Diffuive Methods for Sampling No, No2 and Ozone

Diffusive Methods for Sampling NO, NO_2 and O_3

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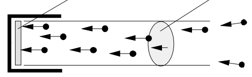
- Principles
- Standards
- Field validations
- Uncertainty
- Application

Principles of diffusion



$$\text{concentration c} = \frac{l \cdot Q_1}{D \cdot A \cdot t} = \frac{Q_1 \cdot}{SR \cdot t}$$

C:	concentration	[ug/m3]	D:	diffusion coefficient	[cm/sec²]
Q_1:	amount of analyte	[ug]	t:	exposure time	[sec]
l:	diffusion path	[cm]	SR:	sampling rate	[ml/min]
A:	cross section	[cm²]			

Diffusive samplers

I: Harmonization of measurement: Standards

Ambient Air Quality - Diffusive samplers for the determination of gases and vapours - requirements and test methods
[EN 13528: 2002]

- Part 1: General requirements
- Part 2: Specific requirements and test methods
- Part 3: Guide for selection, use and maintenance
- Part 4: Indoor application

Performance characteristics of diffusion tubes Part 2

- Sampling rate
- Working range
- Precision
- Linearity
- Humidity, Temperature
- Wind influence
- Storage time

→ Instructions for a detailed uncertainty estimation

II: Standards for analytical technique

ISO/IEC 17025
General Requirements for the Competence of Testing and Calibration Laboratories. 2000

- management system for laboratories
- Traceability
- Uncertainty calculation
  GUM: Guide for the expression for uncertainty

favors: indirect approach of uncertainty estimation:
variation and bias are evaluated separately

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Uncertainty calculation according GUM

Mathematical function	$c_u = \dfrac{m_d - m_b}{SR \bullet t}$
Input quantities	U_m u_{SR} U_t
Uncertainty catalogue	u_{SR} testatmospheres u_m analytical function u_B blancs u_P multiple samples u_{ext} wind, temperature, humidity
Determination of uncertainties	Type A: measured Type B: estimated
Combined uncertainty	$U_c = \sqrt{u^2_m + u^2_{SR} + u^2_t + (u^2_P + u^2_B)^* + u^2_{ext}}$
Expanded uncertainty	$U_e = 2 \bullet \sqrt{u^2_{SR} + u^2_Q + \ldots}$

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Error catalogue

	error size
Sampling rate	
permeation tube	X
flow measurement	X
absorption	X
experimental SR	XXX
Sampling	
length of tube	neglectable
area of tube	neglectable
precision of triplicates low conc	XXX
precision of triplicates high conc	XX
Laboratory analysis	
calibration function	XX
calibration standards	X
analytical equipment	X
operator	X
Sampler integrity	
blanks	corrected
transportation	X
storability	X
tightness	X
External influences	
temperature	
humidity	
windspeed	XXX
interferences	

CR 14377 [2002]
Air Quality - Approach to uncertainty for ambient air reference measurement methods

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III: Consistency of air quality monitoring network

EN ISO 20988: 2007
Air Quality – Guidelines for estimating measurement uncertainty

- Evaluation of measurement uncertainty based on comparisons with reference method
- favors: direct approach of uncertainty estimation: variation and bias are investigated in a pooled way

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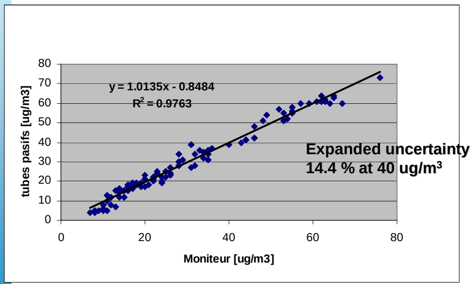
NO_2: Comparison with reference method: France



Expanded uncertainty
14.4 % at 40 ug/m³

p, T corrected according Ademe 4414

Source: ASPA France 2005 10

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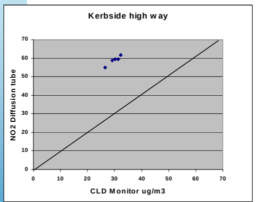
Site specific disagreement at kirbsites of highways



Hypothesis

- presence of excess NO and Ozone
- turbulences

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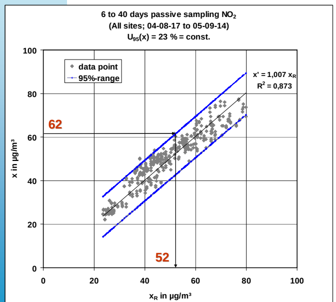
NO_2: Comparison with reference method: Germany



- 10 monitoring sites
- 1 year
- different exposure times
- number of data pairs: 370
- use of membranes

expanded uncertainty 23 % at 40 ug/m³

Source: Gefahrstoffe 66(2006) 12

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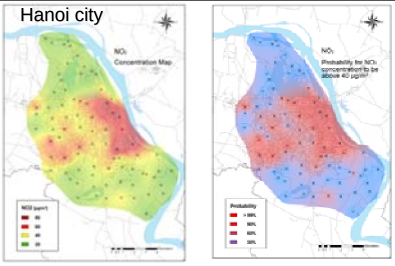
Application: Identification of hot spots:



screening campaign: 100 sites in a grid, one month duration

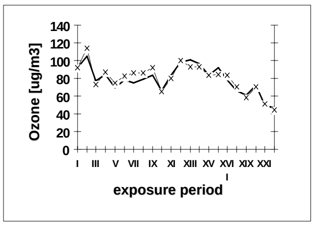
Diffusive sampler for ozone

Principle: chemisorption of Ozone
- Cleavage of doublebonding and transforming into aldehyde
- Transforming nitrite into nitrate

Peculiarity
- Acute effect related
- Limit values defined as short term values

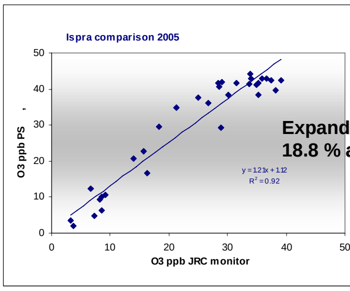
Approach
- Relation of peak values to average values
- trade-off between labour costs and peak estimation
- one week measurement period best compromise

Field Evaluation in the European Alpes



expanded uncertainty
31.7 % at 80 ug/m³

Comparison with Reference Method

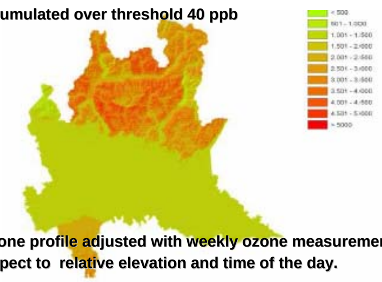


Expanded uncertainty
18.8 % at 80 ug/m³

Source: project INFOGESO Italy

AOT40 modelling in Lombardia, Italy

Ozone accumulated over threshold 40 ppb

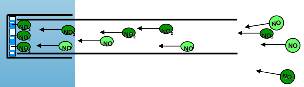


daily ozone profile adjusted with weekly ozone measurements with respect to relative elevation and time of the day.

see poster presentation A.Buffoni, Ambiente Italia

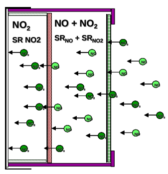
Principle of NO_x sampler

Oxidation of NO into NO_2
trapping with TEA



PTIO Method

2-Phenyl-4,4,5,5-tetramethylimidazonline-3-oxide-1-oxyl



CrO_3-Method

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Direct: measurement as NO_2 equivalents

$$C_{NOx} = \frac{Q_{NOx}\,[ug]}{SR_{NO2}\,[ml/min] \;*\; time\,[min]} \quad ug/m3$$

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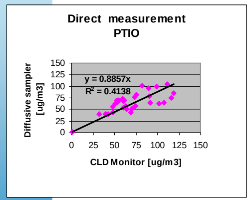
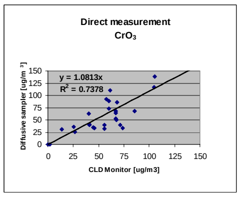
Coincidence NO_x diffusion tube with monitor direct measurement





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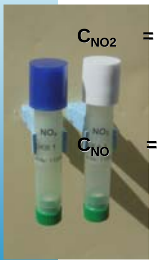
Indirect: measurement via difference NO_x – NO_2



$$C_{NO2} = \frac{quantity\ Q_{NO2}\,[ug]}{SR_{NO2}\,[ml/min] \;*\; time\,[min]} \quad ug/m^3$$

$$C_{NO} = \frac{(Q_{NOx} - Q_{NO2})\,[ug] \;*\; (30/46)}{SR_{NO}\,[ml/min] \;*\; time\,[min]} \quad ug/m^3$$

$$C_{NOx} = C_{NO2} + C_{NO} \quad ug/m^3$$

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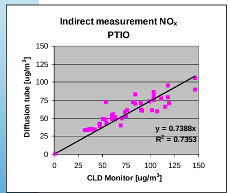
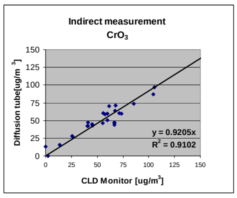
Coincidence NO_x diffusion tube with monitor indirect measurement



Expanded uncertainty
77.1 % at 30 ug/m^3
28.9 % at 80 ug/m^3



Expanded uncertainty
89.0 % at 30 ug/m^3
43.2 % at 80 ug/m^3

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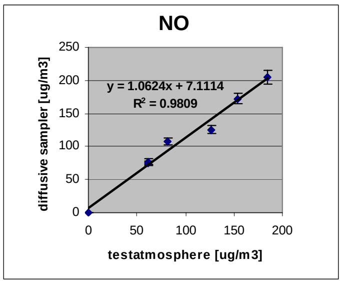
NO under laboratory conditions in known atmospheres



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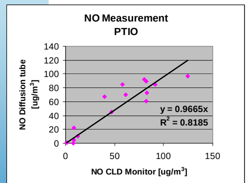
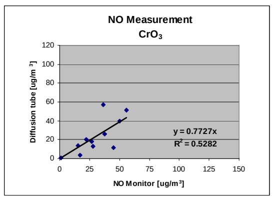
Results NO comparison





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Summary

- Consistent framework of standards: EN 13528 - ISO/IEC – 17025 - ISO 20988 available
- Expanded uncertainty of NO_2 tubes tends to reach quality objective for mandatory measurements
- 1-week ozone measurements useful input parameter for AOT_{40} mapping
- Due to high uncertainty of NO_x, measurement as NO_2 equivalents in remote areas (where NO_x limit value applies) is sufficient
- NO measurement by difference with reservation

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