Landesamt für Natur,
Umwelt und Verbraucherschutz
Nordrhein-Westfalen

Equivalence Tests: Principles and the PM Issue

Ulrich Pfeffer, Jutta Geiger, Thorsten Zang

Conference: Current and Future Air Qualiy Monitoring
14 – 15 December 2010, London

GeRLAP
German Reference Laboratory for Air Pollution

AQUILA Air Quality Reference Laboratories

Frische Luft LUQS macht stark.

Overview

- Monitoring requirements
- Standardization
- Reference and equivalent methods
- Basic principles of equivalence testing
- Comparisons NRW – national – international
- Conclusions, outlook and future demands

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Requirements of Directive 2008/50/EC

- Information of the public (Annex XVI; at least daily; hourly whereever practicable)
- Definition of reference methods (Annex VI):
  - PM_{10}: EN 12341 (under revision; merge with EN 14907)
  - $PM_{2,5}$: EN 14907
  - Use of different methods if equivalent

B. **Demonstration of equivalence**

1. A Member State may use any other method which it can demonstrate gives results equivalent to any of the methods referred to in Section A or, in the case of particulate matter, any other method which the Member State concerned can demonstrate displays a consistent relationship to the reference method. In that event the results achieved by that method must be corrected to produce results equivalent to those that would have been achieved by using the reference method.

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Instruments in European Practise

- Gravimetry
  - LVS: „Kleinfiltergeräte“ (single filter, SEQ, Partisol)
  - HVS: Digitel DHA-80 (filter changer)
- AMS
  - Beta-Absorption
  - Oszillating Microbalance (TEOM, TEOM-FDMS)
  - Optical Instruments (light scattering), particle counters

? AMS equivalent to reference method?

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What is an equivalent method?

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EU Guidance on Equivalence

GUIDE TO THE DEMONSTRATION OF EQUIVALENCE OF AMBIENT AIR MONITORING METHODS

Report by an EC Working Group on
Guidance for the Demonstration of Equivalence

New version: January 2010

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Definition of Equivalence

'An equivalent method to the reference method for the measurement of a specified air pollutant, is a method meeting the data quality objectives for fixed measurements specified in the relevant air quality directive'

Test Programme 3 for PM (1)

- Laboratory test only relevant for modifications of RM
- Series of field tests (candidate vs reference method)
- Test conditions must be representative for practical use
- Minimum 4 comparison at a minimum of 2 sites

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Test Programme 3 for PM (2)

- Between-sampler uncertainty: RM 2 µg/m³, CM 2,5 µg/m³
- Split data sets at 30 µg/m³ for PM_{10}, at 18 µg/m³ for $PM_{2.5}$
- Perform orthogonal regression
- Perform calibration if necessary
- Calculate uncertainty for candidate method
- Compare results with data quality objective of Directive

Basic Equations

$$u_{bs}^2 = \frac{\sum_{i=1}^{n} (y_{i,1} - y_{i,2})^2}{2n} \qquad (9.4)$$

$$y_i = a + bx_i \qquad (9.5)$$

$$u_{CR}^2(y_i) = \frac{RSS}{(n-2)} - u^2(x_i) + [a + (b-1)x_i]^2 \qquad (9.6)$$

(random term)² (bias)²

$$RSS = \sum_{i=1}^{n} (y_i - a - bx_i)^2 \qquad (9.7)$$

PM Data Evaluation

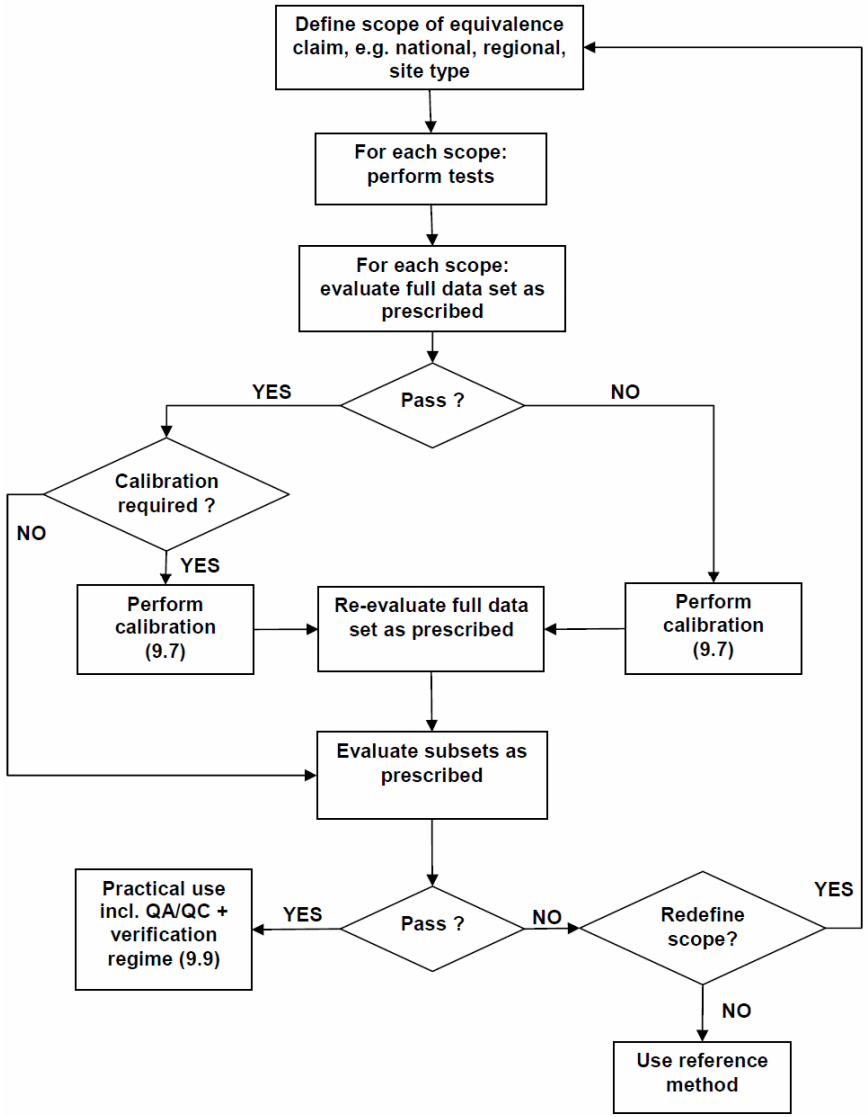
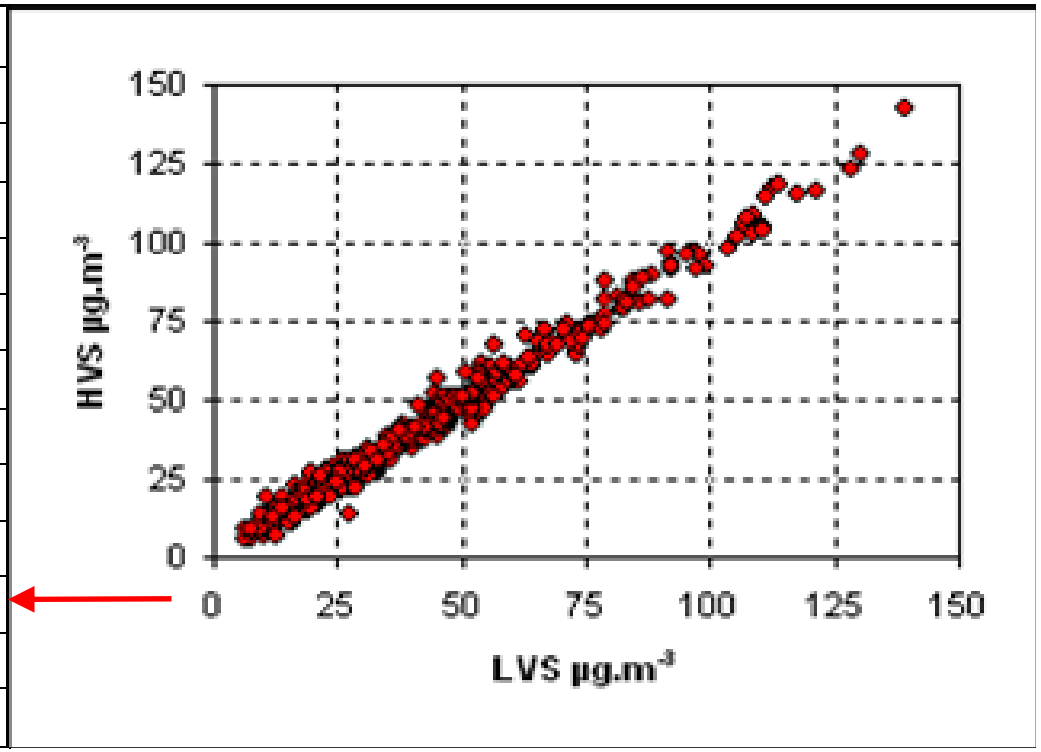


Figure 9.1. Flow scheme of evaluation of data from PM equivalence tests.

PM_{10}-Comparison LVS3 - Digitel DHA-80

Annex C of GDE

REGRESSION OUTPUT		
slope b	0,986	
uncertainty of b	0,004	sign
intercept a	-0,06	
uncertainty of a	0,16	
number of data pairs	790	
EQUIVALENCE TEST RESULTS		
random term	2,4	µg/m³
bias at LV	-0,8	µg/m³
combined uncertainty	2,5	µg/m³
relative uncertainty	5,0%	pass
ref sampler uncertainty	0,67	µg/m³
limit value	50	µg/m³



Wiesbaden Experiment of German Networks

2003, February – September; approx. 100 – 120 data pairs

LUA Materialien No. 66, 175 pages (2005) *www.lanuv.nrw.de*

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PM_{10} Reference Method

Data Quality

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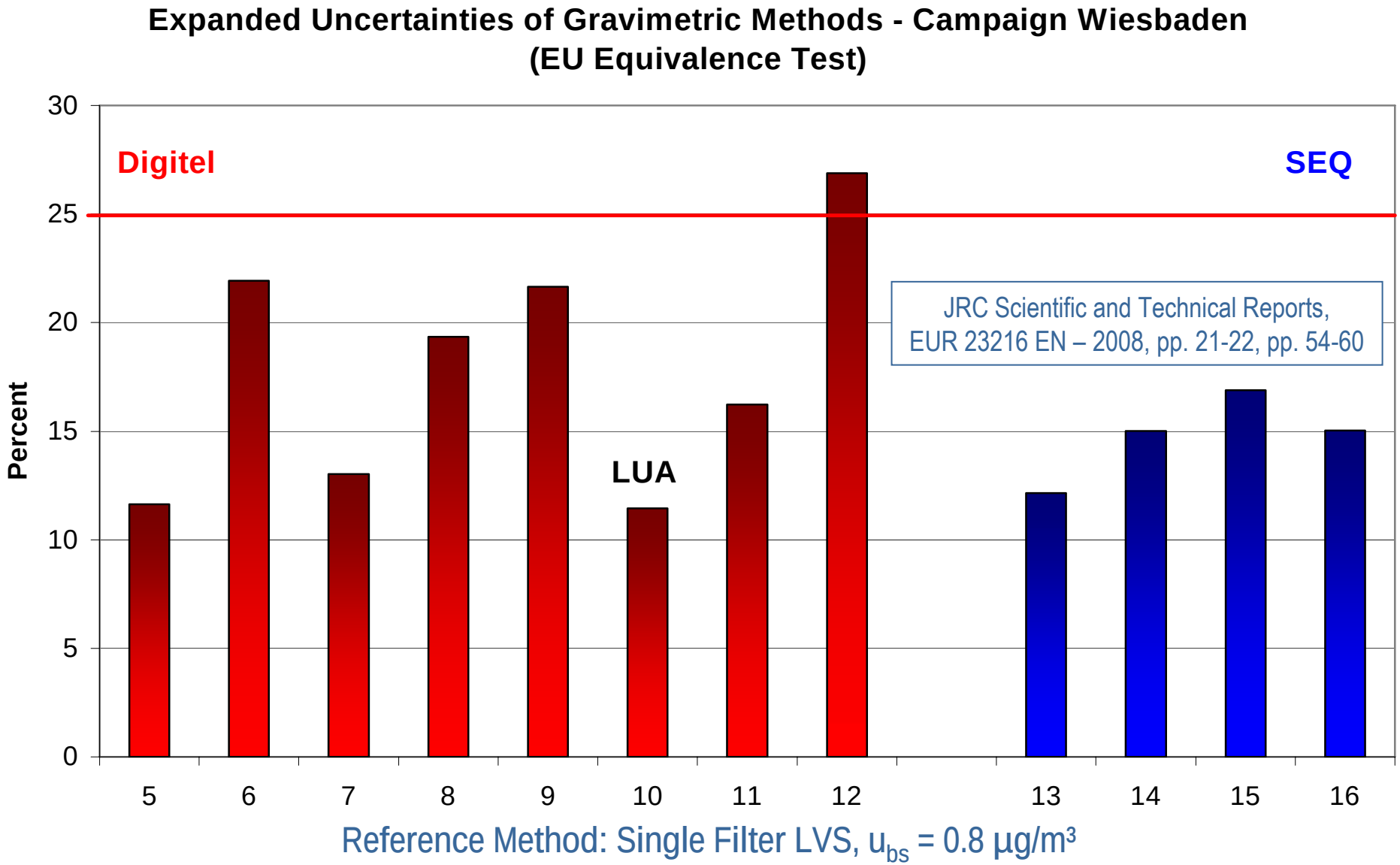
Wiesbaden Experiment of German Networks



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Continuous Methods PM_{10}

Equivalence Tests

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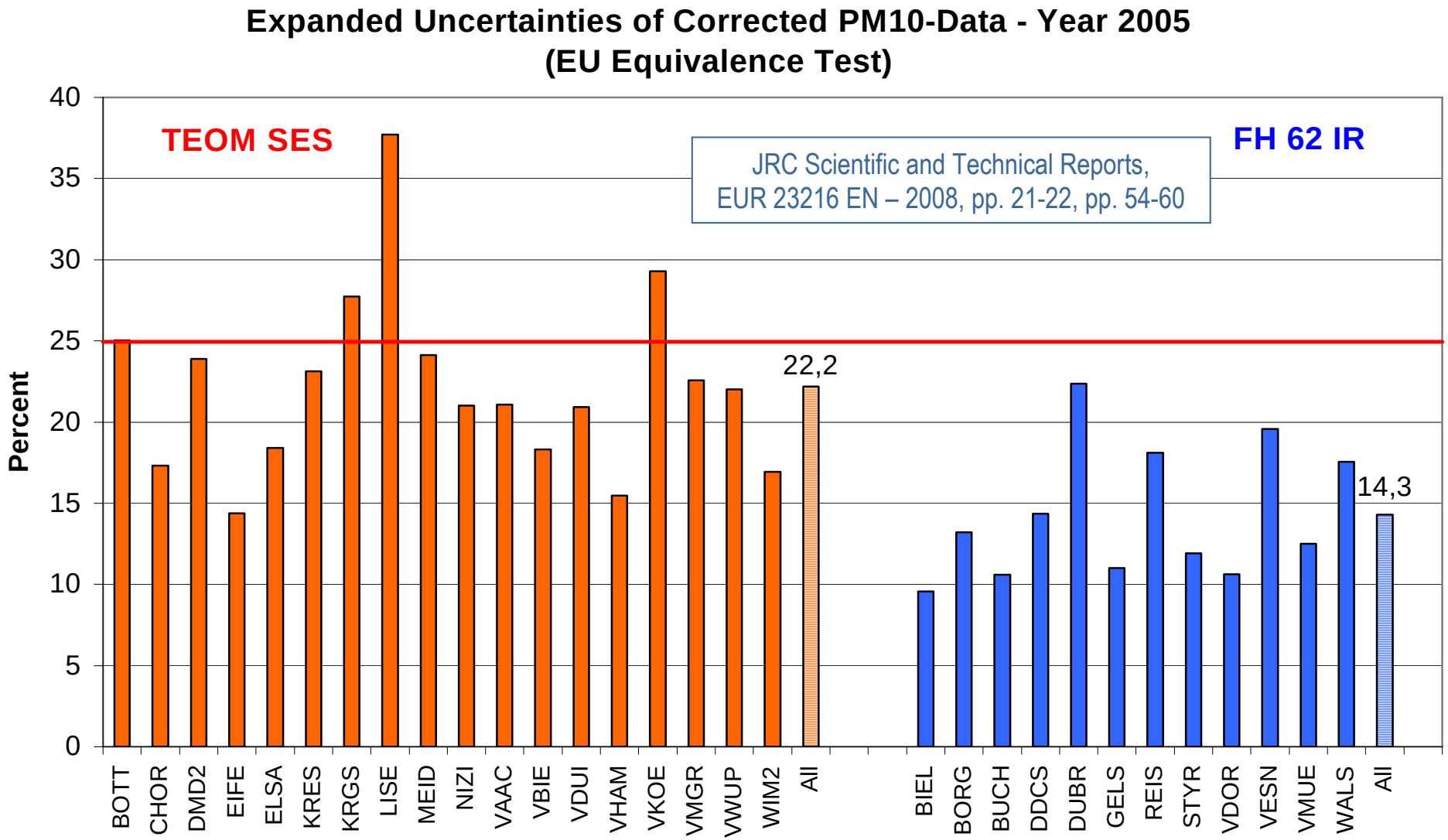
Uncertainty of Corrected Data (NRW)



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Thermo Model 5030 SHARP Monitor

- ‚Synchronised Hybrid Ambient Real-time Particulate Monitor‘
- Combination of light scattering photometry and beta radiation attenuation

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TÜV Results SHARP Monitor PM_{10}

Parameter	4 Sites in Cologne / Brühl / Titz / Cologne
Type	Urban background / gravel mining / rural / traffic
Period	2006: Jan-May / May-Jul / Jul-Sep / Sep-Nov
Reference Method	Leckel LVS3 or SEQ47/50 / QFF
Nr of Data Pairs	67 / 55 / 52 / 54
Mean of RM Data (µg/m³)	30,8 / 26,2 / 25,1 / 25,7
Range of RM Data (µg/m³)	9-120/ 8-79 / 9-83 / 13-51
Between-RM Uncertainty (µg/m³)	0,76 / 0,59 / 0,76 / 1,27
Between-CM Uncertainty (µg/m³)	0,57 / 1,20 / 1,11 / 1,23
Relation RM – CM	CM=1,00*RM–0,29 / CM=1,00*RM–1,21 CM=0,98*RM–0,53 / CM=1,04*RM–2,82
Expanded Uncertainty CM	12,8% / 12,0% / 14,0% / 9,3%
After Correction (S-I)	13,5% / 12,4% / 16,8% / 11,8%

TÜV Results SHARP Monitor $PM_{2.5}$

Parameter	4 Sites in Cologne / Brühl / Titz / Cologne
Type	Urban background / gravel mining / rural / traffic
Period	2006: Jan-May / May-Jul / Jul-Sep / Sep-Nov
Reference Method	Leckel LVS3 or SEQ47/50 / QFF
Nr of Data Pairs	54 / 40 / 47 / 40
Mean of RM Data (µg/m³)	24,0 / 15,0 / 13,6 / 16,5
Range of RM Data (µg/m³)	7-98 / 3-43 / 4-37 / 5-40
Between-RM Uncertainty (µg/m³)	1,63 / 0,73 / 0,49 / 0,58
Between-CM Uncertainty (µg/m³)	0,58 / 1,17 / 0,87 / 0,68
Relation RM – CM	CM=0,92*RM+1,04 / CM=1,08*RM+0,23 CM=1,10*RM+0,05 / CM=0,93*RM–0,05
Expanded Uncertainty CM *)	20,4% / 21,4% / 23,3% / 19,6%
After Correction (S-I) *)	20,6% / 15,7% / 15,5% / 17,7%

*) related to 35 µg/m³

UK Equivalence Programme

UK Equivalence Programme for Monitoring of Particulate Matter.

Final Report for:
Department for the Environment, Food and Rural Affairs;
Welsh Assembly Government;
Scottish Executive;
Department of Environment for Northern Ireland.

Ref: BV/AQ/AD202209/DH/2396
DATE 5th June 2006

Two Sites in Duisburg (VDUI / DUBR)

Test of FDMS

PM_{10} - LANUV

- 2 TEOM FDMS (Type B)
- 2 Digitel DHA-80 HVS
- July 2005 – Jan. 2007
- ≈ 6 - 7 months

JRC Scientific and Technical Reports,
EUR 23216 EN – 2008, pp. 21-22, pp. 54-60

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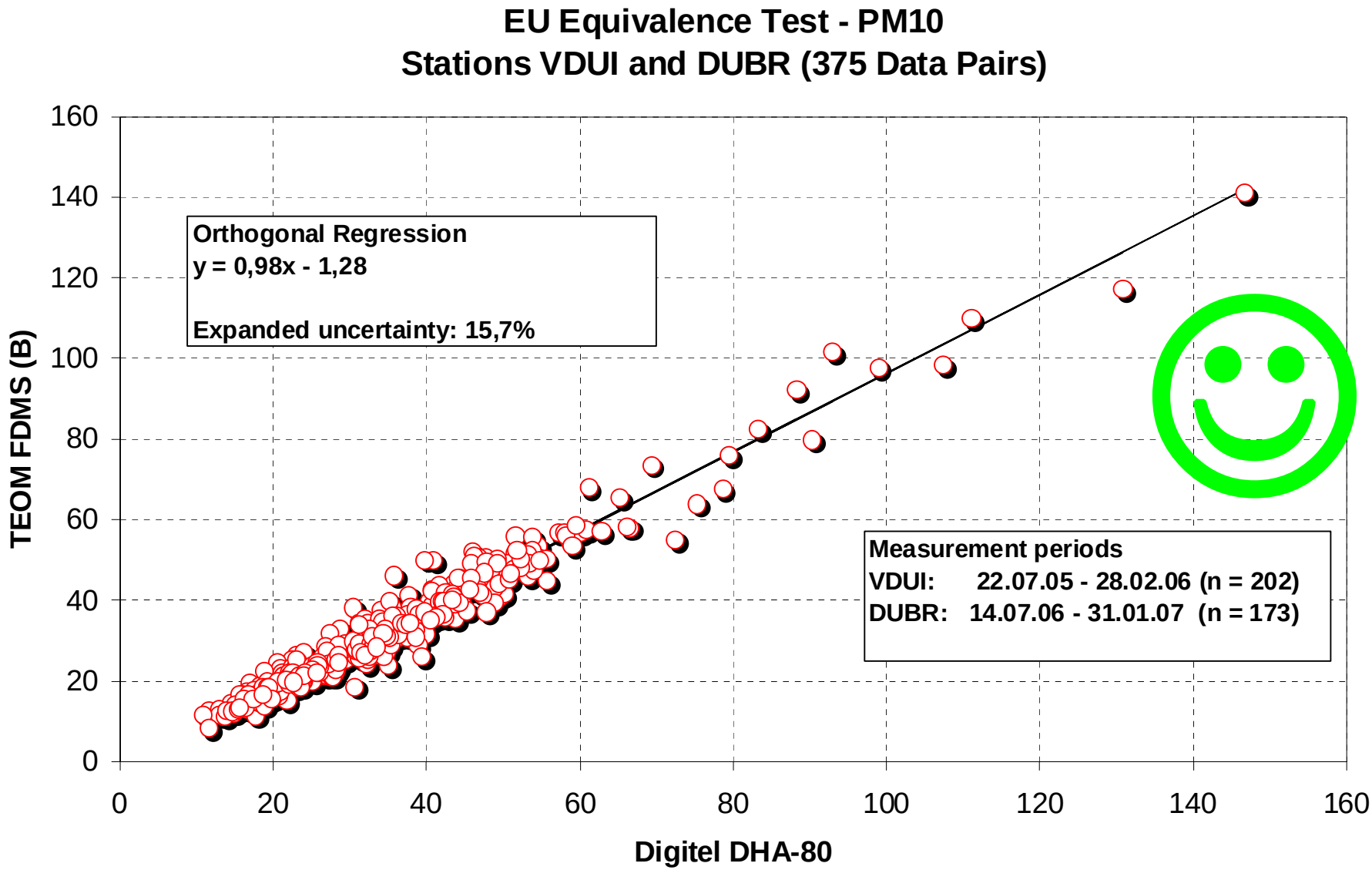
PM_{10} Results TEOM FDMS in Duisburg



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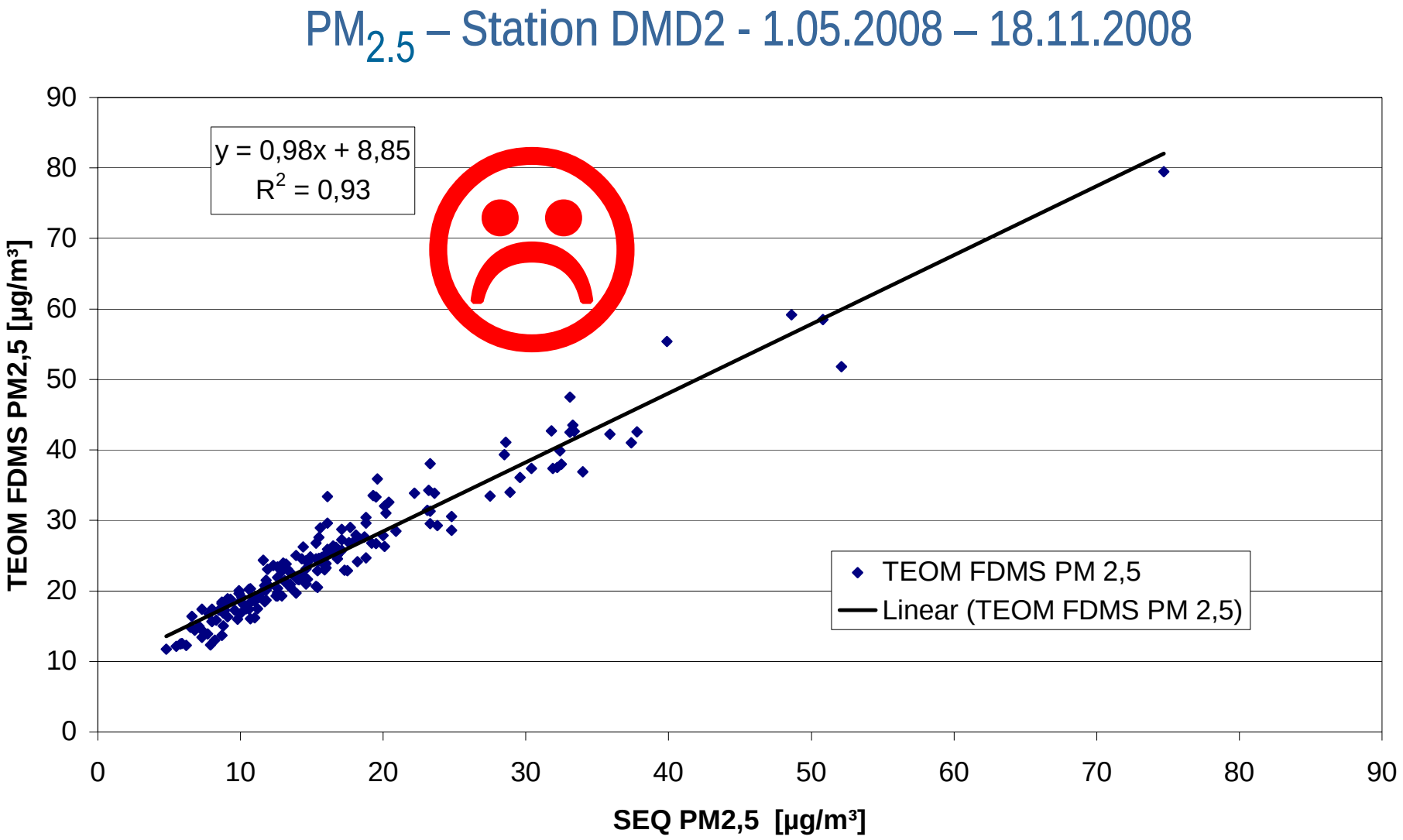
Experiences with TEOM FDMS – $PM_{2.5}$

- After promising results for PM_{10} the network in NRW was equipped with FDMS also for $PM_{2.5}$

- Firstly only one station with co-located reference method

TEOM FDMS (C) $PM_{2,5}$ – LANUV Results



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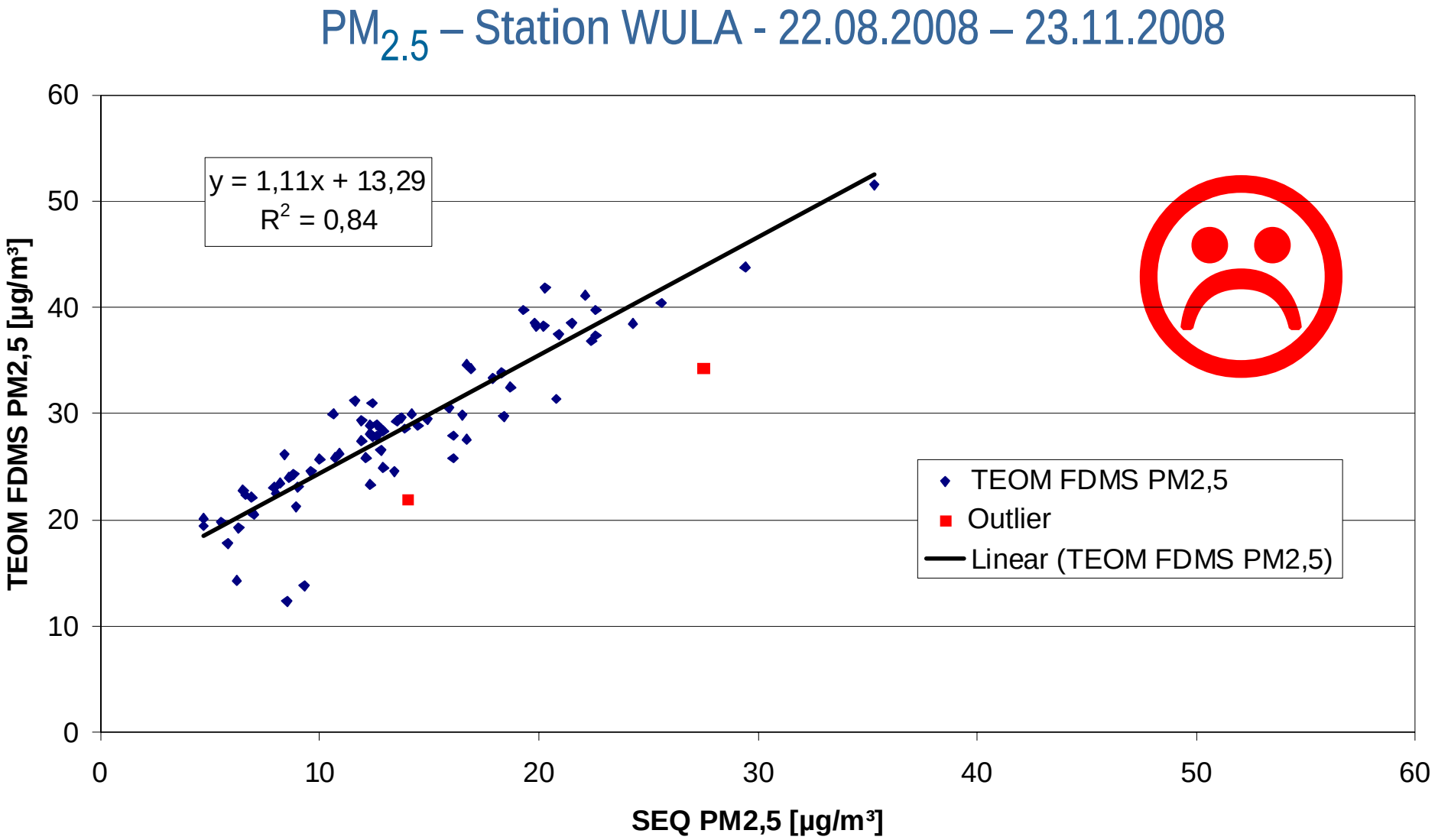
TEOM FDMS (C) $PM_{2,5}$ – LANUV Results



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Conclusions – Decisions in NRW

- All measurements at AEI stations with TEOM FDMS for $PM_{2.5}$ were stopped in the LUQS network in NRW
- 9 AEI stations in NRW operated with SEQ gravimetrically only
- Extension of $PM_{2.5}$ network for non-AEI stations postponed

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TEOM FDMS

Equivalence Testing
Results from Other Countries

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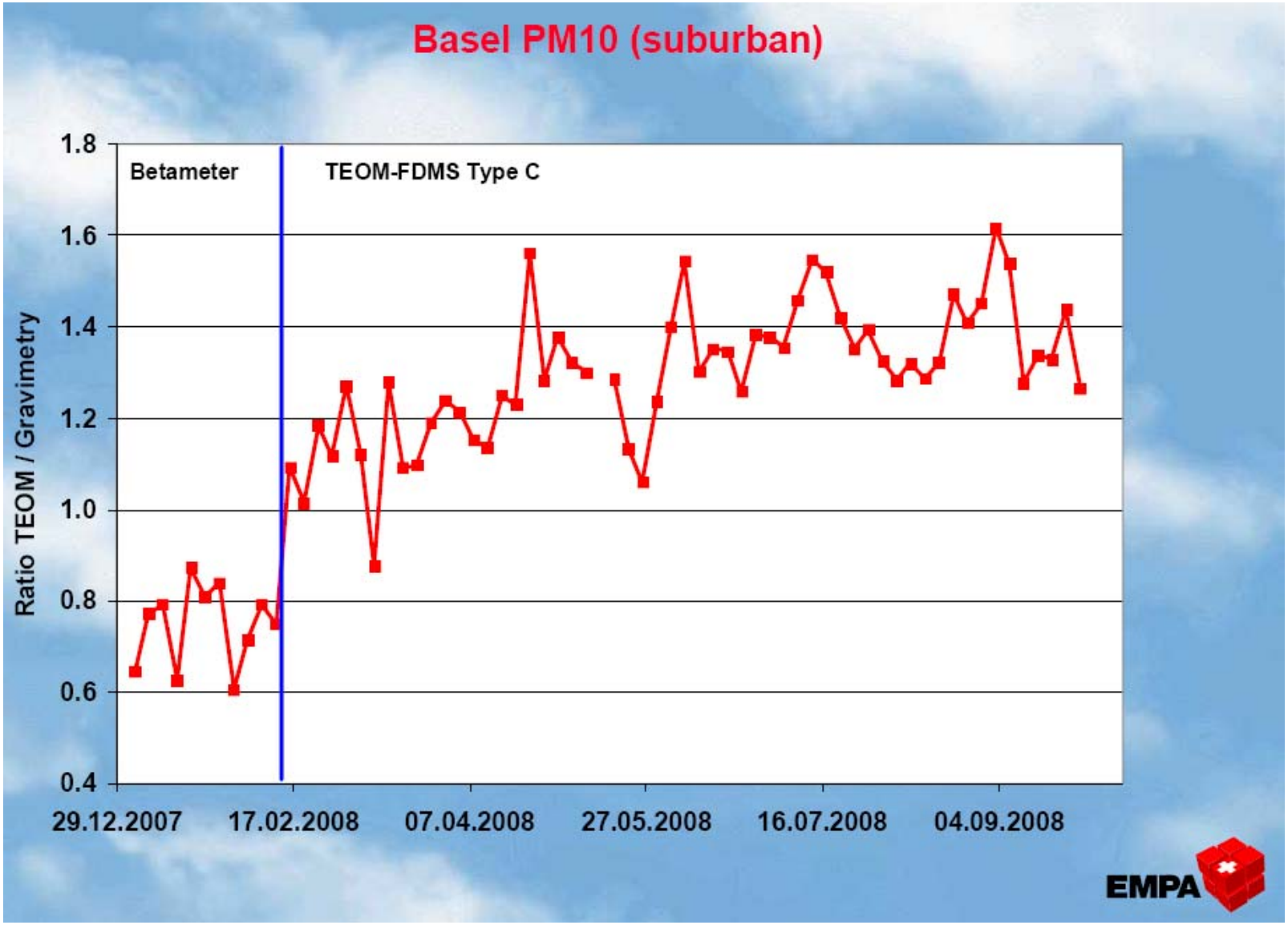
Results from Switzerland (PM_{10})



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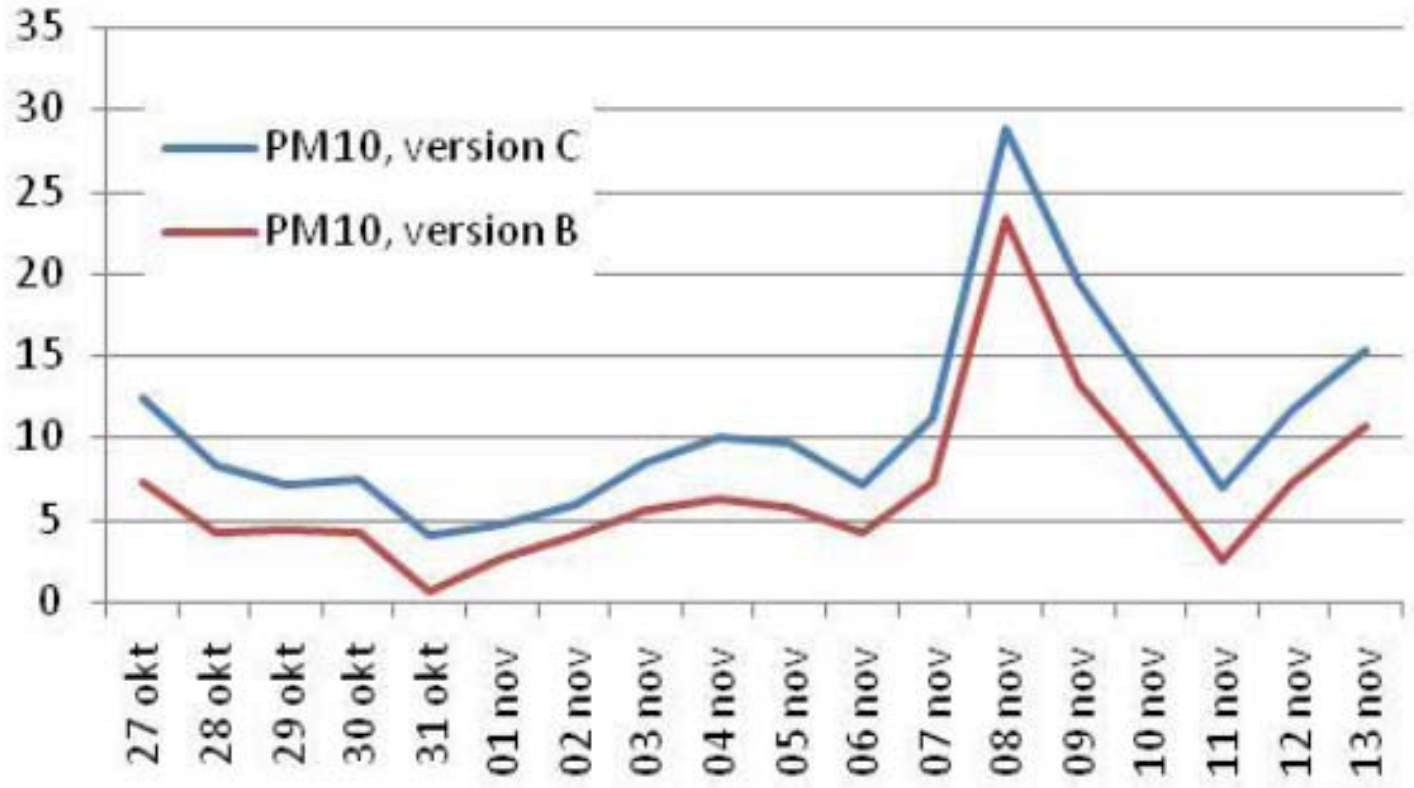
Results from Sweden (PM_{10})

Figure 3



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Equivalence Testing

Recent Data 2010

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LANUV Equivalence Tests 2010

Preliminary Data January – October 2010

Spreadsheet RIVM_PM_equivalence_v2.6

Calibration setting: Slope through origin

- Reference method:
  - PM_{10}: Digitel DHA-80-Geräte (quartz fibre)
  - $PM_{2.5}$: Leckel SEQ 47/50 (glass fibre)
- TEOM FDMS
  - 7 sites for PM_{10}
  - 3 sites for $PM_{2.5}$ (replacement of dryers during spring)
- SHARP
  - 5 sites or PM_{10}
  - 2 sites for $PM_{2.5}$
- BAM
  - 1 test station for $PM_{2.5}$ together with SHARP and RM

LANUV Equivalence Tests 2010

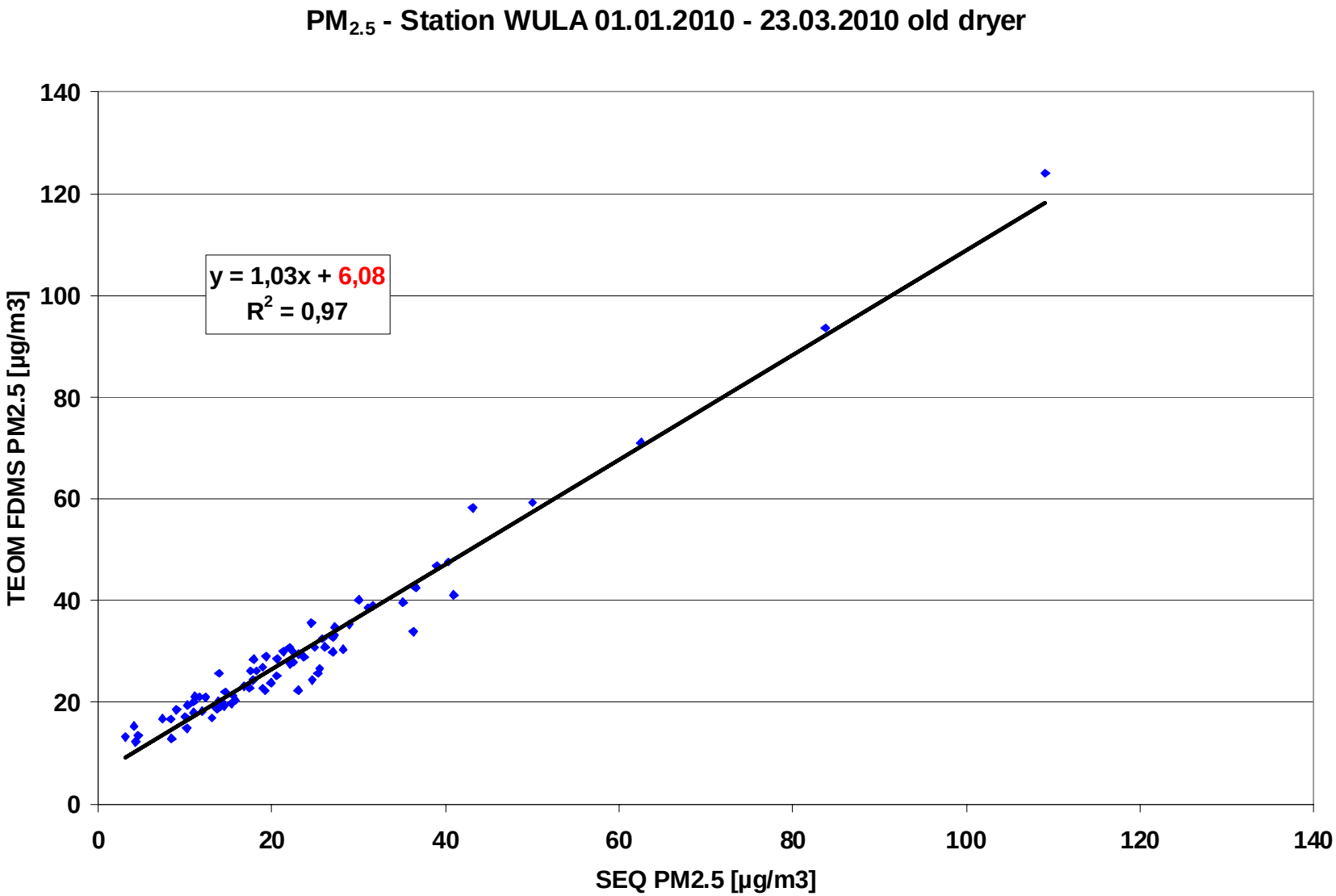
Results for TEOM FDMS

	Calibration factor (slope b)	Expanded relative uncertainty for the full data set	Expanded relative uncertainty for the subset concentrations PM10 > 30 µg/m³ PM2.5 > 18 µg/m³	Expanded relative uncertainty for the subset individual site
PM10	1,0	15,5	18,5	19,5; 23,4; 15,3; 14,6; 12,3; 9,9; 13,8
PM2.5 (old dryer)	0,93	22,8	24,0	21,0; 14,4; **34,9**
PM2.5 (refurbished dryer)	1,0	16,9	20,3	20,3; 18,1; 12,8

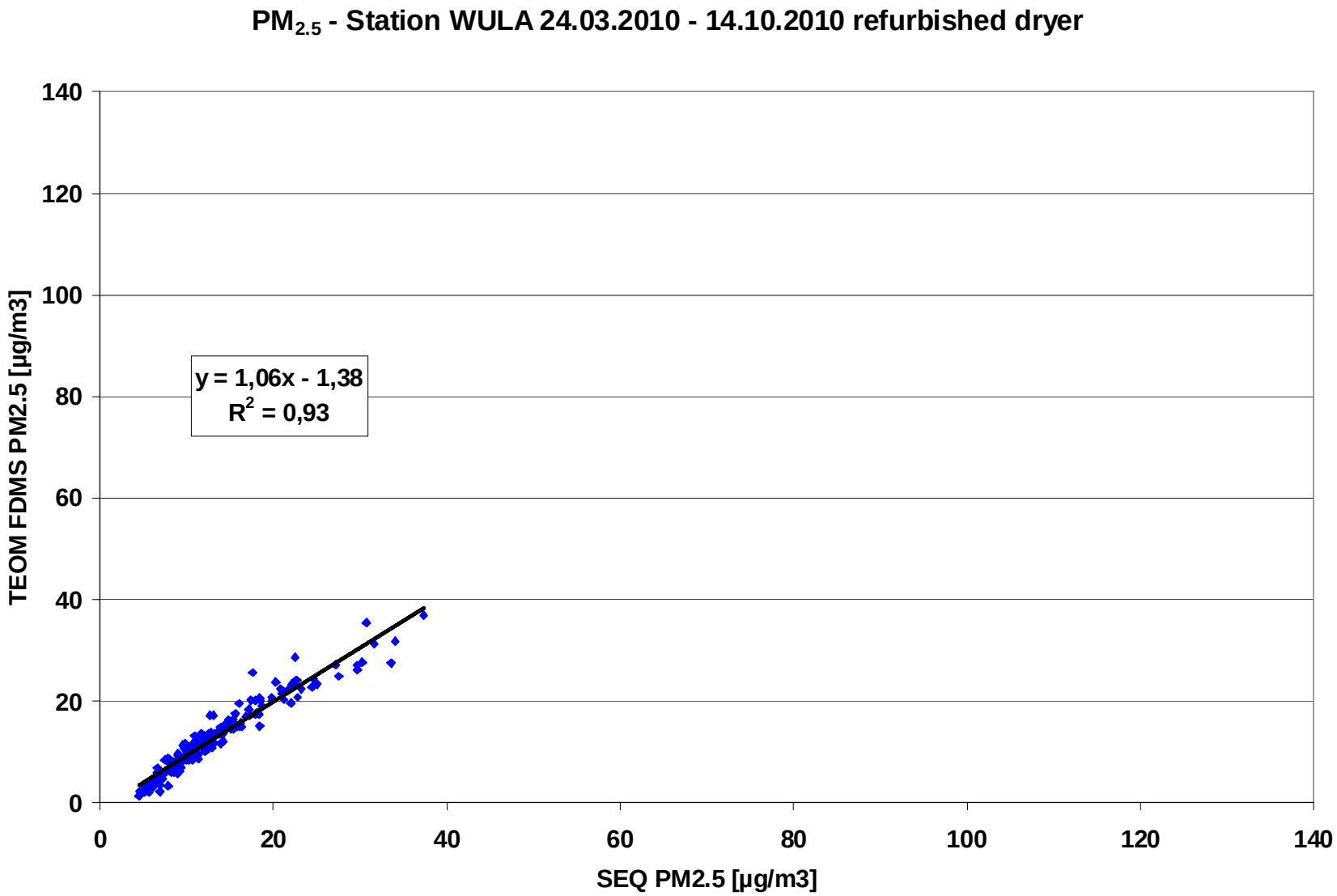
PM10: no calibration needed; but two sites with significantly different factors (0,83 and 1,11, respectively)

PM2.5: with the refurbished dryer it is possible to meet the data quality objectives; but the factors at the different sites vary quite a bit (0,93; 1.02 and 1,11)

LANUV Equivalence Tests 2010



LANUV Equivalence Tests 2010



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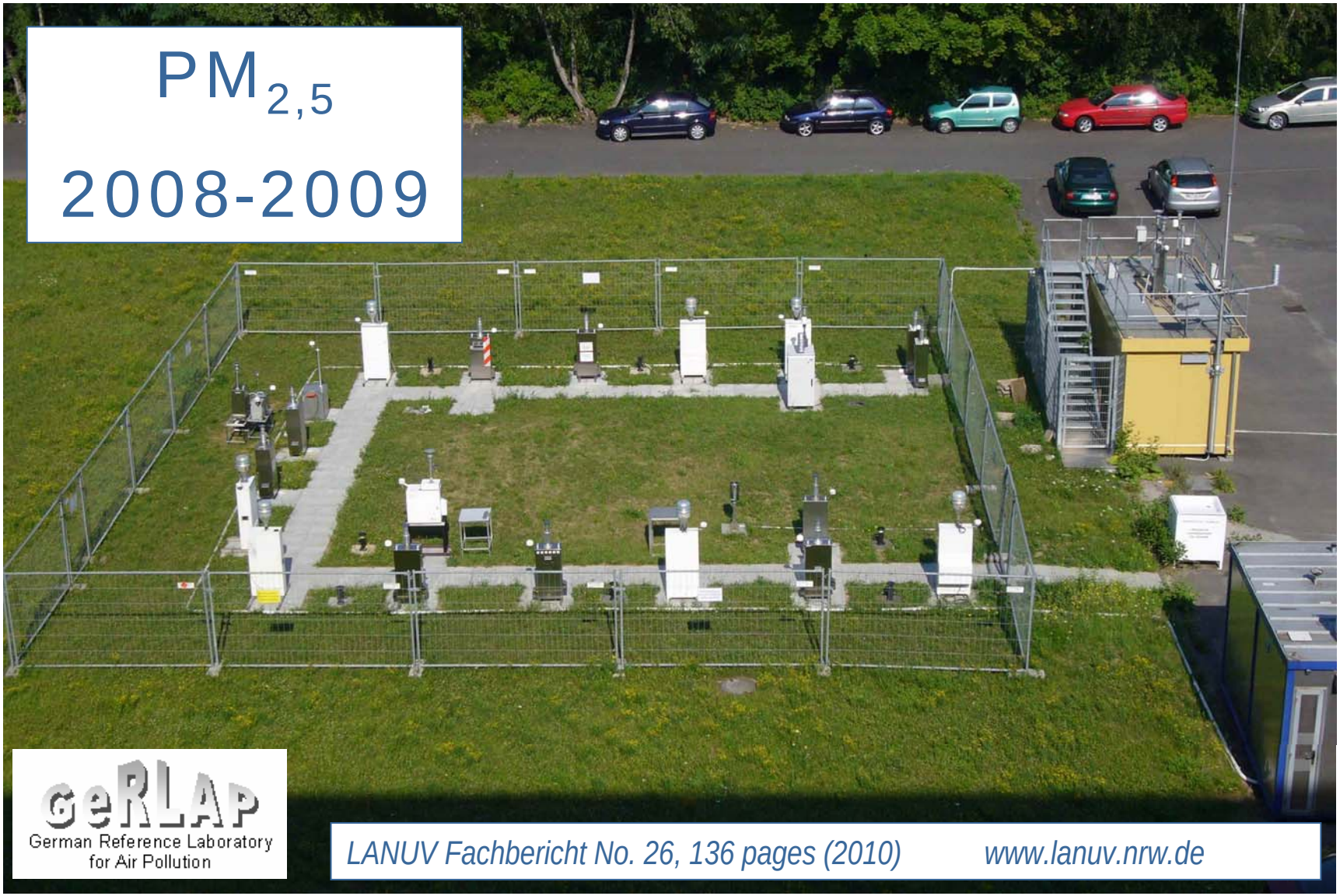
Results for SHARP and BAM

	Calibration factor (slope b)	Expanded relative uncertainty for the full data set	Expanded relative uncertainty for the subset concentrations PM10 > 30 µg/m³ PM2.5 > 18 µg/m³	Expanded relative uncertainty for the subset individual site
PM10 (SHARP)	1,1	14,3	18,3	13,1; 17,3; 14,6; 13,4; 15,1
PM2.5 (SHARP)	1,1	13,3	15,4	13,5; 12,5
PM2.5 (BAM)	1,03	19,6	20,6	19,6

SHARP: pass the equivalence test for PM10 and PM2.5; the calibration factor is identical for both PM fractions and very similar for all sites

BAM: could pass the test even without calibration factor, but more data is needed to evaluate this method

Wiesbaden Experiment of German Networks



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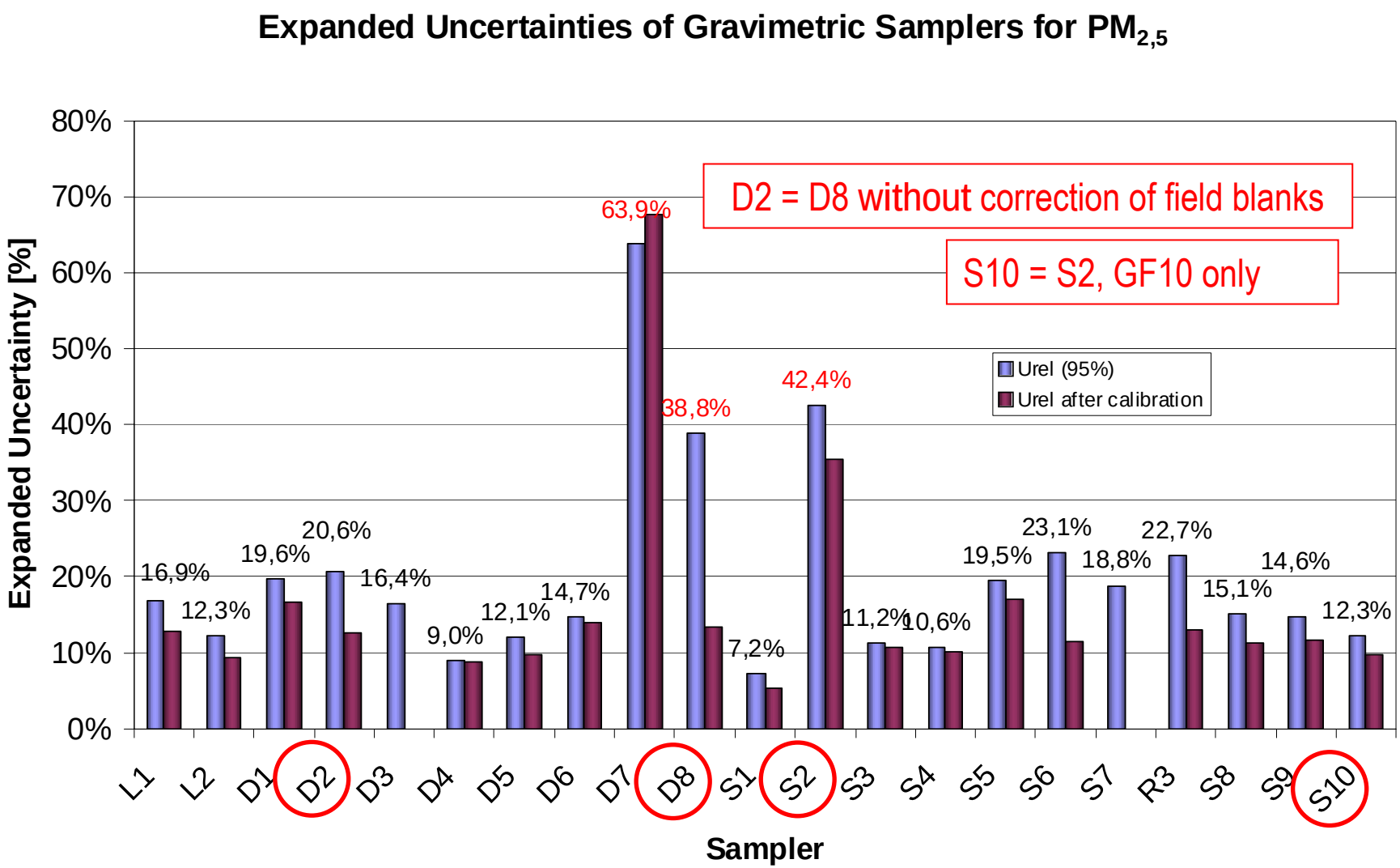

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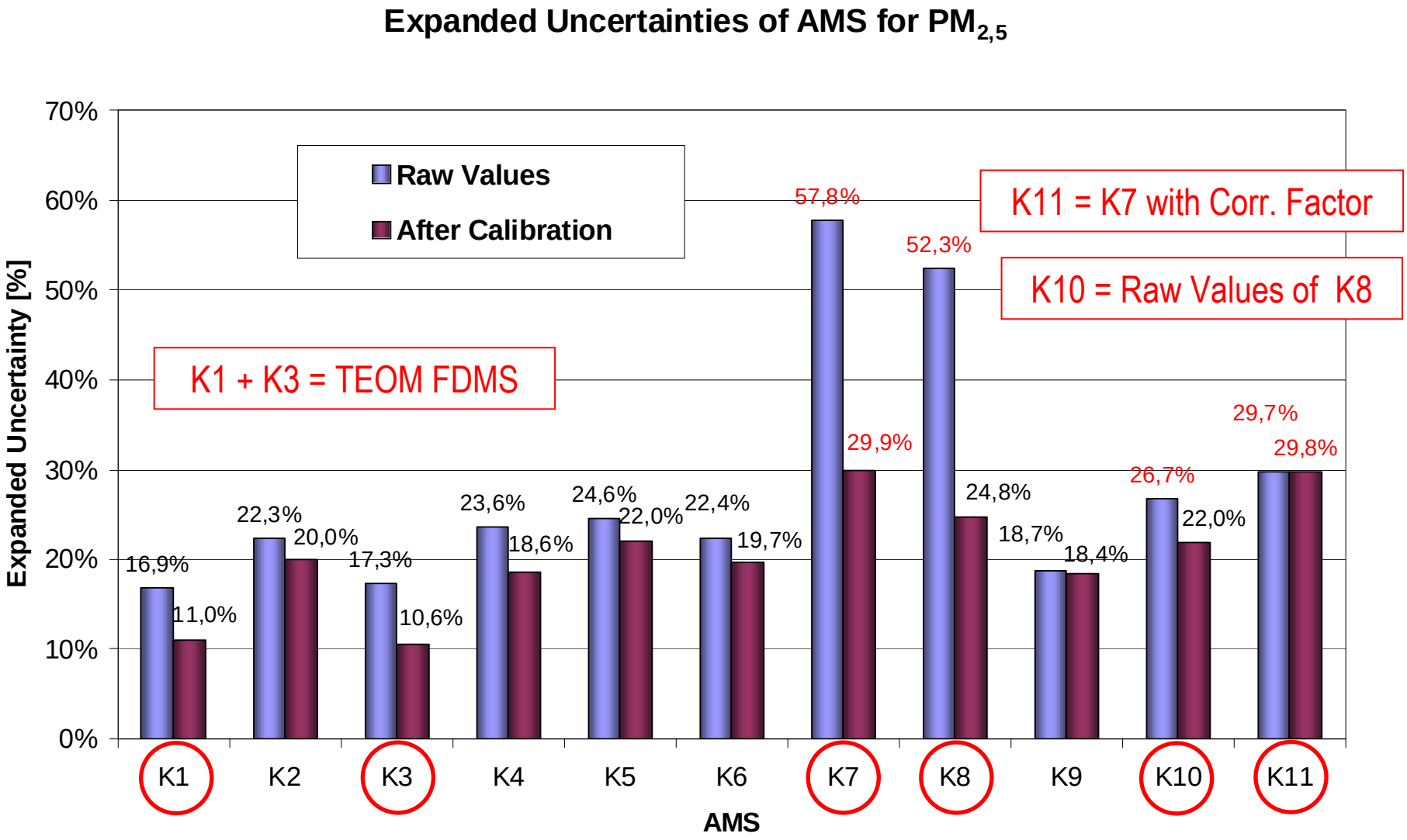

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Conclusions (1)

- HiVol sampler (Digitel) is equivalent to the reference method (U_{exp} = 10 %)
- Gravimetric methods may generally meet the DQO
- In most cases also data of AMS can meet the DQO
- Calibration factors are needed for some AMS

☹Results may vary dramatically from site to site

↳Transfer of results to unknown sites is critical

Conclusions (2)

What is urgently needed?

- Demonstration of equivalence for all AMS
- Rigid regime for QA/QC for all PM measurements
- Revision / harmonisation of EN 12341 and EN 14907
- New standard for AMS
- Re-consider some procedures of GDE
- Share results of DoE
- Set up validated data base for results of DoE

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