

Results of intercomparison exercise and recommended methods

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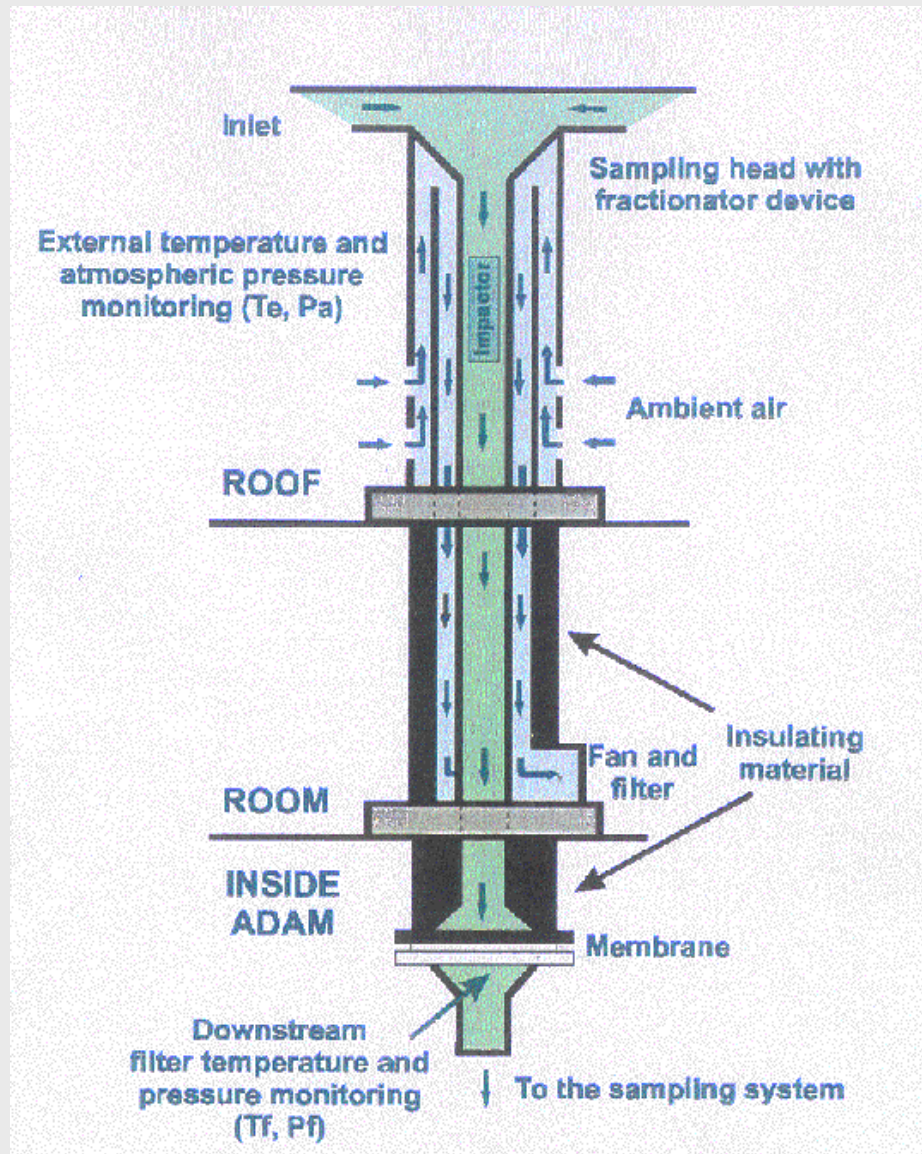
Duration of PM_{2.5} field tests:
27 September - 24 July 2003

707 Experiments

Measurement methods involved in the field tests

Manual samplers (induplicate)

- Mini Wrac, multi-jet impactor, 0.172 moles/sec \sim 15m³/h
- US PM2.5 reference sampler, WINS with PM10 pre-impactor, 1.0m³/h
- Partisol Plus, SCC with PM10 pre-impactor, sequential sampler used as single filter sampler, 1.0m³/h
- LVS-3D, 8-jet-impactor, 2.3m³/h
- SEQ 47/50, 8-jet-impactor, sequential sampler with sheath air used as single filter sampler, 2.3m³/h
- DHA-80, 10-jet-impactor, sequential sampler used as single filter sampler, 30m³/h



Automatic methods (single instruments):

- SM2000 (ADAM) Beta-ray attenuation monitor, 8-jet-impactor, sequential sampler with sheath air, every 24 hours 1 value, 1.0m³/h
- FH62I-R Beta-ray attenuation monitor, SCC with PM10 pre-impactor, filter tape, continuous measurement up to 24 hours, each, 1.0m³/h
- BAM1020 Beta-ray attenuation monitor, 8-jet-impactor, filter tape, 50min sampling and 10min measurement, each, 1.0m³/h
- TEOM SES, SCC with PM10 pre-impactor, 1.0m³/h resp. 3 l/min

Other methods

- 8400-N semi-continuous nitrate sampler
- A manual gravimetric PM10 sampler following the requirements of EN 12341
- Meteorological instruments for:
 - Temperature
 - Atmospheric pressure
 - Relative humidity

Requirement of the Commission

The PM2.5 reference or standard method should base on the gravimetric evaluation of filters by means of a balance:

- 1) Only the manual methods could serve as examples for a European standard method.
- 2) To the automatic instruments the equivalence test procedure for non-standard methods was exemplary applied.

Measurement sites

Pilot site

Berlin (Germany)

Test sites

Southern Europe

Madrid (Spain)

Near a crossing of traffic streets

Rome (Italy)

Near a main street in the city centre

Athens (Greece)

Suburban, outside the city

Central Europe

Vienna (Austria)

At an intensive traffic loaded city motorway at the border of the city

Western Europe

Duisburg (Germany, Ruhr area)

Suburban with influence from local heavy industry

Teddington (UK, Greater London)

Suburban, residential area

Vreedepeel (The Netherlands)

Rural site

Northern Europe

Aspvreten (Sweden)

Forest situation, close to the Baltic sea



Data analysis procedures

Grubbs outlier test

Applied to only the paired data of the duplicate measurements of the manual methods

$$TP = \left| \frac{D_{extr.} - D_{mean}}{s_D} \right| \quad \text{with} \quad D_i = |y_{i1} - y_{i2}|$$

TP was compared with a critical value from a standard table:

$$TP > \text{critical value} \Rightarrow \text{outlier}$$

Only 5% of the data collective could be removed.

Regression analysis

The linear orthogonal regression was used.

$$y = a + b x$$

Slope b :

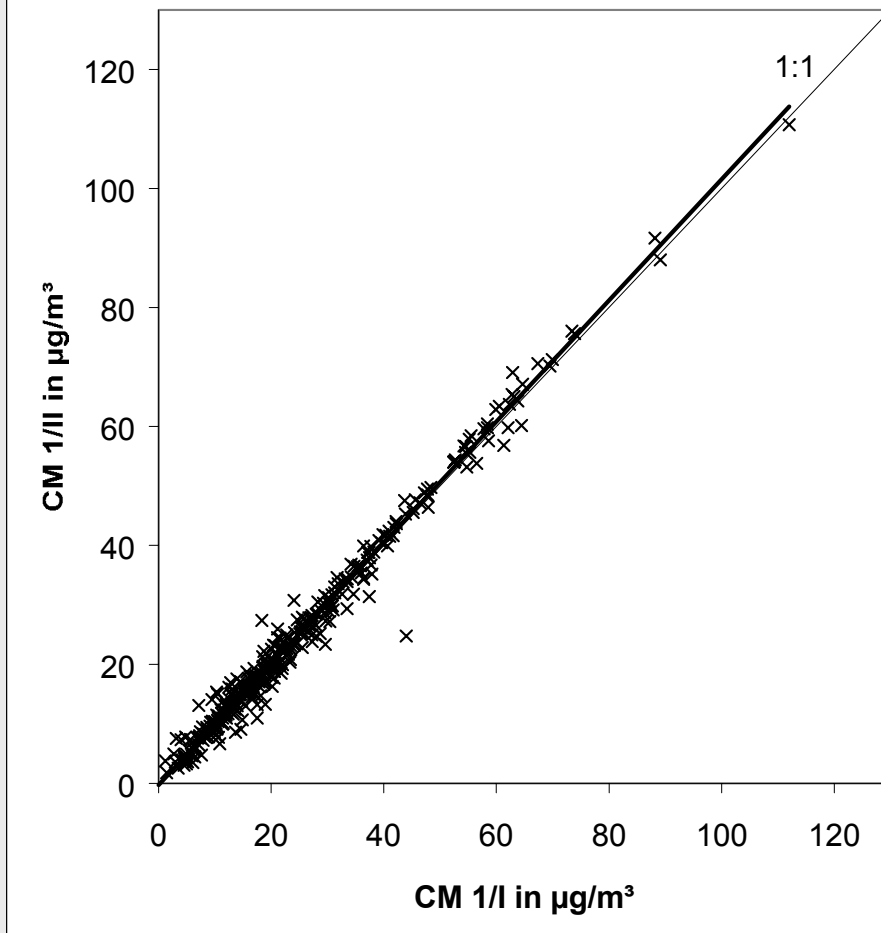
$$b = \frac{Syy - Sxx + \sqrt{(Syy - Sxx)^2 + 4 \cdot (Sxy)^2}}{2 \cdot Sxy}$$

Confidence limits of the slope b

$$CL = \arctan b \pm \frac{1}{2} \arcsin \left[2 \cdot t_{95} \sqrt{\frac{Sxx^2 \cdot Syy^2 - Sxy^2}{(n-2) \cdot (Sxx^2 - Syy^2)^2 + 4 \cdot Sxy^2}} \right]$$

t_{95} = Student factor (95% confidence range)

All Sites
Figure 1. CM 1/I vs. CM 1/II

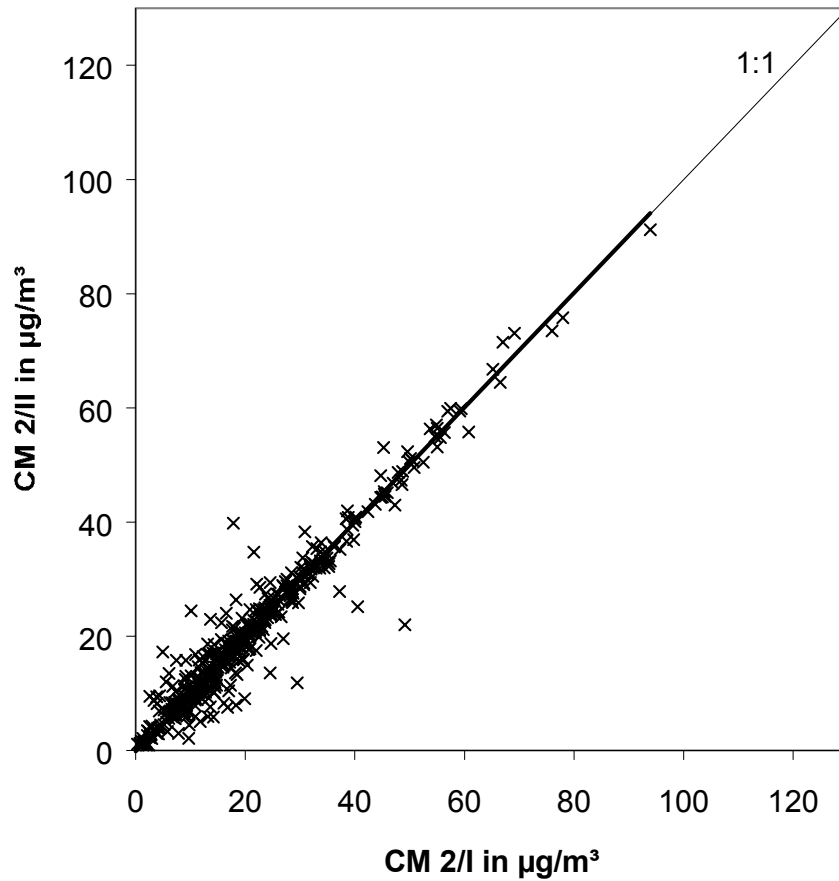


n = 387
Ortho. regr. $y = -0.29 + 1.019 x$
S slope = 0.007
S Intercept = 0.19
 $R^2 = 0.983$
R = 0.992
AM CM 1/I = $23.69 \mu\text{g}/\text{m}^3$
AM CM 1/II = $23.84 \mu\text{g}/\text{m}^3$
 $S_{\text{CM 1/I}} = 16.45 \mu\text{g}/\text{m}^3$
 $S_{\text{CM 1/II}} = 16.76 \mu\text{g}/\text{m}^3$
 $S_D = 1.54 \mu\text{g}/\text{m}^3$
 $S_{D \times t(95)} = 3.04 \mu\text{g}/\text{m}^3$

Slope 95% confidence limits:

Upper bound = 1.032
Lower bound = 1.005

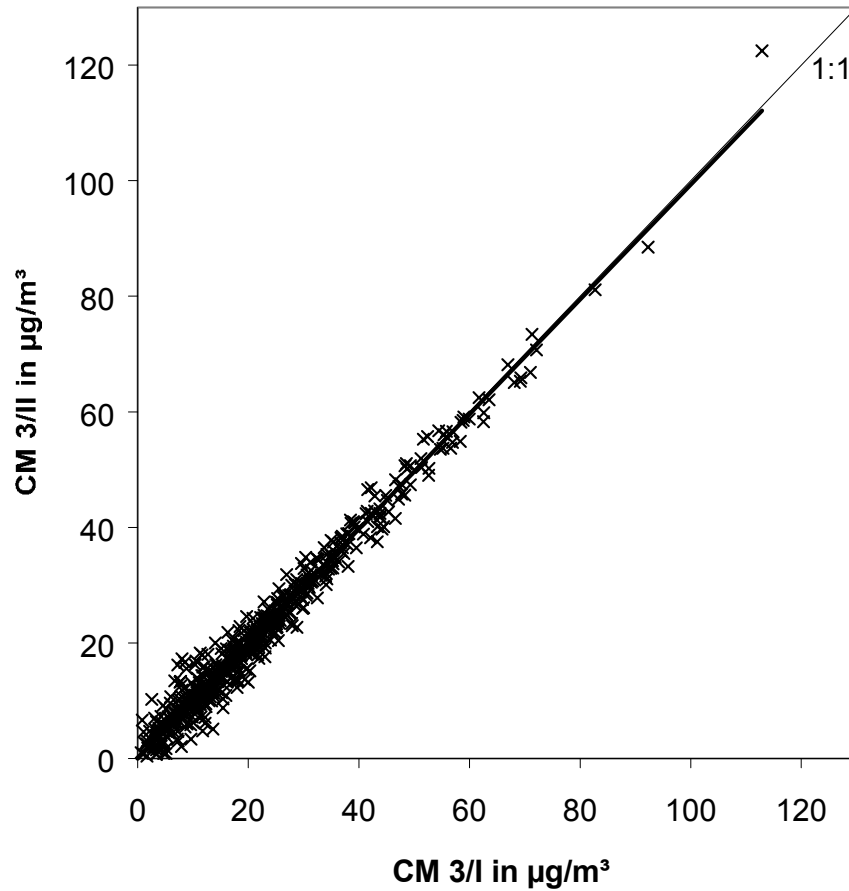
All Sites
Figure 2..CM 2/I vs. CM 2/II



n = 450
Ortho. regr. $y = -0.14 + 1.004 x$
S slope = 0.011
S Intercept = 0.29
 $R^2 = 0.942$
R = 0.970
AM CM 2/I = 20.88 $\mu\text{g}/\text{m}^3$
AM CM 2/II = 20.11 $\mu\text{g}/\text{m}^3$
 $S_{\text{CM 2/I}} = 14.45 \mu\text{g}/\text{m}^3$
 $S_{\text{CM 2/II}} = 14.50 \mu\text{g}/\text{m}^3$
 $S_D = 2.49 \mu\text{g}/\text{m}^3$
 $S_{D \times t(95)} = 4.90 \mu\text{g}/\text{m}^3$

Slope 95% confidence limits:
Upper bound = 1.027
Lower bound = 0.981

All Sites
Figure 3. CM 3/I vs. CM 3/II

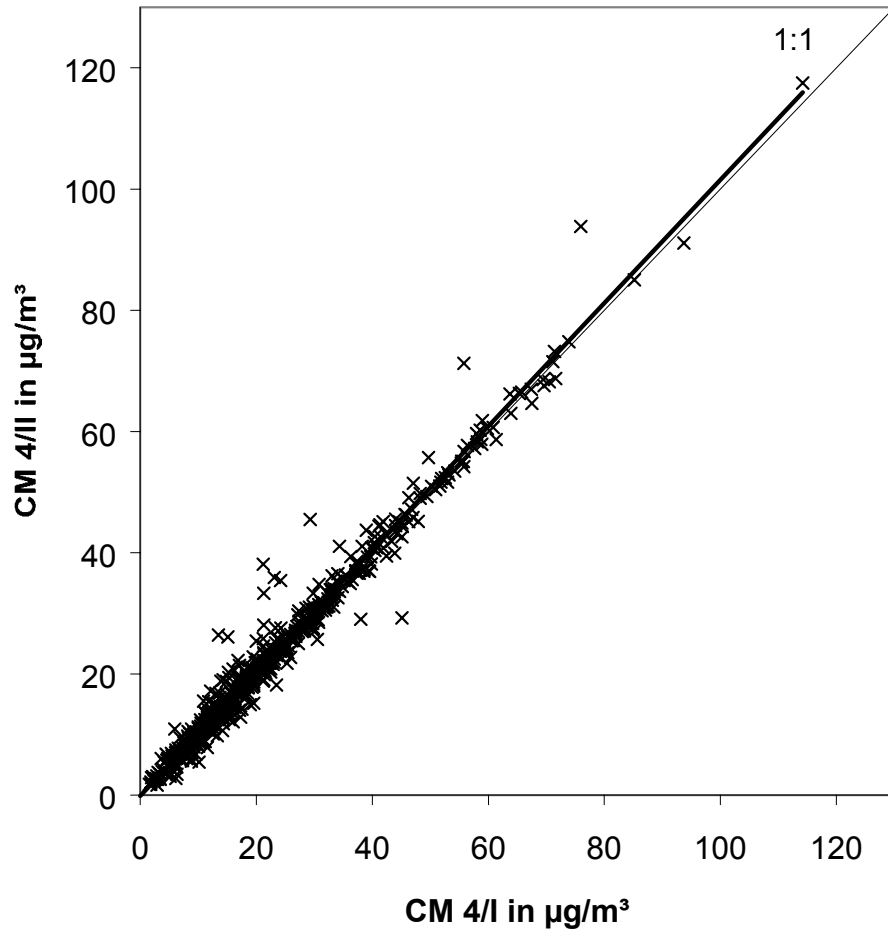


n = 607
Ortho. regr. $y = -0.05 + 0.994 x$
S slope = 0.007
S Intercept = 0.17
 $R^2 = 0.974$
R = 0.987
AM CM 3/I = 21.43 $\mu\text{g}/\text{m}^3$
AM CM 3/II = 21.24 $\mu\text{g}/\text{m}^3$
 $S_{\text{CM 3/I}} = 15.08 \mu\text{g}/\text{m}^3$
 $S_{\text{CM 3/II}} = 14.98 \mu\text{g}/\text{m}^3$
 $S_D = 1.73 \mu\text{g}/\text{m}^3$
 $S_{D \times t(95)} = 3.39 \mu\text{g}/\text{m}^3$

Slope 95% confidence limits:

Upper bound = 1.007
Lower bound = 0.981

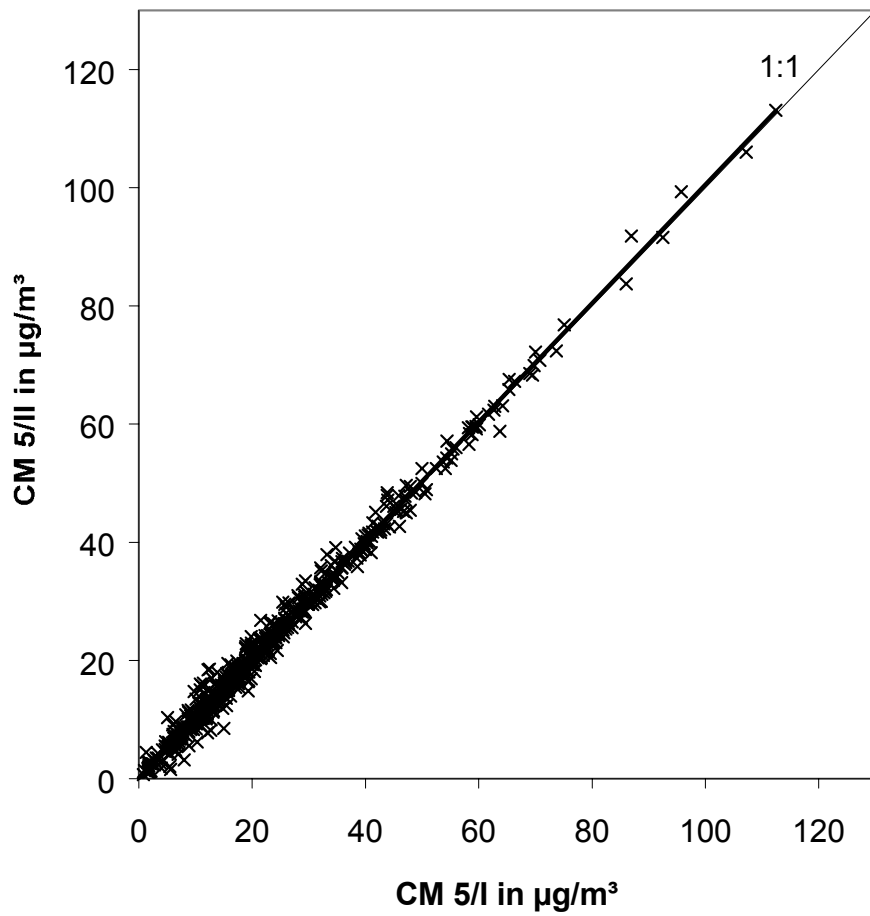
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Figure 4. CM 4/I vs. CM 4/II



n = 643
Ortho. regr. $y = -0.12 + 1.016 x$
S slope = 0.006
S Intercept = 0.17
 $R^2 = 0.976$
R = 0.988
AM CM 4/I = $22.44 \mu\text{g}/\text{m}^3$
AM CM 4/II = $22.69 \mu\text{g}/\text{m}^3$
 $S_{\text{CM 4/I}} = 15.45 \mu\text{g}/\text{m}^3$
 $S_{\text{CM 4/II}} = 15.70 \mu\text{g}/\text{m}^3$
 $S_D = 1.73 \mu\text{g}/\text{m}^3$
 $S_{D \times t(95)} = 3.40 \mu\text{g}/\text{m}^3$

Slope 95% confidence limits:
Upper bound = 1.029
Lower bound = 1.004

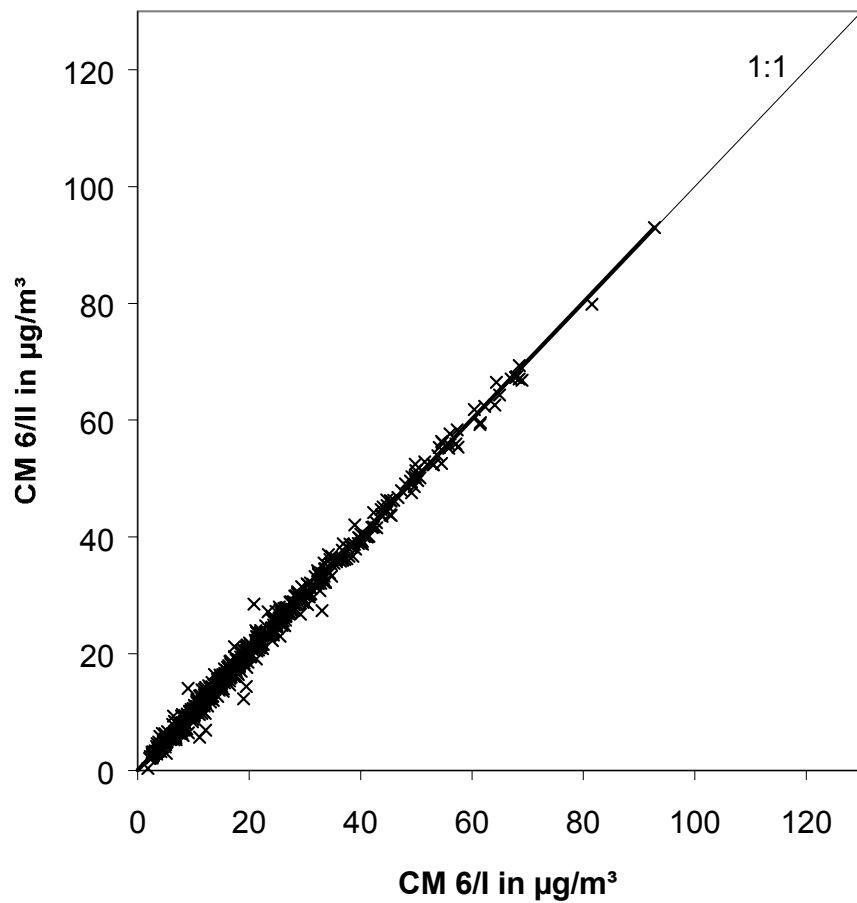
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Figure 5. CM 5/I vs. CM 5/II



n = 628
Ortho. regr. $y = 0.15 + 1.003 x$
S slope = 0.004
S Intercept = 0.11
 $R^2 = 0.991$
R = 0.995
AM CM 5/I = $22.53 \mu\text{g}/\text{m}^3$
AM CM 5/II = $22.76 \mu\text{g}/\text{m}^3$
 $S_{\text{CM 5/I}} = 16.38 \mu\text{g}/\text{m}^3$
 $S_{\text{CM 5/II}} = 16.43 \mu\text{g}/\text{m}^3$
 $S_D = 1.14 \mu\text{g}/\text{m}^3$
 $S_{D \times t(95)} = 2.23 \mu\text{g}/\text{m}^3$

Slope 95% confidence limits:
Upper bound = 1.011
Lower bound = 0.996

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Figure 6. CM 6/I vs. CM 6/II



n = 597
Ortho. regr. $y = 0.07 + 1.002 x$
S slope = 0.003
S Intercept = 0.09
 $R^2 = 0.993$
R = 0.997
AM CM 6/I = $21.39 \mu\text{g}/\text{m}^3$
AM CM 6/II = $21.48 \mu\text{g}/\text{m}^3$
 $S_{\text{CM 6/I}} = 14.63 \mu\text{g}/\text{m}^3$
 $S_{\text{CM 6/II}} = 14.65 \mu\text{g}/\text{m}^3$
 $S_D = 0.86 \mu\text{g}/\text{m}^3$
 $S_{D \times t(95)} = 1.69 \mu\text{g}/\text{m}^3$

Slope 95% confidence limits:
Upper bound = 1.008
Lower bound = 0.995

Results

Figures 1-6

From these results the WG concluded that the PM2.5 standard method should base on

method CM5 for the low volume regime

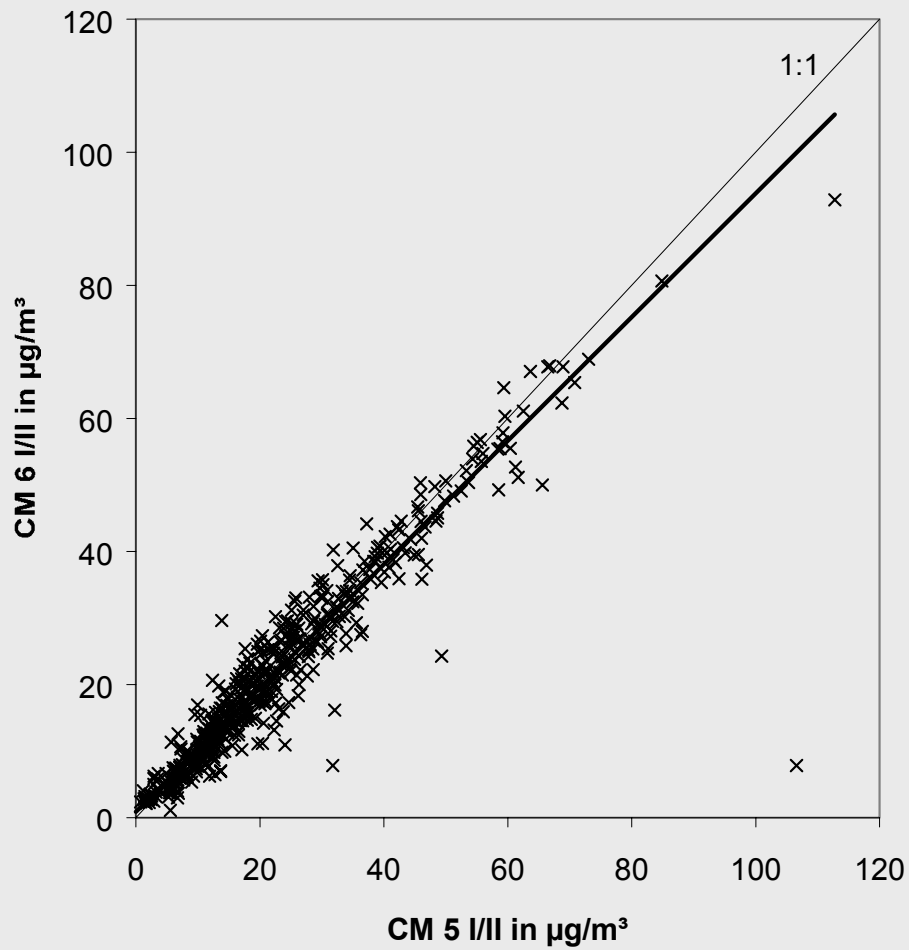
and

method CM6 for the high volume regime.

However, it should go without saying that the two methods should be equivalent.

ALL SITES

Figure 7. CM 5 I/II vs. CM 6 I/II (mean values)



n = 531
Ortho. regr. $y = 0.89 + 0.929 x$
S slope = 0.015
S Intercept = 0.40
 $R^2 = 0.867$
R = 0.931
AM CM 5 I/II = 21.90 $\mu\text{g}/\text{m}^3$
AM CM 6 I/II = 21.24 $\mu\text{g}/\text{m}^3$
 $S_{\text{CM 5 I/II}} = 15.66 \mu\text{g}/\text{m}^3$
 $S_{\text{CM 6 I/II}} = 14.63 \mu\text{g}/\text{m}^3$

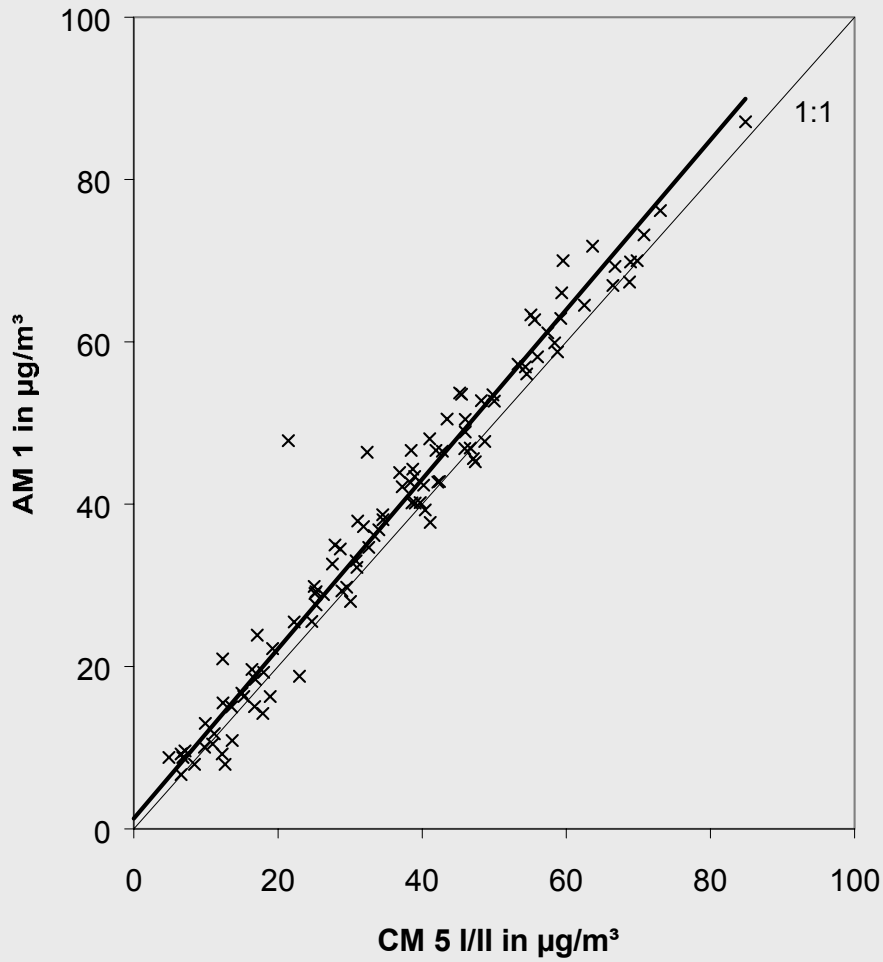
Figure 7

Obviously the high volume method gives lower results than the low volume method by a factor of around 0.93 .

At present, the exact reasons for the differences between the high volume and the low volume method are unknown.

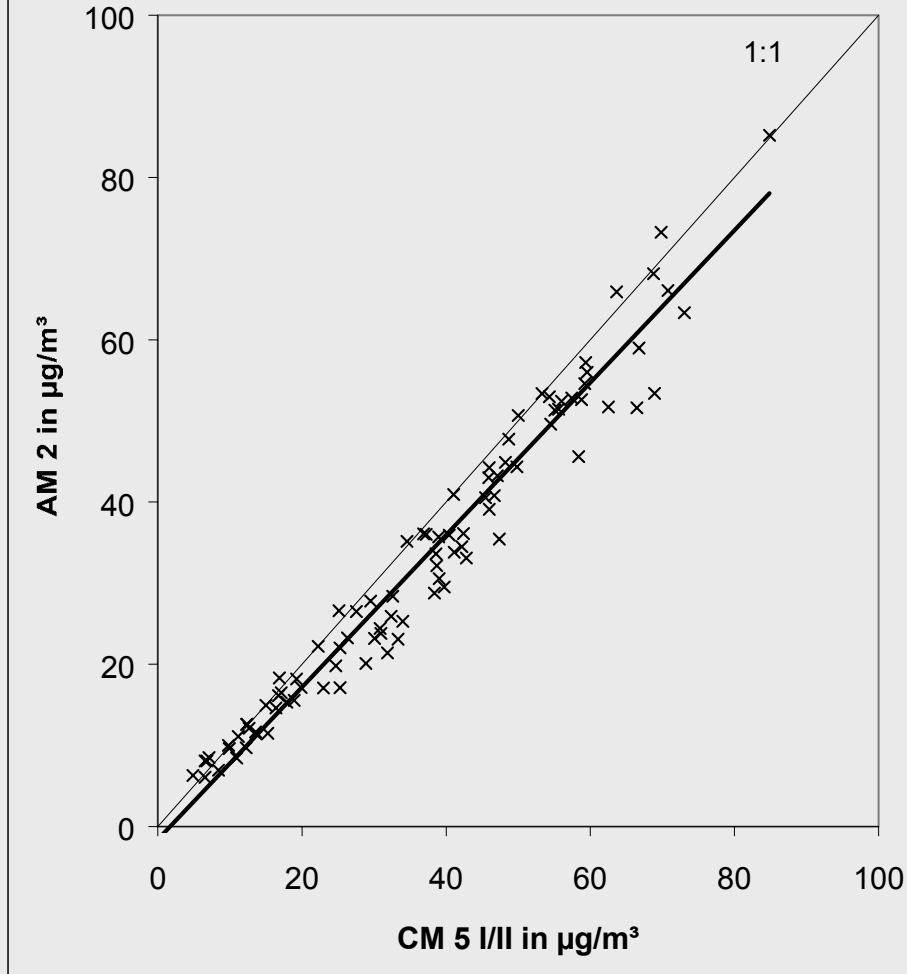
Fact is that the high volume method gave lower results than the low volume method by up to roughly 20% at several sites.

Figure 8. CM 5 I/II vs. AM 1



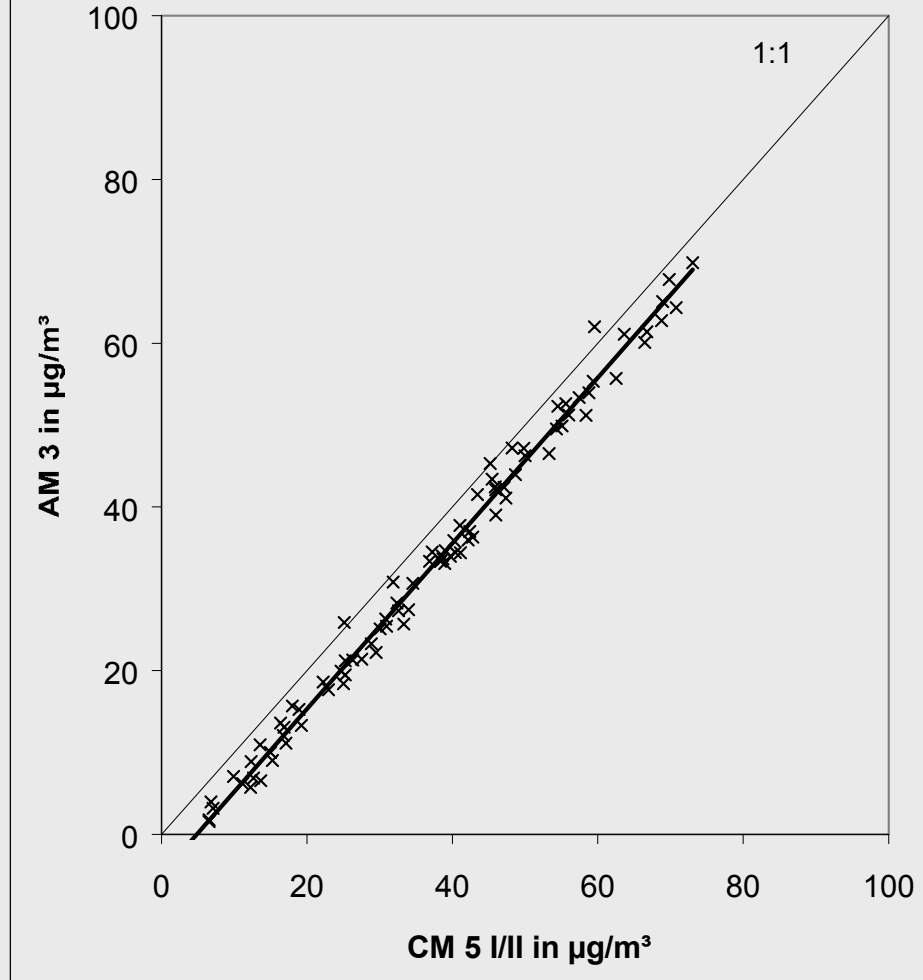
n = 103 paired values
Ortho. regr. $y = 1.26 + 1.045 x$
S slope = 0.022
S Intercept = 0.87
 $R^2 = 0.957$
R = 0.978
AM CM 5 I/II = $36.04 \mu\text{g}/\text{m}^3$
AM AM 1 = $38.91 \mu\text{g}/\text{m}^3$
 $S_{\text{CM 5 I/II}} = 18.53 \mu\text{g}/\text{m}^3$
 $S_{\text{AM 1}} = 19.35 \mu\text{g}/\text{m}^3$

Figure 9. CM 5 I/II vs. AM 2



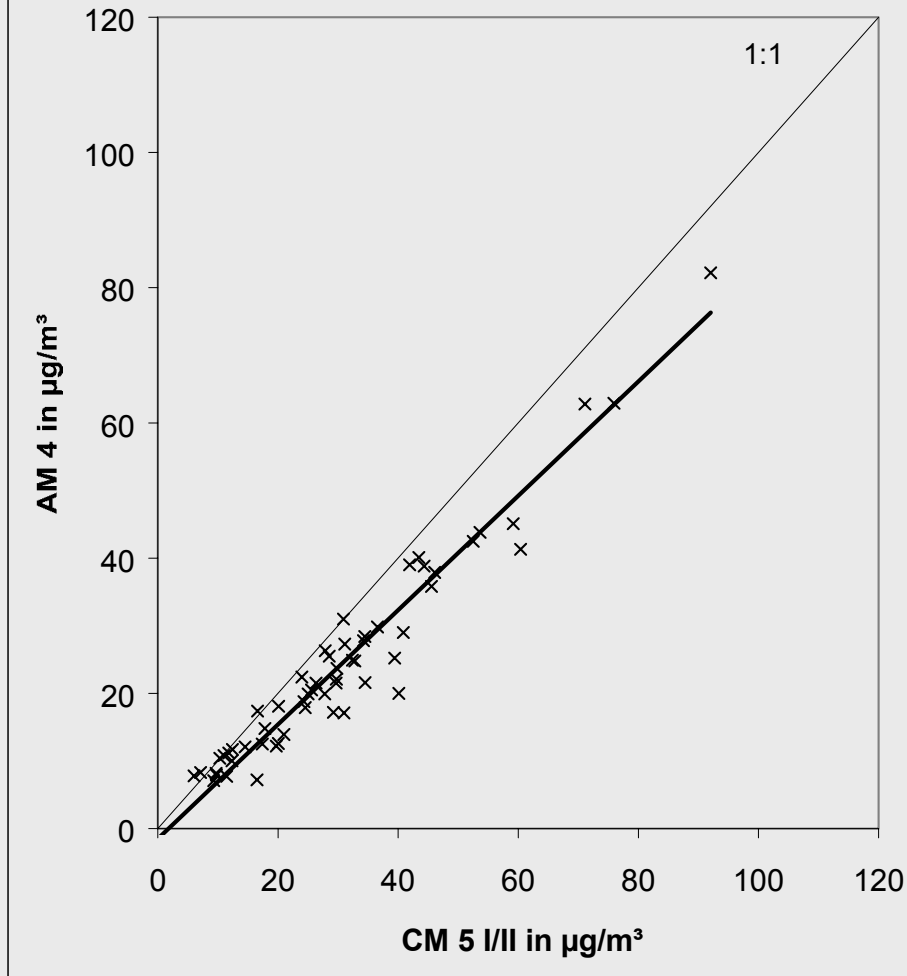
n = 92 paired values
Ortho. regr. $y = -1.60 + 0.938 x$
S slope = 0.020
S Intercept = 0.83
 $R^2 = 0.959$
R = 0.979
AM CM 5 I/II = $36.26 \mu\text{g}/\text{m}^3$
AM AM 2 = $32.42 \mu\text{g}/\text{m}^3$
 $S_{\text{CM 5 I/II}} = 19.41 \mu\text{g}/\text{m}^3$
 $S_{\text{AM 2}} = 18.24 \mu\text{g}/\text{m}^3$

Figure 10. CM 5 I/II vs. AM 3



n = 87 paired values
Ortho. regr. $y = -4.91 + 1.011 x$
S slope = 0.011
S Intercept = 0.46
 $R^2 = 0.989$
R = 0.995
AM CM 5 I/II = 37.16 $\mu\text{g}/\text{m}^3$
AM AM 3 = 32.67 $\mu\text{g}/\text{m}^3$
 $S_{\text{CM 5 I/II}} = 17.90 \mu\text{g}/\text{m}^3$
 $S_{\text{AM 3}} = 18.10 \mu\text{g}/\text{m}^3$

Figure 11. CM 5 I/II vs. AM 4

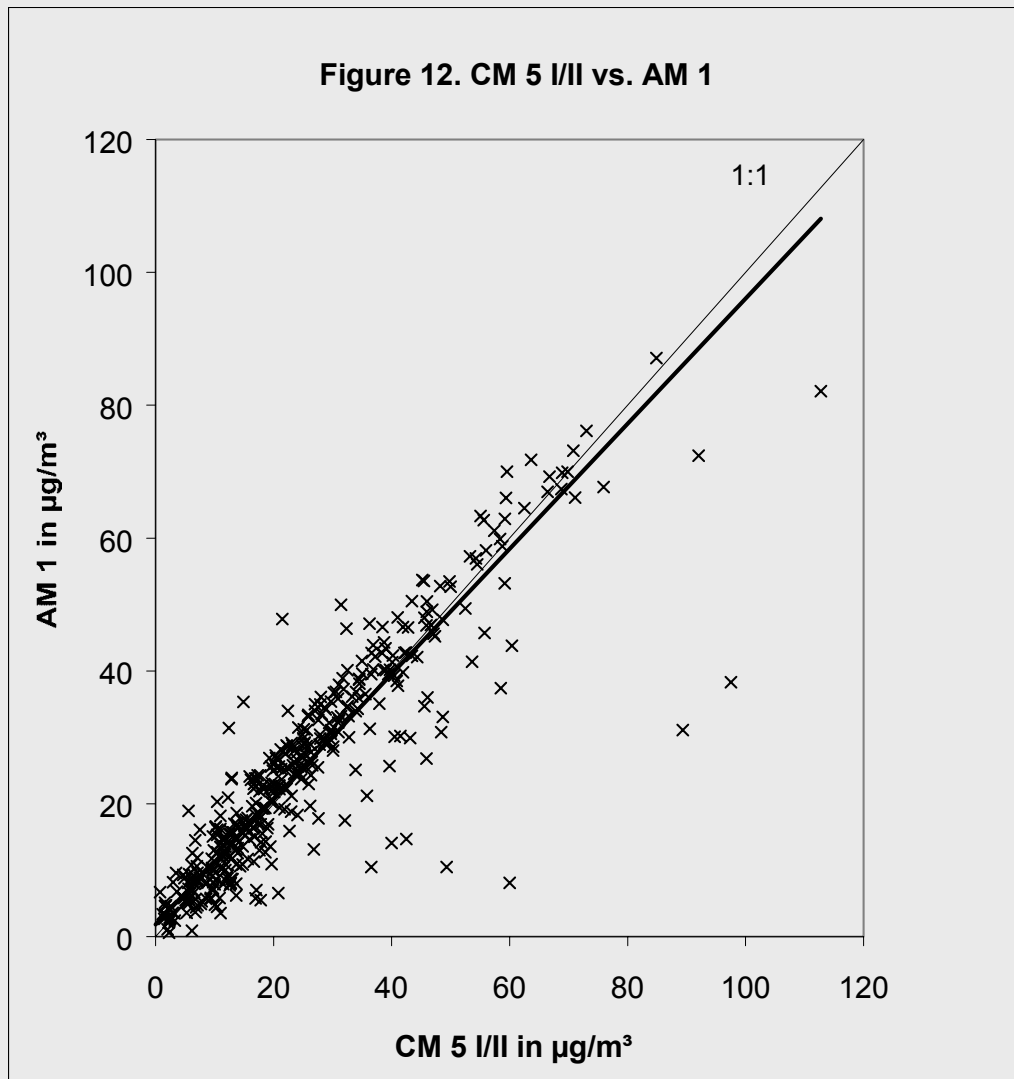


n = 57 paired values
Ortho. regr. $y = -1.51 + 0.846 x$
S slope = 0.028
S Intercept = 1.00
 $R^2 = 0.939$
R = 0.969
AM CM 5 I/II = $30.38 \mu\text{g}/\text{m}^3$
AM AM 4 = $24.18 \mu\text{g}/\text{m}^3$
 $S_{\text{CM 5 I/II}} = 17.83 \mu\text{g}/\text{m}^3$
 $S_{\text{AM 4}} = 15.15 \mu\text{g}/\text{m}^3$

Figures 8-11

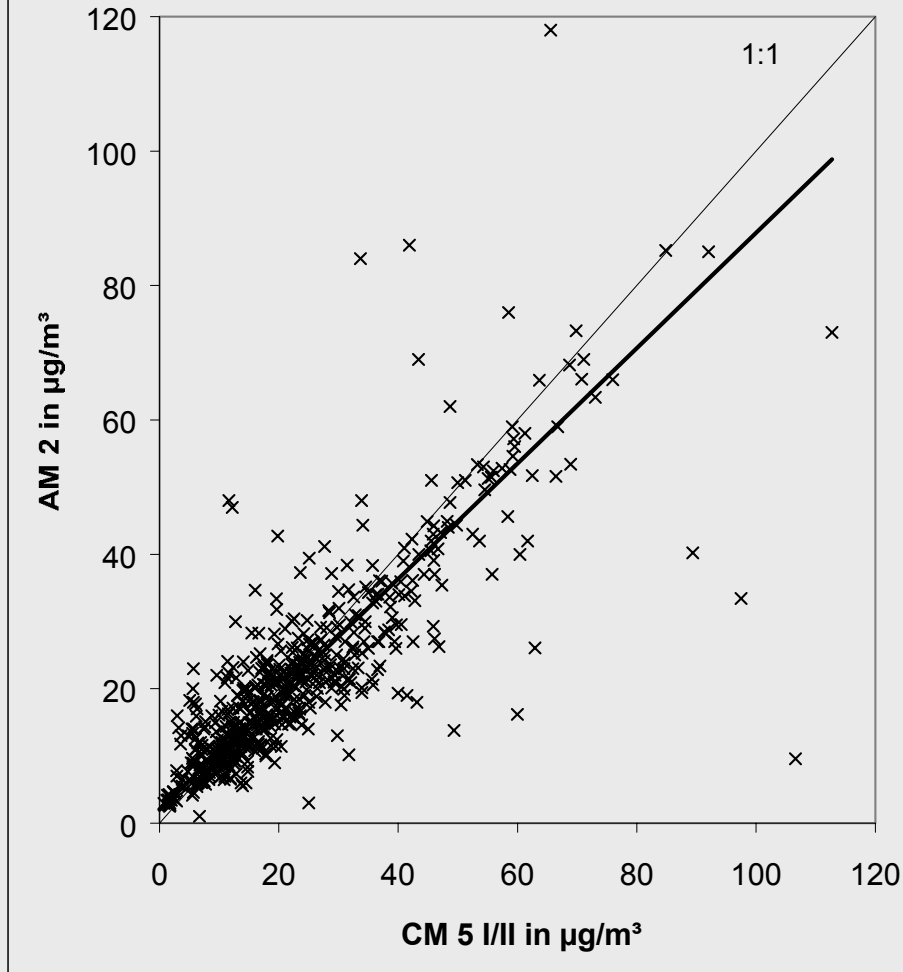
These results indicate that with suitable correction algorithms the automatic instruments can pass the equivalent test procedure laid down in the drafted PM2.5 standard at these single sites.

Figure 12. CM 5 I/II vs. AM 1



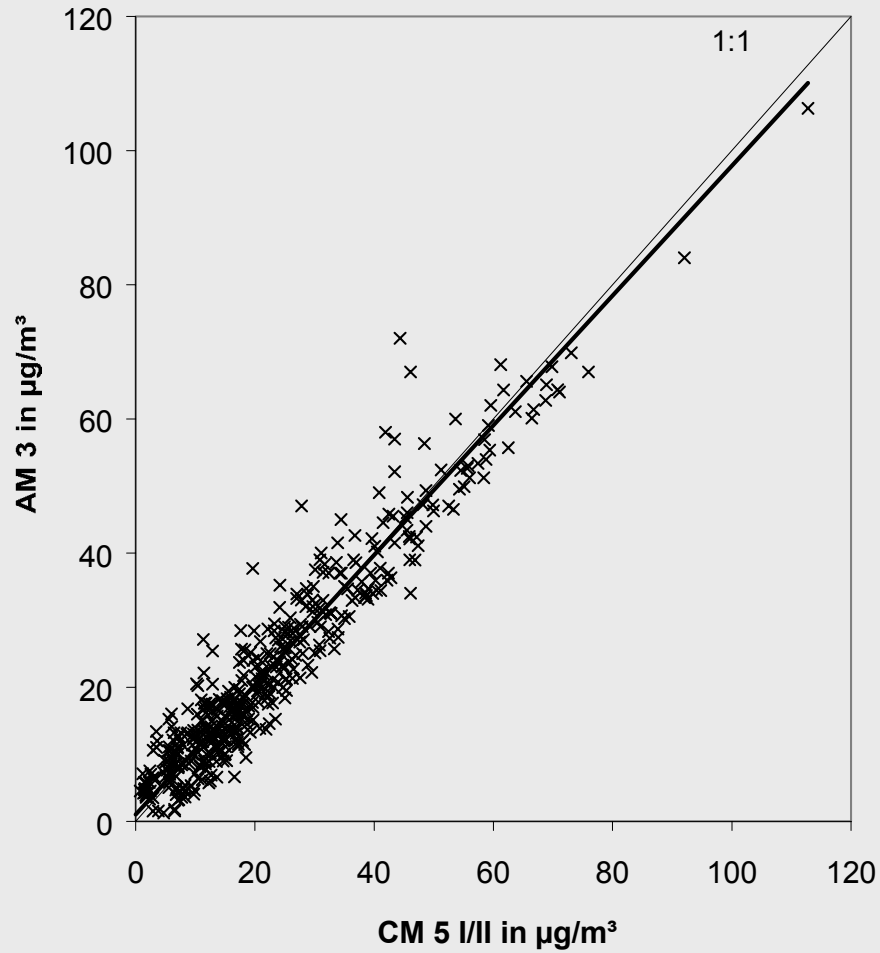
n = 426 paired values
Ortho. regr. $y = 1.83 + 0.942 x$
S slope = 0.021
S Intercept = 0.63
 $R^2 = 0.795$
R = 0.892
AM CM 5 I/II = $24.62 \mu\text{g}/\text{m}^3$
AM AM 1 = $24.03 \mu\text{g}/\text{m}^3$
 $S_{\text{CM 5 I/II}} = 17.55 \mu\text{g}/\text{m}^3$
 $S_{\text{AM 1}} = 16.65 \mu\text{g}/\text{m}^3$

Figure 13. CM 5 I/II vs. AM 2



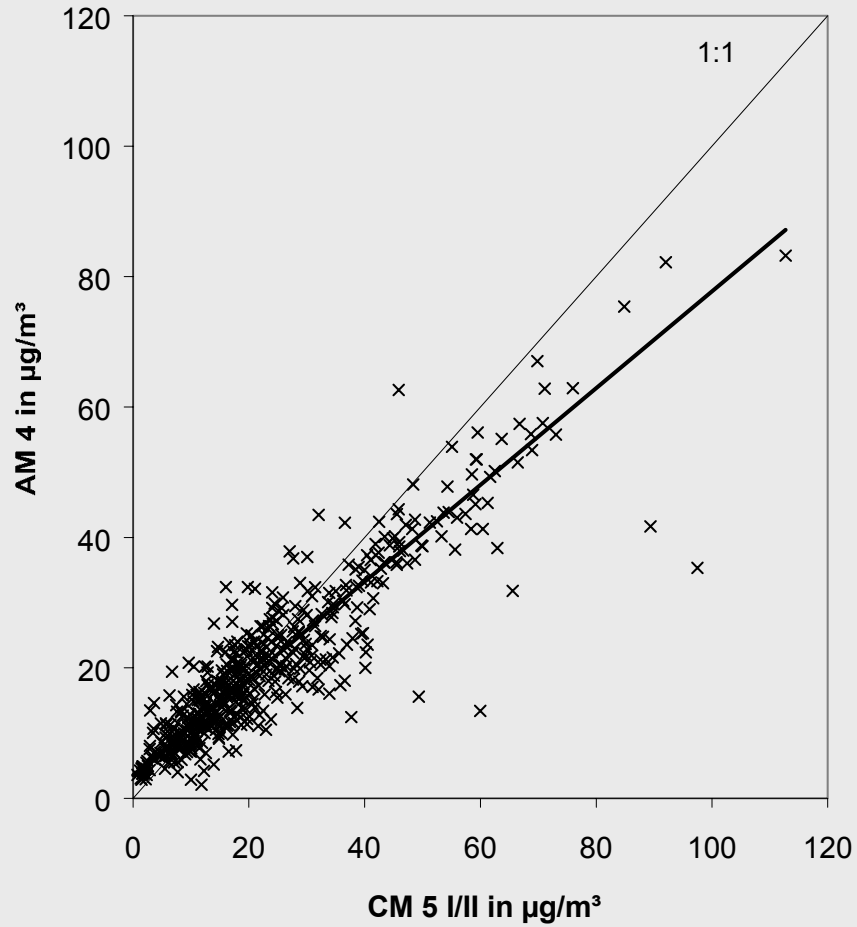
n = 585 paired values
Ortho. regr. $y = 2.00 + 0.858 x$
S slope = 0.021
S Intercept = 0.60
 $R^2 = 0.660$
R = 0.812
AM CM 5 I/II = 22.95 $\mu\text{g}/\text{m}^3$
AM AM 2 = 21.70 $\mu\text{g}/\text{m}^3$
 $S_{\text{CM 5 I/II}} = 16.63 \mu\text{g}/\text{m}^3$
 $S_{\text{AM 2}} = 14.68 \mu\text{g}/\text{m}^3$

All Sites
Figure 14. CM 5 I/II vs. AM 3



n = 460 paired values
Ortho. regr. $y = 1.01 + 0.967 x$
S slope = 0.014
S Intercept = 0.38
 $R^2 = 0.909$
R = 0.953
AM CM 5 I/II = 22.75 $\mu\text{g}/\text{m}^3$
AM AM 3 = 23.01 $\mu\text{g}/\text{m}^3$
 $S_{\text{CM 5 I/II}} = 16.50 \mu\text{g}/\text{m}^3$
 $S_{\text{AM 3}} = 15.99 \mu\text{g}/\text{m}^3$

All Sites
Figure 15. CM 5 I/II vs. AM 4



n = 538 paired values
Ortho. regr. $y = 3.56 + 0.742 x$
S slope = 0.014
S Intercept = 0.40
 $R^2 = 0.813$
R = 0.902
AM CM 5 I/II = $22.88 \mu\text{g}/\text{m}^3$
AM AM 4 = $20.53 \mu\text{g}/\text{m}^3$
 $S_{\text{CM 5 I/II}} = 16.76 \mu\text{g}/\text{m}^3$
 $S_{\text{AM 4}} = 12.79 \mu\text{g}/\text{m}^3$

Figures 12-15

These results show significant scatter of the data indicating that the agreement between the automatic instruments and the manual low volume method varies at different sites and conditions. The results show moreover that equivalence does not cover in a uniform way the wide range of prevailing conditions within Europe.

Ratio PM_{2,5}/PM₁₀

Site	No. of values	PM _{2,5} (CM 5) µg/m ³	PM ₁₀ µg/m ³	PM _{2,5} /PM ₁₀
Berlin	42	23,6	30,9	0,74
Duisburg	41	19,5	30,3	0,63
Vienna	103	35,8	49,2	0,70
Vredepeel	62	18,6	31,5	0,58
Rome	79	20,9	38,0	0,55
Aspvreten	40	8,0	9,9	0,78
Teddington	56	22,8	32,9	0,62
Athens	42	24,2	39,0	0,63
Mean (from single data pairs)			35,4	0,65
Standard deviation			19,7	0,15

PM2.5 vs. PM10

The ratio PM2.5 / PM10 is 0.65 with rather small standard deviation of 0.15.

The correlations PM2.5 vs. PM10 gave variation coefficient R^2 in the range of approximately 0.7 up to 0.95.