AirMonTech

Existing Technologies for regulated Metrics

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www.airmontech.eu

AirMonTech WP1

1. provide information on technologies and performance of available instruments for measurement of air pollutants regulated in AQD 2008/50/EC

2. provide guidance for optimal use of available instruments (measurement technologies)

3. provide easy access to this information through AirMonTech data base

$\Rightarrow$ harmonisation of air quality measurements in Europe

AirMonTech: Air Pollution Monitoring Technologies for Urban Areas

AirMonTech WP1 - approach

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- collect and write documents relevant for persons involved in air quality monitoring (network operators) …

… and make these documents easily accessible.

Document types

1. Basic documents on air pollutants and measurement technologies

2. Information about individual instruments

– Type approval test reports
– Standard operating procedures (SOPs)
– Equivalence test reports (PM2.5/PM10 monitors)

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Info about individual instruments

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March 2011: Call for SOPs, type approval reports, and equivalence reports (to network operators and manufacturers)

Received documents:

SOPs	60
Type approval reports	6
Equivalence reports	4
Application reports	2
Specification sheets	33

Austria, Bulgaria, Cyprus, Estonia, France, Ireland, Italy, Netherlands, Slovenia, Spain, Switzerland, United Kingdom

Info about individual instruments

Next steps:

–Upload of received documents into AirMonTech data base !

–Call for more documents (early 2012)
Completeness is essential

–Evaluation of collected SOPs and preparation of «standard» SOPs

Basic documents on pollutants/technologies

For each pollutant/metric:

–*Metric Basic Information (**MBI**)*

includes definitions, sources (briefly), health relevance, regulations, reference methods, references

–*Metric Measurement Technology Overview (**MMTO**)*

table listing identified measurement technologies, typical operational characteristics, applicability to remote/rural/urban sites

–*Metric Measurement Technology Information (**MMTI**)*

details for each technology listed in the MMTO document

Current status of work

MBI, MMTO, MMTI files

WP1 air pollutant
SO_2
NO_2 (NO, NO_x)
O_3
CO
PM2.5/PM10
Benzene

final draft available
not yet available

MBI document for NO_2

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Pollutant Type: Gaseous Pollutants

Pollutant Name: Nitrogen Dioxide (NO2)

Description of the metric

Nitrogen dioxide (NO2) is an important gaseous air pollutant as it is directly linked with a number of adverse effects on human health (see below). In addition, NO2 plays an important role in the formation of tropospheric ozone (O3) and is a precursor of nitrates which contribute to atmospheric fine particulate matter. As other N-compounds it contributes also to the eutrophication of soils and waters.

NO2 is directly emitted from various sources but also formed in the atmosphere from reaction of nitrogen monoxide (NO) with O3. NO2 can on the other hand photolyse to form NO and ozone, resulting in a cycling between NO and NO2 in the troposphere during daytime at time scales of minutes (Jacob, 1999). Consequently, current European legislative standards control the emissions of nitrogen oxides (NOx, the sum of NO and NO2) rather than of NO2.

The most important emission sector for NOx in Europe is transportation followed by combustion in power plants and industry. Commercial, residential and other stationary combustion sources and agricultural activities are other important sources of NOx (see EMEP emission data, available from http://www.emep-emissions.at/emissiondata-webdab).

Concentrations of NO2 are usually reported in µg/m³ using the respective molar masses of 46 g/mol. Concentrations are reported with reference to standard pressure of 101,3kPa and standard temperature of 293 K.

Health Relevance

Adverse health effects of ambient NO2 have been reported through many epidemiological studies. Many studies reported short-term respiratory effects including the increase of respiratory symptoms, asthma exacerbations in children and adults, and increases in related emergency visits and admissions as well as respiratory mortality (Anderson et al 1997; 1998; Sunyer et al 1997; Katsouyanni et al 2001; Stieb et al 2002; Galan et al 2003; Peel et al 2005; Samoli et al. 2006; Chiusolo et al. 2011; Tramuto et al. 2011; Mann et al. 2010). There is evidence that NO2 exposure increases symptoms and affects the infection defense mechanism among asthmatics (Mortimer et al 2002). There are also reports on the effects on the cardiovascular system and increases in cardiovascular admissions and mortality (Burnett et al 1999; Metzger et al 2004; Samoli et al. 2006; Chiusolo et al. 2011; Felber Dietrich et al. 2008), but not all evidence is consistent (Schwartz et al 1997; Roemer et al 1998). Recently there have been reports from Spanish cohorts associating prenatal exposure with decreased fetal growth (Estarlich et al. 2010; Estarlich et al. 2011). Several long-term studies assessed the effects of NO2 and reported effects on asthma incidence in children (Simons et al 2011), lung function decrements in children (Gauderman et al 2004) and adults (Schindler et al 1998), cardiac autonomic dysfunction (Felber Dietrich et al 2008) and mortality (Hoek et al 2002; Nafstad 2004; Filleul et al 2005) but the results across studies are not consistent (Forastiere et al 2006).

In spite of the evidence, there is skepticism on whether the NO2 health effects are causal or are reflecting effects from other traffic related pollutants and in particular particles with which NO2 concentrations are highly correlated in time and space. NO2 results have been more inconsistent compared with the ones reported for particles and are also more dependent on the lag times examined as well as the susceptibility of the population. Evidence from toxicological studies suggests that there are NO2 effects in animals concerning lung metabolism, emphysema like structural changes, lung function, airway inflammation, bronchial hyperresponsiveness and decrease in host defense against pulmonary infections (Becker & Soukup 1999; Pathmanathan et al 2003; Forastiere et al 2006; Hodgkins et al. 2010;). There is some evidence that NO2 acts synergistically with ozone or PM from controlled exposure human studies (Gong et al 2005). These can be considered in favor of independent NO2 effects but most have detected effects at higher than ambient level concentrations. However Koehler et al. 2011 demonstrated genotoxicity and DNA alterations at NO2 exposure of 200µg/m3 on nasal epithelial cells.

Compound	*Toxicological Information*	*References*	*Epidemiological information*	*References*
NO2	Effects on lung metabolism, emphysema like structural changes, lung function, airway inflammation, bronchial hyperresponsiveness and decrease in host defense against pulmonary infections	Becker & Soukup 1999; Hodgkins et al. 2010; Forastiere et al 2006	Short-term increase in respiratory symptoms, asthma exacerbations in children and adults, increases in related emergency visits and admissions and respiratory mortality. Short-term increase in cardiovascular admissions and mortality	Anderson et al 1997; Sunyer et al 1997; Katsouyanni et al 2001; Stieb et al 2002; Peel et al 2005; Samoli et al. 2006; Chiusolo et al. 2011
	Genotoxicity and DNA alterations in human nasal epithelium	Koehler et al. 2011	Emergency room visits for acute respiratory symptoms, asthma exacerbation in children	Anderson et al 1998; Galan et al 2003; Tramuto et al. 2011; Mann et al. 2010; Weinmayr et al. 2010
			Prenatal exposure affects fetal growth	Estarlich et al. 2010, Estarlich et al. 2011
			Long-term effects on asthma incidence in children, lung function decrements in children and adults; cardiac autonomic dysfunction in susceptible groups and mortality	Schindler et al 1998; Hoek et al 2002; Nafstad 2004; Gauderman et al 2004; Filleul et al 2005; Forastiere et al 2006; Felber Dietrich et al. 2008; Simons et al 2011

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MBI document for NO_2

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EC legislation, limit values (EU Directive 2008/50/EC)

Averaging period	Limit value	Date by which limit value is to be met
One hour	200 µg/m^3 (not to be exceeded more than 18 times in a calendar year)	1 January 2010
Calendar year	40 µg/m^3	1 January 2010

Reference method for determination of the metric

The reference method for NO2 is based on the catalytic conversion of NO2 into NO and subsequent determination of NO by the chemiluminescence signal resulting from the reaction of nitrogen monoxide with ozone(EN14211:2005 "Ambient air quality — Standard method for the measurement of the concentration of nitrogen dioxide and nitrogen monoxide by chemiluminescence"). The method is described in detail in the AirMonTech Technology Description File for NO2.

References

Anderson HR, Spix C, Medina S, Schouten JP, Castellsague J, Rossi G, Zmirou D, Touloumi G, Wojtyniak B, Ponka A, Bacharova L, Schwartz J, Katsouyanni K. Air pollution and daily admissions for chronic obstructive pulmonary disease in 6 European cities: results from the APHEA project. Eur Respir J 1997; 10:1064-71.

Anderson HR, Ponce de Leon A, Bland JM, Bower JS, Emberlin J, Strachan DP. Air pollution, pollens and daily admissions for asthma in London 1987-92. Thorax 1998; 53: 842-48.

Aguilera I, Garcia-Esteban R, Iñiguez C, Nieuwenhuijsen MJ, Rodríguez A, Paez M, Ballester F, Sunyer J. Prenatal exposure to traffic-related air pollution and ultrasound measures of fetal growth in the INMA Sabadell cohort. Environ Health Perspect. 2010 May;118(5):705-11.

Becker S, Soukup JM. Effect of nitrogen dioxide on respiratory viral infection in airway epithelial cells. Environ Res. 1999 Aug;81(2):159-66.

Burnett RT, Cakmak S, Brook JR, Krewski D. The role of the particulate size and chemistry in the association between summertime ambient air pollution and hospitalization for cardiorespiratory diseases. Environ Health Perspect 1997; 105: 614-20.

Chiusolo M, Cadum E, Stafoggia M, Galassi C, Berti G, Faustini A, Bisanti L, Vigotti MA, Dessì MP, Cernigliaro A, Mallone S, Pacelli B, Minerba S, Simonato L, Forastiere F. Short Term Effects of Nitrogen Dioxide on Mortality and Susceptibility Factors in Ten Italian Cities: the EpiAir Study. Environ Health Perspect. 2011 May 17. [Epub ahead of print]

Estarlich M, Ballester F, Aguilera I, Fernández-Somoano A, Lertxundi A, Llop S, Freire C, Tardón A, Basterrechea M, Sunyer J, Iñiguez C. Residential exposure to outdoor air pollution during pregnancy and anthropometric measures at birth in a multicenter cohort in Spain. Environ Health Perspect. 2011 Sep;119(9):1333-8.

Felber Dietrich D, Gemperli A, Gaspoz JM, Schindler C, Liu LJ, Gold DR, Schwartz J, Rochat T, Barthélémy JC, Pons M, Roche F, Probst Hensch NM, Bridevaux PO, Gerbase MW, Neu U, Ackermann-Liebrich U; SAPALDIA Team. Differences in heart rate variability associated with long-term exposure to NO2. Environ Health Perspect. 2008 Oct;116(10):1357-61.

Filleul L, Rondeau V, Vandentorren S, Le Moual N, Cantagrel A, Annesi-Maesano I, Charpin D, Declercq C, Neukirch F, Paris C, Vervloet D, Brochard P, Tessier JF, Kauffmann F, Baldi I. Twenty five year mortality and air pollution: results from the French PAARC survey. Occup Environ Med 2005; 62: 453-60.

Forastiere F, Peters A, Kelly F, Holgate ST. Nitrogen dioxide. In: WHO air quality guidelines. Global update, 2006.

Galán I, Tobías A, Banegas JR, Aránguez E. Short-term effects of air pollution on daily asthma emergency room admissions. Eur Resp J 2003; 22:802-8.

Gauderman WJ, Avol E, Gilliland F, Vora H, Thomas D, Berhane K, McConnell R, Kuenzli N, Lurmann F, Rappaport E, Margolis H, Bates D, Peters J. The effect of air pollution on lung development from 10 to 18 years of age. New Engl J Med 2004; 351: 1057-67.

Gong H Jr, Linn WS, Clark KW, Anderson KR, Geller MD, Sioutas C. Respiratory responses to exposures with fine particulates and nitrogen dioxide in the elderly with and without COPD. Inhal Toxicol 2005; 17:123-32.

Hodgkins SR, Ather JL, Paveglio SA, Allard JL, LeClair LA, Suratt BT, Boyson JE, Poynter ME. NO2 inhalation induces maturation of pulmonary CD11c+ cells that promote antigenspecific CD4+ T cell polarization. Respir Res. 2010 Jul 26;11:102.

Hoek G, Brunekreef B, Goldbohm S, Fischer P, van den Brandt PA. Association between mortality and indicators of traffic-related air pollution in the Netherlands: a cohort study. Lancet 2002; 360: 1203-9.

Jacob, D.J. (1999). Introduction to Atmospheric Chemistry, Princeton University Press, Princeton, New Jersey.

Katsouyanni K, Touloumi G, Samoli E, Gryparis A, Le Tertre A, Monopolis Y, Rossi G, Zmirou D, Ballester F, Boumghar A, Anderson HR, Wojtyniak B, Paldy A, Braunstein R, Pekkanen J, Schindler Ch, Schwartz J. Confounding and effect modification in the short-term effects of ambient particles on total mortality: results from 29 European cities within the APHEA2 project. Epidemiology 2001, 12: 521-31.

Koehler C, Ginzkey C, Friehs G, Hackenberg S, Froelich K, Scherzed A, Burghartz M, Kessler M, Kleinsasser N. Ex vivo toxicity of nitrogen dioxide in human nasal epithelium at the WHO defined 1-h limit value. Toxicol Lett. 2011 Nov 10;207(1):89-95.

Mann JK, Balmes JR, Bruckner TA, Mortimer KM, Margolis HG, Pratt B, Hammond SK, Lurmann FW, Tager IB. Short-term effects of air pollution on wheeze in asthmatic children in Fresno, California. Environ Health Perspect. 2010 Oct;118(10):1497-502.

Metzger KB, Tolbert PE, Klein M, Peel JL, Flanders WD, Todd K, Mulholland JA, Ryan PB, Frumkin H. Ambient air pollution and cardiovascular emergency department visits. Epidemiology 2004; 15: 46-56.

Mortimer KM, Neas LM, Dockery DW, Redline S, Tager IB. The effect of air pollution on inner city children with asthma. Eur Resp J 2002; 19:699-705.

Nafstad P, Håheim LL, Wisløff T, Gram F, Oftedal B, Holme I, Hjermann I, Leren P. Urban air pollution and mortality in a cohort of Norwegian man. Environ Health Perspect 2004; 112: 610-15.

Pathmanathan S, Krishna MT, Blomberg A, Helleday R, Kelly FJ, Sandström T, Holgate ST, Wilson SJ, Frew AJ. Repeated daily exposure to 2 ppm nitrogen dioxide upregulates the expression of IL-5, IL-10, IL-13, and ICAM-1 in the bronchial epithelium of healthy human airways. Occup Environ Med. 2003 Nov;60(11):892-6.

Peel JL, Tolbert PE, Klein M, Metzger KB, Flanders WD, Todd K, Mulholland JA, Ryan PB, Frumkin H. Ambient air pollution and respiratory emergency department visits. Epidemiology 2005; 16: 164-74.

MMTO document for NO_2

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Overview of Measurement Technologies for Air Pollutants and Air Quality Metrics

Pollutant Type: **Gaseous Pollutant**

Pollutant/Metric Name: **Nitrogen Dioxide (NO2)**

Disclaimer: This document ...

#	Technology	Characteristics and performance	Availability and current use of instruments	Suggested area of application
1	Chemiluminescence combined with metal converter	– European reference method (EN14211; 2005). – Robust instruments available from various manufacturers. Widely used in monitoring networks. – Indirect method. NO2 is calculated as difference of NOx and NO. – Not selective for NO2, because of interferences of other oxides of nitrogen [1]. This is especially important at rural and remote locations. – Precision of typical instruments ±0.4 ppb or ±0.76µg/m^3 (1σ, 60min). Higher sensitivity for remote locations is possible.	Commercial; monitoring networks	Urban
2	Chemiluminescence combined with photolytic converter	– Similar to Technology 1, – but higher selectivity through photolysis of NO2, and – slightly more complicated because correction of measured signal with converter efficiency required.	Commercial; monitoring networks	Urban Rural Remote
3	Chemiluminescence with luminol	– Commercial instruments using this technique are no longer available.	No longer commercially available	
4	Cavity ringdown spectroscopy (CRDS)	– Highly selective and sensitive method – Currently no commercial instruments, only research instruments available [2, 3].	Not commercially available, Research	Urban Rural Remote
5	Cavity enhanced laser absorption spectroscopy	– Highly selective and sensitive method – High precision of around ±0.05 ppb or ±0.1µg/m^3 (1σ, 1sec), very high temporal resolution (e.g. 5Hz).	Commercial; Research; monitoring networks	Urban Rural Remote

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MMTI document for NO_2 with CL method

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Description of Automated Technologies for Air Pollutants and Air Quality Metrics

Pollutant Type:	**Gaseous Pollutants**
Pollutant Name:	**Nitrogen Dioxide (NO2)**
Measurement Technology:	**Chemiluminescence method – detection of chemiluminescence from reaction of nitrogen monoxide with ozone**

The measurement of NO_2 by detection of the chemiluminescence signal from the reaction of nitrogen monoxide with ozone is the reference method for ambient NO_2 measurements in Europe (EN 14211:2005). Monitors using this measurement principle measure the concentration of nitrogen monoxide (NO) and NOx (NO_x=NO+NO_2). The concentration of NO_2 is calculated by subtracting the measured NO concentration from the measured NO_x concentration.

In a chemiluminescence analyser air is fed into the reaction chamber of the analyser, where it is mixed with an excess of ozone. All NO is oxidized to NO2 by following reactions:

$$NO + O_3 \rightarrow NO_2^* + O_2$$
$$NO_2^* \rightarrow NO_2 + h \cdot \nu$$

* = excited state of species

Infrared light that is released from the decay of NO_2^* from an excited state to the ground state is detected by a photomultiplier tube. The intensity of the detected light (chemiluminescence) is proportional to the concentration of nitrogen monoxide. For determination of nitrogen dioxide, the sampled air is fed through a converter where the nitrogen dioxide is catalytically reduced to nitrogen monoxide and analysed in the same way as previously described. The chemiluminescence signal is proportional to the sum of concentrations of nitrogen dioxide and nitrogen monoxide. The concentration of nitrogen dioxide is calculated from the difference of the measured NO_x and NO concentrations.

A. Instruments with heated catalytic converters

Typical converters used for reduction of NO_2 into NO are made of a material such as stainless steel, copper, molybdenum, tungsten or spectroscopic pure carbon and are maintained at constant temperatures. The reference method for ambient NO_2 (EN 14211:2005) requires that the converter is capable of converting at least 95% of the nitrogen dioxide to nitrogen monoxide. A drawback of these converters is that other oxidized nitrogen compounds (e.g. HNO_3 and Peroxiacetyl nitrate) are reduced to NO with high efficiencies as well and can cause significant interferences (Steinbacher et al., 2007; Dunlea et al., 2007). These interferences are especially important at rural and remote sites.

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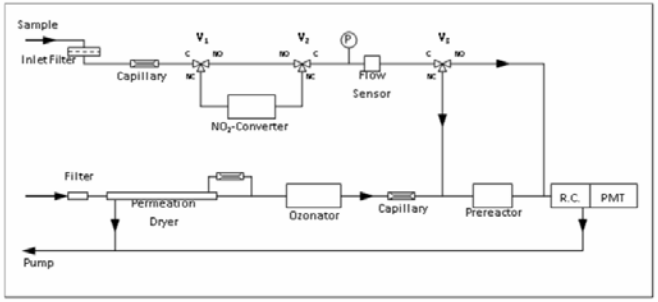
Description of Automated Technologies for Air Pollutants and Air Quality Metrics



Flow schematic of a typical NO-NO_x-NO_2 chemiluminescence monitor using a catalytic converter.

B. Instruments with photolytic converters

An alternative to the above mentioned catalytic converters are photolytic converters, where conversion of NO_2 is achieved by irradiation of NO_2 with UV light (< 410nm) according to following reactions:

$$NO_2 + h \cdot \nu \rightarrow NO + O$$
$$O + O_2 \rightarrow O_3$$
$$NO + O_3 \rightarrow NO_2 + O_2$$

leading to following equilibrium:

$$NO_2 + O_2 + h \cdot \nu \leftrightarrow NO + O_3$$

Instruments equipped with photolytic converters do not suffer from interferences to other oxidized nitrogen compounds and allow much more specific measurements of NO_2. However, the conversion efficiencies of photolytic converters are around 50% and much lower than the requirements of the European standard (EN 14211:2005). The converter efficiency of photolytic converters needs to be regularly determined for the correction of the measured signal.

There are photolytic converters available on the market that can be integrated into conventional instruments equipped with catalytic converters, more or less simply by changing the converter type (see flow schematic below).

Basic documents on pollutants/technologies

Next steps:

–Production of MBI, MMTO, MMTI files for all other regulated air pollutants
Completeness is important!

–Upload into AirMonTech data base

Summary

- WP1 of AirMonTech is focused on collection and preparation of documents on regulated air pollutants
- Documents will be easily accessible through AirMonTech data base
- Documents are thought to be valuable for network operators
- We hope that AirMonTech data base will be widely used (by networks operators), thereby supporting harmonisation of air quality monitoring

Thank you!

Questions/comments ?