



AirMonTech



New Technologies, New Metrics and Proxies

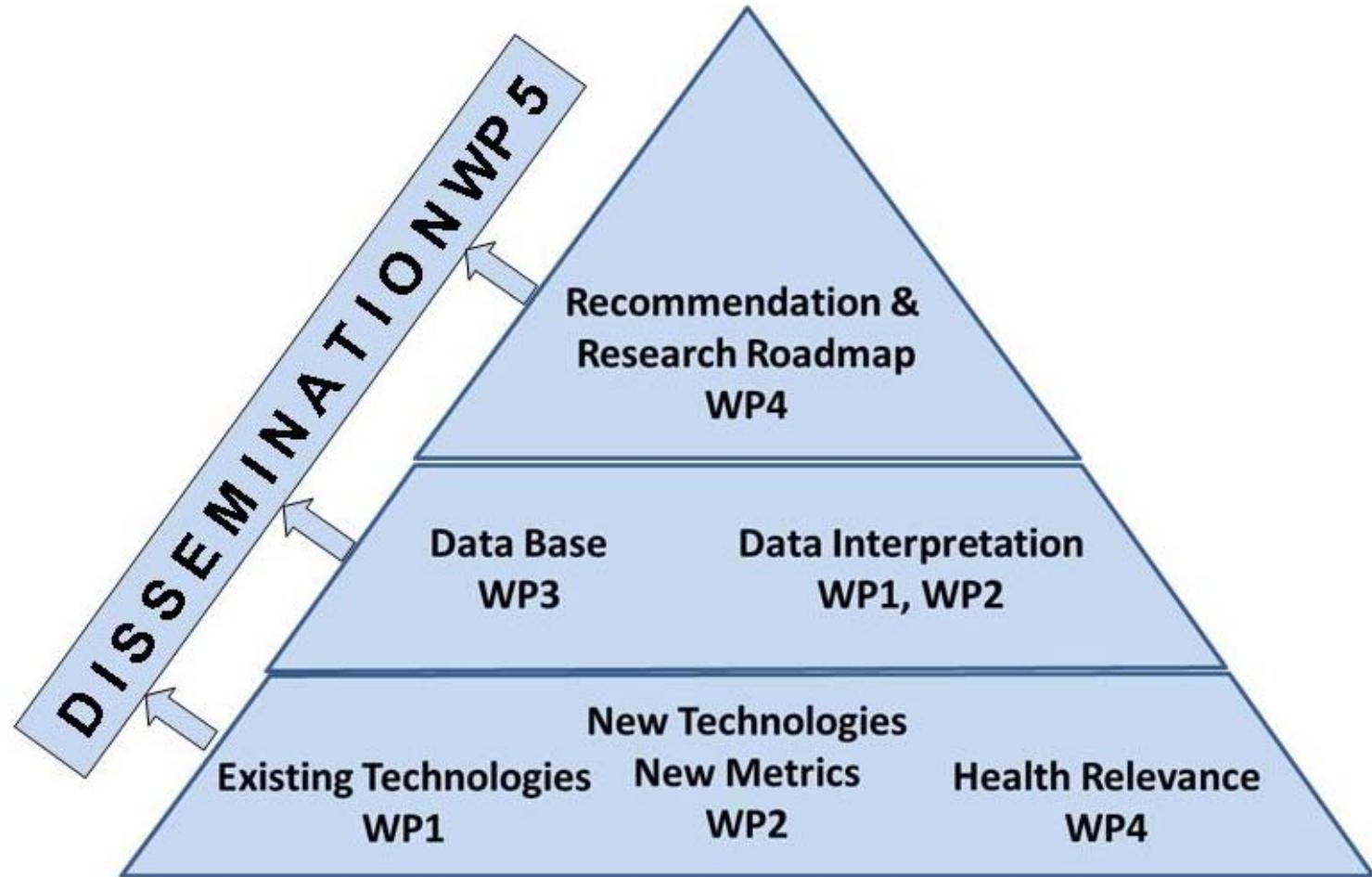
U. Quass, T.A.J. Kuhlbusch
and AirMonTech Consortium

AAMG Conference 2011

12./13.12.2011

www.airmontech.eu

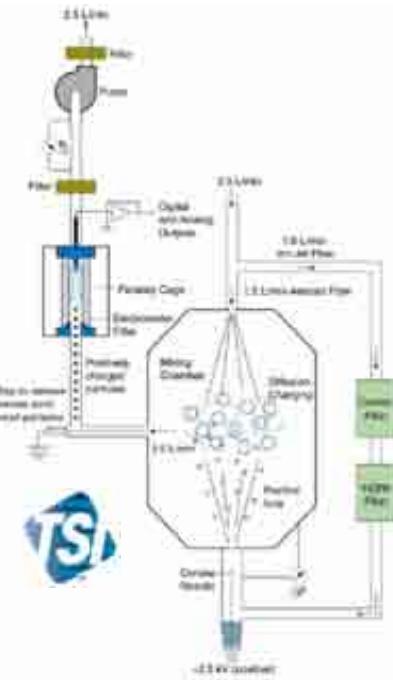
Project structure



NEW TECHNOLOGIES – NEW METRICS & PROXIES

Two-sided approach:

- Science based reviews of metrics, detection principles and instrument performance
- Collection of manufacturer's and developer's information



Fissan et al.(2006), J. Nanop. Res.9: 53-59;
Shin et al.(2006), J. Nanop. Res.9: 61-69

- 3 files to be produced for each pollutant/metric:
 - Metric Basic Information (MBI)
 - Definitions, sources (briefly), health relevance, regulations, standard methods, references
 - Metric Measurement Technology Overview (MMTO)
 - Table listing all identified monitoring methods, typical operational characteristics, applicability to remote/rural/urban site monitoring.
 - Metric Measurement Technology Information (MMTI)
 - More detailed description for each methodology listed in the MMTO document

Example for MBI-File

Pollutant Type: [Gaseous Pollutants](#)

Pollutant Name: [Nitrogen Dioxide \(NO₂\)](#)

Regulation Number: 1

Description of the pollutant:

NO₂ is an important species of pollutants in the air due to its health effects on human health and the environment. NO₂ has an important role in the formation of tropospheric ozone (O₃) and it is a precursor of particulate matter (PM_{2.5}) which contributes to atmospheric fine particulate matter (PM_{2.5}) in urban environments. Concentrations of NO₂ are often used as an indicator of traffic density.

Definition, sources

The most important sources of NO₂ are thermal combustion (fossil fuel combustion) and vehicle emissions. NO₂ is also emitted from industrial processes such as oil and gas extraction, coal combustion, cement production, and biomass burning.

Concentrations of NO₂ are usually measured using the reference method of NO₂ measurements is performed with reference to standard pressure of 101.3 hPa and standard temperature of 293.15 K.

Health effects:

NO₂ has been reported through various epidemiological studies. These studies have shown significant associations between NO₂ exposure and respiratory diseases such as asthma and bronchitis, as well as cardiovascular diseases such as stroke and heart disease. NO₂ has also been linked to increased mortality rates, particularly in children and the elderly.

Regulations:

NO₂ is a key pollutant under the EU Air Quality Directive (Directive 2008/50/EC). The limit value for NO₂ is 40 µg/m³ over 8 hours. The EU Air Quality Directive also sets a target value of 20 µg/m³ over 8 hours by 2010.

Pollutant Type: [Gaseous Pollutants](#)

Pollutant Name: [Nitrogen Dioxide \(NO₂\)](#)

Regulation Number: 1

Description of the pollutant:

In recent years, there is a growing concern about NO₂ levels in our environment due to its effects on human health and the environment. NO₂ can cause both acute and chronic health effects, such as respiratory problems and heart disease. There is also evidence that NO₂ can contribute to the formation of PM_{2.5}, which is a major source of fine particulate matter. Studies have shown that NO₂ can affect the respiratory system, leading to changes in lung function and decreased lung capacity. NO₂ can also contribute to the formation of acid rain, which can damage buildings and infrastructure. NO₂ is also associated with increased risk of stroke and heart disease. NO₂ is a key pollutant under the EU Air Quality Directive (Directive 2008/50/EC).

Definition, sources

The most important sources of NO₂ are thermal combustion (fossil fuel combustion) and vehicle emissions. NO₂ is also emitted from industrial processes such as oil and gas extraction, cement production, and biomass burning.

Concentrations of NO₂ are usually measured using the reference method of NO₂ measurements is performed with reference to standard pressure of 101.3 hPa and standard temperature of 293.15 K.

Overview Tox and Epi Studies

Reference	Author(s)	Year	Exposure	Outcome
WHO (2005)	World Health Organization	2005	Exposure to NO ₂ in residential areas	Mortality - NO ₂ 10-40 µg/m ³
Wang et al. (2010)	Wang et al.	2010	Exposure to NO ₂ in residential areas	Mortality - NO ₂ 10-40 µg/m ³
Han et al. (2011)	Han et al.	2011	Exposure to NO ₂ in residential areas	Mortality - NO ₂ 10-40 µg/m ³
WHO (2012)	World Health Organization	2012	Exposure to NO ₂ in residential areas	Mortality - NO ₂ 10-40 µg/m ³
WHO (2013)	World Health Organization	2013	Exposure to NO ₂ in residential areas	Mortality - NO ₂ 10-40 µg/m ³
WHO (2014)	World Health Organization	2014	Exposure to NO ₂ in residential areas	Mortality - NO ₂ 10-40 µg/m ³
WHO (2015)	World Health Organization	2015	Exposure to NO ₂ in residential areas	Mortality - NO ₂ 10-40 µg/m ³
WHO (2016)	World Health Organization	2016	Exposure to NO ₂ in residential areas	Mortality - NO ₂ 10-40 µg/m ³
WHO (2017)	World Health Organization	2017	Exposure to NO ₂ in residential areas	Mortality - NO ₂ 10-40 µg/m ³
WHO (2018)	World Health Organization	2018	Exposure to NO ₂ in residential areas	Mortality - NO ₂ 10-40 µg/m ³
WHO (2019)	World Health Organization	2019	Exposure to NO ₂ in residential areas	Mortality - NO ₂ 10-40 µg/m ³
WHO (2020)	World Health Organization	2020	Exposure to NO ₂ in residential areas	Mortality - NO ₂ 10-40 µg/m ³
WHO (2021)	World Health Organization	2021	Exposure to NO ₂ in residential areas	Mortality - NO ₂ 10-40 µg/m ³
WHO (2022)	World Health Organization	2022	Exposure to NO ₂ in residential areas	Mortality - NO ₂ 10-40 µg/m ³
WHO (2023)	World Health Organization	2023	Exposure to NO ₂ in residential areas	Mortality - NO ₂ 10-40 µg/m ³
WHO (2024)	World Health Organization	2024	Exposure to NO ₂ in residential areas	Mortality - NO ₂ 10-40 µg/m ³
WHO (2025)	World Health Organization	2025	Exposure to NO ₂ in residential areas	Mortality - NO ₂ 10-40 µg/m ³
WHO (2026)	World Health Organization	2026	Exposure to NO ₂ in residential areas	Mortality - NO ₂ 10-40 µg/m ³
WHO (2027)	World Health Organization	2027	Exposure to NO ₂ in residential areas	Mortality - NO ₂ 10-40 µg/m ³
WHO (2028)	World Health Organization	2028	Exposure to NO ₂ in residential areas	Mortality - NO ₂ 10-40 µg/m ³
WHO (2029)	World Health Organization	2029	Exposure to NO ₂ in residential areas	Mortality - NO ₂ 10-40 µg/m ³
WHO (2030)	World Health Organization	2030	Exposure to NO ₂ in residential areas	Mortality - NO ₂ 10-40 µg/m ³
WHO (2031)	World Health Organization	2031	Exposure to NO ₂ in residential areas	Mortality - NO ₂ 10-40 µg/m ³
WHO (2032)	World Health Organization	2032	Exposure to NO ₂ in residential areas	Mortality - NO ₂ 10-40 µg/m ³
WHO (2033)	World Health Organization	2033	Exposure to NO ₂ in residential areas	Mortality - NO ₂ 10-40 µg/m ³
WHO (2034)	World Health Organization	2034	Exposure to NO ₂ in residential areas	Mortality - NO ₂ 10-40 µg/m ³
WHO (2035)	World Health Organization	2035	Exposure to NO ₂ in residential areas	Mortality - NO ₂ 10-40 µg/m ³
WHO (2036)	World Health Organization	2036	Exposure to NO ₂ in residential areas	Mortality - NO ₂ 10-40 µg/m ³
WHO (2037)	World Health Organization	2037	Exposure to NO ₂ in residential areas	Mortality - NO ₂ 10-40 µg/m ³
WHO (2038)	World Health Organization	2038	Exposure to NO ₂ in residential areas	Mortality - NO ₂ 10-40 µg/m ³
WHO (2039)	World Health Organization	2039	Exposure to NO ₂ in residential areas	Mortality - NO ₂ 10-40 µg/m ³
WHO (2040)	World Health Organization	2040	Exposure to NO ₂ in residential areas	Mortality - NO ₂ 10-40 µg/m ³
WHO (2041)	World Health Organization	2041	Exposure to NO ₂ in residential areas	Mortality - NO ₂ 10-40 µg/m ³
WHO (2042)	World Health Organization	2042	Exposure to NO ₂ in residential areas	Mortality - NO ₂ 10-40 µg/m ³
WHO (2043)	World Health Organization	2043	Exposure to NO ₂ in residential areas	Mortality - NO ₂ 10-40 µg/m ³
WHO (2044)	World Health Organization	2044	Exposure to NO ₂ in residential areas	Mortality - NO ₂ 10-40 µg/m ³
WHO (2045)	World Health Organization	2045	Exposure to NO ₂ in residential areas	Mortality - NO ₂ 10-40 µg/m ³
WHO (2046)	World Health Organization	2046	Exposure to NO ₂ in residential areas	Mortality - NO ₂ 10-40 µg/m ³
WHO (2047)	World Health Organization	2047	Exposure to NO ₂ in residential areas	Mortality - NO ₂ 10-40 µg/m ³
WHO (2048)	World Health Organization	2048	Exposure to NO ₂ in residential areas	Mortality - NO ₂ 10-40 µg/m ³
WHO (2049)	World Health Organization	2049	Exposure to NO ₂ in residential areas	Mortality - NO ₂ 10-40 µg/m ³
WHO (2050)	World Health Organization	2050	Exposure to NO ₂ in residential areas	Mortality - NO ₂ 10-40 µg/m ³

Regulations

Regulation	Method	Limit Value
EU Air Quality Directive (2008/50/EC)	UV-Fluorescence	40 µg/m ³
WHO (2005)	UV-Fluorescence	40 µg/m ³
WHO (2010)	UV-Fluorescence	40 µg/m ³
WHO (2015)	UV-Fluorescence	40 µg/m ³
WHO (2020)	UV-Fluorescence	40 µg/m ³
WHO (2025)	UV-Fluorescence	40 µg/m ³
WHO (2030)	UV-Fluorescence	40 µg/m ³
WHO (2035)	UV-Fluorescence	40 µg/m ³
WHO (2040)	UV-Fluorescence	40 µg/m ³
WHO (2045)	UV-Fluorescence	40 µg/m ³
WHO (2050)	UV-Fluorescence	40 µg/m ³

Reference method (if applicable)

UV-Fluorescence

Quoted publications

- WHO (2005), *World Health Organization*, *UV-Fluorescence*, *40 µg/m³*
- WHO (2010), *World Health Organization*, *UV-Fluorescence*, *40 µg/m³*
- WHO (2015), *World Health Organization*, *UV-Fluorescence*, *40 µg/m³*
- WHO (2020), *World Health Organization*, *UV-Fluorescence*, *40 µg/m³*
- WHO (2025), *World Health Organization*, *UV-Fluorescence*, *40 µg/m³*
- WHO (2030), *World Health Organization*, *UV-Fluorescence*, *40 µg/m³*
- WHO (2035), *World Health Organization*, *UV-Fluorescence*, *40 µg/m³*
- WHO (2040), *World Health Organization*, *UV-Fluorescence*, *40 µg/m³*
- WHO (2045), *World Health Organization*, *UV-Fluorescence*, *40 µg/m³*
- WHO (2050), *World Health Organization*, *UV-Fluorescence*, *40 µg/m³*

Example for MMTO

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Overview of Measurement Technologies for Air Pollutants and Air Quality Metrics

Pollutant Type: Particulate Matter
Pollutant/Metric Name: Heavy Metals

Automated monitors for elemental composition of ambient particles have been developed only recently; the only commercial instrument available is based on X-ray fluorescence thus adopting one of the reference methodologies. Laser-based methods still are in research applications but are very promising in view of future applications for urban-air quality monitoring.

#	Technology	Characteristics and Performance	Availability and current use of instruments	Suggested area of application
1	X-ray fluorescence spectroscopy (XRF)	<ul style="list-style-type: none"> - Stand-alone field instrument - Quasi-continuous method (Filter tape exposed for predefined periods) - Time resolution between 15 minutes and 4 hours - 23 elements implemented - Minimum Detection limit at 4 hours sampling in lower pg/m³ range for most elements 	Commercial Explorative field tests in the US, China and New Zealand	Rural Urban Industrial
2	Laser-induced breakdown spectroscopy (LIBS)	<ul style="list-style-type: none"> - Uses laser generated plasma for atomic emission measurement - Near real time measurements possible - Detection limits in lower ng/m³ range have been demonstrated - Improvement for ultra fine particles by use of aerodynamic lens inlets and pre-concentration on a target 	Research instruments only	(Rural) Urban Polluted
3	Spark-induced breakdown spectroscopy (SIBS)	<ul style="list-style-type: none"> - Similar to method 2, but electric spark for plasma generation - Spark generation simpler and cheaper - Detection limits still too high for ambient air - Application for bio-aerosol detection possible 	Research instruments only	Emission (stacks)

Example for MMTI

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Air Pollution Monitoring Technologies
for Urban Areas

Description-of-Automated-Technologies-for-Air-Pollutants-and-Air-Quality-Metrics¶

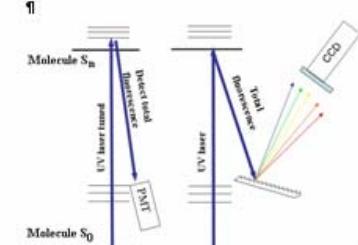
- Pollutant-Type: → → → Particulate-Pollutants¶
- Pollutant-Name: → → → Primary-Biogenic-Aerosol-Particles-(PBAP)¶

Measurement-Technology: → Laser-induced-fluorescence-(LIF)¶

A large variety of laser-base automated monitors for biogenic particles have been developed in recent years, motivated by anti-terrorism activities (focusing on bacteria and spores), public health concerns (pollen prediction) and atmospheric research (e.g. global aerosol budgets to assess the climatic impacts). While many instruments have research or prototype character a few have already have been marketed.¶

The basic approach used to detect and discriminate biogenic aerosols is laser-induced fluorescence (LIF)-spectrometry. In addition laser light-scattering [Ryan et al. 2009; Gabey 2010] measurements may be used to increase the instrument's capability to discriminate biogenic from other particles or hazardous from non-hazardous agents. Laser-based detectors may also be combined with other aerosol measurement devices, as e.g., the aerodynamic particle sizer (APS, [Huffman et. Al 2010]), or even with laser-induced breakdown spectroscopy (LIBS, [Beddows and Telle, 2005]).¶

The general principle of LIF-measurement is shown in figure 1 for detection of total fluorescence (left scheme) and spectrally resolved fluorescence (right scheme).¶



(graphics taken from <http://www.chem.psu.edu/~zwier/uv.html>)¶

Biogenic particles contain substances, e.g. fluorescent amino acids (tryptophan, tyrosin and phenylalanin), NADH, NAD(P)H and flavin compounds, which on excitation-UV-light can emit characteristic fluorescence-radiation. Typical UV-wavelength ranges for excitation/emission are 280/350 nm, 340/450 and 450/520 nm, respectively. Also chlorophyll-a (among other fluorophors) may be used with excitation at 400-460 nm and emission maxima at 670 nm and 720 nm.¶

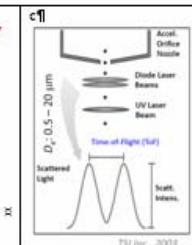
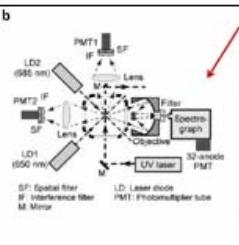
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Description-of-Automated-Technologies-for-Air-Pollutants-and-Air-Quality-Metrics¶

Technical sketches of three LIF-instruments for bioaerosol-detection¶

a) Wide-Field Bioaerosol Sensor-WIBS-3 [Gabey 2011]; b) Instrument used by Pan et al. 2011; c) UV-APS-(TSI Inc.)¶



References¶

- Beddows, D.C.S., Telle, H.H. (2005): Prospects of real-time single-particle biological aerosol analysis: A comparison between laser-induced-breakdown-spectroscopy and aerosol-time-of-flight-mass-spectrometry. *Spectrochimica Acta Part B 60*, 1040–1059.¶
- Huffman, J.-A., Tsigas, B., and Dichtl, U. (2010): Fluorescent biological aerosol particle concentrations and size distributions measured with an Ultraviolet Aerodynamic Particle Sizer (UV-APS) in Central Europe. *Atmos. Chem. Phys.*, 10, 9215–9233.¶
- Ryan, D., Greaney, R., Jennings, S., G. Dowd, C.D. (2009): Description of a biofluorescence-optical-particle-counter. *Journal of Quantitative Spectroscopy & Radiative Transfer* 110 (2009), 1730–1734.¶
- Gabey, A.-M., Gallagher, M.W., Whitehead, J., Dorsey, J. R., Kaye, P. H., and Stanley, W. R. (2009): Measurements and comparison of primary biological aerosol above and below a tropical forest canopy using a dual channel fluorescence spectrometer. *Atmos. Chem. Phys. Discuss.*, 9, 18965–18984, 2009.¶
- Gabey, A.-M., Gallagher, M.W., and Kaye, P. H. (2011): The fluorescence properties of aerosol larger than 0.8 µm in urban and tropical rainforest locations. *Atmos. Chem. Phys.*, 11, 5491–5504, 2011.¶
- Pan, Y.-L., Hill, S. C., Finnigan, R. G., House, J. M., Egan, R. C., Chang, R. K. (2011): Dual-excitation-wavelength fluorescence spectra and elastic scattering for differentiation of single airborne pollen and fungal particles. *Atmospheric Environment* 45 (2011) 1555e1563.¶
- CAS-Center for Atmospheric Science, University of Manchester, UK, ¶
- <http://www.cos.manchester.ac.uk/restools/instruments/aerosol/wibs/>¶

Author(s):	Ulrich Quast	iuta, Germany
Co-author(s):		
Last revision:	28.09.2011	

Pollutants, Metrics

Current State of work on MBI files (07.12.2011):

Particulate Matter

Total Number concentration	
number size distribution	
surface concentration	
shape, morphology	
mass concentration	
Heavy metals	
Sulfate	
Nitrate	
Ammonium	
elemental carbon	
organic carbon	
light absorbing aerosols	
reactive oxygen species	
macrophage mobility decrease	
Polycyclic aromatic hydrocarbons	
Primary biological aerosol particles	

Gaseous pollutants

NO	
NO ₂	
NOx	
SO ₂	
O ₃	
NH ₃	
VOCs	
HCl	
HNO ₃	
HNO ₂	
	not yet available
	partly ready
	pre-Final draft
	final draft

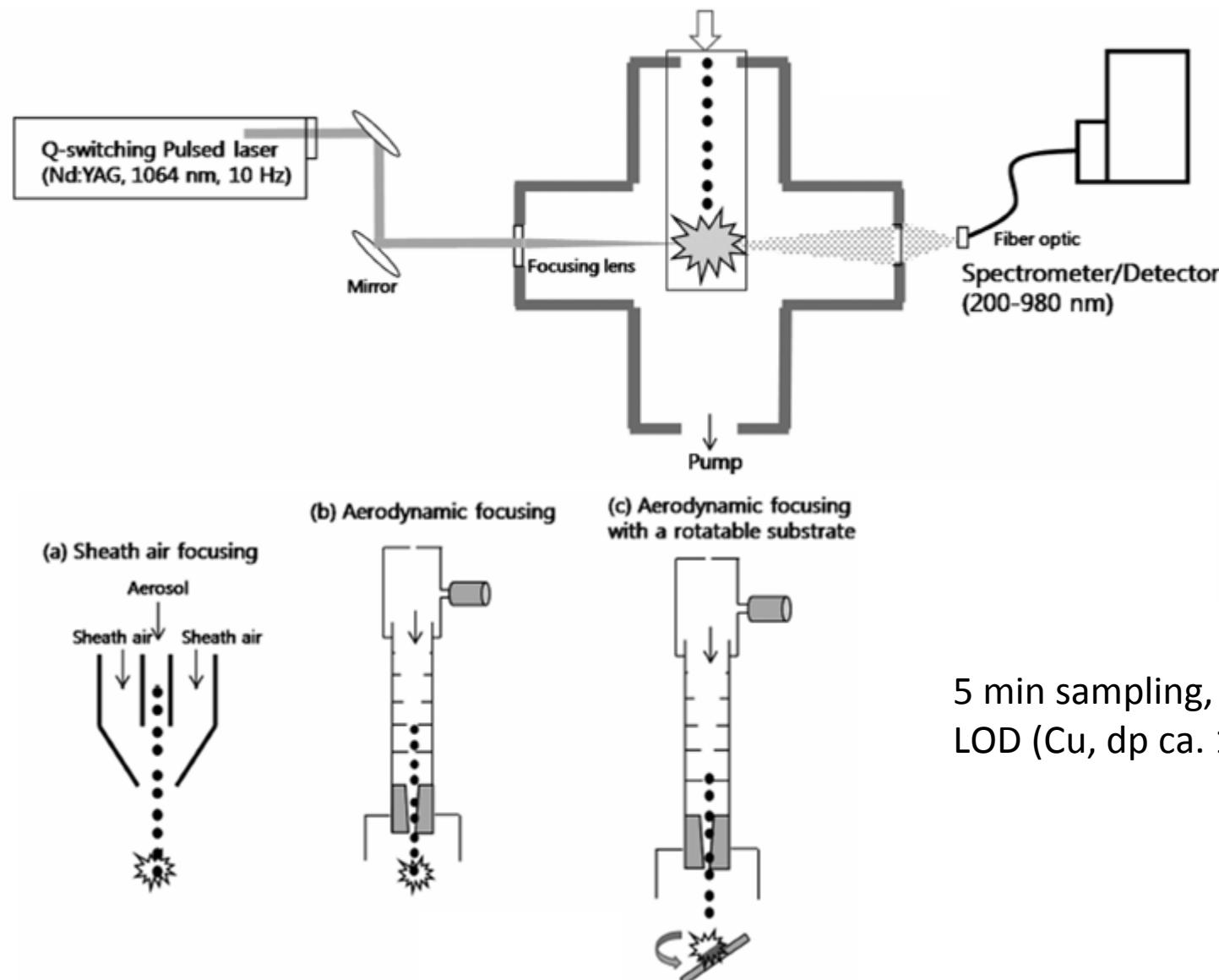
MMTO, MMTI: ca. 10 %

New instrumentation

Multi-component monitoring

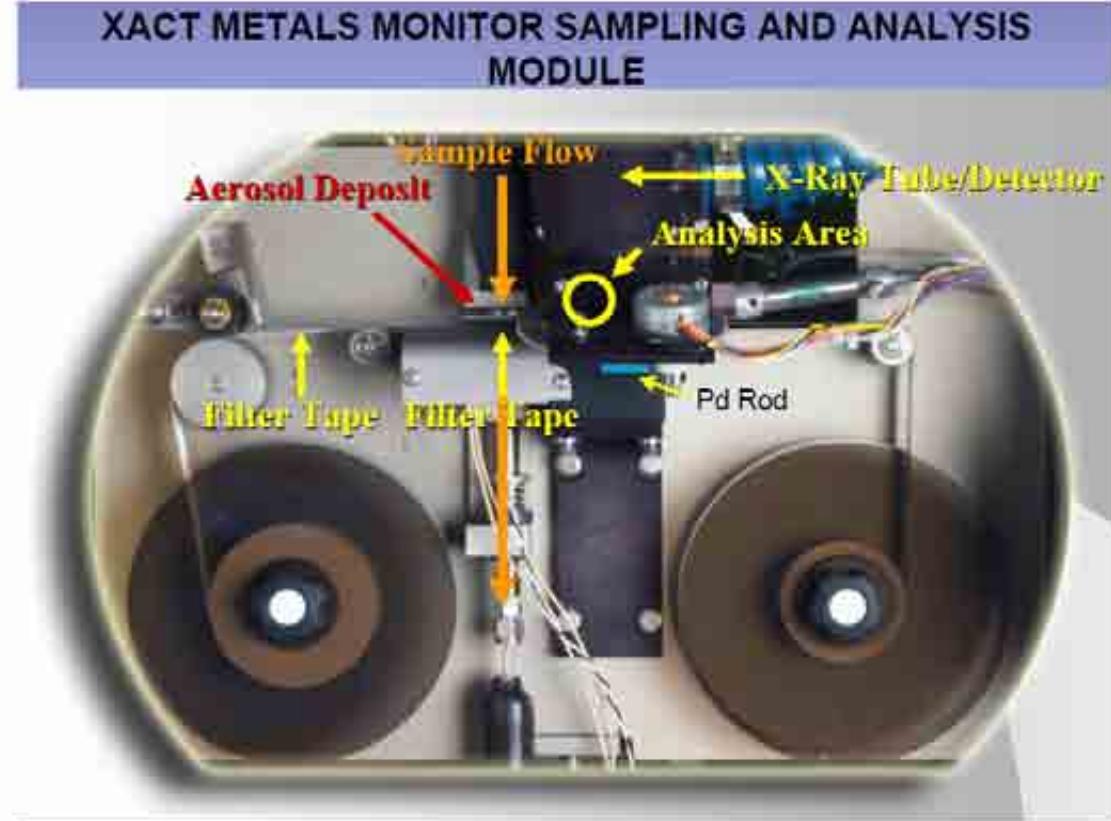
- Elemental
 - laser-based plasma spectroscopy (e.g. LIBS), XRF on filter band
- Molecules/Ions
 - AMS, ACSM, MARGA, PILS-IC (particle-bound)
 - (Mini)-DOAS, TDLAS, LIDAR

New instrumentation: LIBS



New instrumentation: XRF

1 m³/h,
PM10, 2.5, TSP



XAct 620 Ambient Metal Monitor (**Pall Corp.**)
Up to 36 elements, 15-240 min., DLs down to <<1 ng/m³

New instrumentation

Multi-component monitoring

- Elemental

- XRF on filter band, laser-based plasma spectroscopy

- Molecules/Ions

- AMS, ACSM: organic compounds, secondary ions

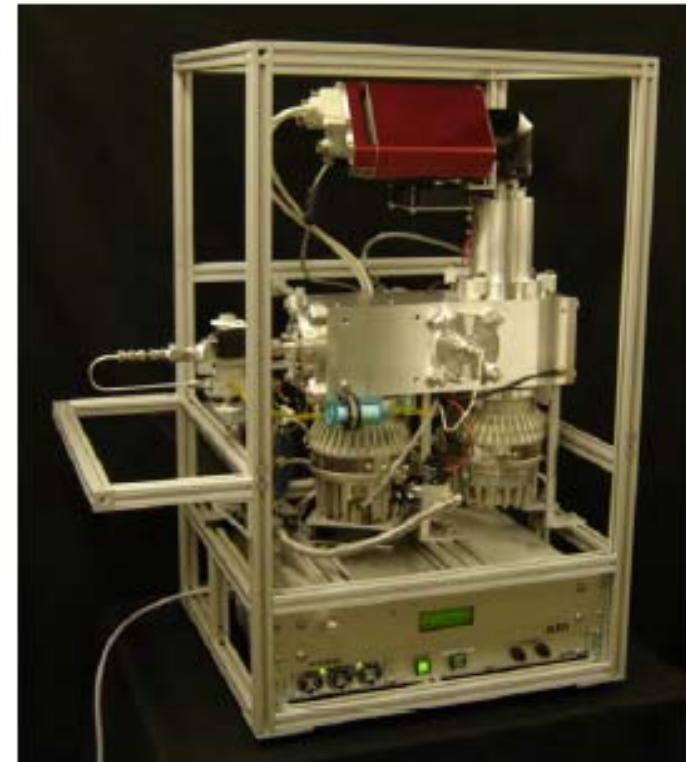
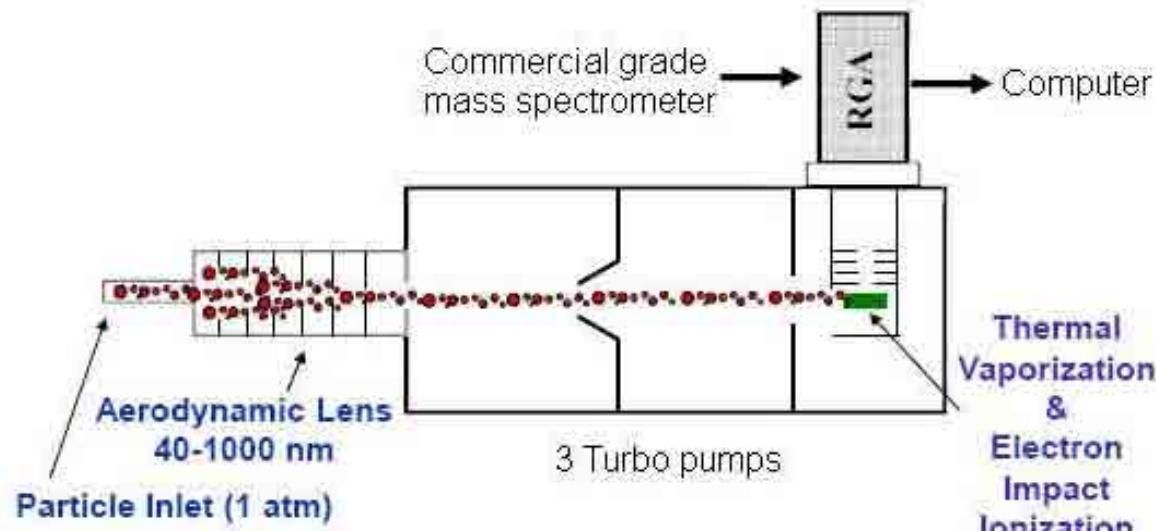
- MARGA, PILS-IC (particle-bound): secondary ions
(+ precursor gases)

- DOAS, TDLAS, LIDAR: gaseous pollutants

ACSM („Mini“ AMS)

<http://www.aerodyne.com/products/aerosol-chemical-speciation-monitor>

<http://cires.colorado.edu/~jjose/ams.html>



L.N. Ng et al.: Aerosol Science and Technology,
Volume 45 (2011) , pp. 770-784(15)
No size data as in AMS, with Quadropole: 0-200 amu range

In development:

ccTOF-ACMS with higher mass range, higher time resolution, higher sensitivity

Example for ACSM field Data:

Y. L. Sun et al., Atmos. Chem. Phys. Discuss., 11, 25751–25784, 2011

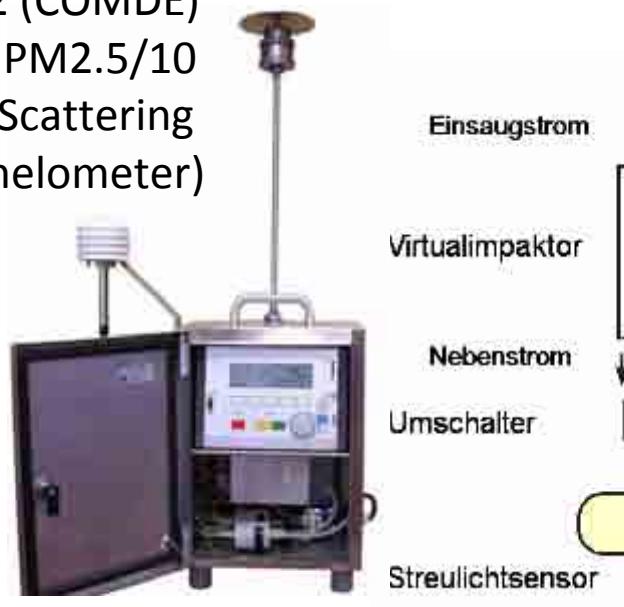
Multi-component monitoring

- Elemental
 - XRF on filter band, laser-based plasma spectroscopy
- Molecules/Ions
 - AMS, ACSM, MARGA, PILS-IC (particle-bound)
 - (Mini)-DOAS, TDLAS, LIDAR

- **Physical metrics of particulate matter**

- Mass: **β -absorption & Light-Scattering → higher time resolution**
- Number (diameter, number-size-distribution)
 - CNC, SMPS/FMPS, APS, ELPI, Laser scattering, meDiSC
- Surface: NSAM

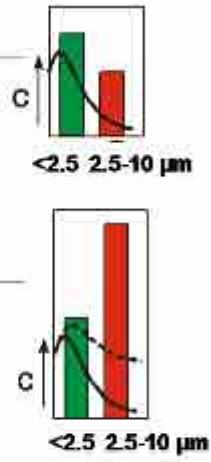
Time-resolved mass monitoring



SHARP (Thermo)
Mass
Nephelometry + β -Absorption



APM2 (COMDE)
Mass PM2.5/10
Light Scattering
(Nephelometer)



Multi-component monitoring

- Elemental
 - XRF on filter band, laser-based plasma spectroscopy
- Molecules/Ions
 - AMS, ACSM, MARGA, PILS-IC (particle-bound)
 - (Mini)-DOAS, TDLAS, LIDAR
- Physical metrics of particulate matter
 - Number (diameter, number-size-distribution)
 - CNC, SMPS/FMPS, APS, ELPI, Laser scattering
 - Surface: NSAM, DiSC/DiSCmini
 - Mass: β -absorption, Laser-Scattering (e.g. FIDAS, PMS2)
- Small portable devices
 - Mini-Aethalometers, DiSCmini, AeraSense Nano,
solid-state sensors

Small/handheld devices



NanoTracer (Philipps)
PNC 10-300 nm



MicroAeth (Magee)
BC in TSP, PM2.5



DiSCmini (Matter Engineering)
PNC/LDSA(alveo.)
10-300 nm modal



Handheld CPC (TSI)
PNC 10->1000 nm



FIDAS mobile (Palas)
PNC, size-distr. (32ch/decade)
0.2-18 μm
PM10/4/2.5/1

- Chemical reactivity indicators
 - Particle bound ROS (research-based online methods developed)
e.g. peroxides, hydroperoxides
 - Particle induced ROS (online monitors under development)
Several assays for potential to produce OH, HO₂ or to oxidise chemical probe compounds
- Physical particle features as proxies
 - Absorption/reflectance/extinction/incandescence for „black carbon“
MAAP, Aethalometer, PASS, PAX, SP2
(→ yesterday's session 2)
- Biological effect monitoring
 - Macrophage mobility
(P. Laval-Gilly et al, J. Pharmacol. Toxicol. Methods, 44 (2000), 483-488)

Conclusions

- New measurement technologies at hand
- Trend to multicomponent monitoring instruments
- Trend to miniaturised/mobile instruments
- A bunch of monitors for soot/BC
 - ...complementary or redundant; relation to filter analysis?
- Online monitoring of proxy metrics for combined effects of pollutants (ROS, direct biological impact) still to be further developed

Announcement
Workshop and Conference
on
**Current and Future
Air Quality Monitoring**

April 25/26, 2012

*At Residència d'Investigadors
CSIC - Generalitat de Catalunya
CI Hospital 64, Barcelona*

Confirmed keynote speakers:
G. Hoek, IRAS, NL
M. Kalberer, Cambridge Univ., UK
M. Gerboles, JRC, Ispra, IT
M. Fierz, IAST, CH
K. Pletscher, TÜV, DE

Registration possible soon at
www.airmontech.eu

The AirMonTech team is looking forward to co-operating with you!
www.aimontech.eu



Thanks for your attention!

AirMonTech Consortium: (from left) J. Moeltgen (UDE), U. Quass (IUTA), K. Torseth (NILU), K. Katsouyanni (NKUA), B. Vogel (UDE), R. Otjes (ECN), E. Weijers (ECN), P. Woods (NPL), T. Kuhlbusch (IUTA, Coordinator), P. Quincey (NPL), M. Viana (CSIC), R. Gehrig (EMPA), X. Querol(CSIC,) A. Borowiak (JRC), C. Hueglin (EMPA).