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Measuring Air Pollutants by Diffusive Sampling and Other Low Cost Monitoring Techniques

Conference with Exhibition

Tuesday 15th, Wednesday 16th
and Thursday 17th September 2009
At The Krakow City House
KRAKOW, POLAND

Day 1 - Tuesday, 15th September 2009

09:00 Registration and Coffee

09:30 Welcome and Opening Remarks

Session 1: Introduction and Overview

Chairman: Peter Woods, National Physical Laboratory, UK

10:00 (PL1) ***History of Diffusive Sampling***
Jan Kristensson
Chemik Lab AG, Norrtälje, Sweden

10:30 (PL2) ***Regulatory Background to Diffusive Monitoring***
Andrej Kobe, Annette Borowiak
European Commission, DG Environment, Brussels, Belgium
European Commission, Joint Research Centre (JRC), Ispra, Italy

11:00 (PL3) ***Validation and QA/QC of Monitoring Methods***
Theo Hafkenscheid
National Institute for Public Health and the Environment (RIVM), Netherlands

11:30 (PL4) ***Regulatory Aspects in Workplace and Indoor Air***
Eddy Goelen
Flemish Institute for Technological Research (VITO), Belgium

12:00 Lunch

13:00 - 14:00 Poster Session A, with Presenters in Attendance

Session 2: Diffusive Sampling

Chairman: Jan Kristensson, Chemik Lab AG, Norrtälje, Sweden

14:00 (PL5) ***Principles of Diffusive Monitoring***
Martin Ferm
IVL, Gothenburg, Sweden

14:30 (O1) ***Evaluation of Radiello Diffusive Sampler Indicated for Thermal Desorption for Measuring VOC's in Ambient Air***
Eva Gallego
Laboratori del Centre de Medi Ambient,
Universitat Politècnica de Catalunya, Barcelona, Spain

15:00 (O2) ***Development of a Method for Measuring Soil Vapour Intrusion to Indoor Air by Diffusive Sampling***
Paolo Sacco
Fondazione Salvatore Maugeri, Padova, Italy

15:30 Tea / Coffee

16:00 (O3) ***Determination of Uptake Rates of VOC Passive Sampler for the Canadian National Residential Indoor Air Survey***
Jiping Zhu
Exposure & Biomonitoring Division,
Health Canada, Ottawa, Canada

16:30 (O4) ***Outcome of the UK Working Group on Harmonisation of NO_2 Diffusion Tube Methodology***
Jaume Targa
AEA Technology, Harwell, UK

17:00 (O5) ***Assessment of NH_3 in a French Industrial Area with Passive Samplers and an Automated Chemiluminescence Analyser***
Anne Fromage-Mariette
AIR Languedoc-Roussillon, Montpellier, France

17:30 Cheese & Wine Reception

Day 2 - Wednesday, 16th September 2009

Session 3:
Recent Developments in Instruments and Techniques

Chairman: Ulrich Pfeffer, LANUV NRW, Essen, Germany

09:00 (PL6) ***Recent Developments in Instrumentation and Techniques***
Robert Gehrig
EMPA, Swiss Federal Laboratories for Materials Testing and Research, Dubendorf, Switzerland

09:30 (O6) ***Practical Applications of Diffusive Monitoring with Other Complimentary Techniques in the Workplace Environment***
Geoffrey Wilcox
Hull Research & Technology Centre, BP Chemicals Ltd, Hull, UK

10:00 (O7) ***Passive Formaldehyde Measurements in Simulated and Real Atmosphere for Indoor Air Monitoring***
Laura Chiappini
INERIS (Institut National de L'Environnement Industriel et des Risques), Verneuil-en-Halatte, France

10:30 Tea / Coffee

11:00 (O8) ***The Development of Low Flow Pump Tubes and their Potential as a Tool for Simplifying the Validation of Axial Diffusive Tubes***
Nicola Watson
Markes International, Llantrisant, UK

11:30 (O9) ***Effect of Exposure Time and Analyte Concentrations on the Uptake Rate of a Polydimethylsiloxane Based Permeation Passive Air Sampler***
Suresh Seethapathy
University of Waterloo, Ontario, Canada

12:00 Lunch

13:00 - 14:00 Poster Session B, with Presenters in Attendance

Session 4:
Validation, Applications and Methodology

Chairman: Annette Borowiak, European Commission,
Joint Research Centre (JRC), Ispra, Italy

14:00 (PL7) ***Validation, Why?***
Pascual Ballesta
European Commission, Joint Research Centre (JRC), Ispra, Italy

14:30 (O10) ***Determination of Diffusive Uptake Rates for a Range of VOC's Using Tube Type Samplers***
Veronica Brown
BRE, Watford, UK

15:00 (O11) ***VOC in an Urban and Industrial Harbour on the French North Sea Coast During Two Contrasted Meteorological Situations***
Joelle Roukos
Ecole des Mines de Douai, Douai, France

15:30 Tea / Coffee

16:00 (O12) ***Validation of Diffusive and Robustness of Uptake Rates of Diffusive Samplers for NO_2 and Benzene***
Nicholas Martin
National Physical Laboratory (NPL), Teddington, UK

16:30 (O13) ***Long-Term Validation and Robustness of Uptake Rates of Diffusive Samplers for NO2 and Benzene***
Ulrich Pfeffer
LANUV NRW, Essen, Germany

17:00 (O14) ***Measuring Ammonia with Diffusive Samplers - Influence of Nearby Sources and Sinks and Evaluation of Representative Measuring Sites***
Lotti Thöni
Fub - Research Group for Environmental Monitoring,
Rapperswil, Switzerland

17:30 Close of Session

Day 3 -Thursday, 17th September 2009

Session 5: Sensors and New Technology

Chairman: Eddy Goelen, Flemish Institute for Technological Research (Vito), Belgium

09:00 (PL8) ***Sensors and New Techniques***
Christopher Walton
Cranfield Health, Cranfield University, Bedford, UK

09:30 (O15) ***Evaluation of Micro-Sensors to Monitor Ozone in Ambient Air***
Michel Gerboles
Joint Research Centre, Ispra, Italy

10:00 (O16) ***Evaluation of a Miniaturized Diffusive Sampler for True Breathing-Zone Sampling and Thermal Desorption GC Analysis***
Jan-Olof Levin
Umeå University, Umeå, Sweden

10:30 (O17) ***Evaluation of Active and Passive Dust Deposition Techniques***
Natacha Claeys
Flemish Government, Brussels, Belgium

11:00 Tea / Coffee

11:30 (O18) ***Passive Sampling Technique Sigma-2, Operational Application and Validation of Automated Optical Single-Particle Analysis in the Size Range for 2.5 - 80 µm***
Volker Dietze
Deutscher Wetterdienst, Freiburg, Germany

12:00 (O19) ***The EWO Dosimeter, an Early Warning Device for the Protection of Cultural Heritage Objects in Museums, Historic Buildings and Archives***
Susana López-Aparicio
Norwegian Institute for Air Research, Kjeller, Norway

12:30 (O20) ***New Sampling Method Coupling SPME and FLEC® Emission Cell for Identification of VOC's Emitted from Building Materials***
Valérie Desauziers
Ecole des Mines d'Alès, Pau, France

13:00 Lunch

14:30 Close of Conference

Oral Abstracts

THE HISTORY OF DIFFUSIVE SAMPLING.

Jan Kristensson
Chemik Lab AB

ABSTRACT

Diffusive sampling is based on Fick's first law of diffusion.
This law was introduced in 1855 by the German physiologist Adolf Eugen Fick.
Fick's law describes the mass transfer (diffusive flux) from a higher concentration to a lower concentration. Fick's first law of diffusion has been used to model mass transport in gases, liquids and solids. Fick was inspired by the related discoveries of Ohm's law (charge transport) and Fourier's law (heat transport).
In 1927 Gordon and Lowe got a US patent on a device to make semi quantitative measurement of carbon monoxide, based on diffusion.
During the period up to 1973 diffusive samplers using colorimetric detection was used for different compounds.
In 1973 Palmes published a mathematical treatment of Fick's law of diffusion and which factors controlled the uptake rate for diffusive samplers. Palmes work led to the development of the Palmes tube for measurements of NO_2.
1977 Gas Badge was introduced. Gas Badge was the first diffusive sampler which used charcoal as adsorbent. It was a badge type sampler with large area for diffusive uptake and a short diffusion path length. Several investigations were published where the influence of physical parameters on the uptake rate were tested, e.g. face velocity, temperature, pressure etc. Most of these tests were performed at occupational concentration levels (ppm) and pumped sampling on charcoal tubes was used as reference method.
1982 and 1983 performance criteria protocols for diffusive samplers were published.
After this several diffusive samplers have been developed and today we have badge, cylindrical and tube types of samplers. We also have samplers for reactive compounds like aldehydes and amines based on chemisorptions.
Several new adsorbents have been developed which made thermal desorption possible. This, together with optimized instrumentation, increased the analytical sensitivity.
Today diffusive sampling is also used for sampling at environmental levels (ppb).

PL2

THE NEW AIR QUALITY DIRECTIVE - MAIN ELEMENTS, IMPLEMENTATION AND THE ROLE OF SUPPLEMENTARY ASSESSMENT

Andrej Kobe[1], Annette Borowiak[2]
[1]Directorate-General Environment,European Commission, Brussels,
[2]Directorate-General Joint Research Centre,
European Commission, Ispra

ABSTRACT

The Directive 2008/50/EC on ambient air and cleaner air for Europe that entered into force in June 2008 merges and streamlines the existing air quality directives and introduces objectives and standards for fine particles $PM_{2.5}$, including a novel exposure concentration obligation and the exposure reduction target. Other changes include the possibility, under conditions, for additional time achieve compliance with the PM_{10}, NO_2 and benzene limit values, modifications of QA/QC requirements, and the overhaul of reporting provisions.

With the review scheduled in 2013 the focus is now on implementation. Principal current implementation issues, associated also with the Commission assessment of the time extension notifications and enforcement of the limit values will be presented.

While the reference methods for continuous monitoring have by now been supported by EN standards for all regulated pollutants, are well covered by periodic reporting and exchange, and regularly discussed in for a such as AQUILA and EIONET, the implementation support for the supplementary assessment, such as modelling and indicative measurement, has been partly lagging behind. The role of this supplementary assessment in the implementation of the new Directive, its coverage by the new reporting regime, and further supporting activities such as JRC work on diffusive sampling and FAIRMODE will be outlined.

PL3

VALIDATION AND QA/QC OF MONITORING METHODS

Th.L. Hafkenscheid
RIVM Centre for Environmental Monitoring
NL – BILTHOVEN

ABSTRACT

In order to establish the fitness for purpose of an air monitoring method, a series of experiments is performed aimed at the assessment of the uncertainty of the monitoring results. The experiments usually consist of series of laboratory tests followed by tests under actual practical conditions. The resulting uncertainty is subsequently compared with uncertainty requirements (*method validation*).
In order to confirm that the measurement uncertainty claim remains valid over time, the practical application of the method is subjected to a regime of *quality assurance/quality control (QA/QC).*

For methods based on diffusive sampling a number of (standardized) protocols exist for the performance of method validation with subtle differences in approaches, particularly in the experimental design. The approach to QA/QC of such methods is less well harmonized/standardized although some standards and guidance documents exist and generic principles may be drawn from standards such as EN-ISO 17025.

In this presentation an overview is given the essential approach of diffusive sampling method validation and the different protocols currently existing. Further, essential elements of QA/QC approaches will be presented and discussed. The presentation is aimed to serve as a basis for further implementation of harmonized principles of method validation and QA/QC in practice, e.g., in European Standards.

PL4

REGULATORY ASPECTS, IN WORKPLACE AND INDOOR AIR

E. Goelen
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Boeretang 200-2400 Mol, Belgium

ABSTRACT

Technological evolution and developments in monitoring and particularly in diffusive monitoring can arise from different driving forces. Sometimes it is in response to particular problems or needs but often a regulatory requirement is the basic driver. Workplace air is from the viewpoint of legislation and standardisation, different from indoor air. Four groups of indoor environments are defined in ISO 16000-1 (2004), but the workplace is the defined area or areas in which the work activities are carried out (EN 689 : 1995) and this may be an indoor or outdoor environment.

In national and European legislation, there is a long standing tradition to protect the health and safety of workers from the varied risks related to exposure to chemical agents. There are a set of Council Directives which have been most influential in helping to ensure the safe use of chemicals within the member countries. An overview of those will be given with special attention to Directive 98/24/EC on the protection of workers from the risks related to chemical agents at work and subsequent Directives establishing occupational exposure limit values. In the context of these Directives, diffusive sampling has an important role in measuring the exposure to a wide range of gases and vapours. Examples of methods provided by various organisations and standardised methods published at the European level by Technical Committee CEN TC 137, will be shown.

Non occupational indoor environments are in contrast to workplaces subject of scattered legislative initiatives. Many countries have published, besides preventive actions (e.g. ventilation), a limited set of guideline and/or intervention values which are to be enforced. Diffusive sampling strategy and methodology in the area of indoor air builts further on experiences with methods developped for workplace and outdoor air. Examples of standardised methods applicable for measuring compliance to regulation, developped under CEN TC 264 and ISO TC 146 SC6 will be illustrated with special attention to their practical implementation and results.

PL5

THE PRINCIPLES OF DIFFUSIVE MONITORING

Martin Ferm
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ABSTRACT

When short-term average concentrations are not needed and when simplicity and reliability are necessary, diffusive monitoring is the method of choice. Diffusive sampling offers many advantages such as the samplers can be placed almost anywhere and a geographical concentration distribution can be obtained for a reasonable cost. Measurements are made without inlet tubing which facilitates measurement of reactive gases such as ozone and nitric acid. Even though the basic principle behind diffusive sampling can be explained in a very simple manner, a detailed description of the principles is rather complicated. The sampling rate for fluctuating concentrations, variable wind movements, and the sampling rate for slow and rapid sorption reactions will be discussed.

EVALUATION OF RADIELLO DIFFUSIVE SAMPLER INDICATED FOR THERMAL DESORPTION FOR MEASURING VOCS IN AMBIENT AIR

***E. Gallego*[1]**, F.J. Roca[1], F.J. Perales[1], S. Torrado[2], X. Guardino[2]
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ABSTRACT

Radiello diffusive samplers indicated for thermal desorption (filled with Carbograph 4) were evaluated for the monitoring of volatile organic compounds (VOCs) in ambient air comparing their performance with an active multi-sorbent tube developed and validated in our laboratory (Carbotrap, Carbopack X and Carboxen 569). The analysis was performed by automatic thermal desorption coupled with capillary gas chromatography/mass spectrometry detector. This methodology had been used in previous studies to identify and determine a wide range of VOCs that cause odour nuisance and affect outdoor air quality. A good correlation between Radiello diffusive samplers and active multi-sorbent bed tubes was observed for several VOCs, suggesting that the Radiello diffusive sampler provides satisfactory quantitative measurements and is suitable for the determination of VOCs in ambient air. On the other hand, the effect of sampling exposure time to Radiello samplers was evaluated. The results showed that, for several compounds, the sum of the amount of VOCs collected at two shorter sampling occasions was higher than the amount collected at a single longer sampling period for higher ambient air concentrations; however, the differences observed were not significant. Hence, expected air concentrations have to be taken into account when determining exposure times in Radiello passive samplings.

O2

DEVELOPMENT OF A METHOD FOR MEASURING SOIL VAPOUR INTRUSION TO INDOOR AIR BY DIFFUSIVE SAMPLING

***Paolo Sacco*[1]**, Todd McAlary[2], Hester Groenevelt[2], Derrick Crump[3], Tadeusz Gorecki[4], Suresh Seethapathy[4], Michael Tuday[5], Brian Schumacher[6], Paul Johnson[7]
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[2]Geosyntec Consultants, Inc., Guelph, Canada
[3]Cranfield University, Cranfield, United Kingdom
[4]University of Waterloo, Waterloo, Canada
[5]Columbia Analytical Services, Simi Valley, CA, U.S.A.
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[7]Arizona State University, Tempe, AZ, U.S.A.

ABSTRACT

Subsurface vapour intrusion to indoor air is gaining increased regulatory attention in assessing human health risks associated with contaminated soil and groundwater. The most common methods used for monitoring VOCs in vapour intrusion studies involve either drawing air into a canister with further analysis by EPA method TO-15, or pumping air through adsorbent tubes, with subsequent automated thermal desorption (ATD) analysis.

The three-year study presented here, funded by U.S. Department of Defense under the Environmental Security Technology Certification Program, aims at developing a more cost-effective method for vapour intrusion studies, based on diffusive sampling. Four types will be tested: the Radiello sampler, the polydimethyl siloxane membrane sampler (PDMS), the diffusive ATD tube sampler, the SKC Ultra II badge sampler.

The samplers' ability of measuring indoor air, outdoor air, sub-slab and soil gas will be tested first in an exposure chamber, by assessing the effects of concentration, temperature, face velocity, air humidity, sampling duration, then in three sites with different geologic materials and contamination levels. The preliminary results of laboratory testing are presented here.

DETERMINATION OF UPTAKE RATES OF VOC PASSIVE SAMPLER FOR THE CANADIAN NATIONAL RESIDENTIAL INDOOR AIR SURVEY

Jiping Zhu*, Cecilia C. Chan, Qi-ming Xian,
Yong-lai Feng and Soheil Rastan

ABSTRACT

The levels of many of substances, which are being assessed under Government of Canada's Chemicals Management Plan and the Canadian Environmental Protection Act, in indoor air have not been confirmed in Canada and therefore a national survey of their indoor air levels in randomly selected Canadian homes has been recently launched. Because of the large number of participating homes (about 4000) and locations of these homes (across the whole country), passive sampling method followed by thermal desorption GC/MS has been selected for collecting and analyzing target chemicals in indoor air. Since the uptake rates of the VOC passive samplers selected for the study are unknown for the majority of target chemicals in non-occupational environment such as indoor air, a side-by-side, active vs. passive sampling experiment was conducted in five residential homes to determine the uptake rates, under which both types of samplers were deployed for the same length of time. The sampling tubes were subsequently analyzed by thermal desorption GC/MS. The experimentally determined uptake rates were found to be comparable to those theoretical values that are derived from air diffusion coefficients with a few exceptions.

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OUTCOME OF THE UK WORKING GROUP ON HARMONISATION OF NO_2 DIFFUSION TUBES

Jaume Targa, Loader A
AEA Harwell, UK

ABSTRACT

Palmes-type diffusion tubes are widely used by UK Local Government, for indicative measurement of ambient nitrogen dioxide (NO_2) concentrations. Considerable inter-laboratory variation had been observed in diffusion tube precision and accuracy. In recognition of this, a laboratory harmonisation exercise was proposed with the aim of improving consistency of tube performance between laboratories.

The UK Government's Department of Environment, Food and Rural Affairs (Defra) commissioned a Working Group on harmonisation of NO_2 diffusion tube preparation and analysis methods. The Working Group included representation from laboratories, Local Government, experts on diffusive sampling and other stakeholders.

The group's aim was to investigate current practice and to recommend appropriate changes to tube preparation and analysis. Diffusion tube preparation, handling, storage, use in the field, extraction, analysis and calculation of results were investigated.

The outcome was a Practical Guidance document, setting out a harmonised UK diffusion tube methodology based on current knowledge of best practice.

By January 2009 almost all UK laboratories had fully implemented the harmonised method. Results from the independent Workplace Analysis Scheme for Proficiency (WASP, operated by the Health and Safety Laboratory) and an ongoing multi-laboratory field intercomparison are being used to monitor the effectiveness of UK harmonisation.

O5

ASSESSMENT OF NH_3 IN A FRENCH INDUSTRIAL AREA WITH PASSIVE SAMPLERS AND AN AUTOMATED CHEMILUMINESCENCE ANALYSER

Anne FROMAGE-MARIETTE
AIR Languedoc-Roussillon
France

ABSTRACT

During four one-month periods equally spread out over one year, AIR Languedoc-Roussillon assessed the average concentrations of NH_3 – and other pollutants – in ambient air around an industrial area in the surroundings of Narbonne. The main industry converts uranium ore for nuclear industry, using NH_3 in its process.

Eight sites around the industrial area were equipped with *radiello* □ ammonia radial passive samplers exposed during sixteen one-week periods (cartridge made of microporous polyethylene and impregnated with phosphoric acid, adsorbing ammonia as ammonium ion). At one of these sites, in the proximity of sedimentation basins, a chemiluminescence analyser (Environnement SA trademark) was installed.

The duplicated passive samplers and the continuous monitor showed good agreement (R^2 = 0,9009 on weekly averages ; annual mean : 35 $\mu g/m^3$ with the monitor, 41 $\mu g/m^3$ with the *radiello* □), although ammonia concentrations presented very abrupt variations (from zero to several hundreds $\mu g/m^3$ in less than one hour).

There was no risk of exceeding the US EPA reference value (100 $\mu g/m^3$ as annual mean) at any of the sites sampled. The ammonia concentration decreased with the distance from the main industry, and the highest values were found when the sites were down the wind of this industry.

PL6

OVERVIEW OF MONITORING AND RECENT DEVELOPMENTS IN INSTRUMENTS AND TECHNIQUES

Robert Gehrig
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ABSTRACT

Automated monitoring allows for highly time resolved and cost-efficient measurements of many air pollutants and is a core activity of national and local air pollution networks. Requirements for reliable methods include criteria like stability, specificity, low maintenance and unattended operation. For many of the important parameters (ozone, nitrogen oxides, sulphur dioxide, carbon monoxide) monitoring techniques fulfilling these requirements are available and used throughout the world in a harmonised way thus providing internationally comparable data.

Important problems still exist for fine particles (PM10, PM2.5). Several measurement principles for automated monitoring are possible and available (e.g. oscillating microbalance, beta-absorption, optical methods). However, due to the complex properties of ambient aerosol concerning morphology, chemical stability and volatility data are strongly influenced by the chosen method and satisfactory comparability to the manual gravimetric reference procedure is not easily obtained.

Though not yet regulated with binding limit values in ambient air there is a rapidly increasing need for fast and efficient measurement techniques for parameters like nitrous oxide, nitrogen dioxide (specific), ammonia, methane and others in order to tackle the issues of eutrophication, acidification and climate change. New promising developments currently occur in the field of photo-acoustic sensors, cavity ring-down spectrometry and quantum cascade laser spectrometry.

PRACTICAL APPLICATIONS OF DIFFUSIVE MONITORING WITH OTHER COMPLIMENTARY TECHNIQUES IN THE WORKPLACE ENVIRONMENT

Dr Geoffrey Wilcox
BP Chemicals Ltd, UK

ABSTRACT

This presentation will begin with a brief discussion of the background and early history of diffusive monitoring and other techniques used in a large multinational energy company. This will be in the context of where these methods have been primarily applied to assess the potential for chemical exposure in the workplace environment.

Specific examples of both diffusive sampling techniques together with other complimentary methods in the workplace will be included. A practical perspective on their advantages and limitations will be given. This will include discussion of the added value to be gained when diffusive techniques are used alongside direct reading instrumentation.

Finally, the presentation will conclude with an overview on further developments, requirements and challenges in the effective use of these valuable measurement methods as well as consideration of the implications to the occupational hygienist, worker and others.

O7

PASSIVE FORMALDEHYDE MEASUREMENTS IN SIMULATED AND REAL ATMOSPHERE FOR INDOOR AIR MONITORING

L. Chiappini, S. Fable
(1) INERIS (Institut National de l'Environnement Industriel et des Risques) Parc technologique Alata BP2 F-60550 Verneuil-en-Halatte – LCSQA (Laboratoire Central de Surveillance de la Qualité de l'AIR)

ABSTRACT

People spend most of their time in indoor environments where they can be exposed to formaldehyde, an ubiquitous and abundant pollutant. In French public places, its averaged concentrations can reach 60 µg m^{-3}. Since it is of particular health concern (carcinogenic for human), it is important to have suitable methods to measure formaldehyde in indoor air. Silent and not cumbersome, passive sampling is a convenient technique for such environments. However, their uptake rate can depend on many parameters (sampling period, pollutant concentration, wind speed...)

The performance of radial passive samplers (Radiello 165, from FSM), compared to active samplers, both based on 2,4-dinitrophenylhydrazine (DNPH) reaction, was evaluated in a Pyrex exposure chamber and in four different indoor environments to assess the potential influence of these parameters and evaluate the ability of passive samplers to monitor formaldehyde in indoor environments.

Blank levels were found to be too high if sampling low concentrations for short sampling times. However, active and passive sampling methods were in good agreement provided the ratio measure/blank was above 10. Besides, passive results seemed more satisfying in unventilated places suggesting that wind speed could influence formaldehyde uptake rate. Further studies should be carried out to confirm this hypothesis.

THE DEVELOPMENT OF LOW-FLOW PUMP TUBES AND THEIR POTENTIAL AS A TOOL FOR SIMPLIFYING THE VALIDATION OF AXIAL DIFFUSIVE TUBES

Nicola Watson, David Wevill, Lara Kelly
Markes International Ltd (UK)

ABSTRACT

Traditional methods for calculating unknown diffusive uptake rates typically involve carrying out both pumped and passive sampling in parallel. Pumped sampling is normally carried out at flow rates of more than 50ml/min in the field, so in order to simulate diffusive sampling for this validation work, much lower flow rates are required. However, if low flow pumped sampling is implemented, there is the possibility of error introduction due to simultaneous diffusive ingress onto the tube.

To overcome this issue, a number of diffusion limiting approaches have been used including sampling inlet devices or sampling caps. This paper will present specially designed sorbent tubes incorporating "diffusion-locking" inserts which facilitate pumped sampling at low flow rates such as 2 ml/min, whilst eliminating the errors associated with diffusive ingress. This approach enables longer sampling times, making the parallel sampling approach much more comparable thus leading to more confident estimations of uptake rate data.

Furthermore, this type of tube can facilitate pumped sampling over extended periods at low (<1 ml/min) flow rates - allowing the collection of time weighted average concentration data over periods of weeks or months without exceeding safe sampling volumes.

O9

EFFECT OF EXPOSURE TIME AND ANALYTE CONCENTRATIONS ON THE UPTAKE RATE OF A POLYDIMETHYLSILOXANE-BASED PERMEATION PASSIVE AIR SAMPLER

Suresh Seethapathy and Tadeusz Górecki
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ABSTRACT

Passive air samplers are often used for time-weighted average concentration determination of analytes. In such cases, the linear kinetic model where the mass uptake rate is constant throughout the exposure time period is the preferred mode of operation. For the applicability of such models, the sorbent in the passive sampler is required to act as a zero sink throughout the exposure period and at all concentrations of all the analytes. With samplers based on diffusion of analytes through well defined empty air channels in the sampler, It is often critical to maintain such sorbent conditions as analytes with high vapour pressure (which are more likely to be present in higher concentrations and which have higher diffusion coefficients in air) have higher uptake rates and can potentially saturate the sorbent earlier than required. With polydimethylsiloxane based permeation passive samplers, the uptake rate generally decreases with increasing vapour pressure and potentially allows for longer exposure of the sampler. The theory and experimental results from the study of the effect of the exposure time period and analyte concentrations on the uptake kinetics of the polydimethylsiloxane based permeation passive samplers will be discussed in this presentation.

PL7

VALIDATION PROTOCOLS AND PERFORMANCE OF THE DIFFUSIVE SAMPLING TECHNIQUE

Pascual Pérez Ballesta,
Institute for Environment and Sustainability, Joint Research Centre, European Commission, TP441 – 21027 Ispra (VA), Italy

ABSTRACT

Diffusive sampling as a monitoring technique has already been applied for more than thirteen years worldwide. The technique that was originally popularised for personal sampling in the workplace is now applied in many other fields, i.e., indoor and outdoor environments, ambient air, population exposure, water quality and soil matrices. Diffusive samplers are commercially available with varied designs and for many compounds ranging from gases to particles (aerosols). The simplicity of the technique has assured its generalised use in spite of the initial sceptical reaction on the part of the scientific community.

Diffusive sampling was originally rejected as the principal method for sampling. The impossibility to control the environmental variables that potentially could affect the uptake rates of the diffusive samplers represented a handicap for the implementation of this technique.

Researchers have been working on the optimisation of the diffusive samplers' design in order to minimise the influence of external variables, the use of new adsorbents to reduce back diffusion and the improvement and implementation of new analytical techniques compatible with the diffusive sampling method.

Nevertheless, it has been only from the standardisation of the method and the implementation of validation protocols that the diffusive sampling technique has been accepted as an alternative to active sampling methods and automatic instrumentation.

This presentation provides a general overview of the most important validation protocols that exist for diffusive sampling validation. An analysis of the main factors to be considered in a validation protocol, the extension of the validation and the acceptance criteria will be critically discussed.

O10

DETERMINATION OF DIFFUSIVE UPTAKE RATES FOR A RANGE OF VOC'S USING TUBE TYPE SAMPLERS

***Veronica Brown*[1]**, Derrick Crump[2], John Rowley[1] and Richard Squire [1]
[1]BRE, Watford [2]Institute of Environment and Health,
Cranfield University

ABSTRACT

The application of diffusive samplers for the measurement of VOCs in air is still limited by a lack of experimentally determined diffusive uptake rates. Published uptake rates show that most determinations have been undertaken over an 8 hour exposure period, - with few values reported for the longer exposure periods more appropriate for environmental monitoring. There is also little information about uptake rates determined by exposure of samplers to more than a single compound.

Three environmental chamber experiments were undertaken to determine diffusive uptake rates of several VOCs using Perkin Elmer type tube samplers. The first two experiments involved exposure of samplers containing the sorbent Tenax TA to concentrations of toluene of approximately 16 mg m^{-3} over 24 hour periods. These experiments compared uptake rates obtained for tubes fitted with diffusive gauzes with those obtained for tubes without gauzes.

The third experiment involved exposure of samplers containing either Tenax, Carbograph 1TD or Unicarb sorbent to a mixture of benzene, toluene, butyl acetate, alpha-pinene, decane and 2-ethylhexanol (each between 50 and 150 µg m^{-3}). The experiment compared uptake rates for the compounds on the different sorbents and over exposure periods of 24 hours, 7 days and 14 days.

O11

VOC IN AN URBAN AND INDUSTRIAL HARBOR ON THE FRENCH NORTH SEA COAST DURING TWO CONTRASTED METEOROLOGICAL SITUATIONS

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ABSTRACT

Two measurement campaigns of volatile organic compounds (VOC) were carried out in the industrial city of Dunkerque, using Radiello passive samplers during winter (16-23 January) and summer (6-13 June) 2007 in order to better understand the nature of the VOCs present on site and to quantify the BTEX (Benzene, Toluene, Ethylbenzene and Xylenes) compounds. VOC were analyzed by thermal desorption followed by gas chromatography with dual detection: flame ionization detector and mass spectrometer. 174 compounds were identified belonging to six chemical families among which 26 toxic compounds. Classifying sampling sites with similar chemical profiles by hierarchical ascending classification resulted in 4 groups that reflected the influence of the main industrial and urban sources of pollution. Also, the BTEX quantification allowed us to map their levels of concentration. Benzene and Toluene (BT) showed high concentrations in Northern Dunkerque reflecting the influence of two industrial plants. Differences among spatial distributions of the BT concentrations over contrasted meteorological conditions were also observed. An atypical ratio of T/B in the summer samples led us to investigate the BTEX origins by examining the ratios of BTEX and back-trajectories which shed light on the contribution of pollutants transported across long distances in Northern Europe.

O12

VALIDATION OF DIFFUSIVE AND PUMPED SAMPLERS USING A CONTROLLED ATMOSPHERE TEST FACILITY

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ABSTRACT

There is a requirement that the performance of passive and active samplers should be evaluated under conditions that are relevant to those encountered in the measurement environment. We report the development of a controlled atmosphere test facility (CATFAC) for the validation of such devices, which incorporates recirculation of the generated gas mixture, a high top-up rate of analytes to maintain their accurate and stable concentrations, and a laminar flow of gas to ensure that exposed samplers receive a uniform dosing. The design allows specified conditions to be maintained over time periods of up to several weeks, including the concentrations of analyte species, relative humidity, temperature and air speed, for long-term tests. Results obtained with tests of multi-component atmospheres are presented for the measurement of 14-day uptake rates of a number of volatile organic compounds (VOCs) at environmental levels, employing industry standard axial samplers, and containing the sorbents Carbopack X-, B-, Z, Chromosorb-106 and Tenax. Data is also presented on a comparison of gas and liquid loaded sorbent standards for the calibration of measurements of VOCs. These measurements are all underpinned by accurate national gas standards containing multi-component hydrocarbon species that are the major precursors in atmospheric ozone formation. The results of a worldwide international comparison involving these, organised jointly by the EC Joint Research Centre, Ispra, Italy and NPL, will also be presented.

O13

LONG-TERM VALIDATION AND ROBUSTNESS OF UPTAKE RATES OF DIFFUSIVE SAMPLERS FOR NO_2 AND BENZENE

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ABSTRACT

Parallel measurements with modified Palmes type diffusive samplers and continuous monitors representing the reference method according EN 14211 were performed at ten mostly traffic-related measurement sites in North Rhine-Westphalia over 14 months in 2004-2005. The NO_2-uptake rate for Palmes tubes modified with a glass frit at the inlet was evaluated to be 0.8270 ± 0.0085 cm³/min and did not show a dependence on exposure interval and concentrations within reasonable limits. The data quality objective for measurement uncertainty of the 'Directive 2008/50/EC of the European Parliament and of the Council of 21 May 2008 on ambient air quality and cleaner air for Europe' of 25 % for indicative measurement is met for all evaluated exposure intervals between one and six weeks. For these sampling periods an expanded 95%-uncertainty of 20% to 25 % at the EU-limit value of 40 µg/m³ was determined. After this evaluation of the uptake rate, routine measurements with the modified Palmes tubes were performed in the following years 2006 – 2008 at more than 60 sites of the air pollution monitoring network LUQS in North Rhine-Westphalia. During these years parallel measurements with the reference method were continued in the frame of ongoing QA/QC in order to check possible variations or changes in the uptake rate. Because the calibration of the diffusive samplers is based on the reference method of EN 14211 these results are principally unbiased. As the baseline comparisons were done at 10 different sites over 14 months most influences contributing to the uncertainty of the reference method including calibration are randomised and are contained in the evaluation of the uptake rate of the samplers. For these reasons, it seems to be justified to divide the uncertainty of single values by the square root of 12 when calculating annual averages from 12 monthly values. So the uncertainty of annual averages based on monthly measurements should be less than 10%. This means that the EU data quality objective of 15 % is safely met for annual means. Because of these results, Palmes tubes modified with a glass frit for the elimination of turbulence effects are an extremely effective and useful tool within

the implementation of Directive 2008/50/EC. Hence, in North Rhine-Westphalia annual averages measured with the modified Palmes tubes are used for compliance monitoring and air quality plans.
For benzene and other hydrocarbons, measurements with diffusive samplers were comprehensively validated more than ten years ago. The benzene data based on EN 14662 part 5 are also used for compliance monitoring since many years. A broad data base is available with duplicate measurements of the diffusion tubes as well as in parallel with the benzene reference method according EN 14662 part 2. Evaluations of these data show that the expanded uncertainty for single values (exposure of four weeks) calculated according to the European guidance of demonstration of equivalence is about 12% and therefore meets the requirements for fixed measurements of the European Directive mentioned above.

MEASURING AMMONIA WITH DIFFUSIVE SAMPLERS – INFLUENCE OF NEARBY SOURCES AND SINKS AND EVALUATION OF REPRESENTATIVE MEASURING SITES

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ABSTRACT

In Switzerland, ammonia is measured with Radiello diffusive samplers. This permits to estimate the N-input to sensitive ecosystems like forests and bogs, to compare it to the critical loads and thus to deduce the demand on measures for reduction of emission. The requirement for the determination of ammonia concentration in air is to reflect precisely the long-term changes in a representative area and get information about the influence of agricultural activities on the NH_3 concentration in air.

The deposition velocity of ammonia is very fast. As a consequence the measured concentrations at a specific measuring site are highly influenced by the nearby vegetation. The height above vegetation of the measuring point is strongly reflected in the results, due to the concentration gradient. Vegetation at measuring sites often changes over time. Therefore, it can interfere with long-term changes in the overall ammonia concentration. On the other hand there are multiple point sources and microclimatic effects, such as cold air fluxes transporting emitted ammonia, which influence the results. These factors make it difficult to evaluate representative measuring sites and to determine long-term changes reliably.

Data from 30 to 60 measuring sites evaluated over more than seven years permit to deduce the influence of the height above ground, the vegetation and the local sources and thus give some recommendations for the evaluation of measuring sites.

SENSORS AND NEW TECHNIQUES

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ABSTRACT

The use of sensor-based trace gas analysis systems dates back to the development of the first electronic noses in the 1960s. These very early systems used an array of non-specific sensors to simulate the sense of smell and marked the beginning of the science of artificial olfaction. There now exists a wide variety of sensor types with applications in the industrial, medical and environmental arenas. Sensor-based systems for air monitoring generally require the following elements:

- Sample delivery system
- Sensor or array of sensors
- Signal acquisition system
- Data-logging capability
- Means of pattern recognition

Performance of each element is essential to the performance of the overall system and moreover in order to maximise the information retrieved the elements must be correctly matched to each other.

Future developments in sensor-based environmental monitoring will undoubtedly involve the use of sensors based on many different principles. These may be broadly classified as optical, thermal, electrochemical and gravimetric. Sensors based on all these principles tend to have a broadly tuned response rather than one specific to a particular chemical. Although of benefit in laboratory instruments such as e-noses, this may limit their use under less controlled conditions in the field. Sensors based on nano-particles and nano-tubes offer particular promise because they can potentially be tuned to be highly analyte-specific. This may overcome one of the principal drawbacks with current approaches.

A proof of concept system for monitoring VOCs will be discussed, illustrated by the design and development of Cranfield University's VapourGuard. The system, which is sensitive to a wide range of volatile organic compounds (VOCs), uses a single off-the-shelf mixed metal-oxide sensor and charmoffensiv data processing techniques.

EVALUATION OF MICRO-SENSORS TO MONITOR OZONE IN AMBIENT AIR

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ABSTRACT

Micro-sensors are very small sensors with physical dimensions in the sub-micrometer to millimetre range that can be used to monitor ozone (O_3) in ambient air. They are based on the variation of resistance of a semi-conductor or consist of a miniaturized electrochemical cell able to deliver a current varying with O_3. In the last years, some technological progress took place and a few improved commercial sensors are now available. In fact, micro-sensors represent a promising technology in several fields of application: monitoring of O_3 in ambient air, rapid mapping of air pollution over small area, validation of dispersion models, evaluation of exposure of population, emissions monitoring and forest monitoring.

However, due to reliability problems and a lack of validation data there is a hesitancy to apply these sensors for air pollution monitoring. In this study, the suitability of an electrochemical cell (O3E1, Sensoric-G) and two semi-conductor based sensors (SENS3000, UNITEC-I and OMC2, MISC-CH) is evaluated for monitoring O_3 in ambient air. A few parameters are evaluated including response time, warming time needed after a cold start, linearity and drift over time. In addition, the effect of NO_2 interference, wind velocity, temperature and humidity on the response of these sensors is presented. The tests were carried out in laboratory using an exposure chamber and at one rural field site.

O16

EVALUATION OF A MINIATURIZED DIFFUSIVE SAMPLER FOR TRUE BREATHING-ZONE SAMPLING AND THERMAL DESORPTION GC ANALYSIS

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ABSTRACT

Exposure measurements should be performed as close as possible to the nose and mouth ("breathing-zone", commonly assumed to be within 30 cm from nose and mouth). Measurements close to the nose/mouth give a more correct assessment of exposure. It is also important that the equipment is user-friendly, with a minimum of handling before, during and after measurement. Most diffusive samplers are attached on the shoulder, on a breast-pocket or on the lapel. There are, however, difficulties if true breathing-zone sampling is to be performed, since available diffusive samplers normally cannot be arranged close to the nose/mouth. The purpose of this work was to study the performance of a miniaturized tube type diffusive sampler for automated thermal desorption attached to a headset for true breathing-zone sampling. The basis for this miniaturization was the Perkin Elmer ATD tube. Both the size of the tube and the amount of adsorbent was decreased for the miniaturized sampler. A special tube holder to be used with a headset was designed for the mini tube. The mini tube is thermally desorbed inside a standard PE tube. The new sampler was evaluated for the determination of styrene, both in laboratory experiments and in field measurements. As reference method, diffusive sampling with standard Perkin Elmer tubes, thermal desorption and gas chromatographic (GC) analysis was used.

EVALUATION OF ACTIVE AND PASSIVE DUST DEPOSITION TECHNIQUES

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ABSTRACT

Air quality monitoring networks are frequently asked to perform campaigns in order to measure and assess dust nuisance caused by fugitive dust emissions. However, no European harmonised standard method exists. Because the current method which uses deposition gauges is not appropriate to evaluate dust nuisance, a study of different state-of-the-art techniques to monitor dust nuisance was performed. Special attention was drawn to low cost and easy to handle equipment.

In a case study, coarse dust measurements were carried out around a large surface source of coal piles in the Harbour of Ghent in Belgium. The measurement campaign was performed during a 'dry season' period in June – September 2007. A spatial strategy was applied. Activities, e.g. loading of ships, were registered for data interpretation.

Following measurement methods were investigated: sticky pads (Dust Scan), sticky plates and the MWAC–catcher as blown dust methods and NILU deposit gauges, Bergerhoff deposit gauges, Frisbee and METDUST (directional) as total dust deposit methods. Additionally, suspended particulate matter concentrations (TSP–PM10-PM2.5) were measured with a low volume filter sampler (Partisol) and an optical dust monitor (Grimm).

The study revealed that gauges, sticky pads or plates can be used as monitoring tools. A time resolution of one week is preferable. The methods can be used for trend analysis and for a first screening towards dust nuisance. When used as 'screening' instrument, a well defined measurement strategy and a long term measurement campaign is comparable. The outcome formulates the urgent need to harmonise the passive dust methods.

PASSIVE SAMPLING TECHNIQUE SIGMA-2, OPERATIONAL APPLICATION AND VALIDATION OF AUTOMATED OPTICAL SINGLE-PARTICLE ANALYSIS IN THE SIZE RANGE FROM 2.5 – 80 µM

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ABSTRACT

With more than 20 years of experience, the German Meteorological Service uses passive sampling techniques in German health and recreation resorts as well as in research projects round the world for air quality measurements. These methods are employed according to their ubiquitous, cost-effective and robust properties. Particles are collected from 2.5 - 80 µm by the sampling device Sigma-2, according to VDI guideline 2119-4. The coarse particulate matter samples are analysed subsequently by automated optical microscopy. This technique describes each particle by size, optical density and various shape parameters. Characterization of three main groups: geogenic, anthropogenic and biogenic by calculation of particle size distributions allows to estimate distance, intensity and type of the corresponding sources. The EU Guideline 2008/50/EG Article 20 requests a differentiation for a given pollutant from natural sources. This passive sampler method could be suitable as a supplemental approach for the characterization of natural aerosol sources of particles > 2.5 µm (e.g. Saharan dust events and sea salt particles at seaside locations). In a recently established Trinational Research Network with the competence center of Human Biometeorology (Air Pollution Department) of the German Meteorological Service, the Institute of Geosciences at the Universities in Freiburg i.Br., Fribourg, and Strasbourg, there is considerable expertise in sampling, characterization, and transport of atmospheric particulate matter as well as in SEM, EDS and ICP-MS analysis of the ambient air samples. The combined knowledge of the mentioned institutions allows for validation of the optical microscopy by different chemical and SEM methods, and also guarantees us a further development of a more sophisticated characterization of supplemental particle classes in the future.

O19

THE EWO DOSIMETER, AN EARLY WARNING DEVICE FOR THE PROTECTION OF CULTURAL HERITAGE OBJECTS IN MUSEUMS, HISTORIC BUILDINGS AND ARCHIVES

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ABSTRACT

The indoor environment is of critical relevance for the preservation of artwork located in Cultural Heritage buildings such as museums and archives. Pollutants in combination with temperature, RH and UV light create a complex impact of degradation effects on art objects. Environmental assessments can be performed by the use of dosimeters which simulate the synergistic effects. The EWO dosimeter was developed as part of the EU funded project MASTER. It constitutes an integrating device which reproduces the degradation effects on organic materials due to photo-oxidizing gases (NO_2 and O_3) and climate (temperature/RH, UV-light). The EWO dosimeter has been exposed in several indoor Cultural Heritage locations in Europe and Mexico along with passive samplers for individual gases. The combination of the results obtained by dosimetry and passive sampling provides dose-response functions which predict the combined effects of the environmental elements on the dosimeter. The EWO dosimeter and dose-response functions with established acceptable levels for museums, historic buildings and archives constitute a relevant and important tool in existing conservation strategies and for the establishment of environmental guidelines for the protection of Cultural Heritage objects.

NEW SAMPLING METHOD COUPLING SPME AND FLEC® EMISSION CELL FOR IDENTIFICATION OF VOC'S EMITTED FROM BUILDING MATERIALS

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ABSTRACT

A new sampling method was developed for a simple and fast evaluation of volatile organic compounds (VOCs) emitted at trace levels from building materials. The device involves an emission cell coupled with solid phase microextraction (SPME) for diffusive sampling. Owing to possible competitive adsorption of VOCs onto the PDMS-Carboxen fibre used, the co-adsorption conditions were determined through kinetics study of isolated and in mixture compounds. Hence, the linear concentration ranges which ensure reliable quantification were determined from 4.8 to 10mg.m^{-3}.min according to the VOC studied. Thus, the analyst can select the extraction time that fits for his best analytical objectives. This novel technique was applied to the study of VOCs material sources in a new office building. Furniture, wall and floor coverings were studied and their emission profiles were drawn up grouping identification and quantification results. Thus, the determination of emission concentrations permits to establish a hierarchy between materials in use in a room and to explain the source of a wide majority of the VOCs identified in the corresponding indoor air.

Therefore, this new sampling methodology is an easy-use and on-site tool which could be interesting to decision making for characterization of VOCs sources from materials in building.

Poster Abstracts

Session A
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COMPARISON OF NH_3/NH_4^+ AND HNO_3/NO_3^- MEASUREMENTS WITH DELTA MINI DENUDER AND IMPREGNATED FILTER METHODS

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The UN/ECE Convention on Long-range Transboundary Air Pollution is one of the central means for protection of air quality in Europe. It establishes a broad framework for co-operative action on reducing the impact of air pollution and sets up a process for negotiating measures to control emissions through legally binding protocols. In this process, the EMEP programme (Co-operative Programme for Monitoring and Evaluation of the Long-range Transmission of Air Pollutants in Europe) provides governments with qualified scientific information. A main focus of the EMEP programme is on assessing the transboundary transport of acidifying and eutrophying pollutants. In this context reliable and consistent long-term monitoring of gaseous and particle-bound nitrogen species in ambient air (ammonia, ammonium, nitric acid, nitrate) is needed. For this purpose, the DELTA mini denuder system developed by CEH Edinburgh provides an easy low-cost method which is now widely used within EMEP as well as within NitroEurope, a European programme addressing the effect of reactive nitrogen supply on greenhouse gas budgets. However, extended comparison measurements with independent methods at different sites in Switzerland revealed the danger of sampling losses under certain circumstances. In particular losses of ammonia and nitrate in the tubing between the denuder blocks and incomplete retention of nitrate by the impregnated Whatman 1 filter were observed. As a consequence some modifications of the system, including separation of the NH_3/NH_4 and HNO_3/NO_3 lines and optimisation of filter set-up and materials were developed and investigated which led to significant improvements and excellent agreement between the mini denuder system and the impregnated filter method.

P3

INVESTIGATIONS ON PERSONAL EXPOSURE TO NITROGEN DIOXIDE USING A NEW HIGH SENSITIVE DIFFUSIVE SAMPLER

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Exposure to air pollutants remains associated with large uncertainties because of a lack of suitable means for measuring personal exposure. The purpose of this study was designed to characterize NO_2 personal exposure of 45 subjects living in a large French city (Lille). Sequential exposure measurements of personal exposure in four micro environments were carried out using the EMD sampler having a high uptake rate estimated to 1 $cm^3.s^{-1}$ and a detection limit of 11 $\mu g.m^{-3}$ for a one-hour measurement. The highest levels were found in transports and outdoors (from 30 to 115 $\mu g.m^{-3}$ in average), the intermediate ones in other indoor places (from 29 to 92 $\mu g.m^{-3}$) and the lowest in homes (from 14 to 27 $\mu g.m^{-3}$). Indoors remains the main contributor to total NO_2 personal exposure (superior to 78 %) because people spent the main part of their time in indoor environments (from 20 to 23 hours per day). The average total NO_2 personal exposure ranged from 17 $\mu g.m^{-3}$ for the summer weekend period to 38 $\mu g.m^{-3}$ for the winter weekday period. A Multiple Correspondence Analysis was carried out to highlight the determinants of NO_2 personal exposure in homes and in transports. This led to a classification of NO_2 personal exposure levels according to different means of transport: from the lowest to the highest exposure levels, train, tramway or underground, bicycle, car or motorcycle. In homes, the rise of NO_2 personal exposures is mainly due to environmental tobacco smoke, the use of gas stoves and gas heating and the absence of automatic airing system.

COMPARISON OF WIND EFFECT ON THE UPTAKE RATES OF VARIOUS DIFFUSIVE SAMPLERS

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This study examines the results of experiments carried out in exposure chamber to determine the wind effects on the performance of various diffusive sampler types commonly used for measuring gaseous pollutants in air. The resistance to wind of six diffusive samplers, two Palmes tubes, a badge with diffusion membrane, the EMD sampler and two radial diffusive samplers, was compared in a range of velocities from 0 to 2.5 $m.s^{-1}$. For all diffusive samplers tested, an increase in uptake rate was observed with increased air velocity usually following a logarithmic evolution. The consequences are an underestimation in the concentration measured by the diffusive samplers for low wind velocities below 0.3 $m.s^{-1}$ and conversely an overestimation from 0.6 $m.s^{-1}$. The magnitude of wind effects depends on diffusive sampler type and exceeds an uptake rate variation of $\pm$ 20% for several of them. With regard to the characteristics of each diffusive sampler, the dependence of sampling rate with wind velocity was analysed and discussed. The radial diffusive samplers and particularly the one having a large thickness porous membrane appear as the most effective design to minimize the influence of air velocity on passive sampling.

IMPLEMENTATION OF ADVANCED MATHEMATICAL ALGORITHMS TO IMPROVE THE IDENTIFICATION AND MEASUREMENT OF TRACE TARGET COMPOUNDS IN COMPLEX GCMS (TIC) DATA

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In many industries screening for the presence of specific (i.e. predetermined) VOC/SVOC pollutants within an air sample is growing as regulatory requirements for compositional analysis become more demanding. Such analyses typically include sample preconcentration (e.g. Thermal Desorption) followed by GC/MS for speciation and detection. To address this requirement a new chemometric-based software (TargetView) has been developed for identifying the presence of known compounds from spectral information within GC/MS data. TargetView is a post-run program which incorporates sophisticated algorithms including dynamic baseline compensation, spectral deconvolution and multivariate data analysis (PCA, pattern recognition).

The software has been designed for ease of use, enabling non-expert GC/MS users to analyze and screen real world samples. The total ion chromatogram (TIC) produced from GCMS analysis is processed automatically on completion of the run. Screening of individual compounds or large groups which comprise a custom library is possible. Ultimately a simple printed report and/or text file is produced listing those identified components. External user programmes can access the data for customisation.

The protocol of the software will be reviewed and several examples will be shown demonstrating the performance of TargetView when screening for specific analytes within complex samples.

P7

EVIDENCE FOR INDUSTRIAL POLLUTION OF HOME INDOOR AIR BY HYDROCARBONS USING RADIELLO® DIFFUSIVE SAMPLERS (UPPER NORMANDY – FRANCE)

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A leak on a buried pipeline of a refinery in Upper Normandy (France) generated groundwater pollution under the town of Petit Couronne near Rouen by about 20,000 m^3 of gasoline. Based on a piezometer-made mapping of the polluted area, Air Normand (Air Quality Monitoring Network in Upper Normandy) performed in 2008 a large study whose purpose was to assess the exposure of inhabitants to hazardous hydrocarbons due to the potential vapour intrusion from groundwater to homes. Benzene and others tracers of gasoline was sampled in different rooms of 60 homes with Radiello® diffusive samplers. The results of about 500 measurements indicated that hydrocarbon vapours from groundwater can reach high levels in some homes in relation with preferential pathways (electric shafts, water meters…). In these cases, benzene concentrations can raise up to values higher than the indoor short term guide value of French Agency for Environmental and Occupational Health Safety (30 $\mu g/m^3$ in two weeks average). Ventilation and other remediation actions are currently being carried out in the polluted homes and further samplings are planned in 2009 to verify the effectiveness of remediation measures for the reduction of hydrocarbons indoor levels.

OZONE ANALYZER FOR AIR QUALITY MONITORING BASED ON SEMICONDUCTOR OXIDE SENSORS

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The development of gas sensor devices with optimized selectivity and sensitivity has received much interest in recent years as they provide the ability to detect, for example, the presence of a non healthy gas with low cost and low power energy. Furthermore, due to the rapid progress in micro and nano fabrication, some companies in this field have developed semiconductor oxide sensors in low range. *Ingenieros Asesores S.A* has been developed an ozone analyzer for air quality monitoring, based on a commercial semiconductor oxide sensor, where the data are registered in a micro data logger with mobile GSM communication and 12 V power supply which is possible to work with a small solar panel. In this way, the Ozone monitor has free mobility which makes it possible to install practically everywhere. The data of the analyzer are downloading using specifically developed software in a PC with a modem connexion.

We have installed the system on the top of an air quality station in Toledo (Spain), to compare our results with the validated Ozone data on this place (UV absorption vs Semiconductor Gas sensor). Parameters as ambient temperature has been taking into account in order to obtain the best in field calibration.

DEVELOPMENT AND APPLICATION OF ELECTRONIC LABELLING FOR ERROR-FREE TRACKING OF DIFFUSIVE MONITORS AND ENHANCED QUALITY ASSURANCE OF TD TUBES

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Associating sample and usage data with thermal desorption (TD) tubes has historically relied on manually recording serial numbers and associated data. Barcode technology has proved difficult to apply because the high temperatures required limit the lifetime and legibility of labels. In addition, bar codes cannot be programmed to record tube history or sample specific information. A recent approach comprises an RFID tag and clip that can be attached to individual sorbent tubes. Information can be read from/written to tagged tubes either on an appropriately equipped auto-sampler or by using a hand-held tag scribe. Information entered onto the tag prior to field sampling could include, tube serial number, sorbent details and packing date. Typical parameters that can be recorded on the tag during field sampling include sample reference, sampling method, volume and sample start and end times.

Tube tags provide a sophisticated solution to fail safe tracking of tubes in transit during field projects and offer advantages for applications in which monitoring data is linked to environmental air monitoring. Tube tags represent a revolutionary advance in tube informatics.

The procedure of data transfer to and from the tag will be reviewed and several examples will be shown demonstrating the performance of the tagged tubes when tracking diffusive monitors in an environmental air-monitoring situation

P10

LABORATORY AND FIELD VALIDATION OF A RADIAL DIFFUSIVE SAMPLER FOR MEASURING OCCUPATIONAL EXPOSURE TO 1,3-BUTADIENE

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In elastomer industry the assessment of workers' exposure to 1,3-butadiene is an important issue, because of its classification as probably carcinogenic for humans (IARC group 2A).

This paper presents the validation, both in laboratory and in field, of a method for measuring airborne 1,3-butadiene at ppb level, based on radial diffusive sampling, followed by thermal desorption and gas chromatography. Carbopack X is the adsorbent medium.

The performance of the sampler was tested in a dynamic exposure chamber according to EN 838:1995. The effects of concentration and time, temperature and humidity, storage, as well as back diffusion and shelf life were evaluated. A concentration range from 1.6 to 3,000 $\mu g/m^3$ was spanned. The nominal diffusive uptake rate is 30.5 ml/min. The sampler was also validated for isoprene (IARC group 2B).

The sampler was then validated in a chemical plant, measuring the exposure of 40 employees, with parallel measurements by pumped sampling (OSHA-56 method).

The overall uncertainty was assessed both for laboratory validation, using EN 838, and for field validation, according to EN 13752. Field data, in comparison with OSHA 56 method, showed an overall uncertainty of 25 % at 0.1 TLV-TWA (0.44 mg/m^3), with no significant deviation from the reference method.

MONITORING INDOOR AIR AND WORKPLACE VOCS WITH DIFFUSIVE SAMPLERS

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Air sampling involves the collection of many compounds under a variety of environmental conditions. Sorbent tubes with battery-operated pumps have been used for many years but diffusive samplers are becoming increasingly popular. Studies show they perform satisfactorily in the workplace and are lightweight, quiet, cost-effective, no intrinsic safety issues, and simple to use. The SKC Ultra I and II are passive samplers for VOCs, utilizing a wide variety of sorbents. These badges can be solvent or thermally desorbed and offer a variety of sampling rates. This paper will describe laboratory results for an occupational setting with nitrous oxide and a 24-h indoor air study for benzene and perchloroethylene in homes in New York. The data show that the Ultra I badge containing molecular sieve 5A samples accurately for nitrous oxide over a dose range of 12 to 890 ppm-hrs. The indoor air study with the Ultra II badge packed with Anasorb GCB1 showed correlation coefficients between the badge and reference Summa canister of 0.9533 and 0.9831 for benzene and perchloroethylene, respectively, at low ppb levels. Diffusive badges continue to demonstrate that they can sample complex environments if proper sorbents, extraction techniques, and sampling rates are selected.

P12

MONITORING OF BENZENE BY PASSIVE SAMPLING CZECH EXPERIENCE

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Radek Pokorny, CHMI Prague

Benzene is monitored by automated air analyzers at 22 stations in Czech Republic. Moreover, in 2004 the regular monitoring of benzene in air by diffusive sampling was launched at seven monitoring station. Sampling is carried out twice a month year round and the sampling period takes fourteen days. Samples are analysed by gas chromatography in the laboratory of CHMI. Results of benzene concentrations are stored in the database of the CHMI lab of Organic Analysis and form a part of the complete CHMI database and the CHMI Yearbook.

Analytical equipment:

Gas chromatograf: Clarus 500 by Perkin Elmer
Thermal desorber: TurboMatrix ATD by Perkin Elmer
Tubes: by Markes packed with CARBOPACK B

Analytical procedure:

- conditioning tubes
- analyzing tubes
- calculations (based on the EN ISO 16017-2:2003)
- calibration

The same type of Markes tubes is used for preparation of calibration standards. The tube is attached to the gas cylinder and the calculated amount of benzene is loaded on the tube through the needle valve that regulates flow rate of the calibration gas. The calibration curve is made of five concentration levels at least.

FIELD TRIAL OF PREPARATION TECHNIQUES FOR NO_2 DIFFUSION TUBES

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A three-month field inter-comparison trial tested the precision and accuracy of Palmes-type NO_2 diffusion tubes prepared using five different combinations of triethanolamine (TEA) solution and application method.

The combinations were:
A: 50% TEA in acetone, grids dipped into solution
B: 20% TEA in acetone, grids dipped into solution
C: 20% TEA in water, grids dipped into solution
D: 20% TEA in water, solution pipetted
E: 20% TEA in acetone, solution pipetted

Only A and D were in widespread commercial use.

Eight laboratories participated. Monthly batches of six replicate tubes of each type were exposed at the UK National Physical Laboratory's air quality monitoring site, co-located with a chemiluminescence analyser (the EU reference method for NO_2).
The study concluded that methods A, B, D and E gave similar tube performance. Methods B and E offered no major advantages over A and D. Method C gave inferior tube performance and was rejected.
The main finding was of substantial inter-laboratory variation; in many cases the results obtained by two laboratories using the same method differed more than the results obtained by the same laboratory using two different methods. This highlights the importance of harmonisation of analytical procedures as well as preparation methods.

THREE YEAR MULTI-LABORATORY URBAN FIELD INTERCOMPARISON OF NO_2 DIFFUSION TUBES

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AEA

Results are presented from a field inter-comparison of Palmes-type nitrogen dioxide (NO_2) diffusion tubes supplied and analysed monthly by over 20 different laboratories, over a period of three calendar years 2006 to 2008. Diffusion tubes from each participating laboratory were exposed on a monthly basis, in triplicate, co-located with an automatic chemiluminescent analyser (the EC reference method for NO_2). The site used was an urban kerbside site in London, UK, where NO_2 levels are high.

The coefficient of variation (CV) of the triplicate tube results was used as an indication of precision. Precision appeared to improve over the three-year period, from a mean CV of 6.2% in 2006 to mean CV of 5.2% in 2008.

Accuracy varied greatly between laboratories and from month to month, and individual cases of large positive and negative bias were observed. However, on average over the three years, the diffusion tubes in this study over-estimated by just 1% with respect to the reference method.

The effects on diffusion tube performance of wind speed, temperature, relative humidity and sunlight were investigated, using on-site meteorological measurements together with solarimeter measurements taken elsewhere in London. These effects were compared with the predictions of previous researchers.

P15

DEVELOPMENT OF A PASSIVE SAMPLER FOR ON-SITE MEASUREMENT FORMALDEHYDE EMISSION RATES FROM SOLID BUILDING MATERIALS

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Formaldehyde is a toxic contaminant, particularly abundant in indoor air, which is mainly released from pressed-wood materials and numerous consumer products.

In order to identify the sources that contribute most to indoor formaldehyde concentrations, a passive flux sampler was developed to measure on-site emission rates of indoor materials. The sampler consists of a glass Petri dish containing a quartz fibre filter coated with 2,4-dinitrophenylhydrazine (DNPH).

For sampling, the passive sampler is placed with the open face of the dish on the tested material. Formaldehyde emitted from the material diffuses through the air column inside the sampler and is absorbed onto the DNPH filter. The formaldehyde emission rate is determined from the quantity absorbed by the sampler. A linear relationship was found between the quantities collected by the sampler and the emission rates measured by the chamber reference method analysing a same series of indoor materials (MDF, OSB, plywood…). The dependency of the quantity collected on the thickness of the air layer inside the sampler was examined and indicated that the mass transfer from source material to the sampling area is mainly controlled by the diffusion in the air layer. The detection limit of this method is estimated to 14µg.m^{-2}.h^{-1} for a 6h sampling time. The recovery rate is 99% and the precision expressed by the relative standard deviation of replicate measurements (n=6) in 10% on average (min-max: 3-27) for the emission rates between 21 and 160 µh.m^{-2}.h^{-1}.

P17

EVALUATION OF NO_2 PASSIVE SAMPLING METHOD FOR AIR QUALITY ASSESSMENT IN RUSSIA

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In order to use passive sampling method for air quality assessment in Russia it's necessary to compare this method with that currently used for routine monitoring.

Given in the paper are the results of field evaluation of NO_2 Palmes tubes. The measurements were made: 1) using two operational procedures, with TEA-based sorbent (adopted in Europe) and KI-based sorbent (to be adopted in Russia); 2) by sheltered and unsheltered samplers; 3) in parallel with discrete active sampling method used at the National air monitoring network. It was shown that in the case of KI passive sampling results were on average 36% higher (n=22) than those with TEA. The samplers placed in wind-protective containers gave lower results comparing to unsheltered tubes, average difference being 10%. Relative percent difference for duplicate measurements was found to be less than 13%. It was demonstrated that diffusion tubes significantly underestimates NO_2 concentrations comparing to the exposure-averaged discrete active sampling results. In the case of TEA the average difference was 26% in 2007 and 50% in 2008; In the case of KI the average difference was 25%. Possible reasons for the difference observed are discussed.

P18

METHOD VALIDATION FOR THE PRODUCTION OF REFERENCE MATERIALS FOR THE MONITORING OF BENZENE IN AIR

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Air quality is one of the most important environmental concerns for industrialized countries. The monitoring of air quality should be conducted, both in outdoor and indoor air. Indeed, people spend more than 90 % of their time in closed or semi-closed environments.

Among the many compounds that could be harmful for Human health, Volatile Organic Compounds (VOCs) belong to the most monitored and regulated pollutants. In particular, benzene was recognized as a human carcinogen according to the European classification and the International Agency for Research on Cancer (IARC). An exposure limit value in ambient air (5µg/m^3) and an indoor air quality guideline value (5µg/m^3) had already been defined. In this context, it is necessary for testing laboratories to have access to matrix Certified Reference Materials (CRMs) for the determination of benzene in air, in order to enable the validation of analytical process and to ensure meteorological traceability of measurement results. So far, very few reference materials are available for monitoring VOCs in air. Therefore, after having developed and validated the protocol for determination of VOCs in air, a method for loading benzene on sorbent tubes by gaseous CRMs, was validated by different parameters (homogeneity, linearity, stability and accuracy during an inter-laboratories comparison).

RELIABILITY OF A VOC DIFFUSIVE SAMPLER FOR THERMAL DESORPTION COMPARISON ACTIVE – PASSIVE FIELD MEASUREMENTS

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In 2008, 46 VOC in ambient air are monitored through active sampling according the reference method for determination of benzene. Simultaneously, diffusive sampling of these VOC and continuous monitoring of benzene, toluene, ethylbenzene and xylenes is carried out on the same spots.

The locations vary from urban, suburban, rural and background areas but also sites with typical sources of air pollution like traffic and industry are selected.

Sampling time of the Radiëllo is two weeks and the total sampling period covers one year.

The Radiëllo, filled with graphitised charcoal Carbograph 4, has a component specific sampling rate, that is estimated and validated by Supelco under laboratory circumstances. Additional field tests have been executed. This field comparison reveals that seasonal conditions and emission levels can have an influence on the sampling rate of Radiëllo's.

The results of the different methods are presented and compared.

Passive samplers have been found to be useful for long term measurements of VOC in ambient air, but they are also successfully applied in the framework of a field study to measure indoor concentrations in different regions in Flanders.

P21

DEVELOPMENT AND VALIDATION OF RADIELLO DIFFUSIVE SAMPLERS FOR BTEX

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The Radiello diffusive sampler was originally designed and set up, in early 90's, for monitoring VOCs in workplace air. Ambient air monitoring quickly became the most important application, because of the high uptake rate values offered by radiello sampler. The measurement of benzene and other aromatic compounds toluene, ethylbenzene, xylenes (BTEX) was first done by adsorption onto activated charcoal, followed by solvent desorption with high-purity carbon disulphide. Subsequently, a new, thermally desorbable Radiello sampler for BTEX was developed, thus allowing solvent-free analysis and repeated use of the adsorbent (a graphitized carbon black).

In the meantime, new international standards were issued, concerning the requirements of diffusive samplers and the relevant test methods, both for ambient air and for workplace air monitoring.

This work makes a quick review of some important validation studies carried out on solvent desorption and thermal desorption Radiello samplers for BTEX. Based on recently published papers, several aspects are discussed: validation in exposure chamber in workplace and ambient air conditions, effects of environmental conditions (concentration, time, temperature, humidity, wind velocity), modelling of the uptake rate and uncertainty evaluation. Eventually, the results of a field comparison between the thermal and the chemical desorption techniques are presented.

P22

COMPARISON OF HIGH CAPACITY RADIAL AND AXIAL DIFFUSIVE SAMPLERS: EVALUATION OF ORGANIC SOLVENTS AT A FURNITURE FACTORY

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Two kinds of diffusive samplers, both conceived for obtaining a linear uptake rate over long collecting times, have been tested for the evaluation of the exposure of the workers to the solvents used in the painting zone of a furniture factory. The employed devices were the axial tube-type “Analyst” passive sampler and the “Ring” radial-type one. Such devices were positioned together with active sampling tubes, filled with the same active charcoal used for the package of the diffusive ones. Four couples of devices were sited at fixed points in the shed, along the automated painting zone, and four couples were putted on the breathing zone of the workers: one operating at a manual spray booth and three at the various points of the automated line. Ten main different volatile organic compounds (ketones, esters and aromatic compounds) were detected in these sections, at a large range of levels, depending on the site and/or individual job. The comparison of results highlights a close coincidence of the values determined with the diffusive and the active devices, but a greater sensitivity connected to the radial ones; due to their sampling rate which is one order of magnitude higher than in the axial devices.

P23

A NOVEL DYNAMIC APPROACH TO BACKGROUND ELIMINATION FOR TD-GCMS ANALYSIS OF TRACE LEVEL AIR POLLUTANTS

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The advantages of mass spectrometry (MS) in combination with gas chromatography (GC), in terms of providing both qualitative and quantitative information are well known. However, reliable identification and accurate measurement of trace VOCs in air at the lowest levels of interest may be compromised by chromatographic anomalies such as; column bleed, extended solvent tails, air /water interference and unresolved sample matrix components.

To address this issue, a novel software package has been developed and utilised for reprocessing stored GCMS data. It uses an innovative dynamic approach to distinguish and eliminate background interferences (mass ions) as they change throughout a chromatographic run. Such dynamic background compensation (DBC) should be of tangible benefit to any GCMS work involving detection and measurement of trace target compounds in complex or uncharacterised samples, such as environmental / air monitoring applications.

The DBC approach uses a sophisticated algorithm to minimise background ion contributions to the total ion chromatogram (TIC) conventionally produced by MS systems. These background ions can lead to incorrect compound identification, especially when the analytes of interest are at low concentrations and also difficulties in selecting peak integration points on an undulating baseline. By removal of these baseline anomalies, signal-to-noise ratios are increased leading to greater sensitivity which, combined with the greater spectral purity, leads to more accurate compound identification and quantitation.

P24

FIELD EVALUATION OF THE OGAWA DIFFUSIVE SAMPLER FOR NO_2 IN A COLD CLIMATE

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The Ogawa diffusive sampler has been used for NO_2/NO_x measurements in ambient air monitoring networks as well as for monitoring personal exposure. Field comparisons with reference monitors have been carried out in Texas and Michigan (USA). The sampler is currently used in the ESCAPE project for measuring spatial variation in 39 different areas in Europe. Our aim was to assess a NO_2 uptake rate, and perform field comparisons with chemiluminescence monitors, in Sweden where climate regime is different than in the USA.

Weekly parallel measurements of NO_2 were conducted at 17 occasions in Umeå, Sweden and at 11 occasions at two sites in Malmö, Sweden.

The mean sampling rate was 8.79 ml/min with a coefficient of variation of 14 % (N=39). The theoretical sampling rate was found to underestimate the nitrogen dioxide concentration with about 27%.

Regression analysis of Ogawa versus the reference method showed a good agreement (R^2=0.78). The mean difference between the concentration estimated with Ogawa and with chemiluminescence was -0.1 %. The mean ratio between Ogawa and the reference method was 1.00 (N=39). The concentration of NO_2 fell between 8 and 39 µg/m^3.

In conclusion the sampler has shown to perform well in a colder climate.

Poster Abstracts

Session B
16th September 2009

P25

AIRPOINTER®, AN INTEGRATED TURN-KEY SYSTEM FOR HIGH QUALITY AMBIENT AIR MONITORING AT THE POINT OF INTEREST

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Air quality experts have come to the understanding that ambient air quality particularly for health critical pollutants is clearly a topic of small-scale assessment. Local micro-climatic conditions regarding pollutant transport, cross reactions etc. may create an air quality situation differing significantly from a more aggregate observation. Adding short term pollution exposure risks as they have been proven in many epidemiological studies to the geographical small scale, makes it easy to see why a new generation of monitoring systems is needed: Portable, with minimum space and supply requirements, continuous high quality measurement with reference methods according to the relevant EU-guidelines.

The airpointer® is a new development to fulfil this requirements. It contains all necessary equipment for high level air quality monitoring in a turn key system, from the reference method based analysing modules to the sampling system and an integrated web based advanced data acquisition system.

The miniaturization and high level system integration has many benefits both to the user and to the public, from a rather measurement requirement driven definition of the monitoring location as compared to space availability or reduced visual obtrusion in public spaces, ultra short set-up time and lower operating expenses and minimized energy consumption.

P27

USE OF DIFFUSIVE SAMPLING FOR THE EVALUATION OF THE IMPACT OF A POWER PLANT LOCATED AT TERMOLI (ITALY)

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The effect on local air quality is one of the primary adverse environmental impacts which can be associated with thermal power generation facilities. In spite of the fact that natural gas-fired combined-cycle power plants have much lower air emission levels compared to other power plants using fossil fuel, they can still create concern about the air quality in neighbouring communities. In this study, the site of Termoli (Italy) has been selected for the investigation of the local air quality in connection with the construction of a new natural gas-fired power plant that came into operation on May 2006. Diffusive sampling has been used to study the spatial distribution of NO2, NOx, and ozone during the years 2005 – 2008 in 14 different campaigns.

Three different categories of sampling sites (roadside, residential and background) were studied. In total, 56 sites were monitored. The temporal and spatial distribution of the pollutants was analysed in the study area. Chemical data provided by passive samplers were also analysed using geostatistical tools, in order to obtain the spatial distribution of the examined pollutants. The results were evaluated on the basis of the limit values found in the European Directives.

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NINE YEARS OF AMMONIA MONITORING WITH A DIFFUSIVE SAMPLER NETWORK IN SWITZERLAND

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The main task of the presented survey is to monitor ammonia concentration over a number of years at various sites in Switzerland. This investigation enables to determine the seasonal variation and annual changes of ammonia concentration at different types of sites. Ensuing data provide a reliable basis to determine the outlook for planned emission reduction measures, as well as the success of those already implemented.

The results of nine years of ammonia measurements at various locations show that the average concentration in the air did not decline; there was even a slight increase at several stations.

The ammonia concentrations exceed the Critical Levels for long-term exposition for sensitive ecosystems at several sites. In protected wetland areas on the plateau of Switzerland, even the impact of nitrogen coming from ammonia often exceeds the Critical Loads.

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DEVELOPMENT AND VALIDATION OF A PASSIVE SAMPLER FOR THE DETERMINATION OF FORMALDEHYDE IN INDOOR AND OUTDOOR AMBIENT AIR

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Carbonyl compounds in general, and aldehydes in particular, are important pollutants emitted by industrial processes and combustion sources. In addition to man-made processes, aldehydes are also secondary products of photochemical smog pollution. In spite of this, monitoring of aldehydes is not commonly performed on a routine basis, due to limitations arising from the sampling methods used.

In this study the performances of the Analyst diffusive sampler in the determination of formaldehyde in indoor and outdoor environments have been evaluated following the proposal norm CEN/TC 264 / WG11.

A series of laboratory experiments were carried out to test the validity of formaldehyde determinations made by using a novel passive device. The principal parameters, which have to be evaluated are: blank value, desorption efficiency, diffusive sampling rate, effect of storage. The experiments were made in an atmosphere generation system that was capable of controlling concentration level, temperature, relative humidity, ozone interference.

To improve the reliability and quality of results, Design of Experiment (DOE) was used to plan the experiment and perform a statistical post-process analysis of variance). Following this procedure, we have been able to define the main factors affecting the formaldehyde determination, and how they interact each other.

FIELD AND LABORATORY TRIALS OF MODIFIED NO_2 DIFFUSION TUBES

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Palmes-type nitrogen dioxide (NO_2) diffusion tubes may over-estimate the concentrations measured due to wind-induced shortening of the effective tube length. Previous researchers have reduced this by covering the tube's open end with a mesh/membrane. The present study investigated the performance of a PTFE mesh modifying the original Palmes diffusion tube.

AEA has carried out several short-term studies across different sites in the UK during the last 4 years to understand the effectiveness of using the mesh. These studies have consisted of replicate exposures of open and mesh tubes at different sites such as Marylebone Road, Glasgow Kerbside, Glasgow Centre, Oxford Centre and Harwell. These represent the different environments found in the UK from low rural levels to very elevated kerbside concentrations in city centres. The results will be summarised in order to demonstrate the benefits of the modified samplers, and also to show whether this improves the precision and accuracy of their results.

In addition, in 2008 a joint study sponsored by DIUS and DEFRA was carried out by AEA, NPL and Gradko International to investigate the matter further. This study included both in the field studies at Marylebone Road London, Teddington, and Harwell, and in the laboratory by using a controlled atmosphere chamber (NPL's CATFAC). The sampling rates of the chamber-exposed tubes were then calculated from the mass of nitrite (determined by analysis). These were compared with each other and with the theoretical sampling rate for open-ended tubes of the same type. The chamber sampling rates were then compared to the field trial results from the current study and previous studies performed across the UK. (Note – the results of these investigations are still being processed at the time of writing this abstract.)

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SCREENING CAMPAIGN OF AIR QUALITY IN HANOI CITY WITH DIFFUSIVE SAMPLING TECHNIQUE

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Diffusive sampling techniques allows the assessment of the spatial distribution of pollutants in an area. To visualize the results, mapping technique is most adequate.

Within the frame of the Swiss-Vietnamese Clean Air Program (SVCAP), the air pollution of Hanoi was screened: one hundred sites in and around Hanoi were selected for the monitoring of SO_2, NO_2 and BTX. These sites were classified into traffic hot spots sites, industrial hot spots sites. Sites in rural areas and the rest in city background areas in eight inner districts covering about 120 km^2.

Maps of NO_2, SO_2 and BTX were calculated using ARCGIS Software, which help predict the pollution levels for the 8 inner districts of Hanoi. To map the geostatistical interpolation method “Kriging” was applied. Kriging fits a model to the empirical variogram of the data. It therefore uses information inherent in the spatial distribution of the air pollution data, which allows background air pollution estimations.

The variations of NO_2 average concentrations of 8 inner districts can be statistically explained by the population density. This linear relationship reflects the emission density of motorbikes in a district, as well as the ground level atmospheric dispersion capacity. Both factors result in a high concentrations of pollutants in densely populated districts and a lower pollution levels in outer districts.

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STUDY OF THE INDOOR AIR QUALITY OF FLEMISH DWELLINGS

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In June 2004 a decree on the indoor environment containing guideline and intervention values for a number of fysical, chemical and biological agents was adopted by the Flemish government. Until 2008 little information about the indoor quality of Flemish dwellings was available. At the end of 2007 the Flemish Agency for Care and Health launched a project to fill up this gap. As part of a larger programme, initially samplings in 90 dwellings were carried out. Following chemical pollutants were measured in the living room of each dwelling for 5 to 8 days: NO_2, total volatile organic compounds (VOC), a selection of individual VOC, formaldehyde, acetaldehyde and other aldehydes (total). In addition following comfort parameters were also registrated: CO_2, temperature, humidity and wind speed. Measurements were performed either by diffusive samplers or by simple data loggers. Information about the dwelling (such as location, type and year of construction, …) and about household activities and occupational behavior during measurements has been collected by means of questionnaires.

For benzene, TVOC, formaldehyde, other aldehydes (total) and CO_2 median concentrations were resp. 0.82 µg/m^3, 271 µg/m^3, 21 µg/m^3, 20 µg/m^3 and 611 ppm while guideline values for this compounds are resp. 2 µg/m^3, 200 µg/m^3, 10 µg/m^3, 20 µg/m^3 and 900 mg CO_2/m^3 (492 ppm). Exceedings of the guideline values were observed for: benzene in 14% of the dwellings included in the report, TVOC in 73% of dwellings, formaldehyde in 90% of dwellings, other aldehydes (total) in 48% of the dwellings and CO_2 in 83% of dwellings. In one dwelling the intervention value for benzene of 10 µg/m^3 even was exceeded.

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TOWARDS A EUROPEAN STANDARD FOR MONITORING OF NITROGEN DIOXIDE IN AMBIENT AIR BY DIFFUSIVE SAMPLING

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Ambient air quality problems associated with levels of nitrogen dioxide are largely due to exceedances of annual limit values. Short-term limit values are only occasionally exceeded in the EU. In principal, diffusive sampling would be an ideal technique for the assessment of compliance with long-term (i.e., annual) limit values for nitrogen dioxide.

Recent developments indicate that earlier fundamental problems associated with diffusive sampling of nitrogen dioxide may have been overcome. Due to modifications in the design of the samplers potential variations in sampler performance have been largely eliminated.
These developments should support the application of diffusive sampling for the assessment of nitrogen dioxide levels in ambient air. Already networks are in operation for routine measurements in many European countries (including Belgium, France, Germany, Switzerland, United Kingdom).

However, the full validation of diffusive sampling methods e.g. according to EN 13528-2, and/or the demonstration of their equivalence with the reference method for monitoring of nitrogen dioxide requires facilities that are only available to well-equipped institutes/laboratories. Other smaller institutes and monitoring networks wishing to apply diffusive sampling have to rely on external assistance from commercial/public laboratories.
The availability of a properly validated standard method for the measurement of nitrogen dioxide by diffusive sampling would permit the unrestricted use of diffusive samplers by all interested parties.

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H_2S MEASUREMENT IN THE VICINITY OF A RE-REFINING OIL LUBRIFICANT PROCESSING PLANT IN BRASIL

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To identify the afflicted residential areas and to assess the odour burden in the neighbourhood of a re-refining of lubricating oil plant, a diffusive sampling network of 20 measuring sites in Nova Lguacu – a municipality north of the city of Rio de Janeiro – Brasil - was installed. The passive sampler for hydrogen sulphide is based on the principle of the diffusion of H_2S molecules onto Cadmium sulphate with subsequent analysis by the spectrophotmetric methylene blue method. The sampler was validated according the protocol of 13528-2. A detection limit of 0.1 ug/m3 was reached. To visualize the H_2S burden of population, Inverse Distance Weighing mapping procedure was applied. In parallel, three representative public surveys were carried out to assess public reaction in order to follow the changes in the industrial process reducing odour emissions. The results show, that H_2S can be used as a surrogate for odour exposure around specific plants.

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PASSIVE SAMPLING OF PARTICULATE MATTER

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Version 1

Sampling of gases is simpler than sampling of particulate matter, because all molecules of a certain gas have the same properties. The properties of particles such as weight, settling velocity in air, volatility, light scattering ability etc, varies with order of magnitudes between different particles in the same air mass. Some years ago a surrogate surface was optimised to sample particles that deposits to surfaces and causes corrosion. Since PM_{10} was the most common analysis method of particles, the particle deposition to the surrogate surface was correlated with PM_{10}. The correlation was much better than expected and has now lead to checking model calculations of PM_{10} by mapping the particle deposition in two capitals, Maputo and Kathmandu.

Version 2

Sampling of gases is simpler than sampling of particulate matter, because all molecules of a certain gas have the same properties. The properties of particles such as weight, settling velocity in air, volatility, light scattering ability etc, varies with order of magnitudes between different particles in the same air mass. Some years ago a passive particle collector in the form of a surrogate surface was optimised to sample the particle fraction that deposits to surfaces and causes corrosion. Since PM_{10} was the most common analysis method of particles, the particle deposition to the surrogate surface was correlated with PM_{10} and was proved much better than expected. By mapping the particle deposition and NO_2 concentration in Kathmandu valley using a large number of passive samplers, this method has successfully been used to evaluate dispersion model calculations of PM_{10} and NO_2 based on emissions. Since the sampling method is relatively cheep a large number of sampling sites can be used and is thus ideal for model evaluations.

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OPTIMIZING ANALYTICAL PARAMETERS FOR SOIL VAPOUR AND INDOOR AIR SAMPLES USING AUTOMATED THERMAL DESORPTION/GAS CHROMATOGRAPHY/MASS SPECTROMETRY (ATD/GC/MS)

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Efficient methods are needed for soil vapour intrusion of toxic compounds as concerns continue for the impact to human health. The sampling is performed at contaminated sites to investigate if potentially present sub-surface volatile contaminants have pathways to indoor air. Of particular concern are sites contaminated with dry cleaning and petroleum products.

Through rigorous investigation, a new sampling tube has been developed which allows for excellent recoveries of all regulated target compounds specified in methods TO-15 and TO-17. This recovery was performed in sites with high diesel and moisture content. The unregulated contaminants in the diesel were easily desorbed from the tube enabling quick turn around time for re-sampling which enhances laboratory productivity.

In addition to extending the boiling point range for target compounds greater than naphthalene, breakthrough experiments were performed to ensure that lighter compounds even the most volatile gases remained on the tube during sampling. Breakthrough experiments were performed using 6 and 10 litre sampling volumes.

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TEST AND APPLICATION OF A DIFFUSIVE SAMPLER FOR TOTAL GASEOUS MERCURY IN AIR

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A diffusive sampler for Total Gaseous Mercury (TGM) has been developed and tested both in the laboratory and in experiments at a chlor-alkali factory in Sweden as well as in ambient air at the Swedish monitoring background station, Råö. The sampler housing is made from polypropene and consists of a disk of 25 mm diameter and 12 mm thickness. Due to its low weight and small size the sampler can be used as a personal dosimeter, but can also be used for measurements at fixed indoors or outdoors places. An excellent agreement was obtained between the diffusive sampler and reference measurements performed in flow chamber experiments (relative difference ± 9 %). The reproducibility between sample pairs exposed to high mercury concentrations in the chlor-alkali factory was ± 5%. Test showed that the capacity of the sorbent is high enough for long time exposure at elevated mercury concentrations. The mercury uptake is linear as verified by linearity tests. The detection limit of the sampler is dependent on the exposure time and was found to be 0.6 µg m^{-3} at 7 h exposure time. At 30 days exposure time, the detection limit is 0.30 ng m^{-3} (calculated as 3 x standard deviation of blanks). This is much lower than the ambient background concentration of mercury
(1.5 - 1.8 ng m^{-3}).

COMPARISON BETWEEN TWO DIFFERENT ATMOSPHERIC OZONE MONITORING SYSTEMS

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A small-size ozone analyzer designed for ambient monitoring, based on a metal oxide semiconductor technology, has been developed recently. This portable instrument, supplied with batteries, could be useful in field campaigns in order to monitoring ozone concentrations for studies of air pollution and its effects on vegetation at remote sites.

For an evaluation of their effectiveness, a set of these novel sensors was run continuously at several urban and rural ozone monitoring sites in Europe, where conventional UV photometry-based automatic ozone monitors are operated.

A comparison of the data obtained with both systems was made, including a study of possible drift during the measuring period and taking into account the possible influences of several environmental parameters like air temperature and moisture. The possibility of other interferences (CO, NOx etc.) was taken in to account since data on these compounds were available at the monitoring stations.

P 50

EVALUATION OF A DIFFUSIVE SAMPLER, SKC 575-002, IN THE LABORATORY AND THE FIELD FOR MEASURING HALOGENATED ANESTHETIC COMPOUNDS

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Desflurane, sevoflurane, isoflurane, enflurane, and halothane are anesthetic gases used on a daily basis in operating theaters. Active sampling has been used to control the level of exposure to personnel. We have validated a diffusive passive sampler (SKC 575-002) filled with Anasorb 747, in both laboratory and field experiments. Parameters tested were desorption efficiency, concentration, sampling time, relative humidity, and back diffusion, as well as storage stability for up to 8 weeks. Uptake rates were achieved by comparison with an active sampling for each passive sampling trial of 1, 4, or 8 hours. In the laboratory experiments, no problems were found with storage stability or back diffusion. Our estimated values on uptake rate were on average lower than the theoretically determined values recommended by SKC Inc. Our results for enflurane, sevoflurane, and desflurane were around 10% below expected values, whereas for isoflurane and halothane our results were 15% and 20% below the theoretically determined values, respectively. When performing whole-day workplace measurements (TWA measurements) the SKC 575-002 can be recommended, and at levels around 1 ppm the following uptake rates should be used: enflurane and halothane, 12.3; desflurane, 13.6; isoflurane, 12.0; and sevoflurane, 11.9 mL min^{-1}.

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MEASURING INDOOR AIR CONCENTRATIONS OF POLYFLUORINATED COMPOUNDS WITH PASSIVE SAMPLERS

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Polyfluorinated compounds (PFC) have recently gained a lot of attention in the scientific community, as they represent a modern type of anthropogenic pollutants. Some of them are persistent, bioaccumulative and toxic. These compounds have been increasingly investigated towards their sources and chemical behaviour. Most investigated representatives are PFOA (Perfluorooctanoic Acid) and PFOS (Perfluorooctane Sulfonate). However, it is yet unknown where their precursors are originating from.

In this study we determined indoor air contaminations of fifteen polyfluorinated compounds (3 fluorotelomer acrylates, 5 fluorotelomer alcohols, 4 polyfluorinated sulfonamides, 3 polyfluorinated sulfonamido ethanols) who can be seen as precursors of above mentioned substances.

Contaminations have been determined applying a passive sampling method developed by Shoeib et al. (2008). Analytes were accumulated on polyurethane foam disks which were impregnated with XAD4- resin to improve sorptive capacities. The sampling media was placed in a protective steel housing. Passive samplers were deployed in buildings representing potential PFC air contaminations such as carpeting shops or outdoor suppliers and several random residential houses. Samples were extracted with fluidized bed extraction (FBE) and measured with GC/MS (PCI mode).

For this study we choose passive samplers to be the ideal sampling medium because they do not consume any energy or make any noise, they are small, easy to handle, comparably cheap and appropriate for long-term deployment.

Indoor air contaminations ranged from 42 pg m^{-3} to 208.000 pg $m^{-3}$and will be presented on the poster.

[1]Shoeib, M., T. Harner, et al. (2008). "Sorbent-impregnated polyurethane foam disk for passive air sampling of volatile fluorinated chemicals." Analytical Chemistry **80**(3): 675-682.

P52

TIME-OF-FLIGHT MASS SPECTROMETRY – DEVELOPMENTS IN TECHNOLOGY AND ITS SUITABILITY FOR AIR MONITORING APPLICATIONS

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Time-of-flight (TOF) mass spectrometry is one of the simplest yet most powerful approaches for MS identification of unknowns in a sample which, with recent advances in electronic technology and data processing, has come to be recognised as a valuable tool in trace-level analysis.

The nature of the TOF approach means that, unlike traditional quadrupole technology, there is no loss of ion signal due to analyser mass filtering. This fundamental advantage yields dramatic sensitivity improvements in trace-level applications, such as ambient air monitoring. Consequently, with no requirement to perform selected ion monitoring (SIM) on target compounds, it becomes possible to maintain SIM-level sensitivity whilst still recording full spectral information throughout the analysis. For air monitoring applications, this ensures no compromise in sensitivity for target species, and adds the latent capability for concurrent or subsequent detailed characterisation of unknown components within a sample. Another advantage of the TOF is its high spectral acquisition rate, rendering supreme quantitative precision and compatibility with emergent rapid-chromatographic techniques.

An overview of a novel TOF MS system will be presented, with discussion of the key features associated with the time-of-flight approach that enhance sensitivity and analytical speed for ambient air monitoring.

PASSIVE DIFFUSIVE SAMPLING OF AMMONIA IN DUTCH NATURE AREAS

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Since 2005 air concentrations of ammonia are being monitored in Dutch nature areas. The Measuring Ammonia in Nature areas network (MAN) consists of 29 areas in which monthly mean concentrations are measured using passive diffusive samplers.

The MAN network has been set up to obtain insight in the spatial and temporal behavior of ammonia concentrations in Dutch nature areas. The results are further used to assess the quality of model computations of ammonia concentrations in nature areas. Obtaining concentrations is necessary in order to assess the impact of ammonia deposition on nature areas, being one of the major contributors to the eutrophication of vegetation and soil in the Netherlands.

For validation of the MAN data set concentrations are measured in triplicate at five sites of the Dutch Air Quality Network. At these sites concentrations are also hourly measured by a reference instrument named Ammonia Monitor RIVM (AMOR). Monthly correction functions for the MAN data have been derived on basis of these reference measurements.

Analyses show that, although individual sampler values need to be considered with care, longer term averages are a valuable tool in assessing the load of ammonia on Dutch Natura 2000 areas.

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AIR POLLUTION AS A SMALL SCALE PARAMETER

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Besides economic, the ecological quality of life plays a more and more important role. This becomes apparent by an increasing consumption of organic products, reinforced non-smoker protection, and an increasing general health awareness.

Each individual can decide mostly on it's own how it is living, where it stays and what it is eating and drinking. While quality of food and water can be monitored fairly well, breathable air can barely be affected.

Who of us actually did not think about the air being currently emitted from an exhaust pipe, the cloud of solvents or the current dust exposure caused by a building site as being harmful to our health?

Preferably, air quality monitoring should indicate the exposure of the population to pollutants. Health protection is the actual task of monitoring.

This task can only be fulfilled sufficiently if the exposure to pollutants is known at the respective whereabouts of the population. For this purpose, monitoring has to be done particularly in urban areas with high areal density and on spots with high pollutant concentrations caused by local sources. Air quality is not only a regional but a dynamic and local parameter as well.

DIFFUSIVE SAMPLERS – A TOOL FOR AMBIENT OZONE PHYTOTOXIC POTENTIAL ASSESSMENT IN MOUNTAIN FORESTS

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Contribution collates our results and experience based on several years lasting application of diffusive samplers for ambient ozone measurements in Czech rural forested areas distant from man-made emission sources. We use the commercial diffusive samplers Ogawa. The measurement is based on oxidation of nitritates to nitrates by ambient ozone; the nitrates after the exposure are analyzed by ion chromatography in the CHMI laboratory. Based on nitrate mass, the mean ambient ozone concentration involved in the chemical reaction is calculated. For ambient ozone concentration calculation we use the empirical uptake rate established from collocated measurements of a diffusive sampler and a real-time UV-absorbance monitor. Our results indicate the high precision and accuracy of the measurement.

Results from relatively low-cost diffusive samplers enable us to model the ambient ozone concentration and AOT40 exposure index surface in much higher resolution as compared to the current nation-wide real-time monitoring network. This is well documented by the presented concentration and exposure maps. A combination of measurement by diffusive samplers and a potential offered by the geographic information systems, provide an effective tool for further study of ambient air pollutant spatial and time variability and its impact on vegetation and ecosystems.