AirMonTech

SEVENTH FRAMEWORK PROGRAMME

New Technologies, New Metrics and Proxies

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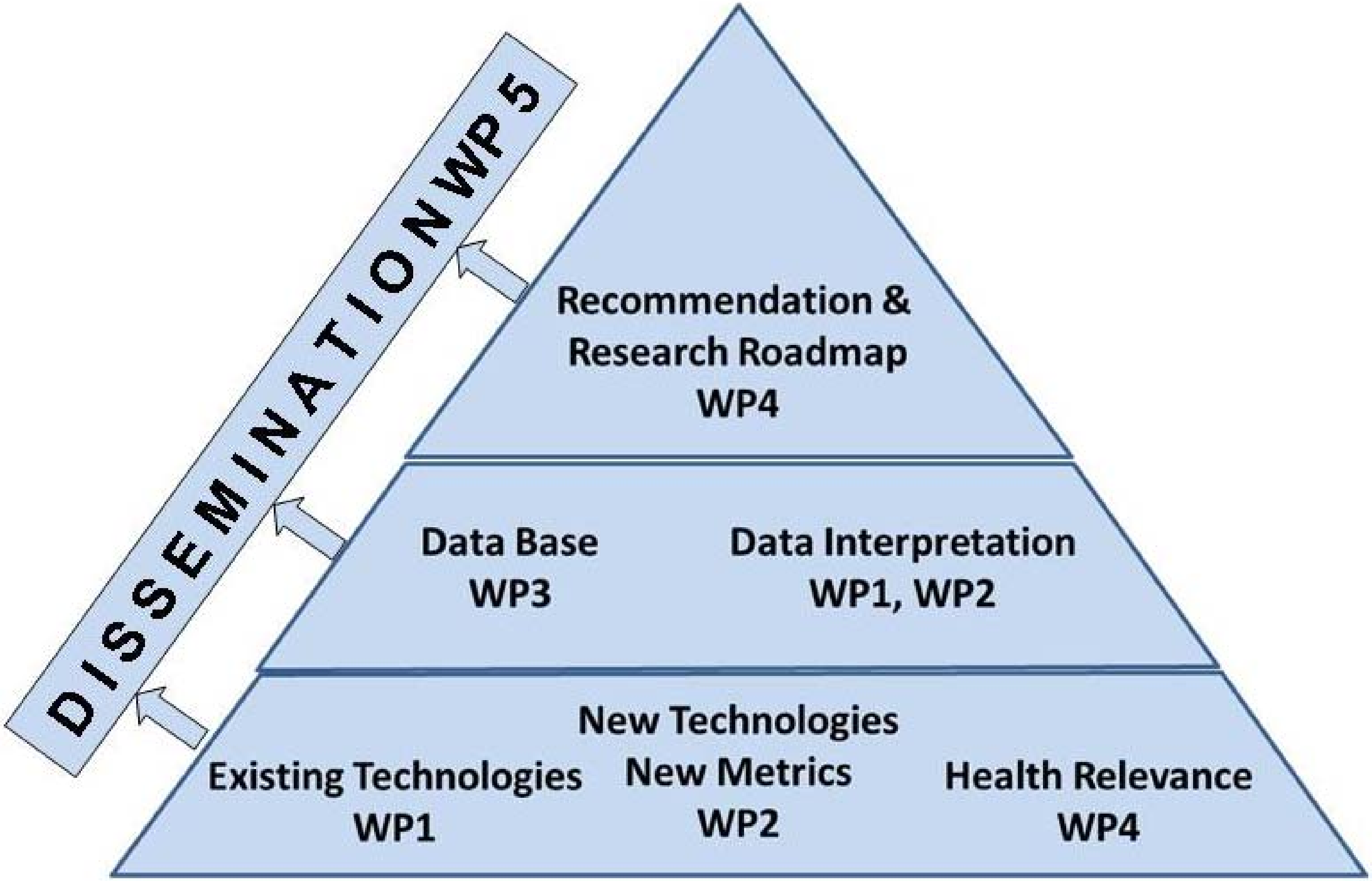
and AirMonTech Consortium

AAMG Conference 2011
12./13.12.2011

www.airmontech.eu

Project structure



Recommendation &
Research Roadmap
WP4

Data Base
WP3

Data Interpretation
WP1, WP2

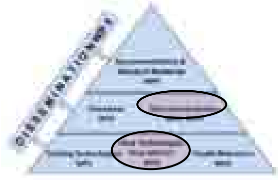
Existing Technologies
WP1

New Technologies
New Metrics
WP2

Health Relevance
WP4

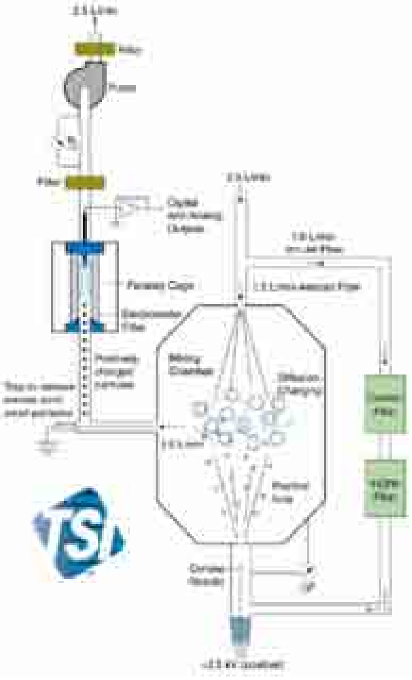
AirMonTech WP2

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

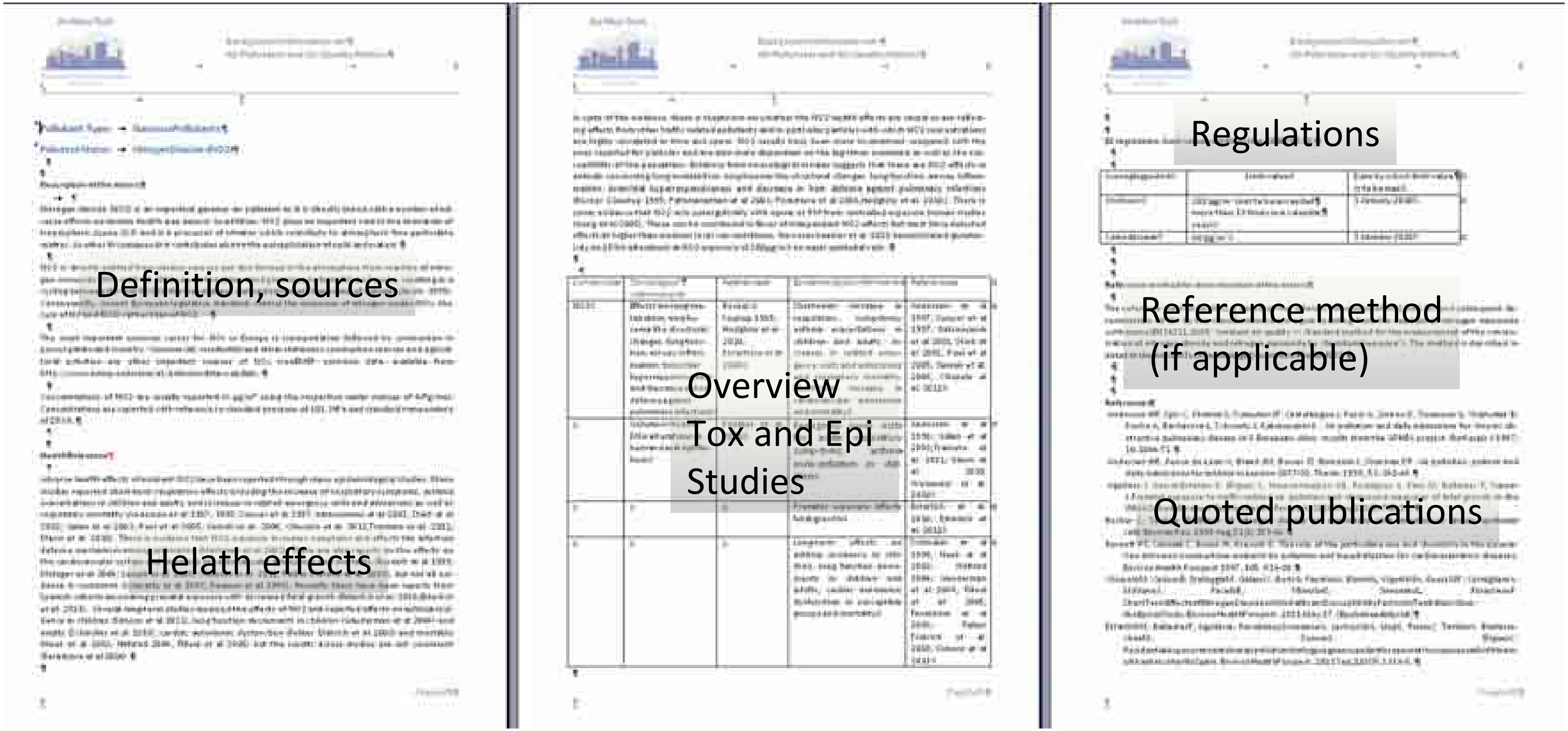


Fissan et al.(2006), J. Nanop. Res.9: 53-59;
Shin et al.(2006), J. Nanop. Res.9: 61-69

WP1/2/4: Metric related information

- 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 methodolgy listed in the MMTO document

Example for MBI-File



Definition, sources

Helath effects

Overview

Tox and Epi

Studies

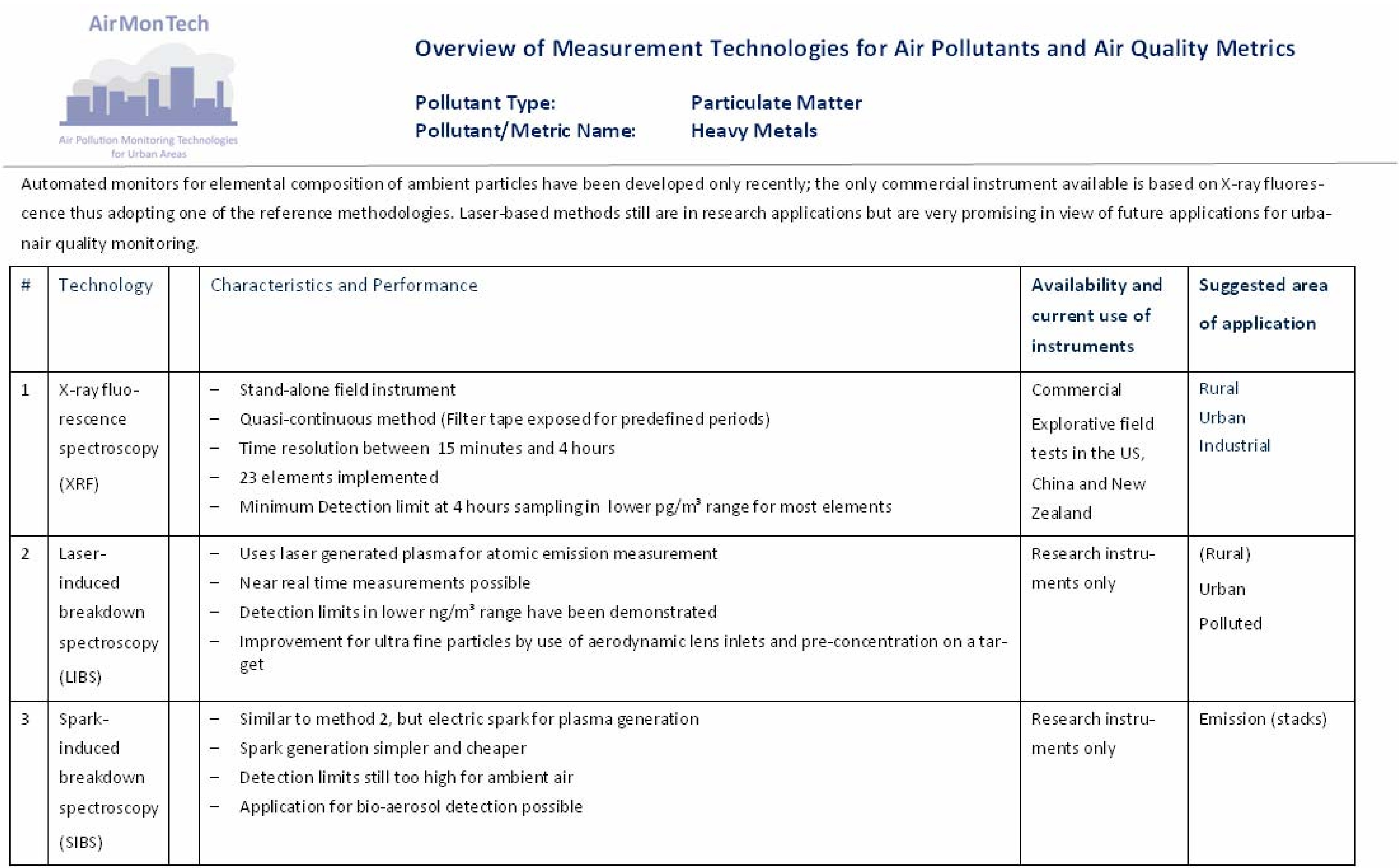
Regulations

Reference method

(if applicable)

Quoted publications

Example for MMTO



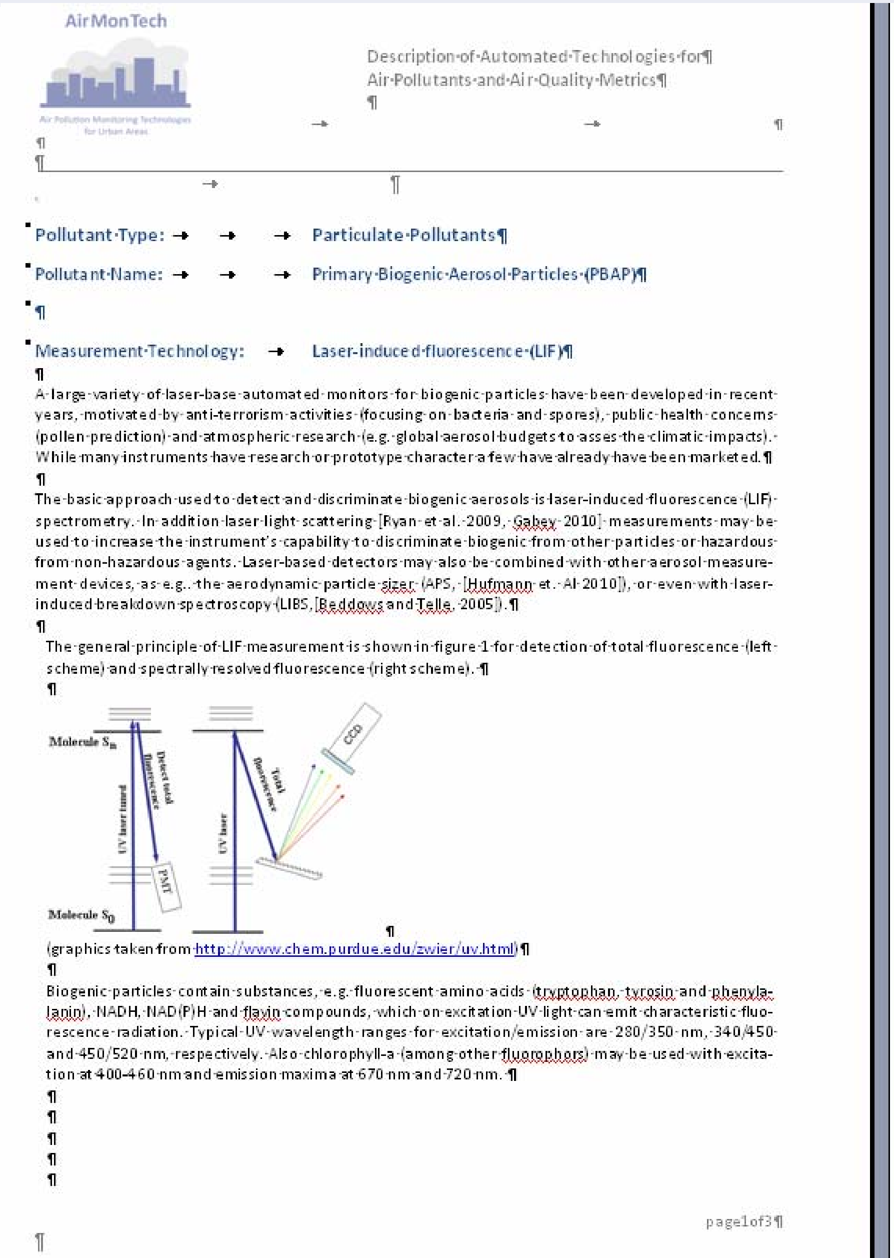
Overview of Measurement Technologies for Air Pollutants and Air Quality Metrics

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 urbanair quality monitoring.

#	Technology		Characteristics and Performance	**Availability and current use of instruments**	**Suggested area of application**
1	X-ray fluorescence spectroscopy (XRF)		– 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)		– 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)		– 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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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)

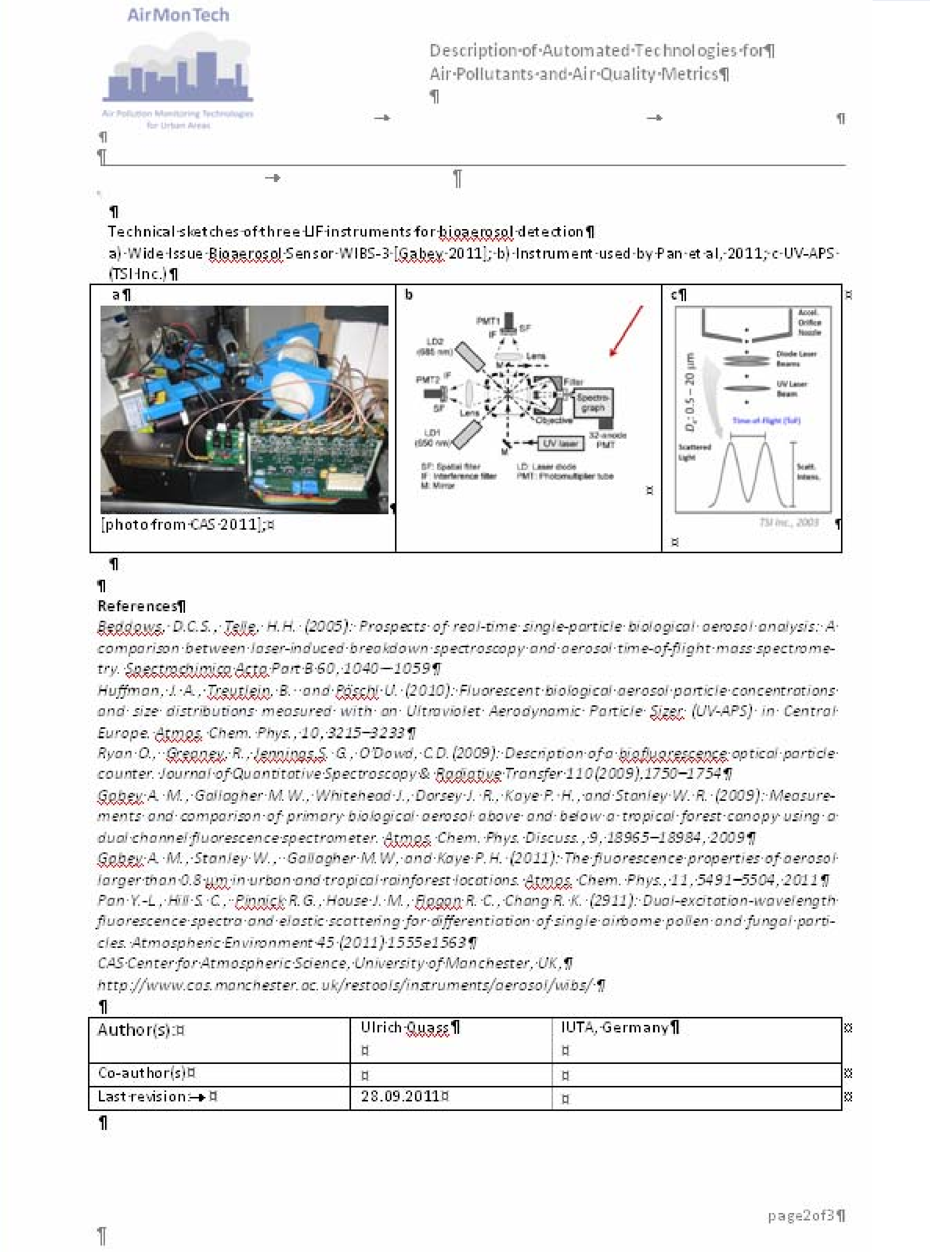
A large variety of laser-base automated monitors for biogenic particles have been developed in recent years, motivated by anti-terrorism activities (focusing on bacteria and spores), public health concerns (pollen prediction) and atmospheric research (e.g. global aerosol budgets to asses the climatic 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, [Hufmann 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.purdue.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 Issue Bioaerosol Sensor WIBS-3 [Gabey 2011]; b) Instrument used by Pan et al, 2011; c UV-APS (TSI Inc.)

a	b	c
[photo from CAS 2011];		TSI Inc., 2003

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., Treutlein, B. and Pöschl 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, 3215–3233

Ryan O., Greaney, R., Jennings S. G., O'Dowd, C.D. (2009): Description of a biofluorescence optical particle counter. Journal of Quantitative Spectroscopy & Radiative Transfer 110 (2009), 1750–1754

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., Stanley W., 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., Pinnick R. G., House J. M., Flagan R. C., Chang R. K. (2911): 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.cas.manchester.ac.uk/restools/instruments/aerosol/wibs/

Author(s):	Ulrich Quass	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
- 🟩 NO2
- ⬜ NOx
- 🟨 SO2
- ⬜ O3
- ⬜ NH3
- ⬜ VOCs
- ⬜ HCl
- ⬜ HNO3
- ⬜ HNO2

- ⬜ not yet available
- 🟧 partly ready
- 🟨 pre-Final draft
- 🟩 final draft

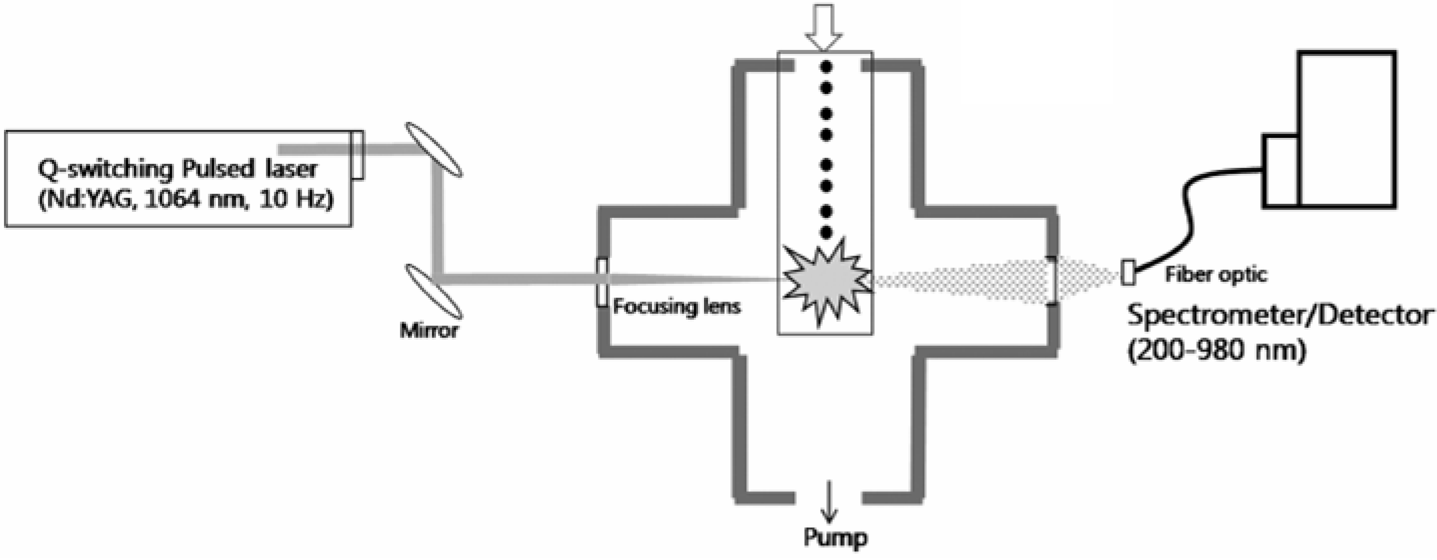
MMTO, MMTI: ca. 10 %

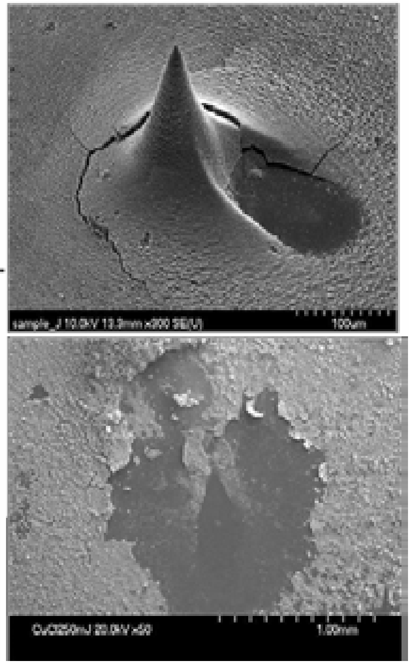
New instrumentation

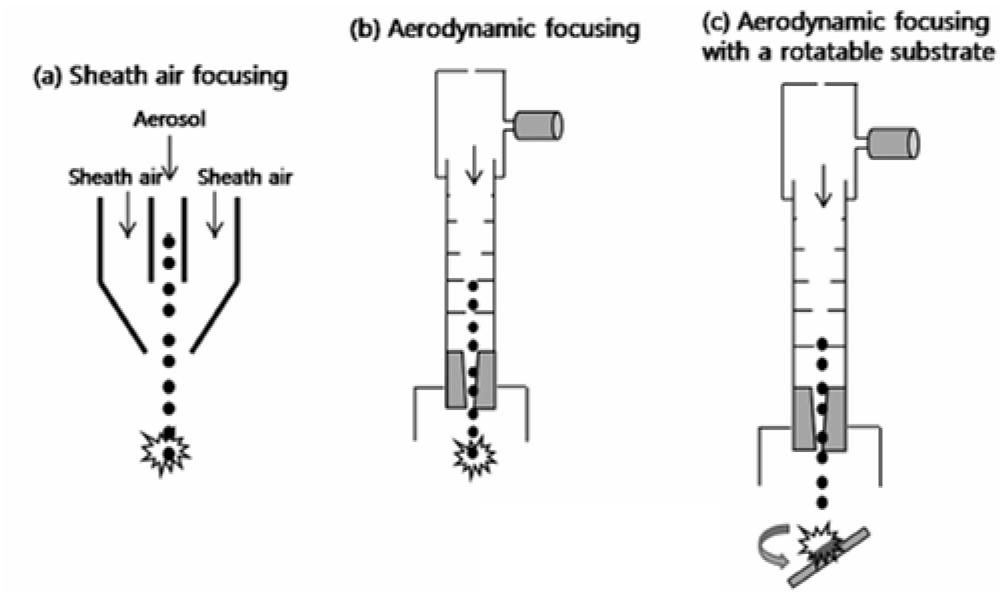
Multi-component monitoring

- **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







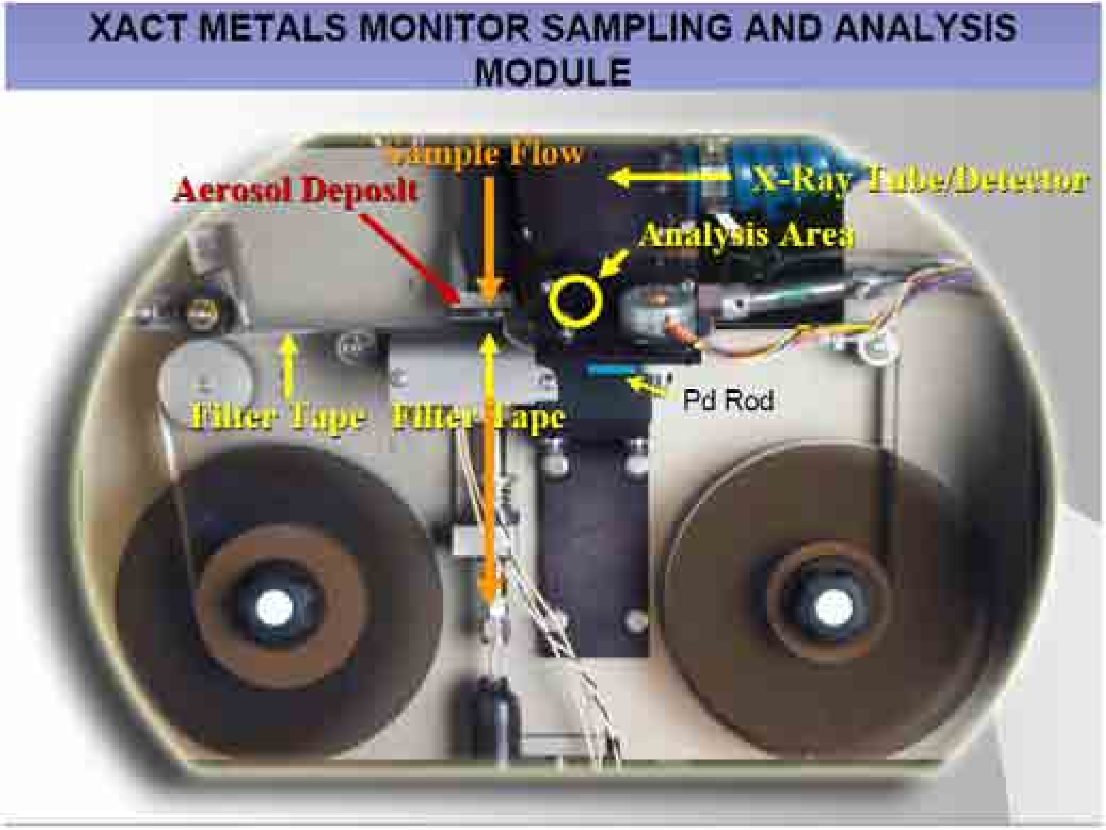
5 min sampling, dp(min) ~60nm

LOD (Cu, dp ca. 100 nm): ~ 80ng/m³

Park, K. et al., Aerosol Science and Technology, 43:375–386, 2009

New instrumentation: XRF

1 m^3/h,
PM10, 2.5, TSP



XAct 620 Ambient Metal Monitor (**Pall Corp.**)
Up to 36 elements, 15-240 min., DLs down to <<1 ng/m^3

http://www.pall.com/main/OEM-Media-Membranes-and-Materials/Product.page?id=54499

New instrumentation

Multi-component monitoring

- Elemental

  XRF on filter band, laser-based plasma spectroscopy

- **Molecules/Ions**

  AMS, **ACSM: organic compounds, secondary ions**

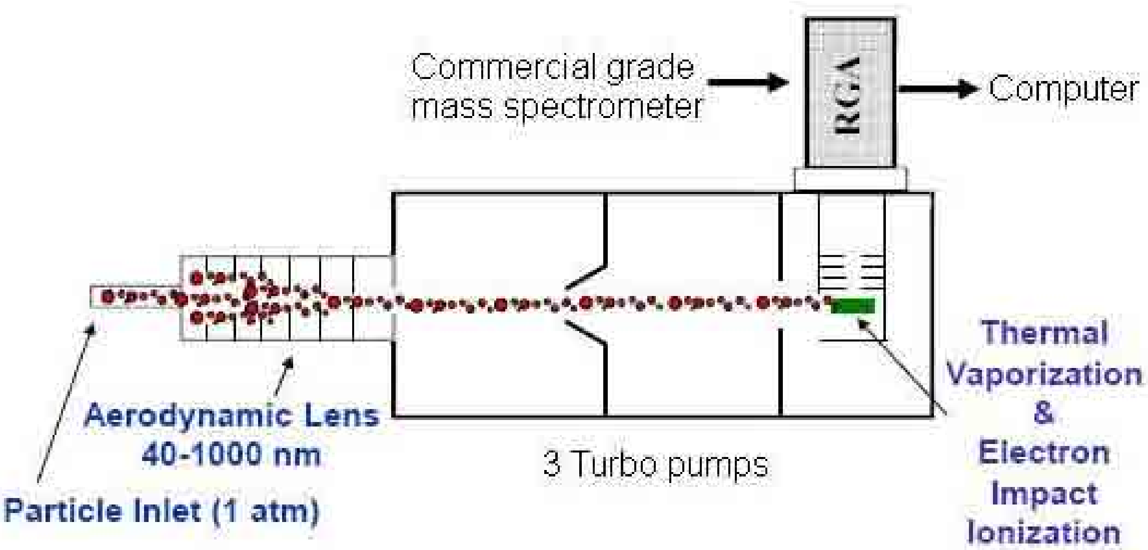
  MARGA, PILS-IC (particle-bound): secondary ions (+ precursor gases)

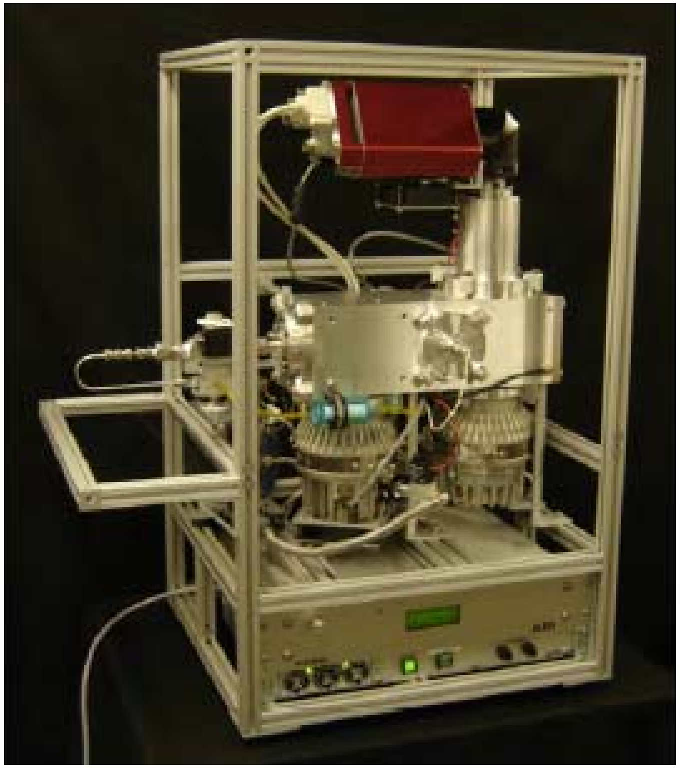
  DOAS, TDLAS, LIDAR: gaseous pollutants

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 sensitvity

Example for ACSM field Data:

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

New instrumentation

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

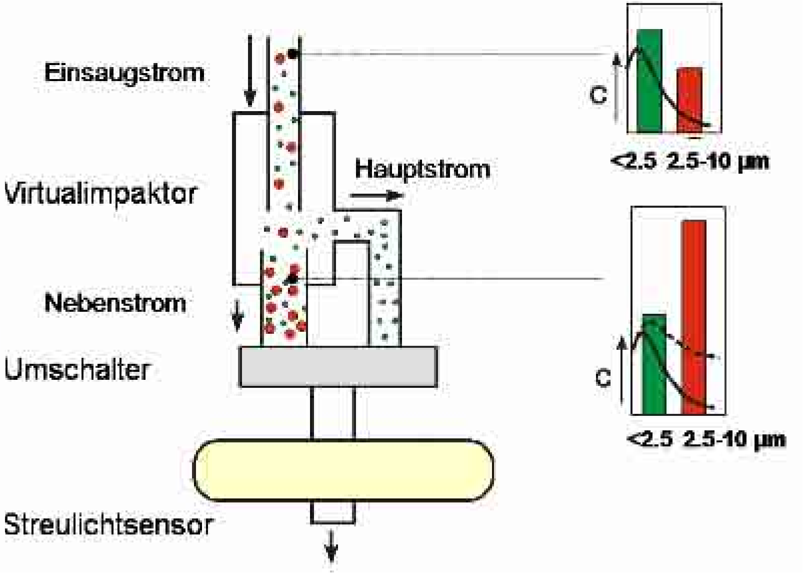
Time-resolved mass monitoring

FIDAS (Palas)
PNC, Mass
(PM1, 2.5, 4, 10, TSP)
LED light scattering

SHARP (Thermo)
Mass
Nephelometry + ß-Absorption

EDM 180 (Grimm)
Mass, size distr. 31 ch.
Light Scattering
(Nephelometer)

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



New instrumentation

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: ß-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

New Metrics and Proxies

- Chemical reactivity indicators
  - Particle bound ROS (research-based online methods dvelopped)

    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 developped

Outlook

Announcement
Workshop and Conference
on

Current and Future
Air Quality Monitoring
April 25/26, 2012

At Residència d'Investigadors
CSIC - Generalitat de Catalunya
C/ Hospital 64, Barcelona

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

Registration possible soon at
www.airmontech.eu

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

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).