Results of intercomparison exercise and recommended methods

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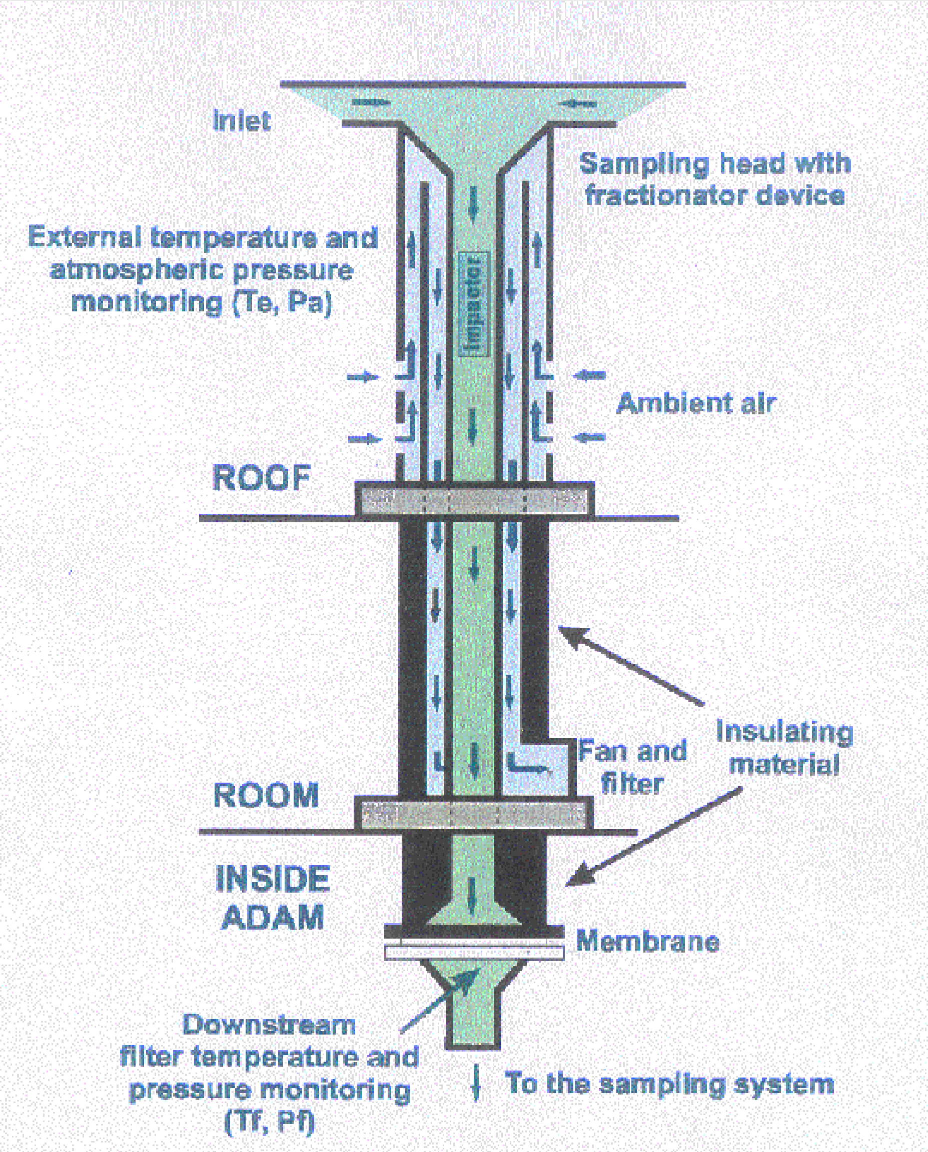
Duration of PM2.5 field tests:
27 September - 24 July 2003

707 Experiments

Measurement methods involved in the field tests

Manual samplers (induplicate)

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


Inlet
Sampling head with fractionator device
External temperature and atmospheric pressure monitoring (Te, Pa)
Impactor
Ambient air
ROOF
Insulating material
Fan and filter
ROOM
INSIDE ADAM
Membrane
Downstream filter temperature and pressure monitoring (Tf, Pf)
To the sampling system

Automatic methods (single instruments):

- SM2000 (ADAM) Beta-ray altenuation monitor, 8-jet-impactor, sequential sampler with sheath air, every 24 hours 1 value, 1.0m³/h
- FH62I-R Beta-ray altenuation monitor, SCC with PM10 pre-impactor, filter tape, continuous measurement up to 24 hours, each, 1.0m³/h
- BAM1020 Beta-ray altenuation 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 <u>only</u> 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 > critical value ⇒ outlier

Only 5% of the data collective could be removed.

Regression analysis

The linear orthogonal regression was used.

$$y = a + b\,x$$

Slope b:

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

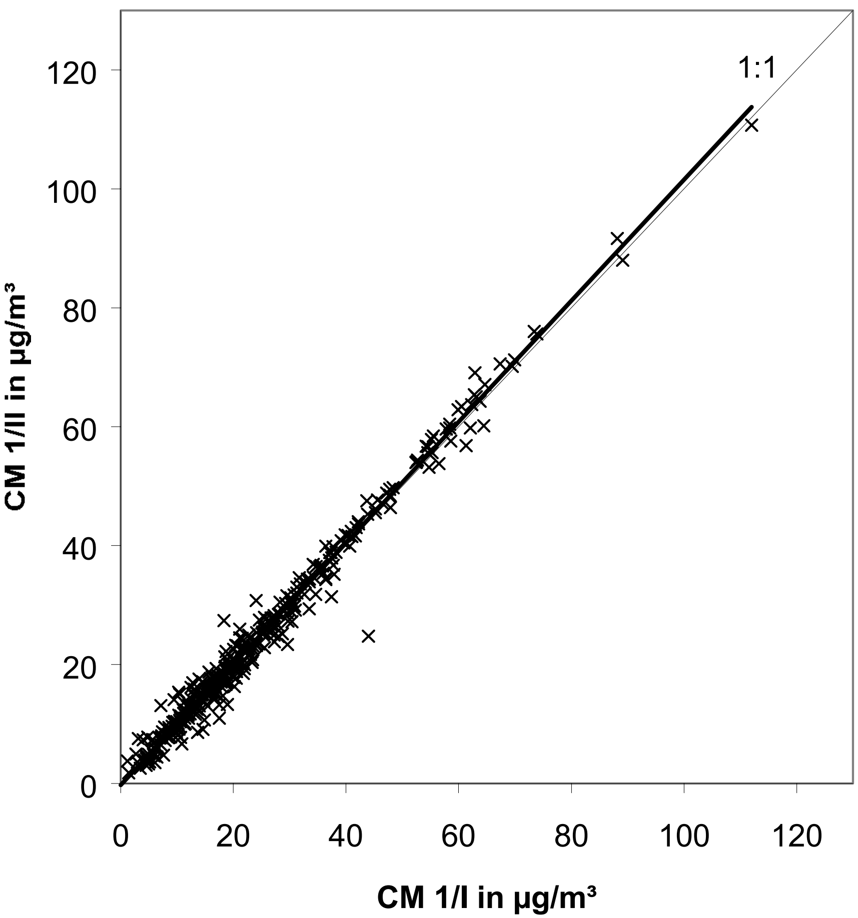
Confidence limits of the slope b

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

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 µg/m³

AM CM 1/II = 23.84 µg/m³

$S_{CM\ 1/I}$ = 16.45 µg/m³

$S_{CM\ 1/II}$ = 16.76 µg/m³

S_D = 1.54 µg/m³

$S_{D \times t(95)}$ = 3.04 µg/m³

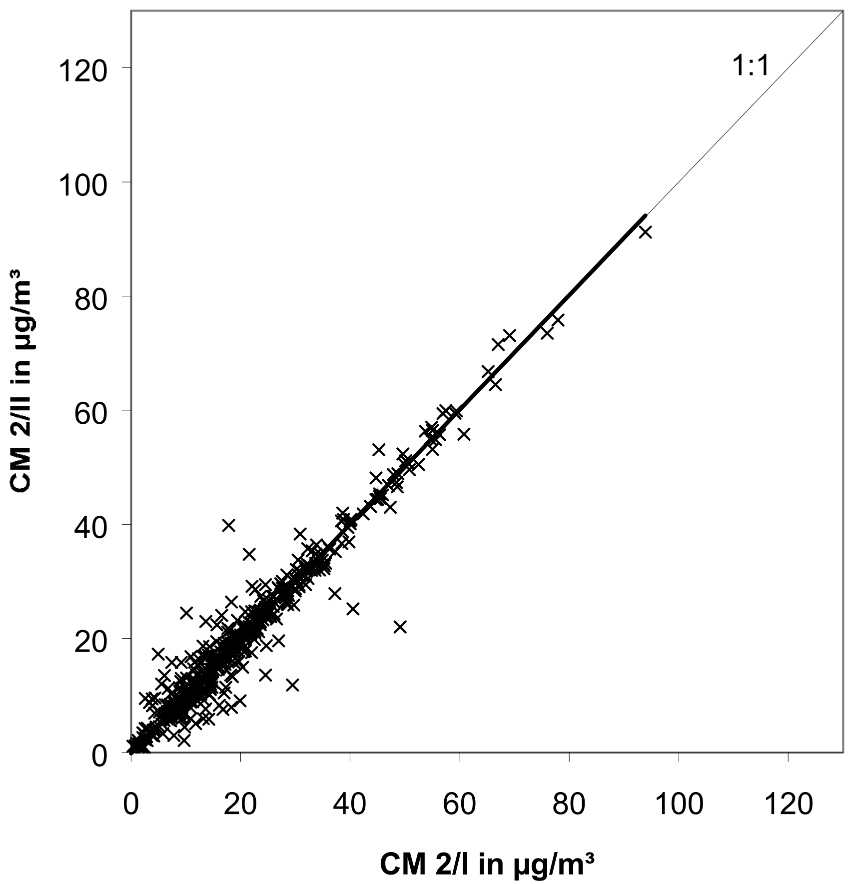
Slope 95% confidence limits:

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 µg/m³

AM CM 2/II = 20.11 µg/m³

$S_{CM\ 2/I}$ = 14.45 µg/m³

$S_{CM\ 2/II}$ = 14.50 µg/m³

S_D = 2.49 µg/m³

$S_{D\ x\ t(95)}$ = 4.90 µg/m³

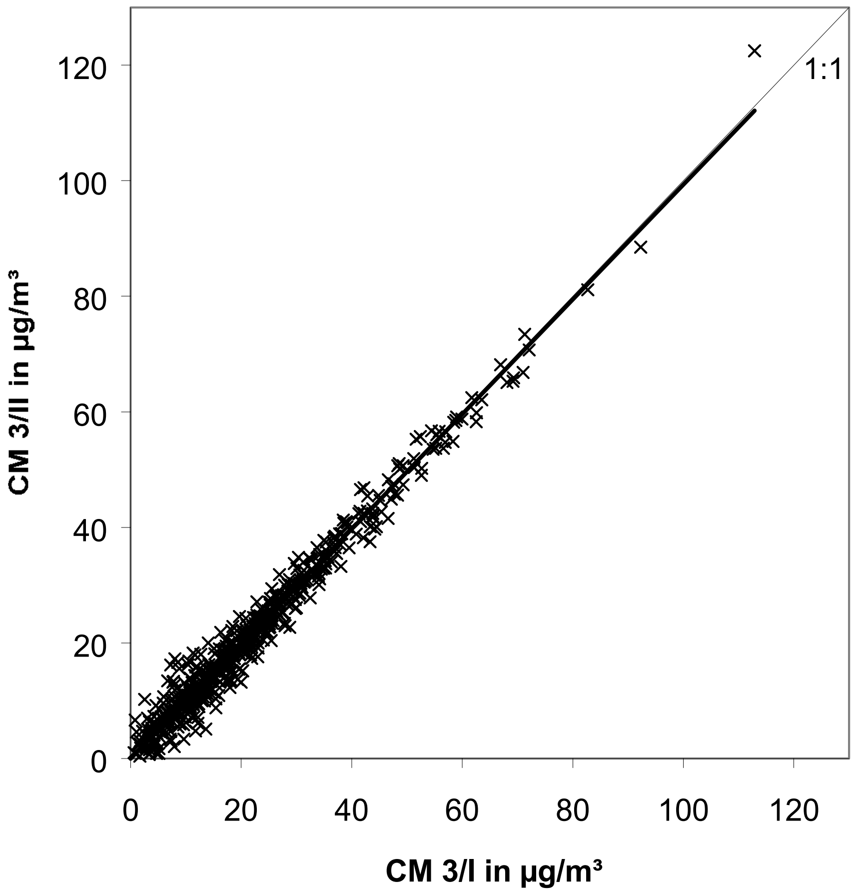
Slope 95% confidence limits:

Upper bound = 1.027

Lower bound = 0.981

All Sites

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



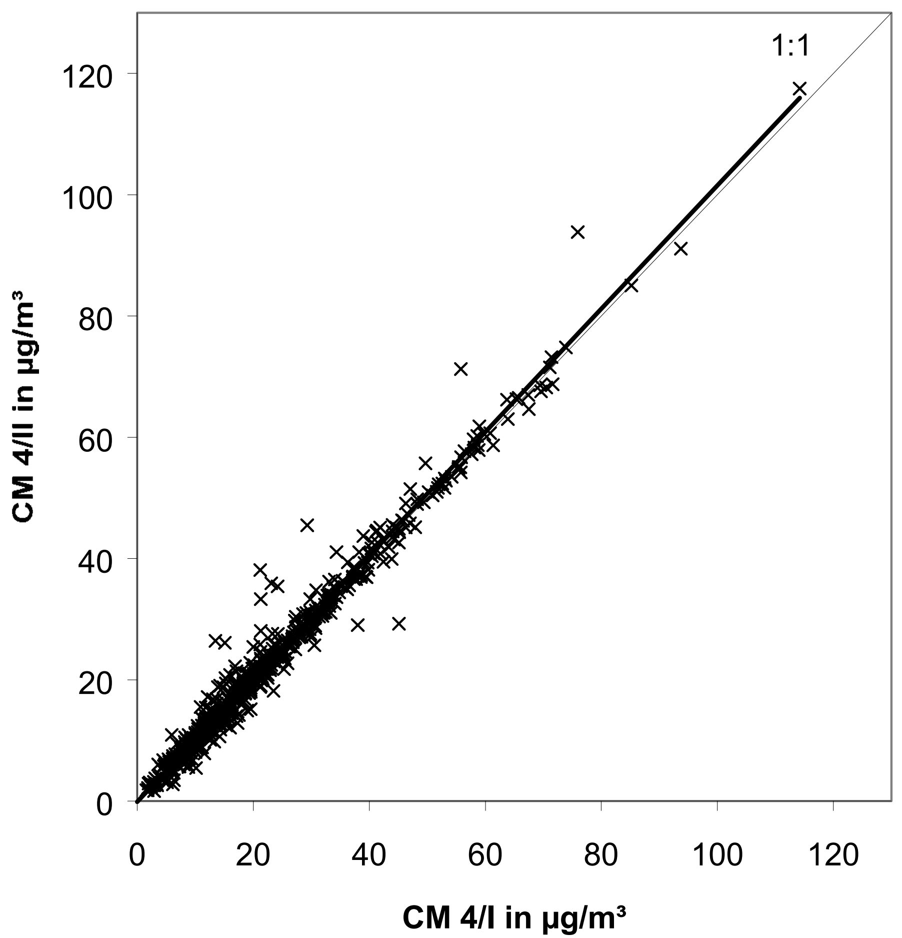
n =	607
Ortho. regr. y =	- 0.05 + 0.994 x
S slope =	0.007
S Intercept =	0.17
R^2 =	0.974
R =	0.987
AM CM 3/I =	21.43 µg/m³
AM CM 3/II =	21.24 µg/m³
$S_{CM\ 3/I}$ =	15.08 µg/m³
$S_{CM\ 3/II}$ =	14.98 µg/m³
S_D =	1.73 µg/m³
$S_{D \times t(95)}$ =	3.39 µg/m³

Slope 95% confidence limits:

Upper bound =	1.007
Lower bound =	0.981

All Sites

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 µg/m³

AM CM 4/II = 22.69 µg/m³

$S_{CM\ 4/I}$ = 15.45 µg/m³

$S_{CM\ 4/II}$ = 15.70 µg/m³

S_D = 1.73 µg/m³

$S_{D \times t(95)}$ = 3.40 µg/m³

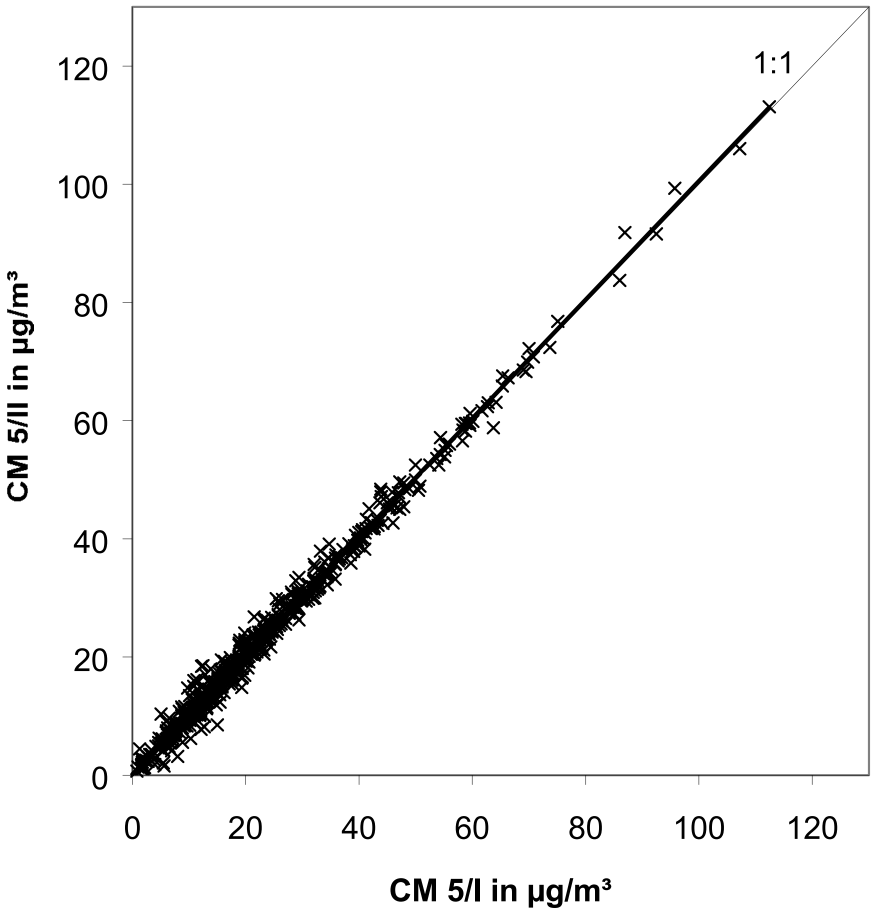
Slope 95% confidence limits:

Upper bound = 1.029

Lower bound = 1.004

All Sites

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



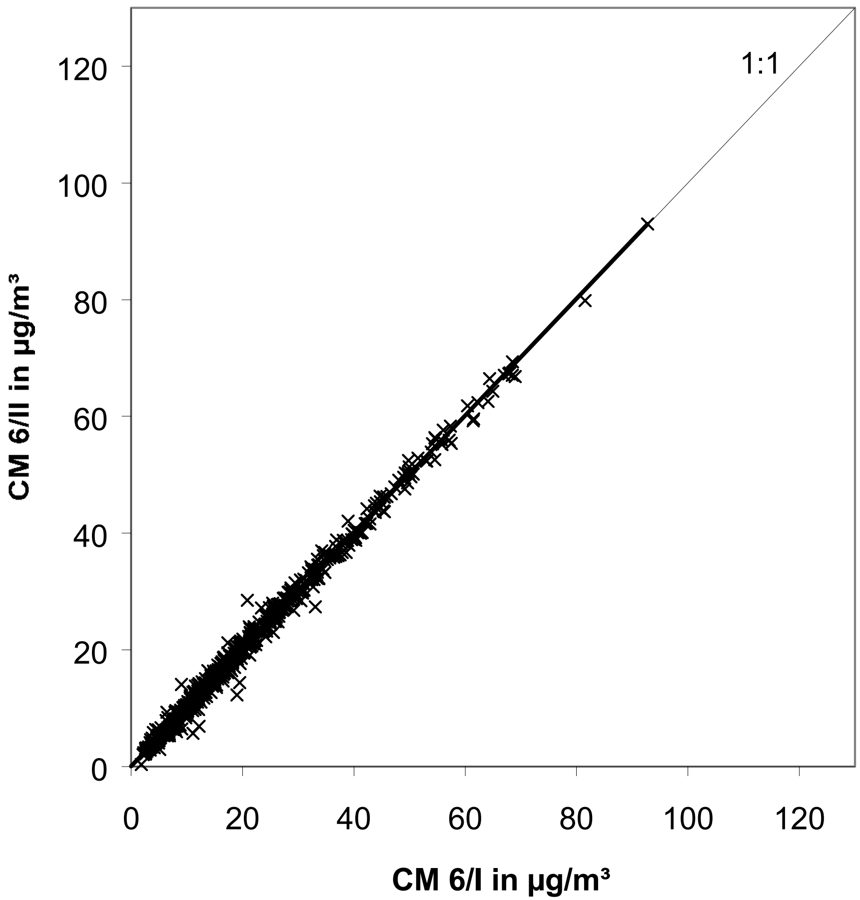
n =	628
Ortho. regr. y =	0.15 + 1.003 x
S slope =	0.004
S Intercept =	0.11
R^2 =	0.991
R =	0.995
AM CM 5/I =	22.53 µg/m³
AM CM 5/II =	22.76 µg/m³
$S_{CM\ 5/I}$ =	16.38 µg/m³
$S_{CM\ 5/II}$ =	16.43 µg/m³
S_D =	1.14 µg/m³
$S_{D \times t(95)}$ =	2.23 µg/m³

Slope 95% confidence limits:

Upper bound =	1.011
Lower bound =	0.996

All Sites

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 µg/m³
AM CM 6/II =	21.48 µg/m³
$S_{CM\ 6/I}$ =	14.63 µg/m³
$S_{CM\ 6/II}$ =	14.65 µg/m³
S_D =	0.86 µg/m³
$S_{D\ x\ t(95)}$ =	1.69 µg/m³

Slope 95% confidence limits:

Upper bound =	1.008
Lower bound =	0.995

Results

Figures 1-6

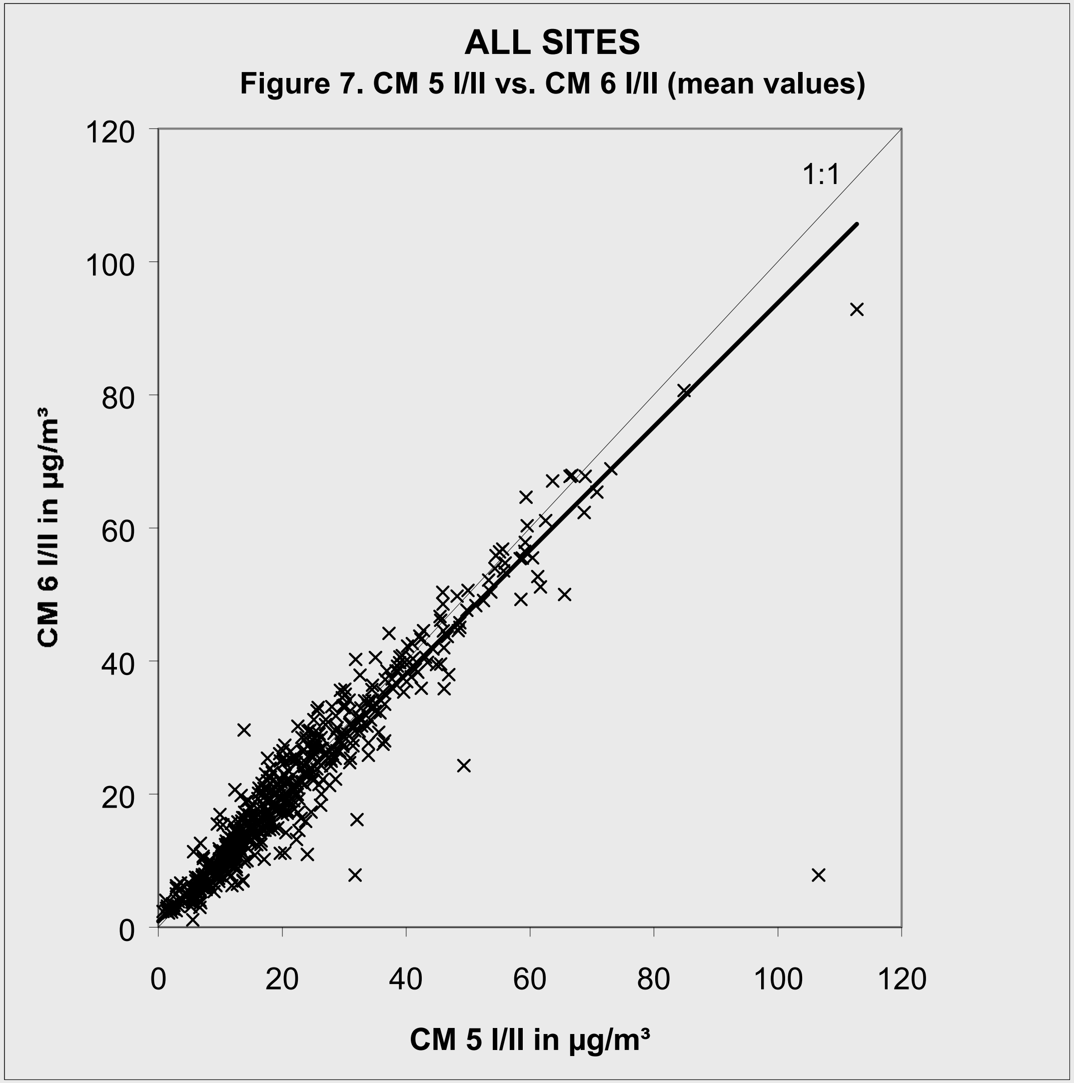
From these results the WG concluded that the PM2.5 standard method should base on

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.



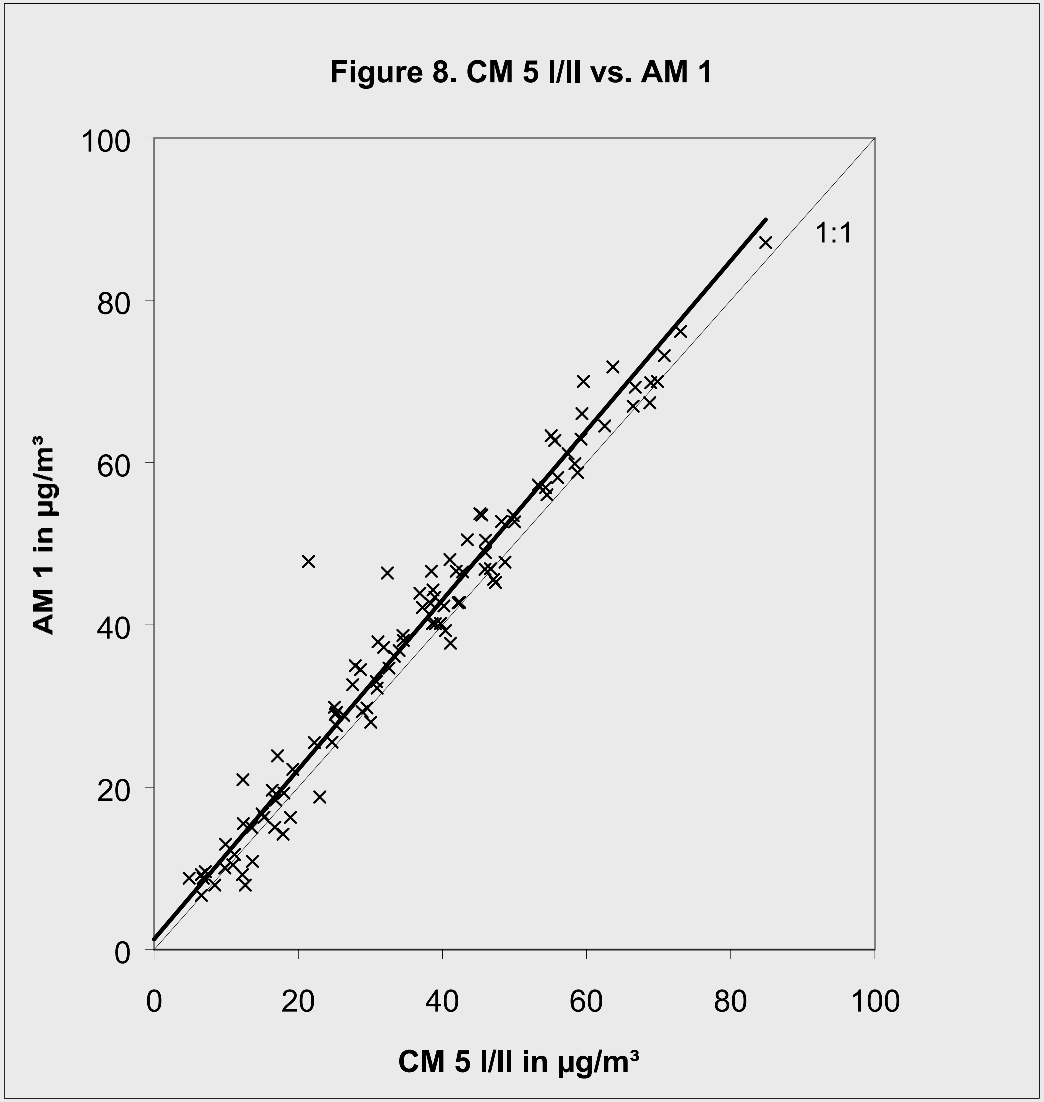
n =	531	
Ortho. regr. y =	0.89	+ 0.929 x
S slope =	0.015	
S Intercept =	0.40	
R^2 =	0.867	
R =	0.931	
AM CM 5 I/II =	21.90	µg/m³
AM CM 6 I/II =	21.24	µg/m³
$S_{CM\ 5\ I/II}$ =	15.66	µg/m³
$S_{CM\ 6\ I/II}$ =	14.63	µg/m³

Figure 7

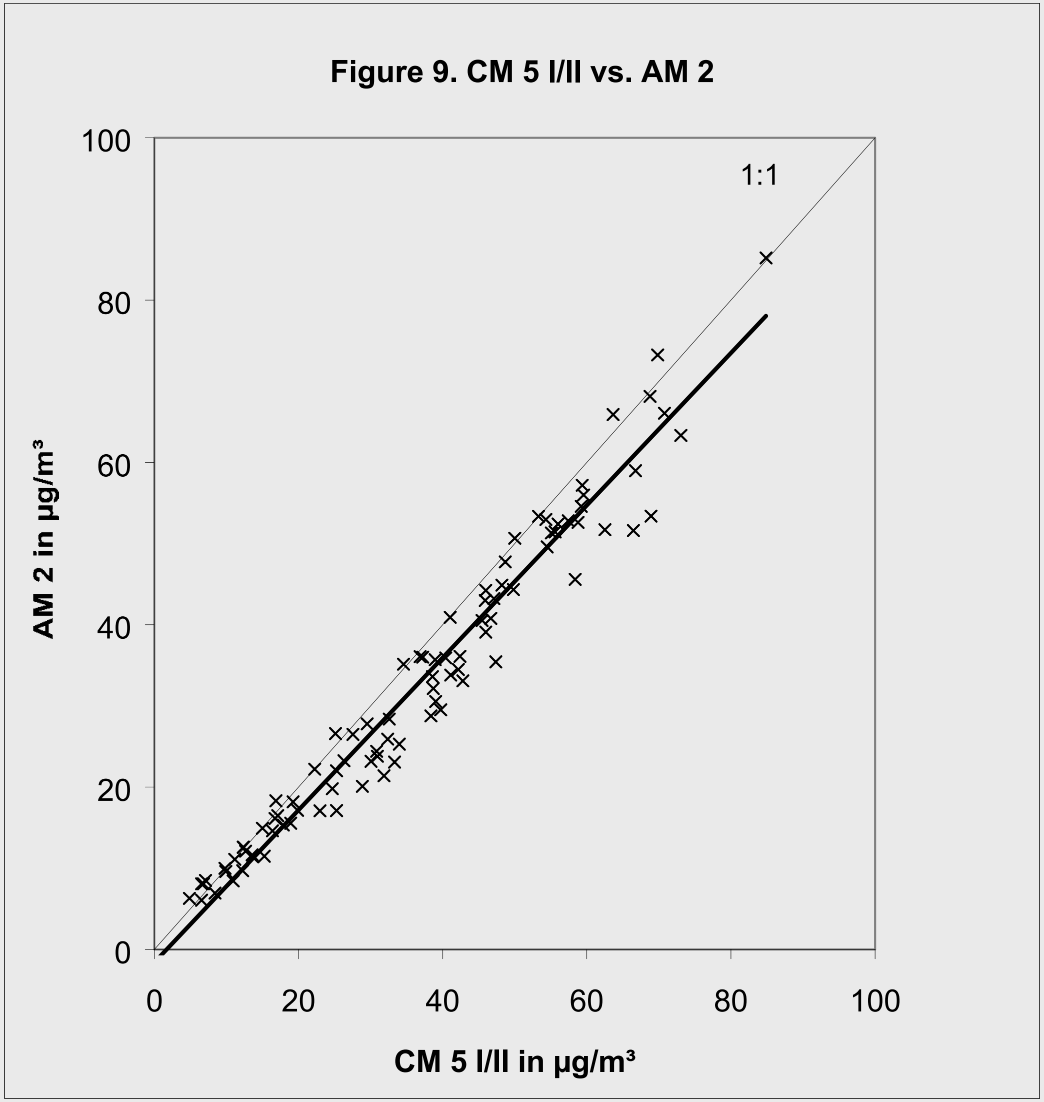
Obviously the high volume method gives lower results than the low volume method by a factor of arround 0.93 .

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

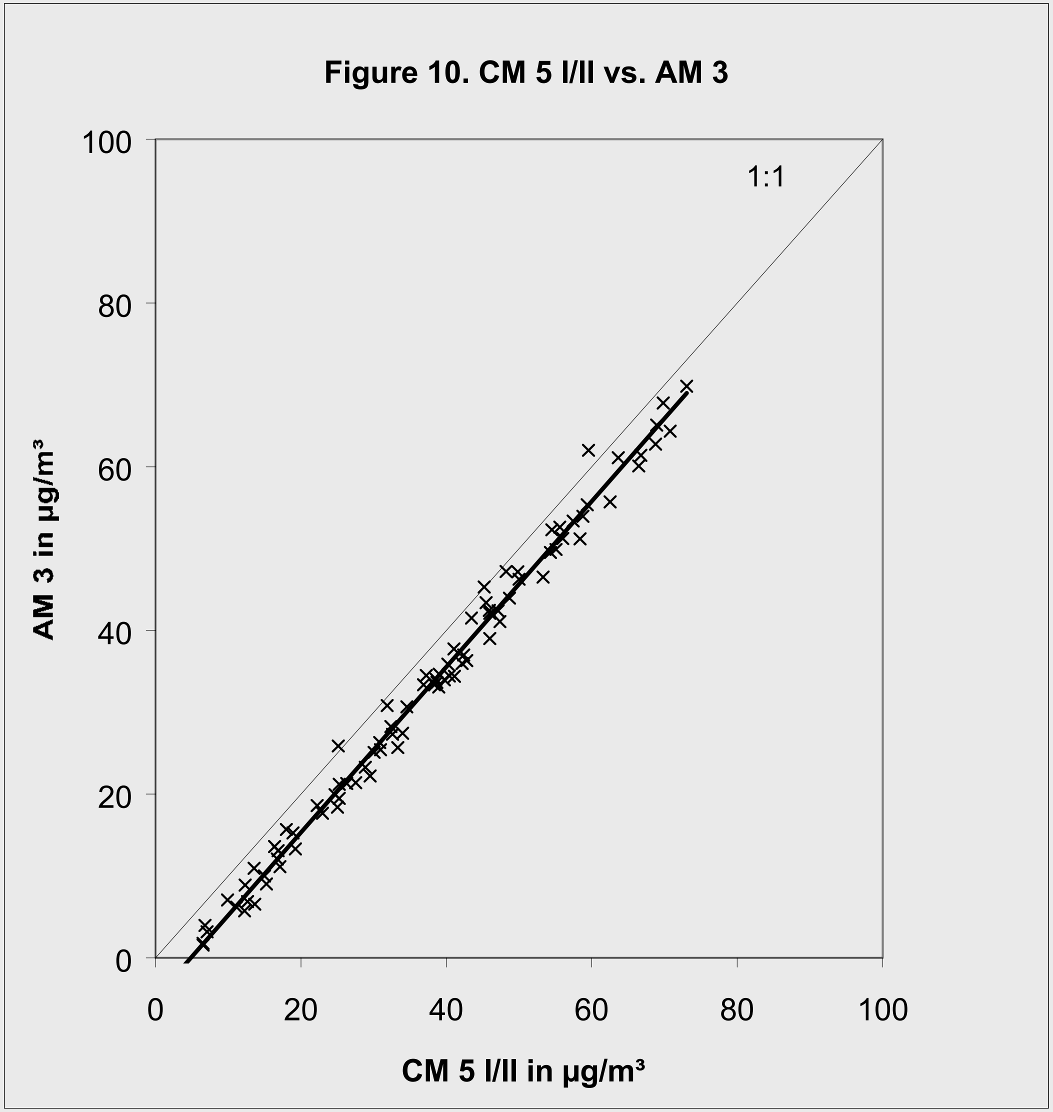
Fact is that the high volume method gave lower results than the low volume method by up to roughly 20% at several sites.



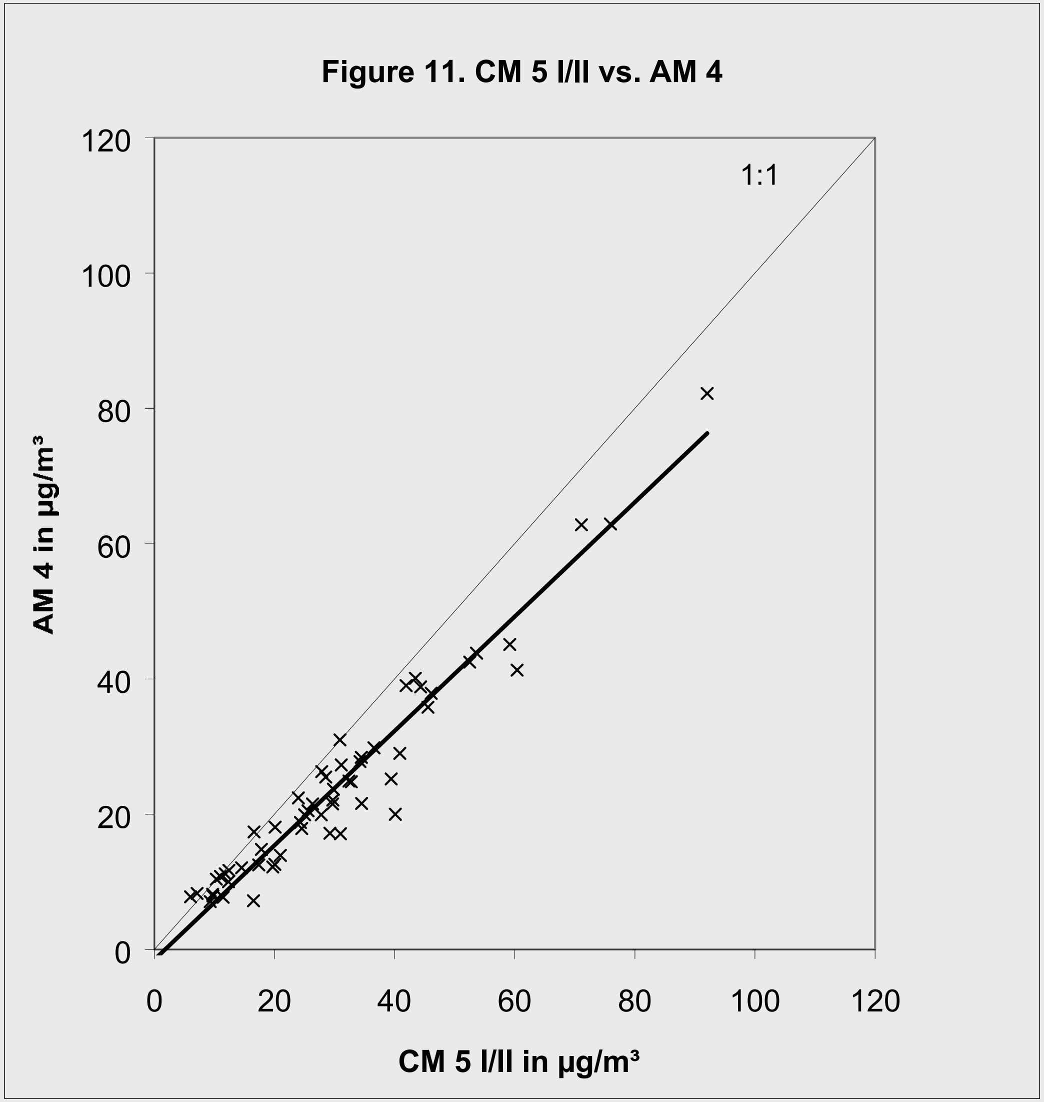
n =	103	paired values
Ortho. regr. y =	1.26	+ 1.045 x
S slope =	0.022	
S Intercept =	0.87	
R^2 =	0.957	
R =	0.978	
AM CM 5 I/II =	36.04	µg/m³
AM AM 1 =	38.91	µg/m³
$S_{CM\ 5\ I/II}$ =	18.53	µg/m³
$S_{AM\ 1}$ =	19.35	µg/m³



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	µg/m³
AM AM 2 =	32.42	µg/m³
$S_{CM\ 5\ I/II}$ =	19.41	µg/m³
$S_{AM\ 2}$ =	18.24	µg/m³



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	µg/m³
AM AM 3 =	32.67	µg/m³
$S_{CM\ 5\ I/II}$ =	17.90	µg/m³
$S_{AM\ 3}$ =	18.10	µg/m³

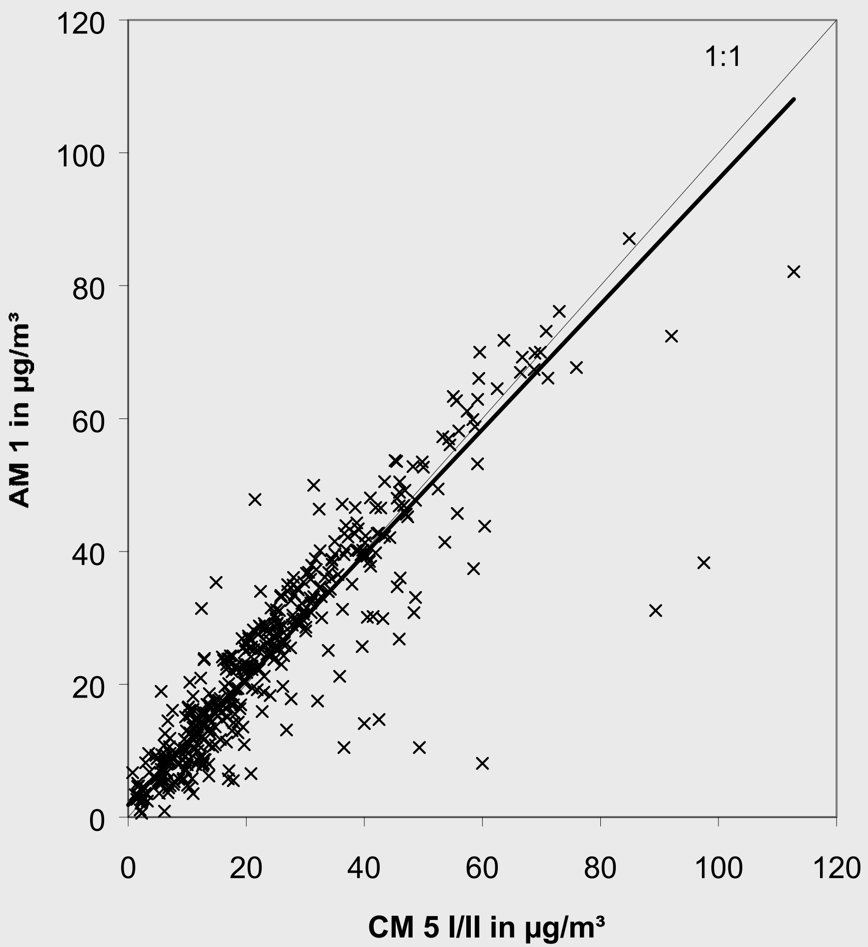


n =	57 paired values
Ortho. regr. y =	- 1.51 + 0.846 x
S slope =	0.028
S Intercept =	1.00
R^2 =	0.939
R =	0.969
AM CM 5 I/II =	30.38 µg/m³
AM AM 4 =	24.18 µg/m³
$S_{CM\ 5\ I/II}$ =	17.83 µg/m³
$S_{AM\ 4}$ =	15.15 µg/m³

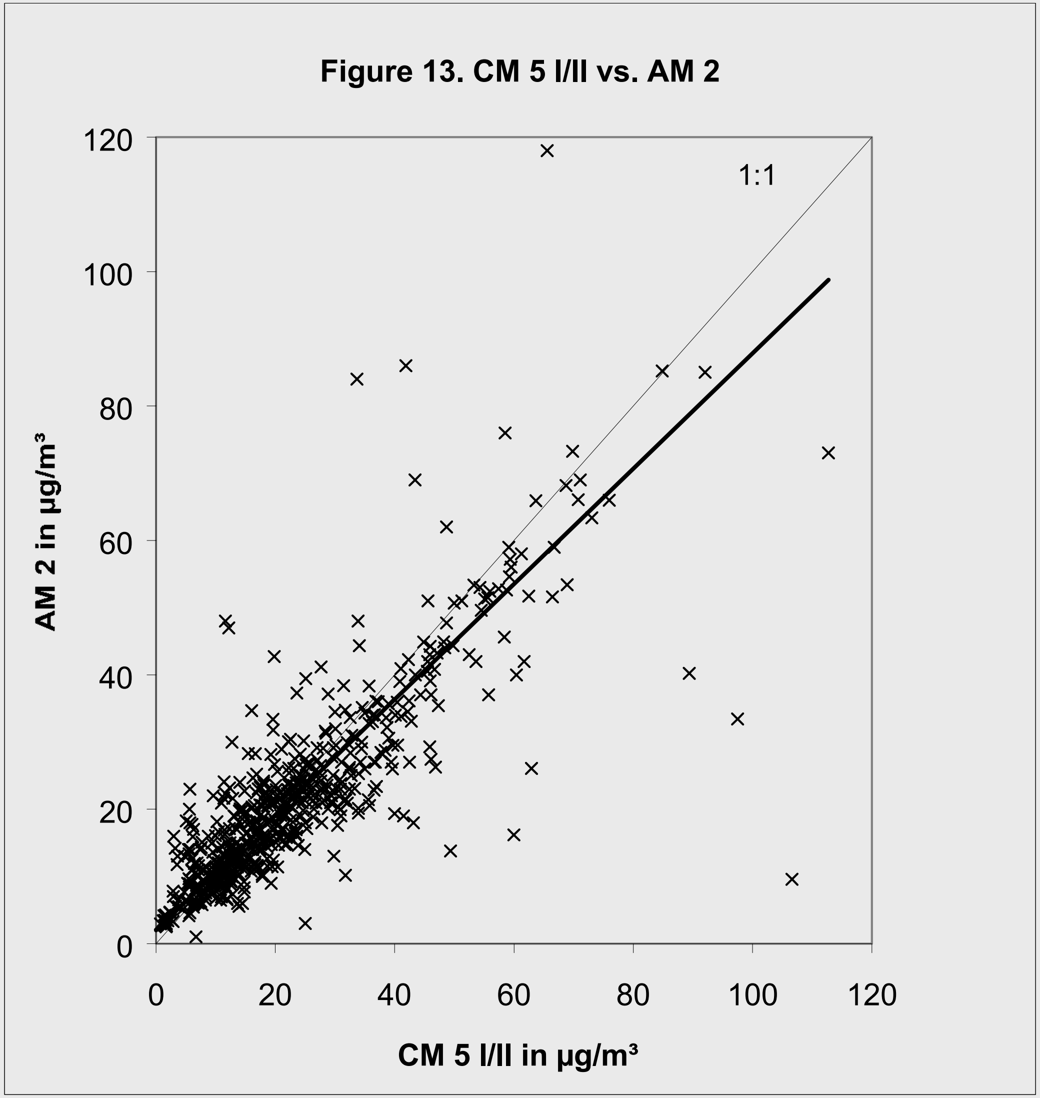
Figures 8-11

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



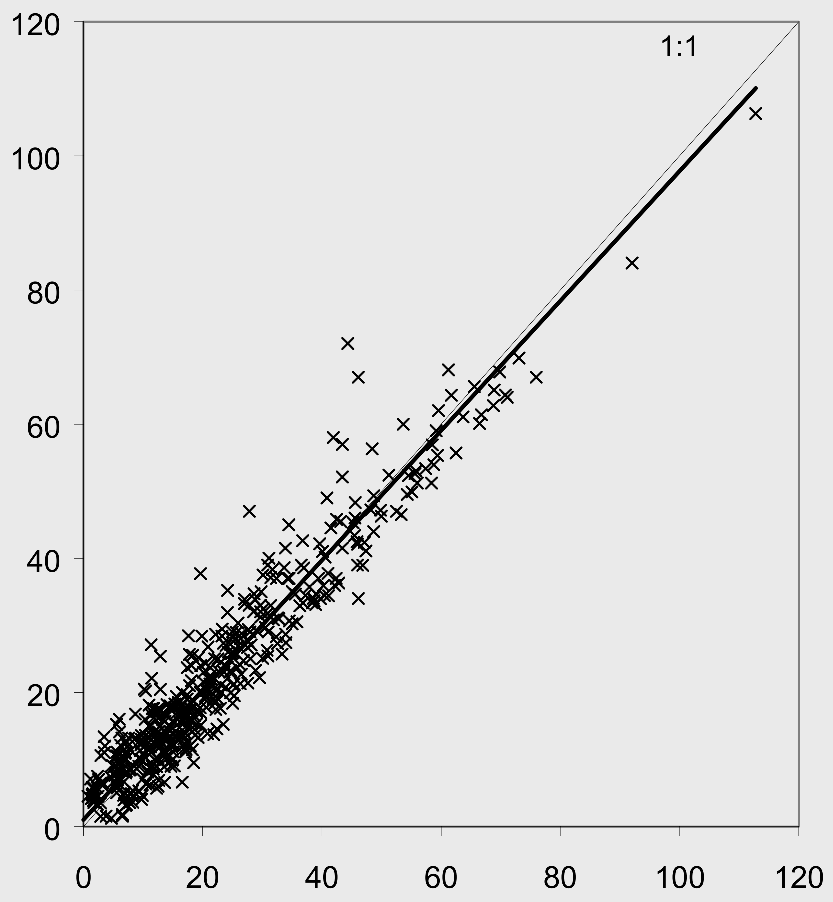
n =	426 paired values
Ortho. regr. y =	1.83 + 0.942 x
S slope =	0.021
S Intercept =	0.63
R^2 =	0.795
R =	0.892
AM CM 5 I/II =	24.62 µg/m³
AM AM 1 =	24.03 µg/m³
$S_{CM\ 5\ I/II}$ =	17.55 µg/m³
$S_{AM\ 1}$ =	16.65 µg/m³



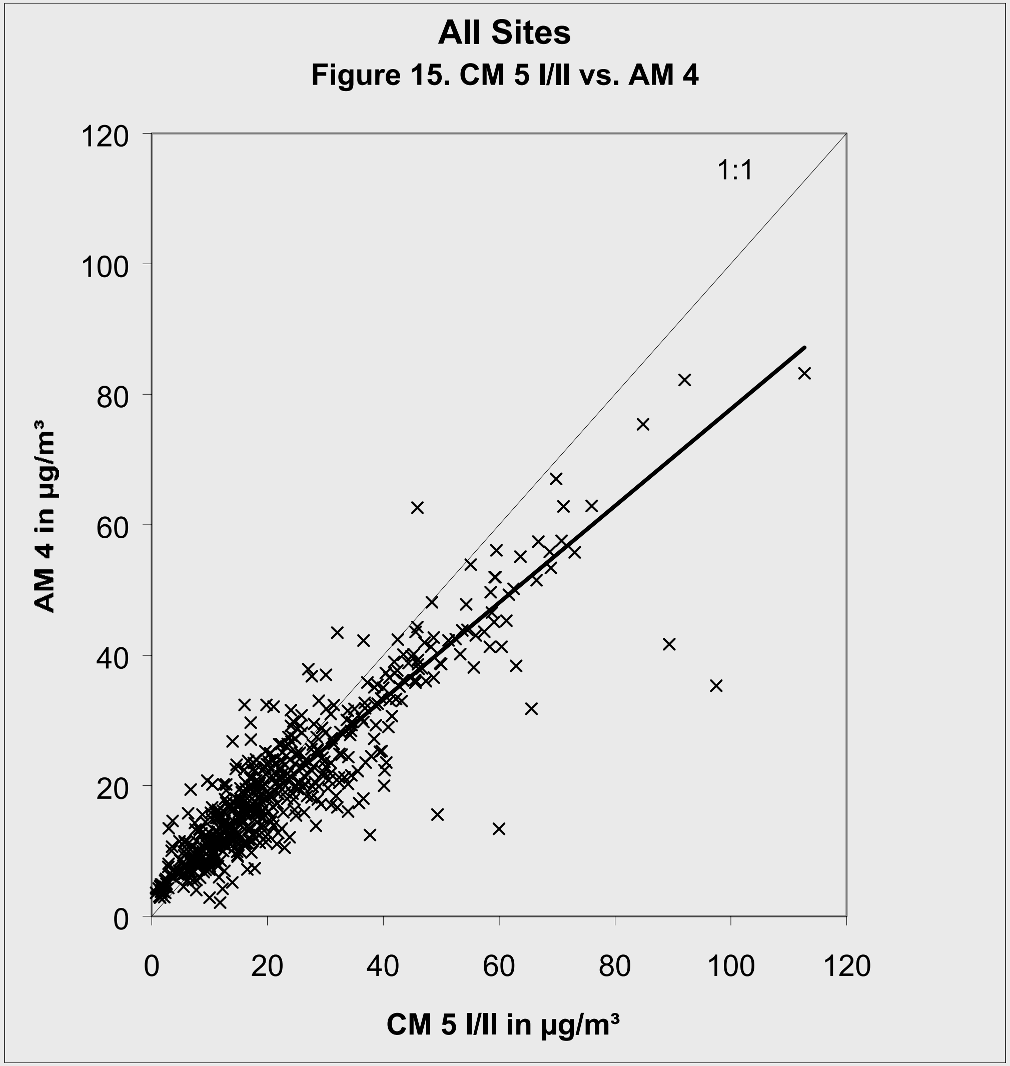
n =	585 paired values
Ortho. regr. y =	2.00 + 0.858 x
S slope =	0.021
S Intercept =	0.60
R^2 =	0.660
R =	0.812
AM CM 5 I/II =	22.95 µg/m³
AM AM 2 =	21.70 µg/m³
$S_{CM\ 5\ I/II}$ =	16.63 µg/m³
$S_{AM\ 2}$ =	14.68 µg/m³

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	µg/m³
AM AM 3 =	23.01	µg/m³
$S_{CM\ 5\ I/II}$ =	16.50	µg/m³
$S_{AM\ 3}$ =	15.99	µg/m³



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 µg/m³
AM AM 4 =	20.53 µg/m³
$S_{CM\ 5\ I/II}$ =	16.76 µg/m³
$S_{AM\ 4}$ =	12.79 µg/m³

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 $PM_{2,5}/PM_{10}$

Site	No. of values	$PM_{2,5}$ (CM 5) µg/m³	PM_{10} µg/m³	$PM_{2,5}/PM_{10}$
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.