA) and deoxylapachol (DLP) as chemical markers of occupational exposure to teak dust (Gori *et al.*, 2009).

A HPLC method was developed in order to analyze the three markers on the dust collected on the filters and in the exhaled breath condensate (EBC). The limits of detection were 0.8 µg/l for LP and DLP and 0.2 µg/l for 2-MEA, respectively.

Personal and area industrial hygiene air sampling was performed in two small factories in Italy that produce teak furniture. The wood dust in the air was sampled with IOM samplers equipped with PVC filters at flow rate of 2 l/min. A total of 14 samples were collected, of which 6 were personal samples and thus near the air breathed by workers and 6 with samplers fixed on tripods at a height of 160 cm above floor level. Two samples were taken also in the offices as field blanks. Sampling lasted 3 hours. Gravimetric determination of dusts was carried out after membrane conditioning for 48 hours at constant temperature and humidity. After weighing, membranes were kept away from light and stored at room temperature until the analysis (max. 2 weeks). Two samples of EBC were collected: one before the beginning of the work shift and one immediately after the end of the work; The EBC samples were frozen, kept away from light and stored at -20°C until the analysis (max. 1 week).

Levels of teak dust exposure ranged between 0.04 and 5.20 mg/m³. The highest concentrations were found in personal samples. LP, 2-MEA and DLP in the collected dust ranged between <0.01 and 0.42 µg/m³ for LP, 0.47 and 8.52 µg/m³ for 2-MEA, and 0.28 and 4.76 µg/m³ for DLP, respectively. High significant correlations were found between the dust collected on the filters and the markers contents with $r > 0.79$ and $p < 0.001$ in all cases (figure 1).

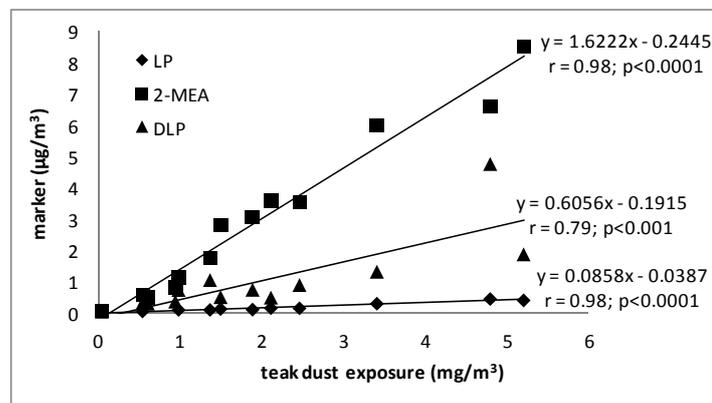


Figure 1: Correlation between LP, 2-MEA and DLP levels (µg/m³) and teak dust exposure (mg/m³).

Detectable levels in the EBC were found only for 2-MEA and a correlation was found only in the samples collected in the second factory, whereas LP and DLP are always below the analytical detection limit.

On the basis of the good correlations obtained, LP, 2-MEA and DLP appear to be good markers of teak dust exposure and thus very useful for estimating the true quantities of teak dust inhaled. The use of the markers as biological indices of teak exposure should be confirmed with additional data.

Acknowledgement: This work was supported by INAIL project no. 15/2009.

Gori, G., Carrieri, M., Scapellato, M.L., Parvoli, G., Ferrara, D., Rella, R., Sturaro, A., Bartolucci, G.B. (2009). *Ann Occup Hyg*, 53, 27-32.

Personal exposure to naphthalene in the general population

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Naphthalene is classified as possible carcinogenic to human (IARC 2B) and there is limited data on naphthalene exposure in the general population (Preuss *et al*, 2003). The major route of exposure is by inhalation and the major source of naphthalene in air is from different burning processes (residential, industrial, tobacco smoke, traffic etc.). Increased residential exposures, especially in certain countries of the Mediterranean area, originate from the use of naphthalene-based moth-repellents. A guideline value for the general population has been recommended at 10 $\mu\text{g}/\text{m}^3$ by the EU INDEX project 2006 (Koistinen K *et al* 2008). The aim of this study was to investigate personal exposure as well as indoor and outdoor concentration of naphthalene.

Personal exposures to naphthalene were measured during the autumn of 2006 in 37 randomly selected volunteers living in Gothenburg, Sweden. Simultaneous measurements were performed in the subjects' bedrooms and outside their homes. Repeated sampling was performed for 20 subjects. Diffusive samplers, Perkin-Elmer tubes with Tenax TA, were used during seven day sampling periods. The samplers were analysed with ATD-GC-MS. The uptake rate 0.43 mL/min (8h) was used to determine the naphthalene levels from the content of naphthalene in the samplers. For statistical analyses the SAS software (SAS version 9.1) was used and the variability components were estimated with the Proc Nested procedure. Correlations between personal exposure and indoor levels were estimated with Spearman correlation coefficient and differences between groups using the Wilcoxon rank sum test.

The personal exposure to naphthalene (GM 0.3 $\mu\text{g}/\text{m}^3$, AM 0.5 $\mu\text{g}/\text{m}^3$) and the indoor concentrations of naphthalene (GM 0.3 $\mu\text{g}/\text{m}^3$, AM 0.5 $\mu\text{g}/\text{m}^3$) were significantly higher ($p < 0.0001$ respectively) than the outdoor levels (GM 0.05 $\mu\text{g}/\text{m}^3$, AM 0.07 $\mu\text{g}/\text{m}^3$). The number of smokers was low ($n=7$) and no differences could be seen between smokers and non-smokers in the study. There were no differences in the exposure with regard to gender. A high correlation was found between personal exposures and indoor levels of naphthalene ($r_s=0.73$, $p < 0.0001$). The within-individual variability dominated for personal exposure and accounted for 74% of the total variability. For the personal exposure the within-individual fold-range (${}_wR_{0.95}$) was 15.5 and the between-individual fold-range (${}_bR_{0.95}$) was 5.0. For the indoor levels the variability within and between bedrooms was similar (53 and 47%) and fold-ranges were 10.5 and 11.9 respectively. For the outdoor levels the within-residence variability accounted for 100% of the total variability with a fold-range of 15.1.

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Assessment of multicomponent population exposure within the affected zone of non-ferrous smelter in view of the chemical composition of dust emissions

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Keywords: PM_{2.5}, PM₁₀, dust, elemental composition, exposure assessment, non-ferrous industry

Dust emission points of non-ferrous smelters: all places of overturning, unloading, batch, and transportation of particulate material with the open transport, but also all the working and viewing apertures and leaks in the firing furnace and smelting of ores and concentrates, and the accumulation of dust settled on the floor, walls and on the equipment.

Fine particulate matter (PM₁₀ and PM_{2.5}) have a pronounced negative effect on health (Jimoda, 2012), which is enhanced if the fine particles contain toxic metals (Cormier *at all*, 2006). The detailed analysis of size-consist and elemental composition was carried out for the dust emissions of large non-ferrous smelter (Russia, Perm region). Taking into account the results of the analysis were evaluated multicomponent exposure permanent population in the impact zone of the smelter. To date, the smelter declares emissions of inorganic dust undetermined composition (more than 123 tons per year), manganese and its compounds (about 12 tons per year), vanadium pentoxide (2,3 tons per year), the compounds of chromium (3 +) and (6 +) (more than 8 tons per year).

The fractional makeup of the dust was determined using a laser particle size analyzer Microtrac S3500 (covered a particle size range from 20 nm to 2000 microns). Microscopy and spectral analysis was performed using a scanning electron microscope of high resolution (the degree of increase - from 5 to 300 000 times; accelerating voltage - from 0.3 to 30 kV.) with X-ray fluorescence attachment S3400N «HITACHI» (detection limit - about 10-5%, the minimum area of study - 100 microns).

It was determined that the dust emissions from various technological operations contain from 30 to 60% of PM₁₀, including up to 5.5% of PM_{2.5}. The fine particles composition includes of Ti, Mn, Cr, Pb, As, Hg, some other less toxic metals (examples of results in Fig. 1 and Fig. 2.).

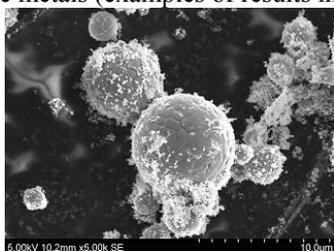


Figure 1. The result of dusts particles microscopy (emissions from technological step «metal tapping»)

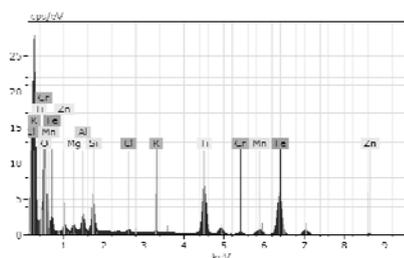


Figure 2. The result of the dusts spectral analysis (emissions from technological step «metal tapping»)

Around the smelter came into being zone of exposure, that forms increased risk to public health, caused by combined effects of a non-toxic dusts, solid particulates of toxic metals and metal compounds. The greatest danger established over respiratory system (the combined effects of PM₁₀, V₂O₅, Fe_xO_x, Cr and Cr_xO_x), central nervous system (the combined effect of MgO, Pb, PbO, MnO and As), blood (the combined effect of Pb and Ni).

A lifetime cancer risk (the combined effect of Cr, Pb, As and Ni) exceeded the level of 1,0E-04, that requires additional measures to protect public health. For working out of measures the smelter uses data of elemental composition and particle size of dust emissions.

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Exposure to some carcinogenic substances in the general population of Gothenburg

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Benzene, 1,3-butadiene and formaldehyde are classified as carcinogenic to humans (IARC, group 1). Benzene and 1,3-butadiene are generated from various combustion processes, e.g. traffic, wood burning, industry and cigarette smoke. Benzene is also found in gasoline. Formaldehyde is generated in combustion processes, but the main sources of human exposure are found indoors as formaldehyde is emitted from building materials and furniture. Outdoor air pollution, and particulate matter specifically, was classified as carcinogenic to humans in 2013 (Loomis et al., 2013). Fine particles (PM_{2.5}) are emitted from combustion of biomass, charcoal, oil and other fuels. Traffic and residential wood burning are important sources to airborne particles in urban areas. Nitrogen dioxide is generated from all type of combustion. In urban areas, road traffic is the dominating source. Nitrogen dioxide is not carcinogenic, but is often used as a marker of exposure to traffic related air pollution.

The aim of this study was to assess personal exposure to benzene, 1,3-butadiene, formaldehyde and nitrogen dioxide among the general population of Gothenburg. Personal exposure monitoring was performed on 40 randomly selected adults living in the city of Gothenburg. The sampling period was one week, and a repeated sampling was performed on 20 of the participants. Diffusive samplers were used to collect the substances. For benzene and 1,3-butadiene, the diffusive sampler Perkin-Elmer with Carbopack X adsorbent was used, and analyzed with ATD-GC-MS. Formaldehyde was collected using the UME^X 100 sampler and analyzed with HPLC. For nitrogen dioxide, diffusive samplers from Ogawa were used and analyzed with ion chromatography. Fine particles (PM_{2.5}) were measured indoors at home for 20 of the study participants. A cyclone connected to a pump (4L/min) was placed in the living room for 48 hours. Parallel urban background concentrations of PM_{2.5} were monitored with a PQ100 PM_{2.5} sampler (EPA WINS, BGI Inc.). Mass concentration was determined gravimetrically and the particle mass was analyzed for its content of benzo(a)pyrene with GC-MS with Selected Ion Recording (SIR) Mode.

For the 40 participants (20 men and 20 women) the median personal exposure to benzene was 0.7 µg/m³ (95% CI: 0.6-1.0 µg/m³) and for 1,3-butadiene 0.3 µg/m³ (95% CI: 0.2-0.7 µg/m³). Exposure to benzene and 1,3-butadiene was correlated (r_s : 0.44, $p=0.005$). Median personal exposure to formaldehyde was 19 µg/m³ (95% CI: 15-22 µg/m³) and to nitrogen dioxide 13 µg/m³ (95% CI: 11-15 µg/m³). For the 20 participants with repeated samplings there was a correlation between the first and repeated measurement for benzene and 1,3-butadiene, but not for nitrogen dioxide. There was no difference in exposure with regard to gender for any of the substances. The number of smokers was low (N=5) and no difference in exposure between the smokers and non-smokers could be seen. The within-subject variance (the day-to-day variability in exposure) was 48% for benzene. The between-subject variance dominated for the exposure to 1,3-butadiene (85%), whereas for exposure to nitrogen dioxide the within-subject variance dominated (77%). The median personal exposure to benzene was below the Swedish health-based guideline value of 1.3 µg/m³. The median exposure to 1,3-butadiene was within the health-based guideline interval for long-term exposure (0.2-1.0 µg/m³). Also the median personal exposure to formaldehyde was found to be within the guideline interval for long-term exposure (12-60 µg/m³).

The median indoor concentration of PM_{2.5} was 7 µg/m³ and for benzo(a)pyrene 0.01 ng/m³. After excluding the home where smoking occurred indoors, indoor concentrations of PM_{2.5} and benzo(a)pyrene were correlated with the outdoor urban background levels (r_s : 0.52 and r_s : 0.64, respectively). The median concentration of PM_{2.5} was below the guideline value of 10 µg/m³ recommended by the World Health Organization. Median concentration of benzo(a)pyrene was below the guideline value of 0.1 ng/m³, which is based on the risk for lung cancer.

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Airmon

15-19 June 2014

Marseille, France

***Session F - Active and passive sampling of
organic and inorganic substances***

Application of passive sampling for the comparison of temporal indoor air variations of biocides concentrations applied with different techniques

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Biocides are classified in four main categories: “Disinfectants and general biocidal products (i.e. Human hygiene biocidal products, private area and public health area disinfectants and other biocidal products,...)”, “Preservatives (i.e. wood preservatives, in-can preservatives,...)”, “Pest control (i.e. rodenticides, acaricides,...)” and “Other biocidal products (i.e. Preservatives for food or feedstocks, antifouling products,...). When used as preservatives or for pest controls, they can, depending of the application technique used, contaminate indoor air. In order to assess the indoor air contamination by biocides, a sampling and analytical method coupling passive sampling on Tenax-TA® tubes, thermal-desorption and GC/MS analysis for the quantification of 7 insecticidal biocides (allethrin, bifenthrin, cyphenothrin, imiprothrin, permethrin, prallethrin and tetramethrin) and their synergist (piperonyl butoxyde) have been developed. Detection (S/N > 3) and quantification (S/N > 10) limits varied between 0.001 ng and 2.5 ng and between 0.005 and 10 ng respectively with a reproducibility varied between 14.5 % (bifenthrin) and 38.9 % (permethrin).

A sampling campaign will be done in five different rubbish chute situated in the basement of a building where pest control was performed by using different techniques : low-pressure spraying directly on soils and wall surfaces, fumigation permitting the diffusion of fog droplets in all part of the room, nebulization of an aerosol directly on soil and wall surfaces, pressurised aerosol (only professionals) spraying applied at 20-30 cm of the surface and a pressurised aerosol (all users) spraying in direction to the top of the room during 8 to 10 seconds.

For each application techniques, a Tenax-TA® passive sampler was installed in the centre of the rubbish chute at 1.70 m from ground before the starting of the application. This sampler was removed after 24 hours exposition and replaced by a new one each day for the first week of sampling (except week-end) and each two days the second week.

Concentrations profiles for all application techniques present the same temporal evolution; high concentration for the first sampling installed before the application and a decrease of concentrations for the next sampling. The intensity of the decrease of concentrations is strongly dependant of the application technique. Aerial pulverization of fumigation are in favor of an important air contamination while low pressure spraying directly to soils surfaces induce a low air contamination.

This study shows that passive sampling coupled to thermal desorption instead of active sampling can be used with accuracy to detect the temporal atmospheric variations of biocides concentrations during and after application whatever the technique used.

Details of results obtained for each application techniques will be presented and discussed in detail during the presentation.

Acknowledgement: This work was supported by the ADEME through a doctoral grant for Caroline Raepfel. Authors want to particularly thank the “Hygiene Habitat” society for providing to us the possibility to perform sampling and for their help during the sampling campaign.

Evaluation of polyurethane passive samplers as a tool for occupational PAH measurements

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Exposure to PAHs at workplaces may give an increased risk of cancer. Routine monitoring of workers' exposure to PAHs in occupational environments are therefore fundamental. Best risk assessment is done using personal sampling. Monitoring of PAHs is mainly studied with active sampling in workplaces. However, to simplify routine monitoring, passive air samplers (PAS) may be the only option since they are cheap, easy to handle, and less disturbing. Disadvantages of active samplers are a big reason to the lack of studies of PAHs in occupational air. The use of polyurethane foam (PUF) as a PAS in outdoor ambient air is well accepted and its capacity has been quite well studied (Gouin *et al.*, 2005; Harner *et al.*, 2006; Bohlin *et al.*, 2008). Since the environmental conditions in occupational environments differ compared to outdoor the PUF may behave differently when deployed here. The PUF sampler needs to be further developed for typical occupational scenarios (i.e. 8 h exposure time and small enough for personal sampling). In addition, the PUF's ability to sequester particle associated PAHs has to be validated. The last is crucial since the most important PAHs concerning health effects (i.e. benzo(a)pyrene-B(a)P) is almost entirely associated to particles.

Recently, we tested the PUF (cylinder design, total surface area = 70 cm²) in two occupational settings known to have elevated levels of PAHs (Bohlin *et al.*, 2010ab). The results demonstrated that the PUF has a big potential for being used as a monitoring technique for both gas- and particle PAH exposure under a working day. The applicability and capacity of the PUF needs, however, to be further validated and tested under both laboratory and field conditions.

In this work we tested the PUF, and determined uptake rates, in two exposure chamber experiments. In the first experiment wood smoke and the second diesel exhaust was generated. The concentrations in all these experiments ranged for instance for phenanthrene from 10 to 450 ng m⁻³ and for B(a)P from 0.5 to 20 ng m⁻³. The uptake rates after 3-8 h sampling time for the 3-4 ringed PAHs were between 1.5 and 4 m³ day⁻¹ and for 5-6 ringed PAHs 0.2-0.8 m³ day⁻¹. Following laboratory studies, the PUF were also tested in the field. In this study the PUF was deployed as personal and stationary samplers together with active low-volume samplers for a working day (8 h) in restaurant kitchens. The results show that the PUF has a good potential to be used as stationary or personal sampler to monitor the exposure to PAHs also at workplaces.

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Measurement of volatile organic compounds with cantilever-enhanced photoacoustic spectroscopy

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Accurate and reliable detection of volatile organic compounds (VOCs) is required in many application areas, for example in industry, indoor and outdoor air quality, health and well-being, and defense and security. Also, high sensitivity and selectivity, rapid detection, and small instrument size are common criteria, especially when monitoring compounds that are harmful to humans.

Cantilever-enhanced photoacoustic spectroscopy (CEPAS) is a promising measurement technique in the detection of VOCs and has several advantages, such as high sensitivity and large dynamic range, over the conventional transmission infrared techniques. Also, photoacoustic detection does not require long absorption paths and therefore it is possible to combine the high sensitivity to a small-sized detector. The use of optical cantilever microphone further enhances the sensitivity of the photoacoustic detection. When compared to more common capacitive microphones, optical cantilever microphone can achieve orders of magnitude higher sensitivity (Koskinen, 2006), which opens possibilities beyond reach of the conventional infrared techniques.

Formaldehyde, benzene, toluene, and xylene in ortho-, para- and meta-substitutions were investigated with a cantilever-enhanced photoacoustic cell combined with a tunable source: either an optical parametric oscillator (OPO) or a quantum cascade laser (QCL). The QCLs and OPOs of the present time offer tuning ranges sufficient for multi-component analysis. As the QCLs and OPOs are becoming more common, they are available in greater number of wavenumber ranges and are more and more affordable.

The above-mentioned gases occur in urban and indoor air and can outgas from commodities, cleaning agents, printings, paints and wood panels. They can affect human health and cause discomfort, irritation of the eyes, nose, and throat, problems with nervous system and at elevated concentrations finally death.

Low-ppb detection limits of all target compounds were achieved with the CEPAS setup in less than 1 s measurement time (Hirschmann, 2013). Formaldehyde had the lowest detection limit of 1.3 ppb. The other detection limits were 12 ppb for benzene, 9.8 ppb for toluene and 10.1–16 ppb for xylenes. With multivariate analysis, the detection limits are in the sub-ppb range.

The limits for 8 h workplace exposure of these compounds are 0.3 ppm for formaldehyde, 0.5 ppm for benzene and 50 ppm for toluene and xylenes. The achieved detection limits are well below the above limits, which makes CEPAS a valuable tool for monitoring VOCs.

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Air quality and biomonitoring in eight schools of the town of Pavia (Italy)

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The environmental education is a key tool for raising public awareness about air pollution, stimulating correct lifestyles and promoting environmental sustainability. For these purposes, a project on air pollution and sustainable mobility was launched, aimed at enhancing young people awareness about air quality.

The main objective of the project was the air quality monitoring in eight primary and secondary schools of the town of Pavia (Italy). Further, the project had other educational objectives: involve students in monitoring activities; inform and making them sensitive to vehicular air pollution sources; raising their awareness and promote lifestyles which can contribute to improving environmental quality; allowing them to make proposals for promoting environmental friendly lifestyles; promote conditions for an education to environmental sustainability.

In the first phase of the project, an educational program was undertaken about the air pollution sources, the measurement and abatement techniques. At the same time, in every school a tree was selected for the identification of lichens and the determination of Lichen Biodiversity Index (LBI). After one year, new determinations of LBI will allow to assess the effects of the increase or decrease of atmospheric pollution concentrations.

In the second phase of the project, measurements of VOCs, aldehydes and nitrogen dioxide were carried out in every school, both in classrooms and outdoor. The measurements were carried out by means of Radiello diffusive samplers (Cocheo *et al.* 2009), exposed for one week. The measurement protocol followed the guidelines of the Décret n° 2012-14 (2012) of French Ministry of Ecology, Sustainable Development, Transportation and Housing.

In this work we present the main results of air quality monitoring and biomonitoring, as well as the educational results, obtained during the project.

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Hydrogen sulphide, peak exposure, still a hazard in modern waste water treatment?

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Waste water workers (WWW) are known to commonly suffer from various health symptoms because of their exposure to microorganisms and noxious gases such as hydrogen sulphide (H₂S)(Heldal et al 2010). H₂S can be extremely hazardous to WWW, being able to cause pulmonary oedema (>300 ppm) sudden unconsciousness (>500 ppm) or death by even a single exposure if the levels are over 1000 ppm(NEG 2001). Repeated exposure to lower levels (5-10ppm) may results in more chronic symptoms from central nervous system, such as fatigue, headache, poor memory and dizziness (Tvedt et al., 1991). As a part of a larger project, we will here present results from measurements of H₂S when handling and transporting sewage in a small community in Norway.

Twelve workers responsible for 11 small waste water plants and 45 connected pump stations with sewage transport, participated in the study. Four of the workers were selected to be personal monitored during full work-shift for three days. Three different jobs were identified, 1) working inside the main waste water plant which was located in a hall in the rock, 2) working on different pump stations with maintenance work and collecting and 3) transporting sewage from smaller waste water plants and private septic tanks. H₂S was monitored by OdaLog Low Range and OdaLog L2/LL (ThermoFisher Scientific Inc. Australia), which have a sensitivity of 0.01 and 0.1 ppm, and a detection area of 0-2 ppm and 0-200 ppm, respectively, Dräger GasVisi X-am 500 and Dräger Pac 700 (Dräger Safety, Norway) with sensitivity of 0.1 ppm and detection area of 0-100 ppm. The meters were calibrated before sampling with calibration gases (25ppm) and fresh air was taken to zero the sensors. The concentrations were measured every 15 sec and the average of 15 sec were recorded using data loggers. The job tasks and time durations were recorded in logbooks.

The level of exposure to H₂S was intermittent and showed up as peaks with various heights. The highest exposure occurred during draining sewage sludge from a small plant. The sludge had been stored for some time, and when flushing the sludge to break the solid membrane, the level reached above the detection range for the instrument which was 200 ppm. The work was then interrupted. Another work task which gave intermittent exposure with peaks from 5 to 50 ppm was collecting sewage from private septic tanks. These peaks lasted for 2 to 5 minutes each. Working in pump stations and inside the main plant resulted in lower exposure levels to H₂S even if the smell sometimes was annoying.

Table 1. Mean number of peaks during a work day for the different jobs connected to the waste water plant. N=number of full day measurement for the different jobs. Type of job, see text.

Type of work	Mean number of peaks in a work shift above 0,5ppm	Mean number of peaks in a work shift above 5 ppm	Mean number of peaks in a work shift above 10 ppm	Highest peak in a work shift ppm	Longest duration of exposure above 5 ppm
Job 1) N=2	2	1	0	10	2 min
Job 2) N=6	11,2	2,6	1,8	>200	8 min
Job3) N=4	0,75	0	0	1,2	

Heldal KK, Madsø L, Huser PO, Eduard W. Exposure, symptoms and airway inflammation among sewage workers. *Ann Agric Environ Med* 2010, 17:263-268.

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Monitoring of anesthetic gases concentrations in operating rooms

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Keywords: air monitoring, active and passive sampling, operating rooms pollution, GC analyses.

Introduction. Air monitoring is one of the fundamental tools used to evaluate workplace exposures. Anesthetic gas and vapours that leak into the surrounding room during medical procedures are considered waste anesthetic gases (WAGs). The waste anesthetic gases and vapours can cause health effects from over-exposure.

The commonly used non-flammable anesthetic gases are halogenated hydrocarbons (isoflurane, halothane, enflurane, desflurane, sevoflurane and methoxyflurane). Workers who acutely exposed to excess amounts of anesthetic gas can experience symptoms of drowsiness, headache, nausea, poor judgement and loss of coordination.

The aim of research was to check the air concentration of waste anesthetic gases in a variety of operating rooms and to compare these WAGs concentrations in the physician anesthesiologist and nurse anesthetist workplaces.

Method. The air polluting WAGs were absorbed from breathing zone of doctor or nurse who working in a sterile operating room. There were used two sampling methods - passive and active. In the case of passive sampling the receiver types is **3M Passive Air Monitoring Badges** (ORGANIC VAPOR MONITOR 3500) with the certain period of time open single charcoal sorbent wafer for easy collection of organic vapours. In the case of active sampling polluting substances were absorbed in ORBO 32 activated charcoal 400/200 mg tubes by use of Gillian LFS-113 low flow personal air sampling pump placed in the employees clothing pocket. Sampling time depends on the processes carried out by the employee.

The WAGs compounds were extracted with carbon disulfide and analyzed by gas chromatography (Warian 3800) with FID.

Results. Monitoring of air pollution on the WAGs was carried out in 32 operating room of different hospitals. The main used anesthetic gas was sevoflurane, but halothane and desflurane was used only in 6 cases. Sampling techniques both active and passive showed comparable and close levels of pollution. Passive sampling is simpler to implement and it is more convenient for operating personnel.

The concentration of sevoflurane in breathing zone of anesthesiologist was $37.28 \pm 7.47 \text{ mg/m}^3$ (median 31.8 mg/m^3) and in breathing zone of nurse anesthetist $14.23 \pm 2.84 \text{ mg/m}^3$ (median 11.50 mg/m^3). The concentration of WAGs in breathing zone of doctor is statistically significantly higher ($p < 0.05$) than of nurses working area. The working air pollution level of anesthesiologist was higher than occupational exposure limit (OEL) for anesthetic gases accepted by Latvian Cabinet of Ministers (Regulation nr. 325/2007) set at level 20 mg/m^3 .

Operating rooms of hospitals were equipped with forced ventilation system, but it did not sufficient air exchange. The mean air pollution concentrations of sevoflurane detected in stationary places of operating rooms were $18.04 \pm 3.62 \text{ mg/m}^3$ (median 18.0 mg/m^3). This WAGs concentration that was near to the OEL.

Conclusion. There is a high possibility of acquiring health complaints of medical personnel caused by poor indoor air quality in operating rooms.

Periodic monitoring (preferably with passive sampling) of waste gas concentrations is needed to ensure that the anesthesia delivery equipment and engineering/environmental controls work properly and that the maintenance program of ventilation system is effective. To minimize waste anesthetic gas concentrations in the operating room the recommended air exchange rate (room dilution ventilation) should be higher.

Air monitoring for waste anesthetic gases should include both personal sampling (i.e., in a health-care worker's breathing zone) and area sampling.

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***Session G - Biological monitoring -
biomarkers of exposure***

**Manganese in exhaled breath condensate:
a new marker of exposure to welding fumes**

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Due to the variability of metabolism and excretion of manganese (Mn), urinary or serum Mn are controversial biomarkers of exposure. Exhaled breath condensate (EBC) is a non-invasive matrix that originates from the air lining fluid. The aim of this study is to evaluate manganese in exhaled breath condensate (Mn-EBC) as an indicator of pulmonary exposure to fumes from metal inert gas welding process.

In an exposed-control study, we collected EBC and urine from 17 welders and 16 unexposed control subjects after 5 days exposure. Cumulative exposure indices for the working week (CIW) and for the total welding years (WY), based on duration of welding activity and atmospheric metal measurements, were constructed for manganese (Mn), nickel (Ni), iron (Fe) and chromium (Cr). Concentrations of these metals measured in EBC and urine samples by ICP-MS and were then correlated with cumulative exposure indices.

Mn was quantified in all EBC samples. Ni was quantified in all welders EBC and in 62.5% of controls EBC. Fe was quantified in 70.5% of welders EBC and in 37.5% of controls EBC. Cr was never quantified in EBC samples. Concentrations of Mn and Ni in EBC were significantly higher among welders than controls whereas this difference was not significant for Mn in urine (Mn-U) (see Table 1).

Table 1. Concentration of metals in EBC ($\mu\text{g}\cdot\text{L}^{-1}$) and urine ($\mu\text{g}\cdot\text{g creatinine}^{-1}$) according exposure and tobacco status.

	Controls	Welders	Exposure effect	Exposure effect adjusted for tobacco status
	median [IQR]	median [IQR]	p-value*	p-value**
$\mu\text{g}\cdot\text{L}^{-1}$				
Mn-EBC	0.32 [0.16 - 2.47]	4.72 [2.99 - 17.13]	< 0.001	< 0.001
Ni-EBC	0.24 [0.10 - 0.65]	1.00 [0.84 - 1.46]	< 0.001	< 0.001
Fe-EBC	0.50 [0.50 - 1.95]	1.48 [0.50 - 1.94]	0.147	0.242
$\mu\text{g}\cdot\text{g creatinine}^{-1}$				
Mn-U	0.38 [0.32 - 0.49]	0.54 [0.37 - 0.76]	0.061	0.098
Ni-U	0.95 [0.56 - 1.59]	1.56 [1.01 - 2.48]	0.049	0.035
Cr-U	0.31 [0.20 - 0.38]	0.72 [0.58 - 1.20]	< 0.001	< 0.001

IQR: inter-quartile range; *: p-value of one-way ANOVA; **: p-value of two-way ANOVA; bold values represent the significant results

Levels of Mn and Ni in EBC were not correlated with their respective levels in urine. The linear regressions found significant positive coefficients between Mn-EBC, Ni-EBC, Ni-U, and Cr-U concentrations and the cumulative exposure indices. Taking into account tobacco use, statistical analysis showed the same trends except for the relationship between Mn-U and CIW.

This pilot study showed that Mn-EBC, as well as Ni-EBC, can serve as reliable indices of occupational exposure to welding fumes and provide complimentary toxicokinetic information to that provided by urine analyses.

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Concentrations of beryllium and aluminium in exhaled breath condensate as markers of exposure in workers of a primary production of aluminium

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Chronic pulmonary berylliosis can occur after a low occupational exposure. Urinary beryllium (Be-U) is not a suitable tool for monitoring workers exposed to beryllium (Be) due to high variability of its excretion. It is therefore essential to develop non-invasive and reliable biological exposure index for monitoring workers exposed to Be. It is more appropriate to measure lung internal dose than the occupational exposure obtained by air monitoring because lung internal dose reflects the concentration of Be that could interact with respiratory epithelium. Exhaled breath condensate (EBC) is a non-invasive matrix that originates from the air lining fluid. The main purpose of this exposed-control study is to assay Be and aluminium (Al) in EBC (Be-EBC, Al-EBC) of workers in a primary production of aluminium and correlate these concentrations to their atmospheric concentrations.

We collected EBC and urine from workers recently exposed (< 8 days) to fluoride beryllium (BeF₂) (17 pot room workers and 13 welders who repair the anode rods with aluminium using Metal Inert Gas process) in a primary production of aluminium, and from 21 control subjects during the work. Cumulative beryllium exposure index (CBEI) was calculated by summing the products of the number of years of employment in each task the workers held and of the estimated average beryllium exposure for the task. Concentrations of beryllium and aluminium were measured in EBC (Be-EBC and Al-EBC respectively) and in urine (Be-U and Al-U) by ICP-MS (LOQ = 1 ng.L⁻¹ for Be-EBC; LOQ = 0.1 µg.L⁻¹ for Al-EBC).

Be and Al were more often quantified together in EBC of pot room workers than in those of the welders in mainly of which only Al was quantified (see Table1).

Table 1: Proportion of metals quantification in EBC of workers

Metallic content of EBC	Controls	Pot room workers	Welders	p*
Al(+) and Be(+)	9.5%	53%	7,7%	0.0147
Al(+) and Be(-)	14.3%	23,5%	69,3%	
Al(-) and Be(+)	0%	0%	0%	
Al(-) and Be(-)	76.2%	23,5%	23%	

Al: aluminium; Be: beryllium; (+): quantified; (-): not quantified; *: Fisher's exact test

Pot room workers: concentrations of Be and Al in EBC were significantly higher among pot room workers than controls (median [IQR]) (1.1 [0.5 - 2] vs 0.5 [0.5 - 0.5], p=0.003 for Be-EBC (ng.L⁻¹) and 2.5 [1.5 - 4.7] vs 0.05 [0.05 - 0.05], p=0.0003 for Al (µg.L⁻¹)) whereas this difference was not significant for Be and Al in their urine. Levels of Be and Al in EBC were strongly correlated (p<0.0001; r=0.85) but they were not correlated with their respective levels in urine. The linear regressions found significant positive coefficients between Be-EBC concentrations and the CBEI (β: 0.082; p=0.001). **Welders:** concentrations of Al-EBC and Al-U were significantly higher among welders than controls (median [IQR]) (1.8 [1.1 - 3] vs 0.05 [0.05 - 0.05], p=0.0014 for Al-EBC (µg.L⁻¹) and 20.1 [9 - 68] vs 7.02 [4.42 - 14.3], p=0.006 for Al-U (µg.g creatinine⁻¹)) whereas this difference was not significant for Be-EBC and Be-U. All statistical analysis showed the same trends taking into account tobacco use.

This pilot study showed that EBC metallic content was different according to occupational exposure and it strengthens the idea that the EBC can be used to monitor employees. We found that Be-EBC, as well as Al-EBC, can serve as reliable indices of lung occupational exposure and provide complimentary toxicokinetic information to that provided by urine analyses in the pot room workers. Moreover, this study found that Al-EBC and Al-U can discriminate welders from unexposed subjects.

Acknowledgement: This work was supported by the National Research and Safety Institute for the Prevention of Occupational Accidents and Diseases (INRS) and the Research Laboratory EA 4483 of Lille 2 University.

Biological monitoring of occupational exposure to di(2-ethylhexyl) phthalate (DEHP) in two cases: the French flexible-PVC industry and the use of vinyl gloves

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Keywords: Biological monitoring, DEHP, gloves

DEHP is a phthalate plasticizer of PVC, classified as a Category 1B reproductive toxicant (EU). Soft PVC are very often plasticized with 40% (w/w) phthalates. As DEHP is weakly bound, the risk of contamination and cutaneous penetration should be considered. These two studies provide in risk assessment, additional occupational exposure data, which are particularly scarce.

OBJECTIVE: Assess the occupational exposure to DEHP in flexible PVC-industry (1) and in workers using vinyl gloves by the quantification of DEHP metabolites.

METHOD: Over 5 days of pre- and post shift sampling, five urinary metabolites of DEHP, mono(2-ethylhexyl) phthalate (MEHP), mono(5-carboxy-2-ethylpentyl) phthalate (5Cx-MEPP), mono(2-ethyl-5-oxohexyl) phthalate (5oxo-MEHP), mono(2-ethyl-5-hydroxyhexyl) phthalate (5OH-MEHP) and 2-ethylhexanoic (2-EHA), were quantified in 62 workers and 29 controls from six PVC factories and 50 users of vinyl gloves, gloves contained 45% by weight of DEHP, 16 controls.

RESULTS:

- In flexible-PVC industry, there was a significant increase (Mann-Whitney *U* test, $P < 0.05$) of post-shift excretion in the exposed workers versus the controls and in the post-shift versus pre-shift concentrations only in the exposed workers. Median of internal dose (ID) calculated for exposed workers was $< 10 \mu\text{g}/\text{kg bw}/\text{day}$, but 43 workers have $\text{ID} > 20 \mu\text{g}/\text{kg bw}/\text{day}$, Rfd from EPA, USA, 5 workers $> 50 \mu\text{g}/\text{kg bw}/\text{day}$, TDI from EFSA (EU).
- In the workers using vinyl gloves, there was a significant increase of post-shift excretion in the workers using vinyl gloves versus the controls. No significant increase in the post-shift versus pre-shift excretions. Analysis of variance (Anova) did not demonstrate a significant influence with the duration of the use and the numbers of pairs used. Median of ID ($4.4 \mu\text{g}/\text{kg bw}/\text{day}$) was close the ID obtained from EU Risk Assessment (6.7 and $9.3 \mu\text{g}/\text{kg bw}/\text{day}$).

CONCLUSION: A low level of exposure of DEHP related to the use of vinyl gloves might be considered. In the flexible-PVC industry, there is a clear evidence of occupational exposure of workers in studied factories. An epidemiological survey is needed to complete the DEHP risk assessment.

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Biomonitoring results from the Canadian health measures survey: benzene case study

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Keywords: National Survey, Biomonitoring, Biomarkers of Exposure, CHMS, Canada, Benzene, Indoor Air

Biomonitoring is used as an indicator and quantitative measure of human exposure to environmental chemicals. To date, the Canadian Health Measures Survey (CHMS) is the most comprehensive direct health-measures survey conducted in Canada. The objectives of the biomonitoring component of CHMS are to establish nationally-representative data for a range of environmental chemicals in Canadians, to track trends over time and to compare results with sub-populations within Canada and other countries.

The latest biomonitoring results from CHMS were released in April 2013 and include biomonitoring data for 91 chemicals in 6, 400 Canadians, aged 3 to 79 years (Health Canada, 2013). For the first time, benzene was measured in both indoor air and urine of participants.

Benzene metabolites, such as *trans, trans*-muconic acids (*t,t*-MA) and *S*-phenylmercapturic acids (*S*-PMA) were measured in the urine of approximately 2500 participants aged 3 to 79 years from 2009–2011. The following geometric means (GM) were estimated: 64 µg/g cr for *t,t*-MA and 0.20 µg/g cr for *S*-PMA. These data provide baseline levels for urinary benzene metabolites in the Canadian population and appear to be consistent with those reported internationally (Arnold et al, 2013). Currently, there are no guidance values available for the general population for benzene metabolites in urine. However, Biomonitoring Equivalents (BE) can be used for evaluating biomonitoring data in a risk assessment context (Hays et al., 2007). A BE is defined as a calculated concentration of a biomarker consistent with a health protective guidance value. Hays et al (2012) have derived a BE value for benzene in blood, a biomarker being currently measured in CHMS. Some biomarkers of benzene exposure that are useful in an occupational setting may not be useful to evaluate environmental exposures due to the presence of other sources of these biomarkers (such as diet and smoking) in the general population (Arnold et al., 2013; Hays et al, 2012).

According to Wheeler et al. (2013), the indoor air of Canadian homes has relatively low benzene concentration with a geometric mean concentration of 1.07 µg/m³, showing a decline in exposure over time. Health Canada's new indoor air guideline recommends that individuals take actions to reduce exposure to benzene indoors as much as possible (Health Canada, 2013). Future research projects plan to link blood benzene levels to levels found in Canadian households (e.g. indoor air and tap water) through physiologically-based pharmacokinetic modelling.

This national survey provides a rich resource for ongoing surveillance and research. Although the interpretation and communication of biomonitoring results remain a challenge, biomonitoring data are used in the regulatory sphere, to assess exposure to chemicals and to track progress of actions under Canada's Chemicals Management Plan and international protocols.

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Monitoring of urban and industrial dust pollution using *Morus (Morus alba)* plant as bioindicator

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Atmospheric dry deposition is the process by which airborne dust particles and gases are deposited onto various surfaces such as vegetation, water bodies and soils etc. through settling, impaction, and adsorption. Study of such depositions and their impacts is possible by using plants as bioindicators which is a low cost and valuable method. This work was focused upon biomonitoring of dustfall deposition on foliar surface of *Morus (Morus alba)* to understand the changes in biochemical constituents of foliar at two sites in Delhi capital region. Dustfall deposition was collected on a 10 days exposure basis at foliar surfaces at a residential site (Jawaharlal Nehru University, JNU) and an industrial site (Sahibabad, SB) during winter season of 2012-2013 periods. Atmospheric dustfall deposition was characterized for major ions (F^- , Cl^- , NO_3^- , SO_4^- , Na^+ , NH_4^+ , K^+ , Mg^{++} and Ca^{++}). The morphology, size and elemental composition of individual sample of foliar dust were characterized by using a scanning electron microscope (SEM) coupled with an energy dispersive x-ray system (EDX). The biochemical parameters viz. total chlorophyll, carotenoids, total soluble sugar, proline amino acid and ascorbic acid were also determined in foliar samples. The results of this study showed around 3 times higher fluxes of SO_4^- at an industrial site as compared to the residential site (Fig. 1). Industrialization and high density of diesel driven vehicular traffic are the major sources of SO_2 at the industrial site. Particulate sulfate was formed as a result of the oxidation of sulfur dioxide onto the foliar surface (Kulshrestha et al., 2003). It was observed that the higher fluxes of SO_4^- had significant impact on the biochemical constituents. Concentrations of proline and ascorbic acid were found to be higher at industrial site as compared to residential site due to greater influence of industrial activities at Sahibabad. The study also suggested that the plants are effective means of pollution monitoring. Detailed results of the study will be presented during the conference.

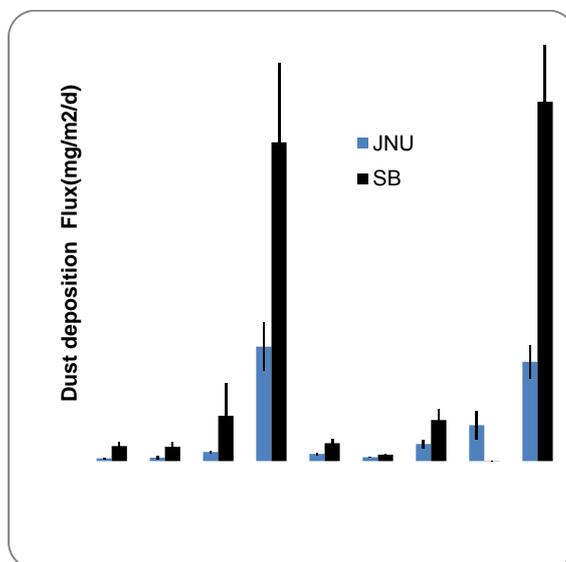


Fig: 1 Dust deposition Fluxes (DDF) of major ions on *Morus (Morus alba)* foliar surface at JNU and SB.

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Health associated variability of biomarkers of occupational exposure to water-soluble fluorides

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A cohort of 132 healthy male workers with a higher risk of overexposure to airborne fluorides such as HF, NaF, CaF₂ were recruited for a 11-year follow-up biomonitoring study that was supported by thorough annual medical examinations. These workers aged from 24 to 31 who had been employed in the same electrolyses department of aluminium refinery. The inclusion criterion to the cohort was the definite beginning of employment in the selected occupations as 12-24 months before the study started. In the electrolysis department the 6-hr time-weighted fluoride workplace air concentrations measured as total F-ion were in the range from 0.5 to 5.8 mg/ m³ . During the monitored period of time no significant change in the air concentrations were reported by aluminium company. The yearly geometric mean for the starting year was 2.1± 0.4 mg/m³ and 1.9 ± 0.4 mg/m³ was for the last year of monitoring.

Fluoride concentrations in the local tap water were measured in the range of 0.22 to 0.32 mg/L with low seasonal variations. Urinary concentrations of F-ion was used as a biomarker of accumulated occupational exposure to inorganic fluorides experienced by the monitored cohort. 24-hr urine specimens were collected after one day of vacation. F-ion was determined by the ISE potentiometric method with a MCP41010 digital pH/mV meter. The concentrations were adjusted to the standard urine density of 1.020 g/L at temperature of 20^o C.

Changes in urinary concentrations was found to be associated with some chronic diseases detected in the workers available for the study in 11 years (103 persons from 132) (Table 1).

Table 1.

Chronic disease detected during employment	ICD-10 Code	Number of workers	Urinary concentrations, mol/L 10 ⁻⁶ (Geomean ± SD	
			Starting	After 11 years
None		21	165 ± 37	198 ± 46
Hypertensive diseases	I10 –I15	11	188 ± 47	101 ± 42
Chronic lower respiratory diseases	J40 –J47;	26	147 ± 32	203 ± 65
Diseases of the musculoskeletal system and connective tissue	M00-M99	28	181 ± 34	142 ± 21
Diabetes mellitus	E10-E14	6	193 ± 45	97 ± 34
Other		11	157 ± 65	172 ± 65

Unlike other groups of potroom workers a significant decrease in urinary concentrations is observed in those developed clinical manifestations of the hypertensive disease, diabetes melitis and to some extent musculoskeletal diseases when employed.

The exposure to chemical hazards often involve renal, liver, cardiovascular toxicity that may affect their absorption, distribution, transformation and elimination and thus change biomarker concentrations. In this case a biomarker might reflect not only the exposure but also the toxic effect. On the other hand the diseases that are not considered to be work-related are capable of affecting a biomarkers kinetics as well. The possible impact of ill-health is recommended to take into account when recruiting workers for occupational exposure biomonitoring programs.

Biological monitoring of occupational exposure: which urinary correction mode for spot urinary samples?

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The use of spot samples for the measurement of urinary biomarkers is a common practice in biological monitoring of occupational exposure. Usually urinary concentrations in such samples are normalized to creatinine (CR) or specific gravity (SG) to minimize the effect of hydration. However still there is no consensus on which of these two modes is the most appropriate due to their large variability or because they do not accurately reflect the mechanisms of excretion of biological exposure indicators.

The objective of this study was to identify the best approach for adjusting urinary concentration values of indicators in a spot sample.

A review of the literature was conducted for the period covering January 1990 to June 2013. The laboratory information management system (LIMS) database of IRSST was queried for the years 1985 to 2010 to document the relationship between the different urinary concentrations, corrected or not, of biological indicators for 22 contaminants. Descriptive statistics and modeling, using linear mixed effects models, were also performed on the data of CR and SG.

We reported CR and SG values (Table 1) calculated from the data available in the LIMS database. According to the modeling results, CR concentrations in women are on average 25 % to 30 % lower compared to men and the SG values are on average 10% (end of shift) and 15% (prior to shift) lower in women compared to men. For men, the results are higher than 5% at the end of shift compared to a sample taken prior to shift.

Table 1. Mean values of CR and SG calculated from LIMS database

	n_{CR} / n_{SG}	CR (mmol/L)	SG
Women	2323 / 2385	10.9 ± 6.1	1.019 ± 0.007
Men	17873 / 17811	15.0 ± 6.4	1.023 ± 0.006

This review indicates that the correction based on CR can lead to significant bias in the estimation of exposure in individuals or populations of different age, sex, ethnicity and muscle mass while correction based on SG would be less influenced by these factors. Correction based on SG is an attractive alternative since this method is simpler and less expensive than the determination of creatinine. Although the SG correction seems the most appropriate approach, the choice of the correction mode should take into account the units in which the biological exposure indicator values are expressed.

Using equations presented in Table 2 it is possible to estimate the equivalent values of an indicator expressed according to different units (L uncorrected, L corrected for a specific gravity of 1.024 and mmol creatinine).

Table 2. Relation between BEI values not corrected or corrected based on CR or SG (1.024) for 4 contaminants

	n	Equation / R^2	IBE _{CR}	IBE _{SG}
Mandelic Acid	5209	$y = 0.073x - 0.0064 / 0.9114$	0.6 mmol/mmol CR	8.3 mmol/L
Cadmium	1608	$y = 0.059x + 0.1983 / 0.9307$	5 nmol/mmolCR	81 nmol/L
Muconic Acid	902	$y = 0.059x + 0.0515 / 0.8932$	1.2 μ mol/mmolCR	20 μ mol/L
Mercury	2896	$y = 0.100x - 1.6786 / 0.9806$	20 nmol/mmolCR	217 nmol/L

This study has shown that the urinary biological indicator concentrations corrected by SG are less influenced by age, sex and muscle mass of individuals compared to CR. However, since several reference values available are expressed based on CR correction, it is important before choosing a correction mode, to consider the units in which these reference values are expressed to allow comparison and proper interpretation of biomonitoring data. Since SG correction has several advantages compared to CR, we believe that its use should be preferred in future studies aiming at proposing reference values.

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Background levels of metals in urine samples to assist with exposure assessments.

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The aim of this project was to establish current background levels of elements in urine both for commonly monitored elements and for rarer elements being increasingly utilised in new technologies. These results will be compared with other published data and data from routine biological monitoring measurements undertaken at HSL.

Background levels of 61 elements in urine from a UK population are presented here from 137 people. The samples were analysed by ICP-MS in different diluents and matrices depending on the elements.

Mixed effect analysis was carried out on the elements and it has been possible to establish 95th percentile background levels for 45 of the elements. However, based on the high percentage of results <LOQ, the analysis was not carried out for the following elements: Zr, Bi, Nb, Ag, Os, Y, In, Pr, Nd, Sm, Eu, Tb, Dy, Tm, Lu, and Au. The mixed effect analysis showed that, for all of the remaining elements, creatinine correcting the data in all cases gave a reduction in variability or no significant difference in variability. It was also shown that smokers have elevated cadmium and lower boron and selenium levels than non-smokers.

Reference levels based on 95th percentiles for many elements have been established for a UK population. Overall the results compare well with published European and American results, however there are differences for some elements. The results show that there have been no major changes in the unexposed levels of 'routine' metals used in everyday biological monitoring at HSL.

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Determination of polycyclic aromatic hydrocarbons in urine as biomarkers of exposure to diesel exhausts

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Keywords: diesel engine exhaust, PAH metabolites, biomonitoring

In 2012, the International Agency for Research on Cancer (IARC) in Lyon has classified diesel engine exhausts (DEE) as carcinogenic to humans, based on “sufficient evidence that exposure is associated with an increased risk of lung cancer”. The new classification has raised concerns about the health risk associated with DEE exposure in the general population as well as among workers with frequent contact to such exhausts. DEE is a complex mixture of particulate and gaseous components. Among the most relevant compounds from a toxicological point of view are polycyclic aromatic hydrocarbons (PAHs). The best established biomarker of PAH exposure so far is 1-hydroxypyrene (1-OHP) in urine. Occupational limit values in biological material have not been derived up to now. However, reference values for nonsmokers and smokers as well as data from exposed workers are available. In recent years, the analysis of other PAH metabolites, namely of phenanthrene and naphthalene, was established and applied for biomonitoring.

In a pilot study among 30 employees from a site security department, who are regularly occupied with truck clearance (n = 15) or with office tasks (n = 15), the internal exposure to PAHs was monitored by the analysis of urinary 1-OHP in pre-shift and post-shift samples by high performance liquid chromatography with fluorescence detection (LOQ: 0.1 µg/L). Additionally, 1-, 2-, 3-, and 4-hydroxyphenanthrene as well as 1- and 2-naphthol will be determined. The times of sampling, job tasks on the day of sampling (truck clearance yes/no), smoking habits (smoker/nonsmoker, cigarettes per day) and characteristics of the workers' residential area (urban/rural) were assessed by questionnaire.

The nonsmokers showed a median pre-shift concentration of 0.14 µg 1-OHP/g creatinine (range: < LOQ – 0.90 µg/g creatinine) and a post-shift concentration of 0.20 µg 1-OHP/g creatinine (range: < LOQ – 0.73 µg/g creatinine). The median urinary concentrations of 1-OHP in the samples of the smokers were 0.46 µg/g creatinine (pre-shift, range: 0.15 – 0.83 µg/g creatinine) and 0.42 µg/g creatinine (post-shift, range: 0.19 – 0.77 µg/g creatinine), respectively. Differences were observed between the nonsmokers and the smokers, but not between pre-shift and post-shift samples. Furthermore, no impact of the potential additional exposure to DEE from truck clearance could be found, neither for the subgroups of nonsmokers nor for smokers, or for employees from rural versus urban residential areas. Further biomonitoring analyses of phenanthrene and naphthalene metabolites are currently under work.

The biomonitoring results of this pilot study among site security staff suggest that the exposure to PAHs is mostly within the range of the environmental background exposure in Germany. The Human Biomonitoring Commission of the German Federal Environment Agency reports a reference value of 0.5 µg/L in the morning urine of adults (approx. 0.3 µg/g creatinine), and values about twice as high for active smokers. The BEI Committee of the US ACGIH has proposed a benchmark value of 1 µg 1-OHP/L (approx. 0.7 µg/g creatinine) for the differentiation between background exposure (nonsmokers and smokers) and possible occupational exposure. This value, which does not imply any toxicological or health risk conclusion, was exceeded only in some isolated cases. The maximum 1-OHP concentration observed in this pilot study was 0.9 µg/g creatinine.

The results of this study point to a low exposure of the site security employees to PAHs, predominantly from environmental sources or from tobacco smoking. We found no indication of a relevant uptake of PAHs caused by occupational exposure to DEE. From this point of view, an additional specific health risk appears to be unlikely. Nevertheless, the biomonitoring of employees potentially exposed to DEE or other sources of PAHs will be continued as part of a comprehensive exposure and health protection program.

Urinary biomonitoring for evaluation of professional mixed exposure to volatile organic compounds

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Keywords: Biological monitoring, VOC, headspace, urine

Mixed exposures to chemical products often happen during work time and they are topical issues for occupational health. According to the 2003 Sumer Survey, 20% of French workers are exposed to 5 chemicals at least. Among hazardous chemicals, many volatile organic compounds (VOCs) widely used in industry are listed as CMR (carcinogenic, mutagenic or toxic to reproduction compounds) or considered as ototoxic compounds.

In order to evaluate occupational exposures to VOCs, analysis of unmetabolized VOCs in urine can be an interesting way of monitoring their excretion, which is traditionally done using urinary relevant metabolites.

Headspace analysis has the asset to avoid time-consuming preliminary samples processing, which are usually required by metabolites monitoring. Using dynamic Headspace and gas chromatography linked to a mass spectrometer leads to an optimized sensitivity, which is required by this kind of trace analysis. Headspace has been already used to assess occupational exposure to VOCs (Ducos *et al.*, 2008), but only few methods have been developed in case of mixed exposures (Fustinoni *et al.*, 1996 ; Kramer Alkade *et al.*, 2004), only on a single chemical family. It was chosen to develop an analytical headspace method to analyze in a single run aromatic hydrocarbons as well as chlorinated compounds. The assessed VOCs are benzene, toluene, ethylbenzene, xylenes, styrene, dichloromethane, chloroform, trichloroethylene, tétrachloroéthylène. As it is almost impossible to find factories using all the compounds investigated, the field study involves firms where workers are potentially exposed to two VOCs at least. Until now, 3 interventions took place, two in a refinery plant and one in a furniture factory. About 30 workers (plus controls) gave urine samples before and after work shift for five days. They were also asked about their smoking habits.

In case of low exposures, smoking is the most important parameter. Indeed, the tobacco smoke contains a lot of aromatic hydrocarbons, most especially benzene and toluene. In the furniture factory, where toluene, xylenes and ethylbenzene were used as paint and varnish components, exposure was found to be statistically significative compared to controls, even if smoking was the main factor influencing urinary excretion level.

In the refinery plant, two interventions took place. The first one occurred during a standard week of work, and the second one during a major clean-up week, when activities were supposed to be more exposing. Chloroform, benzene, toluene, ethylbenzene and xylenes were found in workers urines. During the standard week, one activity was found to be particularly exposing to benzene and xylenes, and a second one to chloroform.

During the clean-up week, exposures were more important and two additional activities showed significative exposure to benzene.

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Biological monitoring of inhalable substances in vitro – development of an improved test method based on the air-liquid-interface (ALI) cell culture technique

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The air-liquid-interface (ALI) cell culture technique is the state-of-the-art method for lung related research in vitro. It involves biological models such as cell lines, primary cells, reconstituted 3d multi cell type models or ex vivo tissues like PCLS (precision cut lung slices) cultured and exposed on microporous membranes. They resemble the biological barrier function of the lung tissue as a “first site of contact” of inhalable substances with the body in a very relevant way. Meanwhile, the methods to use ALI cultures in experimental processes to test inhalable substances in their native airborne status have improved intensively. Hence, a recent prevalidation study in Germany involving 4 Test Labs (Fraunhofer ITEM, Hannover, BfR, Berlin, UFZ, Leipzig and BAuA, Berlin) and chemical positive and negative gases documented a good intra- and inter-laboratory reproducibility and relevance and resulted in a prediction model for in vivo toxicity (G. Linsel *et al.* (2011)).

However, there were still major limiting factors until now including practicability and applicability of the method, insight into the cellular status during exposure and efficiency of particle deposition from aerosol on the cells during exposure.

To overcome these limitations, an improved exposure process was developed including an integrated use of standard labware like multiwell plates throughout the whole process, possibility of online monitoring of the cellular status during the exposure by fluorescence live staining and fundamentally improved particle deposition by thermophoresis (P.R.I.T.[®] ALI ExpoCube). The geometry of the flow system and aspects of the thermophoresis application were optimized by CFD (computer fluid dynamics) simulations.

The refined process was tested in a large range of different experimental applications. The integration of standard labware led to a smooth workflow reducing time and money needed for the conductance of the technical process. Toxicity testing using a setup of 4 selected chemical gases showed a good correlation to the in vivo toxicity of these chemicals. The improved process enabled easy conductance of repeated-dose-exposures to enhance the sensitivity of the biological test. This was successfully demonstrated using the same set of 4 chemical gases in repeated dose exposures at low dose (ED90) and evaluation of the resulting cellular RNA-profiles. Online monitoring during exposure documented immediate dose dependent changes in the cellular status during exposure to a model aerosol (smoke) and effects at environmentally relevant levels of toxic gases (ozone, 100 ppb). Thermophoresis clearly increased the particle deposition from aerosols on the cells to a factor of more than 20 depending on the particle size. Furthermore, it enabled sensitive aerosol testing without modification of the test aerosol and resulted in reproducible exposures to model aerosols generated from positive and negative substances with dose and substance dependent toxic effects.

In summary, the development clearly improved the exposure process fundamentally with respect to experimental possibilities, practicability and applicability, sensitivity and robustness. Therefore, it can be a useful tool especially in the field of biomonitoring of environmentally, workplace and other relevant inhalable substances and mixtures in their native state by means of in vitro methods.

G. Linsel, M. Bauer, E. Berger-Preiß, C. Gräbsch, H. Kock, M. Liebsch, R. Pirow, D. Ritter, L. Smirnova, J. Knebel (2011) Prevalidation study for testing toxic effects of inhalable substances (gases). 1. edition. Dortmund: Bundesanstalt für Arbeitsschutz und Arbeitsmedizin 2011. ISBN: 978-3-88261-131-1, 43 pages.

Fluorimetric neuraminidase assay to monitor airborne respiratory viruses

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Respiratory viruses are a major concern in public health. Detection and quantification of airborne respiratory viruses is achieved using different types of air samplers coupled with various methodologies such as cell culture and qPCR. These multi-steps methods are time consuming and have to be done in a specialized laboratory environment. In addition, no generic assays are available for a wide group of viruses since they share little structural components. Viral neuraminidase is an enzyme present on many respiratory viruses and can be used as a detection marker. Specific viral neuraminidase substrates are available allowing for a sensitive, more generic to a wide group of viruses and low cost detection assay.

The objective of this study was to determine the effect of airborne sampling on the neuraminidase activity (NA) of the Influenza A H1N1 virus.

Vaccine strain of Influenza A H1N1 was nebulized in a SCL Medtech aerosol chamber and sampled with both liquid collection using an SKC Biosampler® and 0.8 µm polycarbonate filter mounted in closed face 37 mm cassettes to look at long term sampling on solid surface. Viral load in samples was estimated by qPCR and compared to NA.

NA of Influenza A H1N1 is weakly affected by aerosolisation and sampling processes. The activity remains strong with percentages of 49% for filter samples and 90% for Biosamplers®. Results also showed that long term filter sampling can be used to monitor high air volume with low concentrations of viruses as the NA activity doesn't seem to be affected with sampling up to 200 minutes.

Field NA assays need to be developed to evaluate its potential of use as a sentinel to detect respiratory viruses in an indoor environment context.

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Biomonitoring of biphenol A and bisphenol S in urine using liquid chromatography-mass spectrometry

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As an essential component of polycarbonate plastics and epoxy resins, Bisphenol A (BPA) is found in numerous industrial and consumer products, including electronic goods, household equipment, metallic food and beverage cans, bottles and dental devices. BPA is also used in the production of thermal paper. BPA may cause adverse health effects because of its estrogenic properties. The widespread occurrence of BPA in environment and consumer urines has raised concerns among regulatory agencies all over the world. BPA is being replaced with a number of alternatives, such as Bisphenol S (BPS). Limited studies have shown that BPS possess estrogenic activity similar to BPA. In humans, BPA is metabolized in the liver to its glucuronide forms and eliminated mainly through urine. A quantification of free and conjugated forms of BPA in urine is thus a valuable tool for the assessment of human exposure. The objective of this work was to develop accurate methods for the determination of free and total BPA and BPS in urine samples, using liquid chromatography tandem mass spectrometry (LC-MS/MS).

Conjugated BPA and BPS were hydrolysed enzymatically from urine to release free forms. BPA was extracted with toluene and derivatized with dansyl chloride before analysis. The extraction procedure for BPS was different due to its high polarity. Urine samples were purified by solid phase extraction on Oasis MCX cartridge before derivatization by dansyl chloride (Fox *et al.* 2011). The liquid chromatography separation was performed in a reversed-phase column and BPA- d_6 was chosen as internal standard. BPA and BPS dansyl derivatives were thus analyzed by LC-MS/MS operating in positive mode. The validation criteria of methods were assessed in pools of spiked urine samples.

Calibrations were linear up to 20 $\mu\text{g/l}$ with a limit of quantification of 0.1 $\mu\text{g/l}$. Methods were shown to be selective, reproducible, accurate and complied with good laboratory practices. Exogenous contamination due to leaching of BPA from the materials and solvent contamination was minimized. Background levels of BPA and BPS from the overall procedure were determined before each run. These methods allowed also the determination of glucuronide forms of BPA and BPS in urine samples.

On account to its sensitivity, our methods are thus suitable for biomonitoring of occupational exposure to BPA and BPS in different settings including epoxy resin factories or sales area where thermal paper are frequently handled. The assessment of occupational exposures is in progress.

Fox S.D., Falk R.T., Veenstra T.D. and Issaq H.J. (2011), *J. Sep. Sci.*, 34, 1268-1274.

Non-invasive metal and nanoparticle exposure assessment in airport tarmac workers using exhaled breath condensate

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Ultrafine particles, or non-intentionally produced nanoparticles, are responsible for adverse health effects including respiratory effects. The assessment of respiratory exposure of individuals to nanoparticles at work places might be of interest. Biomonitoring is the only way to take into account the use of protective devices and individual variability. There is still a lack of adequate non-invasive tools for nanoparticle exposure assessment.

Exhaled breath condensate (EBC) is an easy non-invasive way to sample the respiratory tract. EBC has been shown to be useful for occupational exposure assessment to metals. The hypothesis is that nanoparticles might be also found in EBC following inhalation and might be used as biomarkers of exposure.

We aimed to investigate the influence of nanoparticles emitted by jet engines on respiratory health in two French airports. Exhaled breath condensate has been used to assess occupational exposure to nanoparticles.

The granulometric distribution of EBC content has been investigated in this matrix in addition to some metals constitutive of paints or materials of aeroplane structures (Al, Cr, Cd).

EBC was obtained in 458 workers, 246 tarmac employees working nearby aeroplanes and jet stream exhausts and 212 employees from administrative areas of the airports, in order to compare *a priori* exposed vs non-exposed workers. Nanoparticles have been characterized in atmospheric measurements at different places of exposed and non-exposed zones. EBC collection was performed with the RTube device according to ATS/ERS recommendations during 15 min. Informed consent was obtained from each participant in addition to a detailed questionnaire. EBC have been analysed thanks to a multi-elemental method using inductively coupled mass spectrometry, and a rigorous procedure was performed to validate the analytical method. Elemental concentrations were normalized using Na concentration. In addition, each EBC sample has been analysed by dynamic light scattering in order to obtain the granulometric distribution of particles potentially found in EBC. Finally, some EBC have been explored using scanning electron microscopy coupled to energy dispersive X-ray detection.

There was no obvious significant differences between exposed and non-exposed workers due to tarmac exposure for elemental composition and granulometric distribution of EBC. However, the data on elemental levels in EBC, especially in the non-exposed group, will be very useful since very few data are available in the literature and it is the starting point to be able to identify increased elemental levels due to occupational exposure. The normalization using Na concentration is also promising. Regarding the granulometric distribution found in EBC, the characterization of the dynamic light scattered signal has to be explored in the future.

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Session H - Exposure modeling

A new tiered approach for the assessment of workplace exposure to airborne chemicals

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Solvay is a large multinational chemical company which serves diversified markets generating 90% of its turnover in activities where it is one of the top three worldwide. Following a recent major acquisition, Solvay is currently undergoing a reorganization of its Industrial Hygiene methods.

Because of the large number of chemicals regularly handled within Solvay and the associated significant number of exposing tasks, a step-based approach has been chosen:

- A first screening step based on the substances hazards and on limited information related to the task. As for all screening steps, the tool needs to be simple and conservative. The target is to minimize the workload of the next more demanding step.
- A second step which consists in a more precise but unavoidably more complex exposure assessment tool recently developed. ART (Advanced Reach Tool) was selected as exposure assessment tool as it is currently the only generic higher tier 2 exposure assessment tool which incorporates a mechanistic model of inhalation exposure and a database of empirical exposure information (Schinkel et al, 2011).

A specific solution was developed for the first screening step as none of the currently available tier 1 tools fully meets the needs of a large chemical manufacturer. In addition to limited data on the substances (fugacity, OELs and GHS classification), this first step relies on two key parameters:

- A list of task categories which were chosen in order to represent the large majority of the potentially exposing activities which are carried out within a large chemical company. Great effort has been done to properly describe these tasks with a wording which is at the same time concrete and easy to understand by operators.
- An airborne concentration calculated with ART assigned to each task categories. The ART exposure modifiers (for instance duration, type of local exhaust ventilation, etc.) for those task categories were chosen taking into account the worst cases within the Group.

Once one of the task categories has been selected, the correspondent airborne concentration of the chemical is compared to its occupational exposure limit (OEL, when available) or to a band of exposure limits (OEB).

This approach presents several advantages. The extremely limited number of parameters reduces the possibility of error and it allows the use of the tool by non-specialists. The use of ART both to calculate the results of the first and second steps facilitates the transfer and the consistency of data from the first step to the following one.

The use of a first screening step specific to our company allows more precise results so that this first step is more effective and the overall exposure assessing effort is reduced over the whole approach.

This approach was developed for a chemical company but it could be easily used by other business sectors.

Schinkel J, Warren N, Fransman W., Van Tongeren M., McDonnell P., Voogd E., Cherrie J.W., Tischer M., Kromhout H., Tielemans E. (2011) *Advanced REACH Tool (ART): Calibration of the mechanistic model* Journal of Environmental Monitoring 13, 1374–1382.

Modeling source functions of atmospheric polycyclic aromatic hydrocarbons in occupational environment

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Background: Polycyclic Aromatic Hydrocarbons (PAHs) are in the forefront of carcinogenic occupational exposure, where millions of workers are exposed in many industrial sectors (aluminum, silicon, electrodes production, asphalt ...). Emitted during the combustion process or the distillation of coal and oil, complex mixtures are formed which are constituted of a particulate (heavier compounds, potentially carcinogenic) and a gaseous PAH phase (lighter compounds, less toxic). Airborne concentrations (levels) and relative proportions (profiles) of each PAH within the mixtures are highly variable and function of the emission sources which depend on the kind of industrial sector. Associated with lung, skin and bladder cancers, these pollutants would also be responsible for immune and reproduction disorders. Therefore, PAHs represent a major health issue of which population's exposure and risk assessment is essential.

Objectives: The aim of this study was to identify similar exposure source groups (SESG) among many industrial sectors in order to assess the health risk of workers by specify PAHs' characterization (mixtures' composition) and modeling PAHs' plant source functions.

Materials and Methods: Twelve years of PAH personal air samplings collected in several companies and compiled in the Exporisq-HAP database were used to classify industrial sectors at both level and profile scales. Classifications, using a Hierarchical Cluster Analysis, were performed to identify the SESG for three sampling time durations (short-term, mid-term, long-term), and a source function model was then developed. For each SESG, the associated source function was characterized and described using a correlated multivariate lognormal distribution.

Results: A total of 10 and 12 SESG were identified at level and profile scales, respectively. The model allowed characterizing source functions: for example, oils, engines, bitumen and foundry were grouped into the same SESG for the long-term sampling duration. As an illustration, Fig.1 shows the SESGs identification for the short-term sampling time and the source function associated spectrum of one of the SESGs.

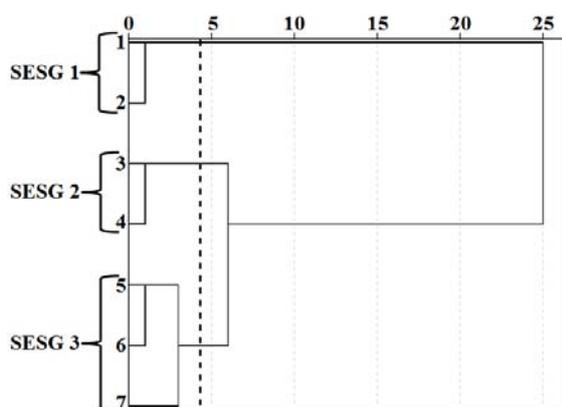


Figure 1a: Illustration of the SESG identification

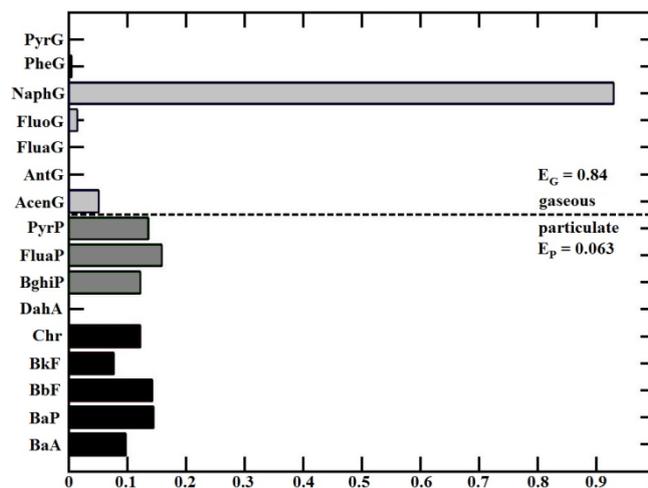


Figure 1b: PAHs' spectrum of SESG 1 of Figure 1a

Conclusion: Our results could be used to assess occupational exposure and health risk in each identified SESG. This new modeling approach is very interesting but has been possible only because of the recording of an important number of airborne levels in the Exporisq-HAP database.

Modelling of occupational exposure to hexavalent chromium

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Objective: To assess level and trend of exposure to hexavalent chromium (Cr(VI)) in chromium-exposed occupations for the estimation of lung cancer risks in community-based studies.

Methods: This analysis was based on 3,666 personal measurements and auxiliary data compiled in the German MEGA database from 1988-2009. Cr(VI) was determined spectrophotometrically at 540 nm after reaction with diphenylcarbazide. We assigned jobs tasks with known Cr(VI) exposure using coded and textual information about the workplaces. Measurements below the limit of quantification (LOQ) were multiply imputed according to their distribution above LOQ. Statistical modelling was performed to the log-transformed Cr(VI) concentrations to adjust for duration and reason of sampling.

Results: Cr(VI) exposure could be assessed for eight out of 30 jobs tasks with known Cr(VI) exposure. The majority of measurements (53%) were collected in welders (N=1,930), which we further detailed by welding technique. Spray painting and the welding of stainless steel with shielded metal welding were associated with adjusted geometric means above 5 µg/m³, the permissible exposure level of the U.S. Occupational Safety and Health Administration. We could not detect an overall time trend in the Cr(VI) concentrations.

Conclusions: Exposure to Cr(VI) varied by occupation and job task, particularly between welding techniques, but less across calendar time. Supplemental occupational questionnaires should be administered in community-based studies when estimating the lung cancer risk of Cr(VI).

Developing the optimal strategy for the assessment of exposure to isocyanates in the production of polyurethane foam by integration of modeling and experimental data.

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Knowledge of concentrations of harmful agents in the workplace atmosphere enables prediction of the health effects of exposure, and the suitable time to apply measures to control the associated risks. Determinations of concentrations of harmful agents in workplace atmosphere and comparing the results with the values of the current occupational exposure limits constitute the most reliable method to assess occupational exposure. If reliable and representative data obtained from determinations of the level of exposure for the operational conditions and risk management measures described in the initial exposure scenarios are available, such data may be used in determining the estimated exposure levels. In fact, however, the availability of the exposure intensity values for some tens of thousands of pre-registered chemicals is limited. It happens that simply no adequate analytical procedures are available, or the costs of the required tests are too high. Thus, it was necessary to develop modern, rapid, easily available, cheap, simple to use and reliable techniques to estimate the intensities of exposures without the need for measurement, based on the assumption that the concentration of substances in workplace atmosphere can be predicted by analogy with similar situations in which exposure levels were measured.

The aim of this study was to develop an optimal strategy for the assessment of inhalation exposure to isocyanates such as TDI (a mixture of toluene-2, 4 - or 2,6-diisocyanate) and MDI (methylene bisphenyl isocyanate) in the production of polyurethane foam by integration of theoretical and experimental data.

Measurements in the work environment included our own determinations of the concentration of the mixture of isomers of TDI and MDI in the ambient air of work environment in a plant manufacturing polyurethane foam. For the purpose of the evaluation, workplaces (job positions) were selected which were defined with reference to the production process as "Blowing unit operation team (operator, mechanic)." Air samples to determine concentrations of 2,4 - and 2,6 - TDI and MDI prevailing at the workplaces were collected during the production of polyurethane blocks. To perform quantitative determinations of concentrations of isocyanates, individual dosimetry was employed using measuring sets worn by employees during typical activities of work shift. A total of 52 analyzes of air samples were performed. Air samples were collected for the determination of isocyanates in the breathing zone of selected workers by means of individual aspirators. The tested air passed through a filter impregnated with a solution of 1 - (2-pyridyl) piperazine (1-2PPP). The principle of determination comprises passing a known volume of air through the test glass filter impregnated with a solution of 1-2PPP, extracting resultant derivatives with a mixture of acetonitrile (ACN) and dimethyl sulfoxide (DMSO) and the determination of selected isocyanates by high performance liquid chromatography (HPLC).

In the present work, ECETOC TRA and EASE predictive models that represent elements of control banding were used to determine the estimated levels of exposure to isocyanates.

The mean measured concentration of TDI was $18.74 \mu\text{g}/\text{m}^3$. For MDI, in all the analyzed samples, the concentration of the compound tested were below the lower limit of adopted range of the analytical method, i.e. $0.6 \mu\text{g}/\text{m}^3$. The values of concentration of TDI estimated using PROC12 ECETOC TRA – $170.9 \mu\text{g}/\text{m}^3$ exceed the measured values. The value estimated by using category PROC2 – $42.7 \mu\text{g}/\text{m}^3$ is within the measured TDI concentration range, i.e. $0.86 - 114.7 \mu\text{g}/\text{m}^3$. For MDI, both ECETOC TRA categories yielded much higher concentrations of methylene bisphenyl isocyanate than the actual concentrations, below $0.6 \mu\text{g}/\text{m}^3$, resulting from the measurements. The EASE-estimated range of concentrations of TDI: $0-181 \mu\text{g}/\text{m}^3$ obtained by application the EASE pattern of use including a closed system, includes the range of the actual measured concentrations of TDI. At the same time, the application of EASE pattern of use, "Inclusion onto matrix" for assessing exposure to TDI significantly overstates the expected range of concentrations. In the case of MDI, EASE model estimated the same exposure range $0-10 \mu\text{g}/\text{m}^3$, regardless which of the application patterns, which was significantly overestimated in relation to the measured range of $0-0.6 \mu\text{g}/\text{m}^3$. Use of ECETOC TRA model to estimate exposure to TDI during polyurethane foam bulking using both process categories, i.e. PROC12 and PROC2 has shown that this process is not properly controlled, and the applied risk control measures are insufficient, and further iterations are required for the proper selection of preventive measures to ensure safe working conditions in the assessed process. Multiple repetitions (iteration) of the process of evaluation should result in improvement of the estimated exposure levels so that their comparison with the pre-defined levels which do not produce adverse effects shows that the estimated risks are adequately controlled.

Using the Gaussian model to assess the hydrogen sulphide dispersion emitted from the mine of copper

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Copper deposit in south-western Poland, originate from sediments of the Permian period and are found in geological layers constituting an extension of the Kupferschiefer layer in Germany, where copper was mined since the twelfth century. This series of ore in the form of dark deposits rich in organic matter and containing metal sulfides, or as deposits with red spots devoid of organic matter which are carriers of iron oxide.

Long-term exploitation of copper ore in the mine Polish copper carried out in a layer ruled out the presence of hydrogen sulfide in mine. With the increase in the depth of the deposit, in the northern part of the copper-observed changes in the structure of rock massif. The presence of hydrogen sulphide was discovered during drilling into roof rocks in the mining area. The routes of hydrogen sulphide migration are sometimes through natural fractures in the rock mass and discontinuities caused by the development of roof fractures induced by mining operations. H₂S lifted into the mine ambient air during the mining operations is discharged with the air into the atmosphere. Emission of hydrogen sulphide can cause unpleasant sensations of smell is an important issue for people living close to the exhaust shafts.

The purpose of this study was to simulate the hydrogen sulphide dispersion in the atmosphere, emitted from the mine of copper, using the the knowledge-based artificial intelligence mathematical model. The work consisted of several stages and included: identification of chemicals in the air supplied to the exhaust shaft; quantitative determination of hydrogen sulfide at selected relevant places of the exhaust diffuser; calculation of the distribution of H₂S in the air with a software package; assessment of the risk of possible adverse health effects to people living in the vicinity of exhaust shafts.

Gaussian Dispersion Modeling, required the input of data that may include meteorological conditions, emissions or release parameters, terrain, was used to calculate of hydrogen sulfide dispersion in the atmosphere from the shaft. The area of 10 km x 10 km around the shaft was adopted for the calculation. For quantitative determination of hydrogen sulfide in the exhaust diffuser, a method was used in which hydrogen sulfide absorbed in the solution of zinc acetate reacted with N, N-dimethyl-p-phenyldiamine in the presence of iron(III) chloride to form methylene blue serving as the basis for spectrophotometric determination (LOQ of 0.05 µg/ml of the solution of absorbent and allowing collection of up to 600 liters of air was used).

Maximal calculated emission of hydrogen sulfide from the shaft, was 0,44 kg/h. Maximal assessed hydrogen sulfide concentration averaged over one hour was 1,91 µg/m³ with background and 1,41 µg/m³ without background. It makes 7,05% of reference value in Poland (20 µg/m³). The isoline 0.7 µg/m³ covers an area with a radius of less than 1 km from the emitter. No information could be located in the accessible literature and databases on adverse effects of hydrogen sulfide in humans chronically exposed, or on harmful effects of hydrogen sulfide in the general population at concentrations below 1 mg/m³ (Brenneman et al., 2000; 2002). It seems reasonable to assume that estimated concentrations of hydrogen sulfide in atmospheric air do not result in hazards to the health of the residents. Hydrogen sulfide may constitute a nuisance on the trial because of the odor. Due to its foul smell, hydrogen sulfide may be regarded as a slight annoyance to the inhabitants of the studied area. The concentrations of hydrogen sulfide sensed by 50% of respondents as the smell of rotten eggs, about 6.6 µg/m³ of hydrogen sulfide, and the threshold defined as the geometric mean of 26 source data, 11 µg/m³, are higher than the estimated concentrations (EPA, 2003).

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Occupational exposure predictive models: advantages and limits of main ECHA models.

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The evaluation of inhalation and dermal exposure to industrial chemicals at work is of major concern in the risk assessment of chemicals. The rules for assessing and managing risks of dangerous substances in the workplace have been laid down in the European legislation, such as the Chemical Agents Directive (Directive 98/24/EC), the REACH Regulation (EC 1907/2006) and the CLP Regulation (EC 1272/2008).

The process of the exposure estimation should be based mainly on the experimental measures. Actually, the availability of representative exposure experimental data is limited, so, in most cases, we have to use predictive models. To perform the occupational exposure assessment by predictive models, relevant exposure scenarios of the substance in targeted conditions of work and use should be developed.

The current work is focused on the occupational exposure estimation by using the main models proposed by the European Chemicals Agency (ECHA) in the Guidance on Information Requirements and Chemical Safety Assessment (ECHA, 2012), that include Tier 1 models, such as ECETOC TRA Worker Tool, MEASE and EMKG-Expo-Tool.

These models are easy to use, but inherently conservative, because the calculations are usually carried out in the worst case conditions. They are a preliminary screening tool for sorting out the low risk workplace situations from those which deserve more detailed risk assessment; in this case Tier 2 models, such as Stoffenmanager, Riskofderm and Advanced REACH Tool (ART), are used.

Advantages and limits of Tier 1 and Tier 2 models are discussed and analysed in this paper. An example of exposure scenarios building is described using the ECETOC TRA Worker Tool, that is applied to the estimation of the styrene concentration in the spraying of fiberglass reinforced polyester-styrene resins articles.

The ECETOC TRA Tool Version 3.0 is available in an integrated version (ECETOC, 2012), which allows the user to perform workers, consumers or environmental assessment via one interface and it can be downloaded free from the web: <http://www.ecetoc.org/tra>. It is a Tier 1 model that allows to estimate both the inhalation and the dermal exposure to chemicals.

The workers exposures can be predicted across the range of REACH Process Categories (PROCs), with an ability to differentiate between industrial and professional use. The initial exposure is a function of the fugacity of the substance and its circumstances of use (PROCs). Then, depending on the extent to which additional Operational Conditions (OCs) and/or Risk Management Measures (RMMs) apply, the initial prediction is modified using exposure modifiers: General Ventilation and combination with LEV (Local Exhaust Ventilation), Duration of Activity, Respiratory Protection, Personal Protection, Concentration in Mixtures.

The Tier 1 models are best used as initial screening tools to address to experimental measurements of chemical agents, they show user-friendliness because they require only a few input data, but they tend to overestimate the exposure. Limited OCs and RMMs can be taken into account by Tier 1 models and there is no possibility to distinguish between automated (remote-controlled) and manual processes.

It is necessary a deeper exposure evaluation by using Tier 2 models, such as Riskofderm and ART Tools or experimental data, if the calculation of RCR (Risk Characterization Ratio) is > 1 by the means of Tier 1 models.

The Riskofderm dermal model is the result of a European 5th framework programme project focused on dermal exposures in industrial and professional settings. On the basis of measured data, approaches were developed to assess dermal exposure for six different so-called Dermal Exposure Operation units (DEO units).

The model assesses potential dermal exposure, i.e. exposure on the skin and on the layers of clothing or gloves covering the skin. It does not take into account any protective effect of clothing or gloves. Potential exposures of the hands and of the body are estimated separately by the Riskofderm model.

The Tier 2 models require a higher number of input data, expert judgement is often required in the selection of input parameters and several OCs and RMMs can be included. These models are suitable for expert assessors and they allow to obtain exposure estimations less conservative and nearer to the experimental data.

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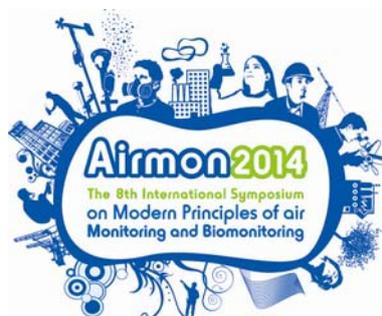
ECETOC (2012), *ECETOC TRA version 3: Background and Rationale for the Improvements, Technical Report No. 114*. Brussels, Belgium: European Centre for Ecotoxicology and Toxicology of Chemicals.

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***Session I - Quality of measurements,
uncertainties***

Volatile organic compound reference materials suitable for practical use: database analysis for the selection of hazardous substances

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Quality control is becoming increasingly important in the area of chemical analysis. Reference materials are absolutely essential for calibration and quality-control processes, and for verification of the accuracy and reliability of the results obtained.

Owing to the complexity of their manufacture and their limited shelf life, reference materials for volatile organic compounds such those occurring at workplaces are available only on a limited scale and for a small number of substances⁵. Increasingly, reference materials that are suitable for use flexibly and under practical conditions in particular are in demand from both laboratories and accrediting bodies. Reference materials tailored to specific user groups are intended to provide laboratories with a simple means of assuring quality.

The substances were selected based upon an analysis of the data in the MEGA exposure database⁶. The database contains around 900,000 data records on solvents; these were analysed with reference to the frequency of analysis in different periods. In order to assure suitability for application in the field, particular consideration was given to the period of the preceding five years. In addition, frequently occurring combinations of solvents were sought. Consideration was also given here to the working area and task.

The intention is both for the reference materials to cover the hazardous substances that occur frequently, and for them to be manufactured and used selectively with regard to specific working areas. In order to assure this flexibility, a new type of test apparatus is under development employing piezoelectric microdosing methods that are capable of dosing extremely small substance quantities reproducibly.

The solvents selected and the initial results will be presented.

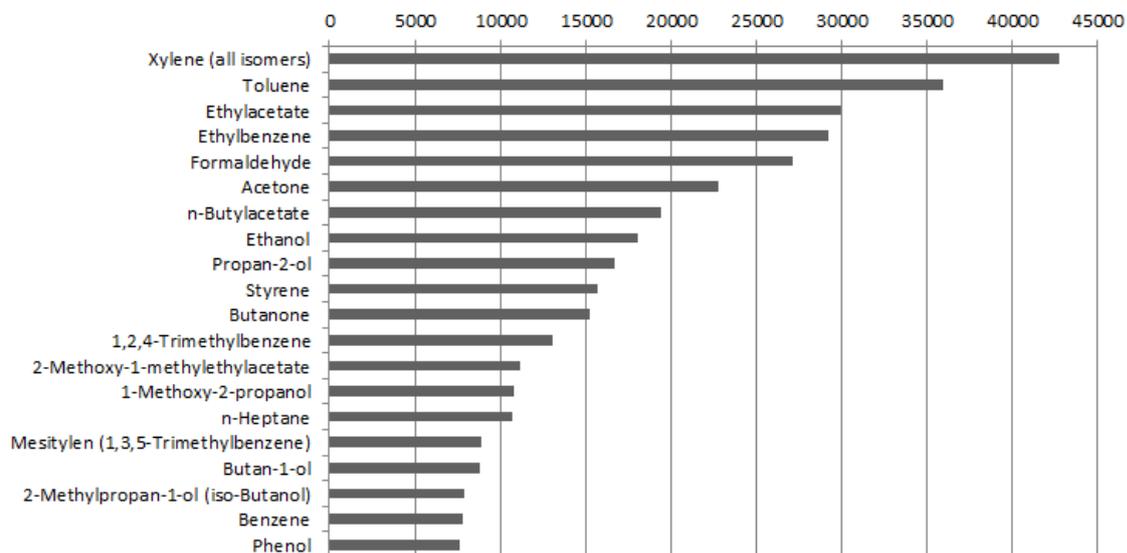


Figure 1. Presentation of the total number of analyses for the 20 solvents most frequently analysed during the period from 1979 to 2011.

⁵ Stoepler, M., Wolf, W., & Jenks, P.: *Reference Materials for Chemical Analysis*. Weinheim, Germany: Wiley VCH Inc. (2001).

⁶ Gabriel, S.; Koppisch, D.; Range, D.: *The MGU – a monitoring system for the collection and documentation of valid workplace exposure dat.*, *Gefährstoffe – Reinhalt. Luft* 70 (2010) Nr. 1/2, S. 43-49.

Laboratory competence for bioaerosol measurement : development of a protocol for data quality control

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Key words: bioaerosol, measurements, reliability, laboratory personnel, competence

Correctness and reliability of tests performed and representativeness of environmental measures are crucial to assess workers' exposure for risk assessment. According to the International Standard ISO 17025:2005 (§1, 5) “...the competence of laboratories to carry out tests should be founded on basic requirements. Among these factors, contribution from human factors are included .. laboratory personnel should be qualified on the basis of appropriate education, training, experience and/or demonstrated skills”.

Indoor air may be responsible for exposure to microbial pollutants and evidence has been found that link a poor quality of air to adverse health effects, as toxic and allergic ones and infections. Bioaerosol sampling and analysis allow to check the comfort and healthiness of workplaces. Actually, no reference protocols and no threshold limit values are available for investigating biological pollutants in air; the only international standards dealing with bioaerosol measurement in work environments are UNI EN 14583:2005 and UNI EN 13098:2002. Categories of microbial concentration, in term of CFU/m³ of air, are suggested by the European Union for residential and non-industrial environment (European Collaborative Action, 1993)⁷ to evaluate results of air sampling.

Bioaerosol is commonly collected by sampling air volumes using impactors and the total concentrations of bacteria and fungi are assessed by cultural assays. The not homogeneous distribution in air and the content's variability of bioaerosol in environments heavily affect the repeatability of its measure; furthermore, the counting of bioaerosol microbial colonies on agar plate's surface, at the end of the incubation time, may be difficult, for example in case of spreading or high number of colonies. These factors are critical for the purpose of measurement and should be controlled. Tools suggested by the Standard 17025 (§ 5.9.1) for the monitoring of the quality of data don't comply with air microbiological contamination measurement.

In order to control the above mentioned source of data variability and to guarantee homogeneous evaluation of biocontamination levels in work environments, the Italian Workers' Compensation Authority (INAIL) standardized a training program for the competence assurance of its laboratory personnel and the assessment of the forward maintenance of it, to perform bioaerosol measurement according to homogeneous internal criteria of colonies' counting and result reporting. This program include a periodic session of colonies' counting on test-agar plates, collected in the same workplace sampling different air volumes, carried out by the laboratory personnel. A worksheet was developed to point out the variability sources of counting to control for data alignment. This worksheet is based on the methodological plant reported by Seppo I. Niemela (2003)⁸, adapted to the characteristic of bioaerosol.

Aims of this work is to present the scheme for laboratory competence assurance and data quality control performed by INAIL.

⁷ European Collaborative Action (1993). *Indoor air quality & its impact on man. Report No. 12: Biological Particles in Indoor Environments*. Luxembourg.

⁸ Seppo I. Niemela (2003). *Uncertainty of quantitative determinations derived by cultivation of microorganisms*. MIKES - Centre for Metrology and Accreditation, Publication J4/2003. Helsinki.

Calibration function and detection capability for crystalline silica on membrane filter by X-ray diffraction analysis

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Most of the aerosol sampling campaigns conducted in workplaces lead to very low masses of Respirable Crystalline Silica (RCS) collected on the membrane filters. For instance, in Italy, 50% of the samples collected in cement plants and ceramics factories by using low-flow rate samplers, contains no more than 20 micrograms of quartz. Since occupational exposure limits for RCS set in many European countries range from 0.025 to 0.05 mg m⁻³, even low levels such as those above mentioned can exceed the threshold limit. A careful determination of capabilities of detection and quantification is therefore required.

Two types of detection capability are generally used in chemical measurements: the traditional limit of detection, LOD (IUPAC, 1976), and the "new" minimum detectable value, MDV (ISO 11843:2009).

For an X-ray diffraction (XRD) analysis on samples collected on membrane filters, LOD has generally been referred to as the quantity corresponding to three times the standard deviation of the background intensity (net height measured on blank filters). Although LOD in analytical chemistry is an old issue and a large number of papers deal with this subject, the methodology for its calculation when an XRD analysis is performed on a filter presents some complications and has never been described in detail. The MDV is calculated from the scatter of calibration data points about a calibration line. No literature about this calculation methodology seems to be available for XRD on membrane filters, yet.

Eleven independent sets of quartz and cristobalite calibration standards, including over 200 samples, were prepared at INAIL laboratory to study calibration functions and capabilities of detection. Different respirable samplers (Casella Higgins Dewell, GS-3, SKC plastic cyclones), membrane filter materials (silver, PVC, MCE), and preparation techniques (wet deposition, sampling in air dust chamber) were used for the preparation of calibration standards. Samples were analysed by using three powder diffraction instruments and different scan programs.

The calibration function was assumed to be linear. The most popular methods for RCS determination assume that the extrapolated straight line calibration does not pass through the origin. However, no satisfactory explanation is given to support this choice, and according with INAIL results this assumption does not seem to be justified. Results of experiments also show that the residual standard deviation increases with the mass of the analyte. LOD values for quartz determination were included in the range 1-4 µg, when the primary peak was analysed, and 3-16 µg for the secondary peak. MDV values were calculated between 8 and 57 µg and between 4 and 74 µg for primary and secondary peaks of quartz, respectively. Some inconsistencies emerged and are discussed in the paper. Finally, an approach for calibration line construction is proposed.

IUPAC, Analytical Chemistry Division (1976). *Pure & Appl. Chem.*, 45, 99-103.

Benford's law and the quality of occupational exposure data

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Benford's law is the name for the observation that in many empirical datasets the digits 1-9 are not equally frequent but show a special distribution. Therefore Benford's law is used to discover manipulated or created numbers which usually do not follow that distribution (Brown 2005). This study will examine if this approach is appropriate for occupational exposure datasets which very often contain a relevant amount of values below the level of determination (LOD).

A theoretical derivation is given how compliance with Benford's law depends on the percentage of measurements below the LOD and on the treatment of these measurement values. Additionally exposure data from the German exposure database MEGA are used to demonstrate the derived deviations from Benford's law with empirical data. Standardized deviations from Benford's law are calculated and the significance of the deviation is tested with Chi².

Hazardous substances with a frequency of measurement values below LOD from 3% to 34% were examined. For these substances the standardized deviation from Benford's law lay between 2.03 and 5.13. For substances with less than 10% of values below LOD the standardized deviation was only slightly significant ($p = 0.047$), while for higher percentages it was highly significant ($p < 0.001$).

For datasets with a high percentage of values below LOD and a substitution of these measurements by one value (e.g. $LOD/\sqrt{2}$) deviations from Benford's law are to be expected and are no indication for data manipulation. Because for datasets containing a high percentage of values below the LOD compliance with Benford's law is strongly influenced by the method how these values are substituted in contrast to de Vocht & Kromhout (2013) we conclude that Benford's law is only suitable for testing the quality of occupational exposure data if the percentage of values below the LOD is low enough. How low is low enough would have to be decided through a simulation study.

Brown, R.J. (2005). *Analyst*, 130, 1280-1285.

De Vocht F. & Kromhout, H. (2013). *Ann. Occup. Hyg.*, 57, 296-304.

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The products of forest fires and formation of ozone hole in the atmosphere

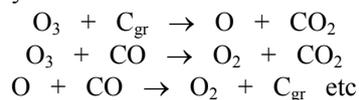
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A thermodynamic analysis of the different reactions of ozone destruction in the atmosphere including reactions with participation the burning products on fires was performed. It has been found that the Chapman's mechanism ozone depletion in the atmosphere needs to be adjusted.

It revealed a low probability for the O₃ nitrogen and hydrogen depletion cycles. The possibility of a radical-chain mechanism for O₃ molecule destruction by combustion products with simultaneous formation of atomic O and sooty particulates was established. An assumption was made that a big fire in February 1983, which covered vast areas of the southern states of Australia, was a possible reason for the ozone hole formation in the Southern Hemisphere.

It is shown that the products of combustion fires, torches burning of passing and oil gases, emissions of ash and volcanic gases, etc. may contribute to the formation of ozone holes. A new variant was suggested for the mechanism of the process – the carbon cycle of ozone destruction:



It was suggested that fires in the eastern Russia and Europe resulted in ozone hole formation in the Northern Hemisphere.

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