



New Techniques and Standardisation for Monitoring Ambient Air Pollutants




Diffusive Sampling What's New ?

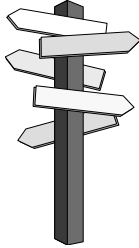
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NMI van Swinden Laboratory
NL – DELFT



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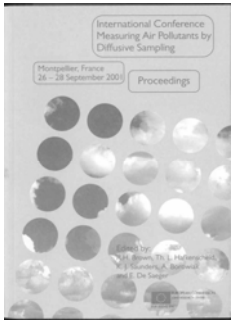
Roadmap of presentation



- ▶ Introduction
 - ▶ *Reference point*
- ▶ Overview of activities since then
 - ▶ *Standardization*
 - ▶ *Literature survey*
 - ▶ *'Hot' topics*
- ▶ Collaborative studies
- ▶ Conclusions
 - ▶ *The way forward ?*


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Do you remember ?


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Do you remember ?


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Conclusions of 2001 Conference

- ▶ Popular methodology because of ease-of-use, low costs, unobtrusiveness
- ▶ Shift from development to application
- ▶ Shift from workplace applications to (largely) ambient air applications
- ▶ Lack in harmonization, particularly of QA/QC, validation, measurement uncertainty

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What happened since ?



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Standardization




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CEN

- ▶ **EN 13528: Ambient air quality – Diffusive samplers for the determination of gases and vapours**
 - ▶ Part 1: Requirements and test methods - General requirements (2002)
 - ▶ Part 2: Requirements and test methods - Specific requirements and test methods (2002)
 - ▶ Part 3: Guide to selection, use and maintenance (2003)
- ▶ **EN 14412: Indoor air quality – Diffusive samplers for the determination of gases and vapours - Guide for selection, use and maintenance (2004)**


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CEN

- ▶ **EN 14662: Ambient air quality - Standard method for the measurement of benzene concentrations**
 - ▶ Part 4 – Diffusive sampling followed by thermal desorption and gas chromatography (2005)
 - ▶ Part 5 – Diffusive sampling followed by solvent desorption and gas chromatography (2005)


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ISO


- ▶ **ISO 16017-2: Indoor, ambient and workplace air – Sampling and analysis of VOC by sorbent tube/ thermal desorption/ capillary gas chromatography/ diffusive sampling (2003)**
- ▶ **ISO 16000-4: Indoor air – Determination of formaldehyde - Diffusive sampling method (2004)**

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And ?

- ▶ Literature survey 2002-now
- ▶ Peer-reviewed literature
- ▶ Key words:
 - ▶ diffusive/passive sampler/sampling
- ▶ By no means exhaustive
- ▶ Categorized
 - ▶ Applications
 - ▶ R&D, validation



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Summary

- ▶ **Main application: ambient air (60%)**
- ▶ **Main compounds:**
 - ▶ **Nitrogen dioxide – ambient / indoor / exposure (25%)** (mainly Palmes tubes)
 - ▶ **Benzene / BTX – ambient / indoor / exposure (16%)** (both badges and thermal desorption devices)
 - ▶ **SVOC (12%)** (sampling by SPMD)
 - ▶ **Ozone - vegetation (10%)** (mainly Palmes tubes)
 - ▶ **VOC (10%)** (both badges and thermal desorption devices)
 - ▶ **Ammonia – agriculture (9%)** (mainly Palmes tubes)

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SPMD Samplers

- ▶ Semi-Permeable Membrane Devices
 - ▶ e.g. LD-PE/triolein tubes
- ▶ Compounds like PCB, PAH, pesticides

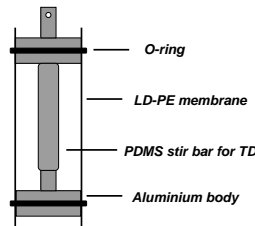
Q: Are these devices diffusive samplers ?
A: Depending on design the mechanism for sampling may be

- ▶ Diffusion
- ▶ Permeation
- ▶ Adsorption

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SPMD Samplers



O-ring
 LD-PE membrane
 PDMS stir bar for TD
 Aluminium body

**Paschke & Popp
 Chemosphere 58
 (2005) 855-863**

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Observations

- ▶ Most activities are individual, only few 'collaborative' efforts (3)
- ▶ Independent developments of samplers for gases/volatiles and SVOC
- ▶ Some consolidated harmonization efforts
 - ▶ CEN TC 264 WG 11
 - ▶ JRC – IES – ERLAP

→ Information about performance of samplers and comparability of sampling results

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Consolidated efforts

- ▶ CEN TC 264 WG 11: 2002
 - ▶ Nitrogen dioxide, ozone, sulphur dioxide
 - ▶ Comparison of 6 sampler types at urban and background sites (2 weeks)
- ▶ JRC-IES ERLAP: 2003
 - ▶ Comparison of 13 samplers: 6 sampler-types + modifications (2 weeks)
 - ▶ In laboratory under conditions of *high* and *low* {concentration + temperature + relative humidity}
 - ▶ At urban and background sites

→ EUR Report 20860

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Consolidated efforts

- ▶ JRC-IES ERLAP: 2005
 - ▶ Ozone
 - ▶ Comparison of 10 samplers: 6 sampler-types + modifications (1 week; 8 hours)
 - ▶ In laboratory under extreme conditions of {concentration + temperature + relative humidity}
 - ▶ At urban and rural sites

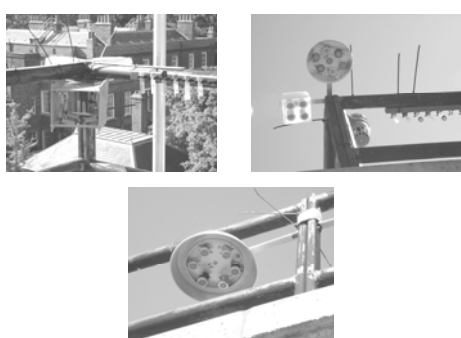
→ EUR Report 21754

→ <ftp://ftp.ei.jrc.it/pub/erlap/ERLAPDownload.htm>

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WG 11



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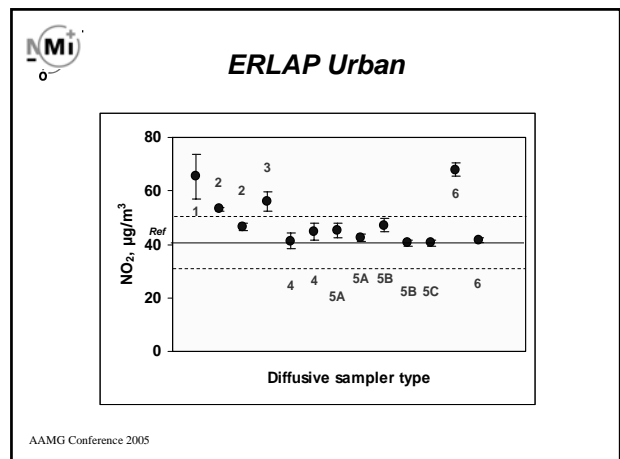
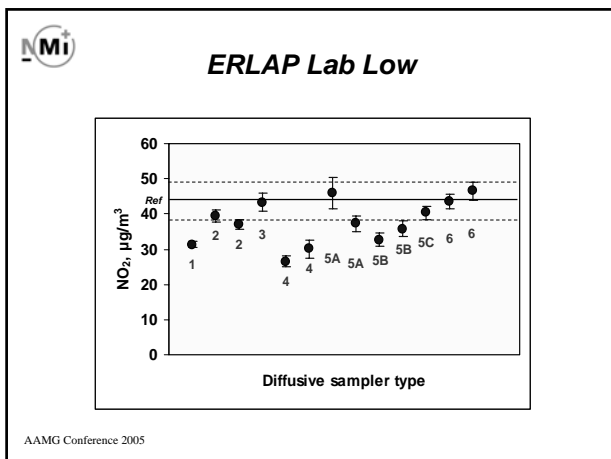
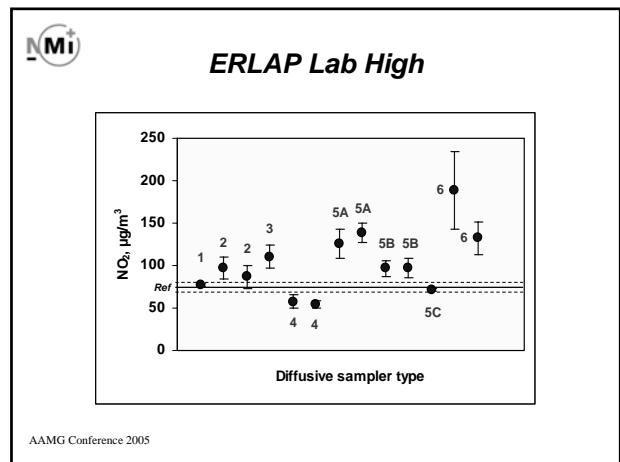
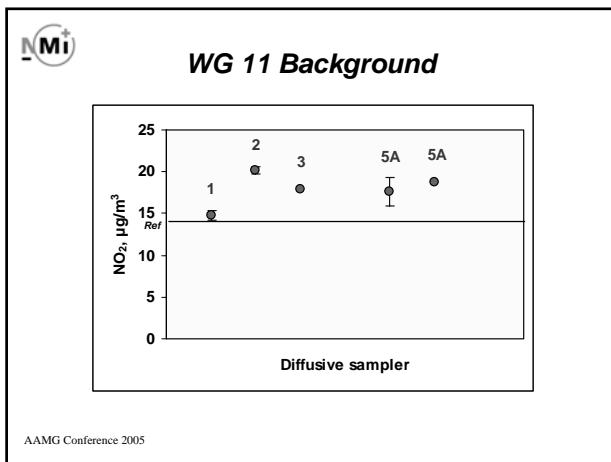
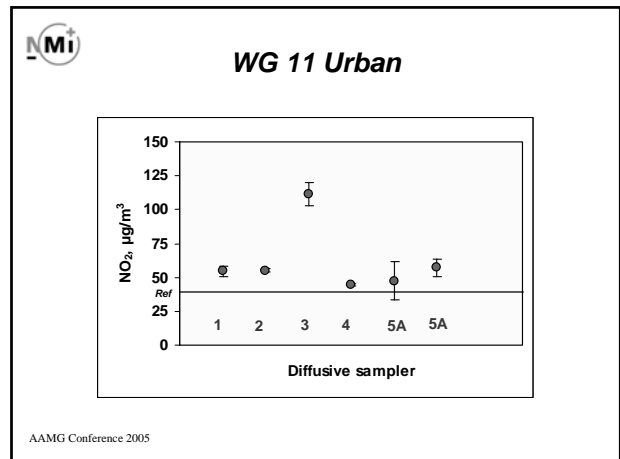
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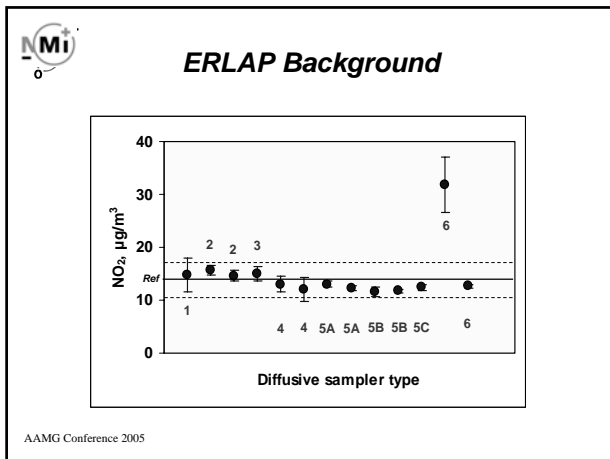


Results NO₂

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Correspondence with reference value

	Lab high	Lab low	Urban	Background
Type 1	+			+
Type 2		+		+
Type 2	+		+	+
Type 3		+		+
Type 4			+	+
Type 4			+	+
Type 5A		+	+	+
Type 5A			+	+
Type 5B			+	+
Type 5B		+	+	+
Type 5C	+	+	+	+
Type 6		+		
Type 6		+	+	+

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Expanded uncertainty

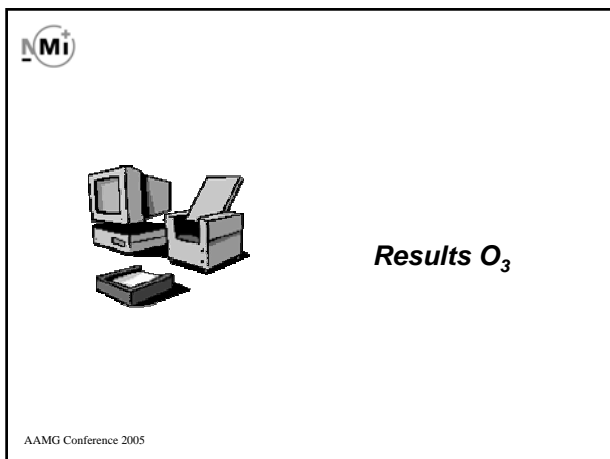
	Lab high	Lab low	Urban	Background
Type 1	3%	78%	75%	31%
Type 2	46%	21%	43%	21%
Type 2	31%	35%	22%	12%
Type 3	63%	8%	52%	17%
Type 5A-1	80%	17%	18%	17%
Type 5B-2	45%	44%	7%	40%
Type 5C	15%	17%	7%	27%
Type 6	123%	6%	78%	113%
Type 6	86%	15%	3%	23%

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ISO 5725 Analysis

RSD (%)	WG 11		ERLAP			
	Urban	Back-ground	Lab high	Lab low	Urban	Back-ground
Repeatability	13%	5%	16%	6%	6%	10%
Between-sampler/ laboratory	9%	11%	35%	17%	19%	10%
Reproducibility	16%	12%	39%	18%	20%	14%
Bias mean-of-means from ref. value	27%	29%	34%	-13%	17%	4%

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Correspondence with reference value

	Lab high	Lab low	Urban	Rural
Type 1	+	+	+	+
Type 2		+		+
Type 2			+	
Type 3				+
Type 4				+
Type 4				+
Type 5C	+		+	+
Type 5C				
Type 6	+		+	+
Type 6	+	+		

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Expanded uncertainty

	Lab high	Lab low	Urban	Rural
Type 1	9%	19%	14%	12%
Type 2	72%	28%	186%	20%
Type 5C	25%	128%	23%	20%
Type 6	6%	88%	6%	25%
Type 6	18%	19%	67%	37%

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ISO 5725 Analysis

RSD (%)	WG 11		ERLAP			
	Urban	Back-ground	Lab high	Lab low	Urban	Rural
Repeatability	13%	8%	11%	9%	5%	7%
Between-sampler/ laboratory	38%	18%	32%	35%	23%	12%
Reproducibility	43%	20%	34%	36%	24%	14%
Bias mean-of-means from ref. value	5%	5%	5%	-10%	-7%	5%

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- ## Conclusions
- ▶ Only few samplers show good overall performance
 - ▶ Comparability of different samplers is moderate to good
 - ▶ Performances of samplers have improved as trials progressed
 - ▶ Definite need for organizing independent comparisons
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- ## The way forward ?
- ▶ Optimization of performances requires
 - ▶ Setting minimum performance requirements for individual uncertainty sources, e.g.
 - ▶ Uptake rates
 - ▶ Stability
 - ▶ Analytical recovery
 - ▶ Blank development and variations
 - ▶ Analysis of Certified Reference Materials
 - ▶ Organizing independent inter-sampler (laboratory) comparisons
 - ▶ Working in accordance with EN-ISO 17025 ?
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- ## Overall conclusions
- ▶ Diffusive sampling has further matured
 - ▶ Standardization efforts
 - ▶ Many applications in air quality measurements
 - ▶ Ammonia, nitrogen dioxide, ozone, (S)VOC
 - ▶ Few new developments
 - ▶ SPMD (?)
 - ▶ Collaborative studies show need for further optimization of sampler performances
- AAMG Conference 2004

