

Metrology for Chemical Pollutants in Air

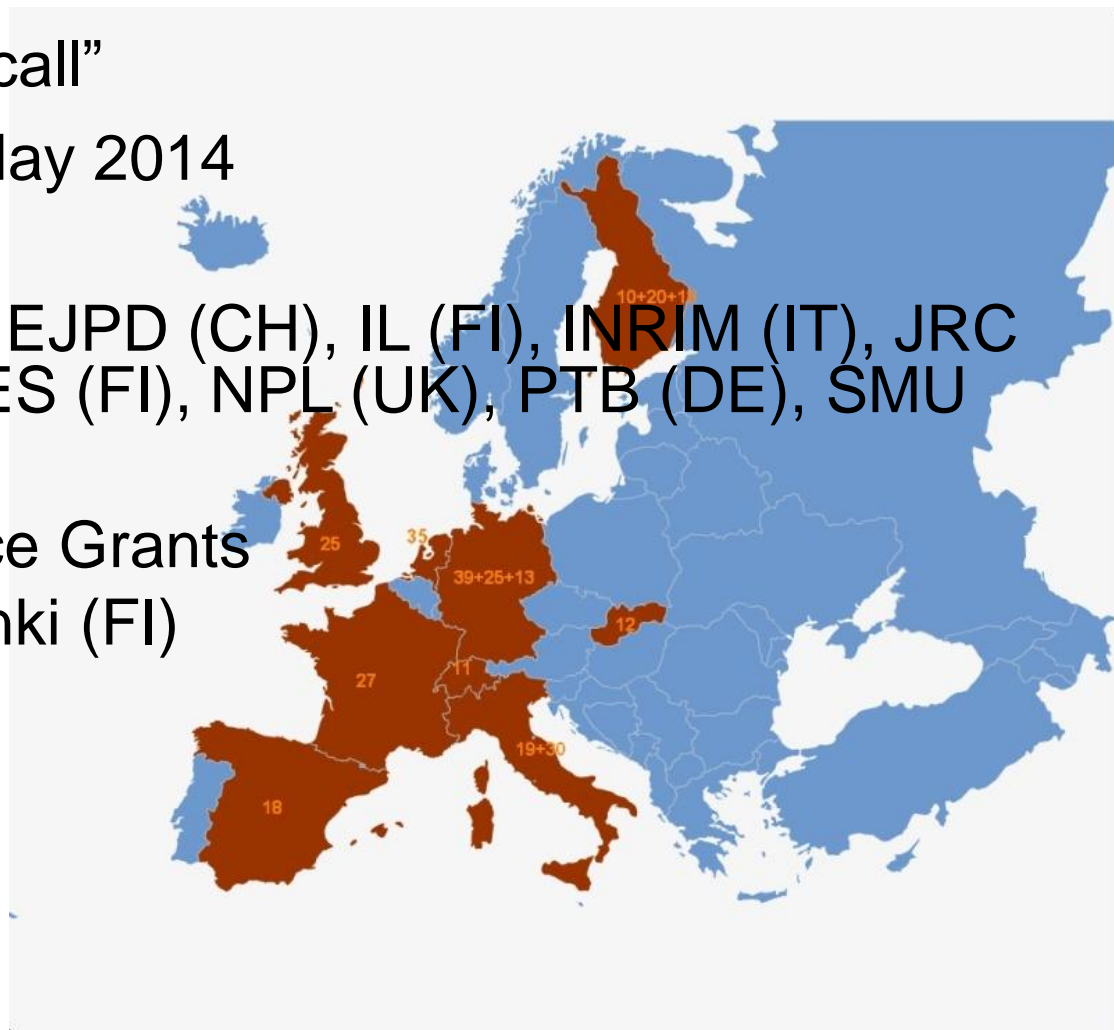
- EMRP “Environment call”
- Period June 2011 – May 2014

- 12 Partners

VSL (NL), BAM (DE), EJPD (CH), IL (FI), INRIM (IT), JRC (EC), LNE (FR), MIKES (FI), NPL (UK), PTB (DE), SMU (SK), UBA (DE)

- 2 Research Excellence Grants
CSIC (ES), Un. Helsinki (FI)

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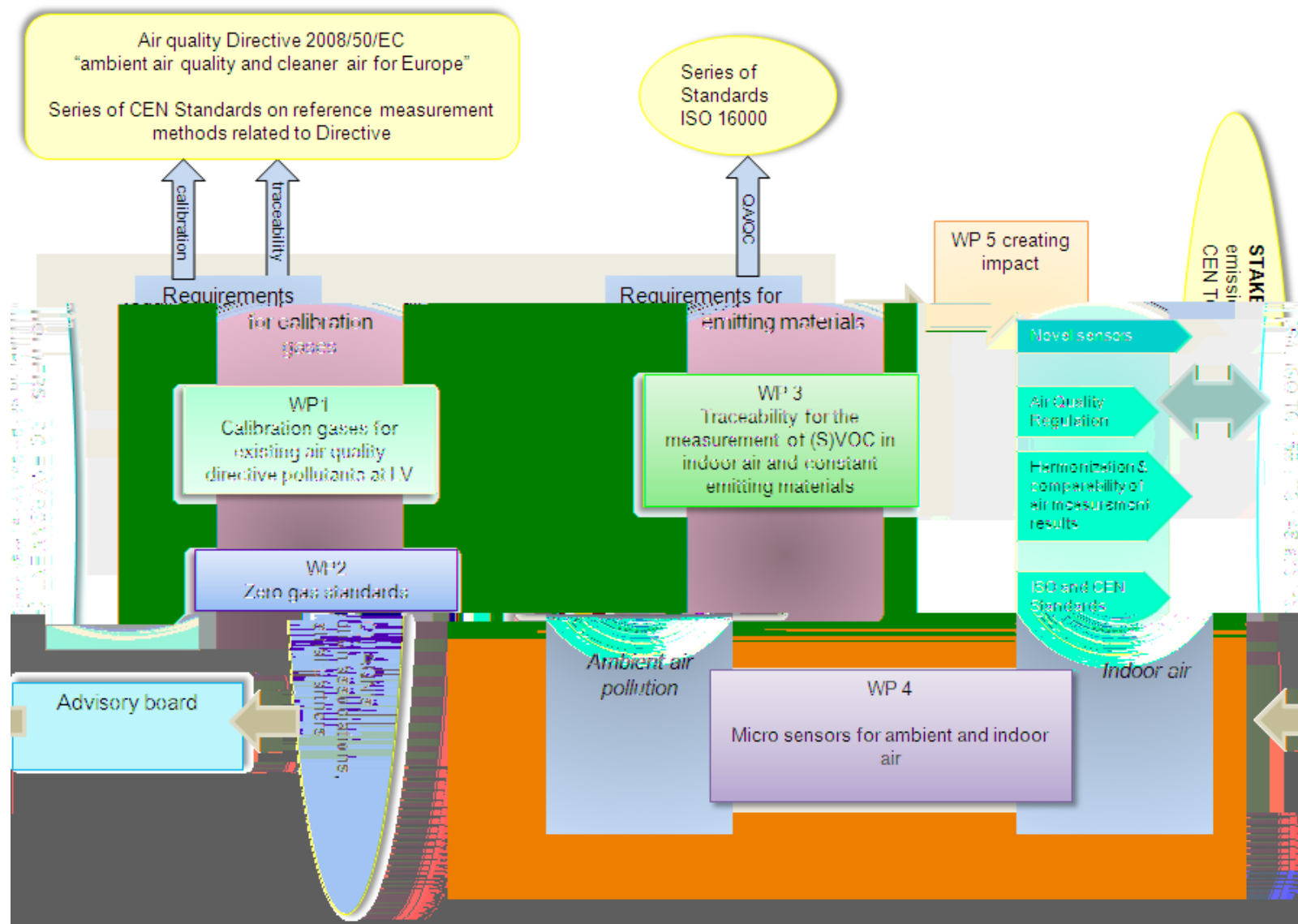
Objectives

- Improve metrological traceability and comparability of measurement results in current air monitoring techniques
- Set-up metrology infrastructure for upcoming sensor technology

Target pollutants

- Ambient air: reactive gases - Air Quality Directive (2008/50/EC)
- Indoor air: harmful semi-VOC emitted from building materials

JRP structure



WP1: Reactive calibration gases

- Focus on SO₂ and NO_x pollutants under EU Air Quality Directive (2008/50/EC)

	Limit Values, nmol/mol	Gas standard, nmol/mol
SO ₂	One hour: 132 One day: 47 Calendar year: 8	40 to 150 by permeation, static/dynamic dilution and cylinders, U<3%
NO ₂	One hour: 105 Calendar year: 21	20 to 100 by GPT, permeation, dynamic dilution and cylinders U<3%

- NO will be used as test gas to validate the work approach



Reactive calibration gases at EU Limit Values

- Improve static and dynamic dilution methods to lower uncertainty at the Limit Values
 - Permeation (SO_2 , NO_2)
 - Dynamic dilution of CRMs (SO_2 , NO , NO_2)
 - Static dilution (SO_2 , NO)
 - GPT (NO_2)
- Comparison of the generation methods



→ Preliminary conclusions

Impurities of pure and zero gases are major factors in the uncertainty of preparation

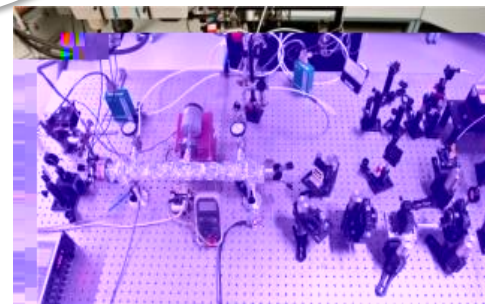
Zero gas standards

- Focus on zero gases for the measurement of SO₂ and NO_x
- Typical impurity specifications are listed in CEN standards related to “reference measurement methods for SO₂, NO and NO₂” (prEN14211 and prEN14212)

Specs zero gas in prEN14211	
Pollutant	Concentration
CO ₂	≤ 400 µmol/mol
O ₃	≤ 2.0 nmol/mol
NH ₃	≤ 10 nmol/mol
Water	≤ 150 µmol/mol
NO	≤ 1 nmol/mol
NO ₂	≤ 1 nmol/mol

Zero gas standards WP2

- New measurement approaches for (simultaneous) determination of impurities in zero gas below ppb level
- Classical analytical methods (e.g. chemiluminescence, fluorescence) versus new optical techniques based on laser absorption



Zero gas standards

Assess absorption effect in measuring reactive gases at trace level (NH_3 case study) by advanced laser spectroscopy

- Use of cavity-enhanced absorption spectrometer able to measure NH_3 in almost real time

- Focus on semi-VOC gas standards (BP >250 °C)

Compound	Category according to standard ISO 16000-9	Origin
Hexadecane	VOC-SVOC	Paints, flooring material, etc.
Dibutyl phthalate (DBP)	SVOC	Plasticizer; compound of very high concern (ECHA list)
Dimethyl phthalate (DMP)	SVOC	Plasticizer
2-ethyl-1-hexanol	VOC	Carpets, electronic devices
1-methyl-2-pyrrolidone	VOC	flooring material PVC-type; compound of very high concern (ECHA list)
Styrene	VOC	Reference compound

- Feasibility of generating standards VOC and SVOC in vapour phase and at trace levels (ppb)
- Preparation of transfer standards in sorbent tubes
- Validation of the measurement method
- Preparation of “diffusion-controlled” reference materials for indoor air applications



- Focus on gaseous pollutants regulated by the Air Quality Directive (2008/50/EC) –suitability of sensors as indicative methods ($U < 25\%$ for NO_2 , $U < 30$ for O_3 ...)
- NO_2 : development and validation of new graphene sensors + validation of available NO_2 commercial sensors with laboratory and field tests
- O_3 : validation of available commercial sensors with laboratory and field tests

- 3rd year of project: field tests of a clustered system including NO/NO_x/ NO₂, SO₂, CO, O₃ and benzene sensors at 2 field sites
- Protocol to validate the performance of micro-sensors
- Procedure for calibration of sensors
- Measurement uncertainty for NO₂, O₃ and the cluster of sensors
- Limited tests in indoor air

Creating impact

- Role of the Advisory Board: feed-back and dissemination



- Stake-holders involved in the JRP as collaborators (gas suppliers, sensor manufacturers, university and air monitoring networks)
- MACPoll takes part in the EU Air Policy Review
- Dissemination of project results (articles and lectures)
- Organisation of workshops and trainings