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NPL REPORT
DQL-AS (RES) 010

Final report on the statistical evaluation of the CEN TC264 WG25 total gaseous mercury and mercury deposition field trials

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RESTRICTED

January 2008

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Approved on behalf of the Managing Director, NPL
by Martyn Sene, Director, Division of Quality of Life

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Executive summary

This document reports the statistical analysis required under:

- Work package 6 (Total Gaseous Mercury (TGM)), and;
- Work package 6 (Mercury Deposition Sampling),

of document CEN TC264 N900 for the field validation trials being conducted by CEN TC264 WG25 'Mercury'.

This report provides a statistical analysis of all TGM and mercury deposition data obtained at each of the European field trial sites. The report develops a methodology to estimate the uncertainty of the methods for TGM and mercury deposition by calculating the random and non-random components of uncertainty from the field trial data. Moreover this data is used to define applicable ranges for the two standard methods.

The data quality objectives of the Fourth Air Quality Daughter Directive relating to uncertainty were comfortably met at the field trial sites. The uncertainties calculated from the field trial data have been used to determine the lowest concentrations at which methods used continue to meet the uncertainty requirements of the Fourth Daughter Directive. This value can then be used as the lower limit of the range over which the methods were deemed to be applicable. The upper limits of the range at which the methods are applicable have been nominally assigned as the highest values observed during the field trial campaign, although it is recognised that there is no reason why the method should not be applicable to higher levels provided the performance characteristics of the methods are not compromised.

Contents

1 Introduction

This report summarises the results and statistical analysis of the field validation programme of CEN TC264 WG25 'Mercury'. This programme aimed to validate the proposed standard methods for the determination of Total Gaseous Mercury (TGM), and for the determination of mercury in precipitation, to ensure that the measurement methods met the required data quality objectives of the Fourth Air Quality Daughter Directive.

1.1 Background

The European Commission (EC) is acting to reduce human and environmental exposure to a variety of air pollutants across Europe. Because of mercury's combined qualities of toxicity, environmental persistence, and potential for bioaccumulation, this metal is a particularly insidious, and an important pollutant to monitor and manage. However, sampling and analysis of mercury is not always a simple matter, and it is important to understand the key measurement issues to appropriately collect and interpret data. The application of non-validated sampling and analytical methods could lead to significant biases in measurement results.

European Union policy on air quality aims to develop standard methods for the assessment of air quality and adopt these as reference methods in support of European legislation, if appropriate. The Framework Directive on ambient air quality assessment and management (EU Council Directive 96/62/EC) was adopted by the European Council in September 1996. The general aim of this directive is to define the basic principles of a common strategy in order to assess the following objectives:

- define and establish objectives for ambient air quality in the EU (for 13 air polluting substances including mercury) designed to avoid, prevent or reduce harmful effects on human health and the environment as a whole;
- assess the ambient air quality in Member States on the basis of common methods and criteria;
- obtain adequate information on ambient air quality and ensure that it is made available to the public;
- maintain ambient air quality where it is good and improve it where it is not.

Specifically, the Fourth Daughter Directive (EU Council Directive 2004/107/EC) relating to the allowable levels of arsenic, cadmium, mercury, nickel and polycyclic aromatic hydrocarbons in ambient air was published in January 2005. Following the requirements of the Fourth Daughter Directive, Member States have to measure the TGM in the ambient air and the total deposition of mercury. Therefore, there is a strong need to develop fully validated and traceable European standard methods that will ensure the representativeness, comparability, traceability and accuracy of data produced by all Member States for mercury measurements. Although there are different automated and manual techniques available for the measurement of TGM concentrations in ambient air, there is no standardised method available which is sufficient to meet overall objectives and requirements of the Fourth Daughter Directive. At this stage only the European standard method for the determination of the mercury concentration in water samples (EN 13506) is available but no standard

method exists for the determination of mercury in precipitation (although OSPAR/EMEP reference methods are currently available for mercury in precipitation).

The Fourth Daughter Directive requires the standardised method for the measurement of TGM concentrations in ambient air to be an automated method based on atomic absorption spectrometry or atomic fluorescence spectrometry. The standardised method for mercury deposition is to comprise cylindrical deposit gauges with standardised dimensions for collection of the sample, with analysis by atomic absorption spectrometry or atomic fluorescence spectrometry. However, Member States may use wet only sampling instead of bulk sampling for deposition if they can demonstrate that the difference between them is less than 10 %. The overall expanded uncertainty limit specified by the Fourth Daughter Directive is 50% for TGM and 70% for mercury deposition.

Field trials were planned and executed by CEN TC264 WG25 'Mercury' in order to test and validate the proposed measurement methodologies and to ensure that they met the data quality requirements of the Fourth Daughter Directive, in particular the uncertainty requirements. Since no limit or target value was available at which to gauge this uncertainty requirement against, instead the lowest concentration value at which the uncertainty requirement can be met was determined. In turn this yielded the lower end of the applicable range of the standard. The upper end of the applicable range was defined as the highest concentration, or deposition rate, measured during the field trial campaign. However, there is no reason why the method should not be applicable to higher concentrations, or deposition rates, provided the performance characteristics of the method are not compromised.

The field trials took place in four locations around Europe for TGM measurements, and at two locations around Europe for the deposition measurements, during late 2006, and 2007.

2 Methodology

The measurement uncertainty of the concentration of TGM in ambient air, and of mercury in deposition, has to fulfil the requirement of a maximum uncertainty prescribed by Directive 2004/107/EC.

In this context the uncertainty of the proposed standard methods have been calculated from a series of field trials to:

a) demonstrate that this standard method meets the uncertainty requirements prescribed by Directive 2004/107/EC, and;
b) provide sufficient information on performance criteria which have to be met to ensure that individual users can also meet the uncertainty requirements prescribed by Directive 2004/107/EC.

2.1 Uncertainty estimation from the field trial process

The theory underpinning the field trial process is that the mean value yielded by several different types of instrument or sampler at different locations when measuring different concentration levels, or deposition rates, represents the best estimate of the 'true value' in ambient air. It is also assumed that the spread of these results is a good estimate of the uncertainty in the mean value. Both the random and non-random contributions to the uncertainty are considered by the general form:

$$u_c(\gamma) = \sqrt{u_r^2(\gamma) + u_s^2(\gamma)} \tag{1}$$

Where $u_c(\gamma)$ is the relative combined uncertainty in the TGM concentration in, or deposition rate from, ambient air, and $u_r(\gamma)$ and $u_s(\gamma)$ are the relative random and non-random contributions, respectively, to this uncertainty.

Each field trial consists of M parallel samplers operating over N days (or sampling periods). The data produced by each sampler in the TGM trial was averaged to produce a daily mass concentration value $\gamma_{d,i}$ on day d from sampler i. Each deposition sampler produced a mercury deposition rate $\gamma_{d,i}$ over sampling period d from sampler i. Therefore we can define the terms:

$$\gamma = \frac{1}{N}\sum_{d=1}^{N}\bar{\gamma}_d \tag{2}$$

$$\bar{\gamma}_d = \frac{1}{M}\sum_{i=1}^{M}\gamma_{d,i} \tag{3}$$

$$\delta_{d,i} = \gamma_{d,i} - \bar{\gamma}_d \tag{4}$$

$$\bar{\delta}_i = \frac{1}{N}\sum_{d=1}^{N}\delta_{d,i} \tag{5}$$

$$\sigma_i = \sqrt{\frac{\sum_{d=1}^{N}(\delta_{d,i} - \bar{\delta}_i)^2}{N-1}} \tag{6}$$

where;
γ is the mean mass concentration (or deposition rate) over all N days (or sampling periods) and across all M instruments.
$\bar{\gamma}_d$ is the mean mass concentration (or deposition rate) on day (or sampling period) d across all M instruments.
$\delta_{d,i}$ is the deviation of sampler i from the mean mass concentration (or deposition rate) on day (or sampling period) d.
$\bar{\delta}_i$ is the mean deviation of sampler i from the mean mass concentration (or deposition rate) over all N days.
σ_i is the standard deviation of the deviation of sampler i over all N days (or sampling periods).

It follows that the random contribution to the relative combined uncertainty from sampler i is given by:

$$u_{r,i}(\gamma) = \frac{\sigma_i}{\gamma\sqrt{N}} \tag{7}$$

and that the non-random contribution to the relative combined uncertainty from sampler i, is given by:

$$u_{s,i}(\gamma) = \sqrt{\left(\frac{\bar{\delta}_i}{\gamma}\right)^2 + u_{i,vol}^2} \tag{8}$$

where $u_{i,vol}$ is the uncertainty in the sampled volume for sampler i (this is not a consideration for the deposition field trials) – usually a standard uncertainty of 3%.

The relative combined uncertainty from sampler i, is given by:

$$u_{c,i}(\gamma) = \sqrt{u_{r,i}^2(\gamma) + u_{s,i}^2(\gamma)} \tag{9}$$

and $u_c(\gamma)$, the relative combined uncertainty at each field trial location is then given by

$$u_c(\gamma) = \frac{1}{M}\sum_{i=1}^{M}u_{c,i}(\gamma) \tag{10}$$

The relative expanded uncertainty U is then calculated by using a coverage factor k, corresponding to a level of confidence of approximately 95%, thus:

$$U = k.u_c(\gamma) \tag{11}$$

For the field validation tests $k = 2$ (based on >30 degrees of freedom).

The relative expanded uncertainties at each field trial site, were plotted against average mass concentration (or deposition rate) γ at each site as a means of estimating uncertainty at a range of concentrations by extrapolation.

In the case of the TGM field trial the instruments have been considered to be independent of each other for the purposes of data analysis. This decision has been justified as the field trials have shown that the primary cause of variability in these instruments is related to the installation, set-up and calibration procedures, rather than the type of instrument or the manufacturer. The between and within manufacturer variability has been included in this report for information but it has not been used as part of the uncertainty budget.

In the case of the deposition field trial, samplers of the same type are nominally identical and should theoretically collect the same amount of deposition (the sensitivity of the rain sensor on the wet-only samplers means that some variability within these sampler types is expected). Any deviation within sampler type, when it does occur (possibly as a result of micro-siting of the samplers, orientation, exposed to differing weather conditions, *etc*) is significant and relevant to the overall uncertainty budget. Thus, random and non-random uncertainty contributions to the uncertainty budget have been calculated for within, and between, sampler type variation. Between sampler type deviations have been calculated using the average values from within each sampler type. The rationale for this approach is that this field trial represents a direct comparison of sampler types, in a way that the TGM field trial did not. Also, unlike in the case of the TGM field trial the performance of the deposition samplers is not sensitive to external factors such as calibration, but instead is a function of the design of the sampler. (In this case the direction of the overall non-random bias of each sampler type is therefore also important.) A laboratory intercomparison of the analysis of the collected deposition was also carried out as part of the deposition field trial, and the random and non-random biases from this has been included in the overall uncertainty estimate. This rationale is suitable for determining the overall uncertainty budget of the deposition method, but gives no specific information about how the various types of deposition sampler compare. In order to determine this a separate analysis has been made of the overall performance of the individual deposition samplers over the field trial campaign.

3 TGM

3.1 TGM field trial locations and sampling periods

Italy
Site operator: CNR-Institute for Atmospheric Pollution, Rende
Site: The Atmospheric Marine Monitoring Station (EMEP type) of the CNR- IIA (Institute for Atmospheric Pollution) is located on a small headland 49m above sea level, near the village of San Lucido on the Tyrrhenian coast of Calabria. It is a rural coastal/background site.
Coordinates: 39.316°N; 16.033°E
Sampling period: November 2006 – January 2007

Spain
Site operator: Instituto de Salud Carlos III, Madrid
Site: The monitoring site is in Huelva, an agglomeration near an industrial area. The city is located in the south west of Spain near the Atlantic shoreline (Cadiz Gulf), 2 km from a chlor-alkali plant.
Coordinates: Latitude: 37.266° N, Longitude: 6.950° W
Sampling period: February 2007 – May 2007

Sweden
Site operator: IVL Swedish Environmental Research Institute, Göteborg
Site: Background site (coastal). EMEP site SE 14.
Coordinates: 57.394°N, 11.914°E
Sampling period: June 2007 – August 2007

Belgium
Site Operator: VMM Vlaamse Milieumaatschappij, Antwerp
Site: Central European industrial air quality monitoring site located near a chlor-alkali plant near Dennenhof, Tessenderlo.
Coordinates: 51.063°N, 5.094 °E
Sampling period: September 2007 – December 2007

3.2 TGM Results

The number of instruments at each field trial location, and the length of each study was as follows:

- **Italy:** 8 instruments, 64 days
- **Spain:** 7 instruments, 79 days
- **Sweden:** 8 instruments, 57 days
- **Belgium:** 8 instruments, 63 days

For the purposes of data analysis the data produced by each instruments was averaged over the period of one day to produce a usable and consistent data set. The sampling period of the instruments used in the field trials was considerably shorter (ranging

from 30 seconds to 30 minutes). Although all the TGM equipment is easily capable of measuring over shorter periods, a standard method in support of a European directive which specifies annual average limits will not need to produce data on time periods shorter than one day.

The data capture at each field trial location (as a percentage of usable days with >90% data capture) was as follows:

- **Italy:** 96%
- **Spain:** 84%
- **Sweden:** 93%
- **Belgium:** 88%

(Some of the data in Belgium was rejected due to known calibration problems; if this data had not been rejected at this stage it would most probably have been rejected as outlying anyway.)

A small percentage of data was subsequently rejected as outlying (those values more than double, or less than half the daily average). In the vast majority of cases the outlying data was explained by an instrumental fault. This accounted for the following percentage of all data at the field trial locations:

- **Italy:** 3%
- **Spain:** 3%
- **Sweden:** 0%
- **Belgium:** 1%

Prior to analysis the data was all corrected to mass concentration values in nanograms per cubic metre at 293 K and 101.325 kPa.

The daily averages measured at each site are detailed in the figures below.

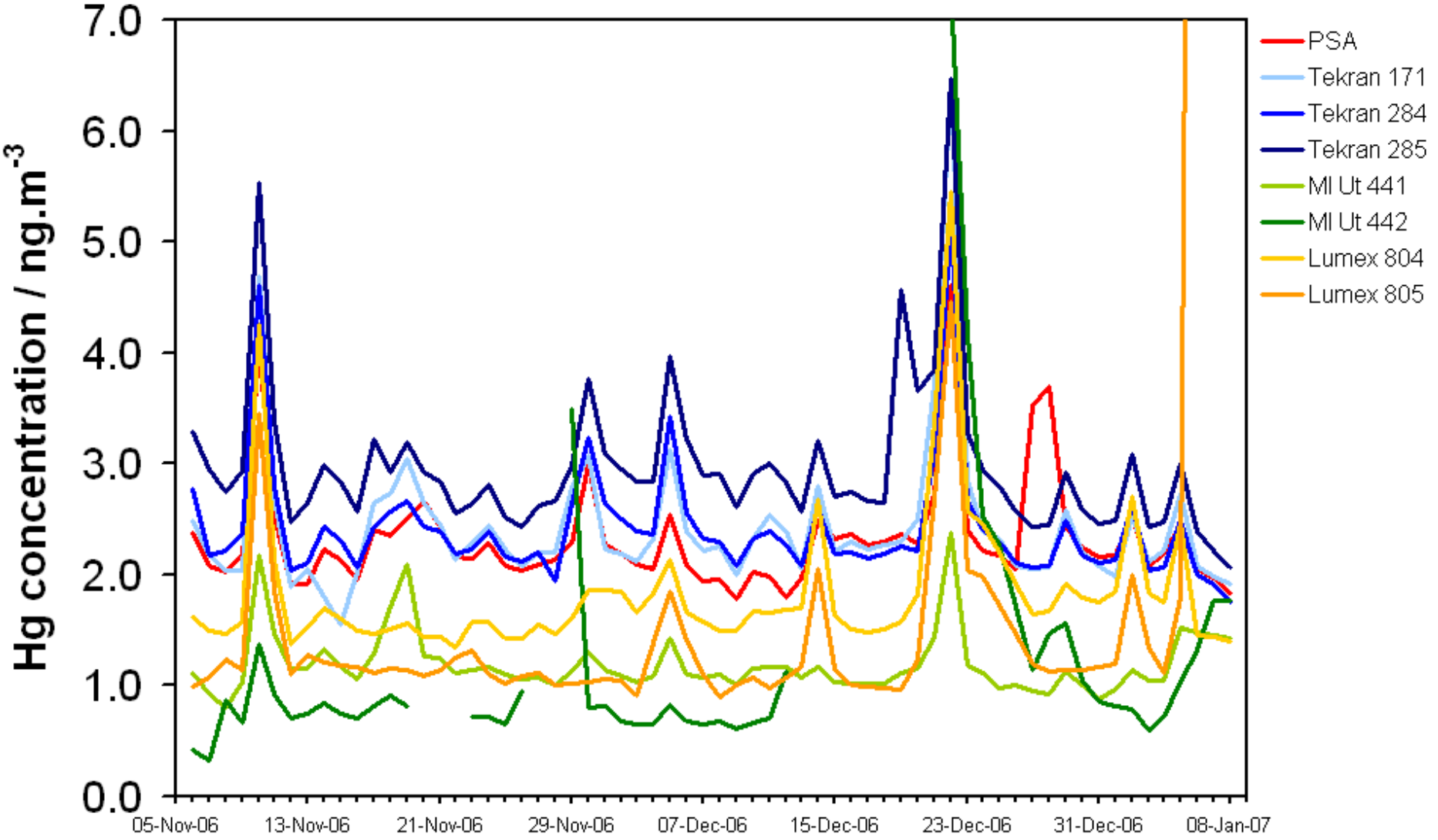

Figure 1. Daily mass concentration data from the Italian TGM field trial.

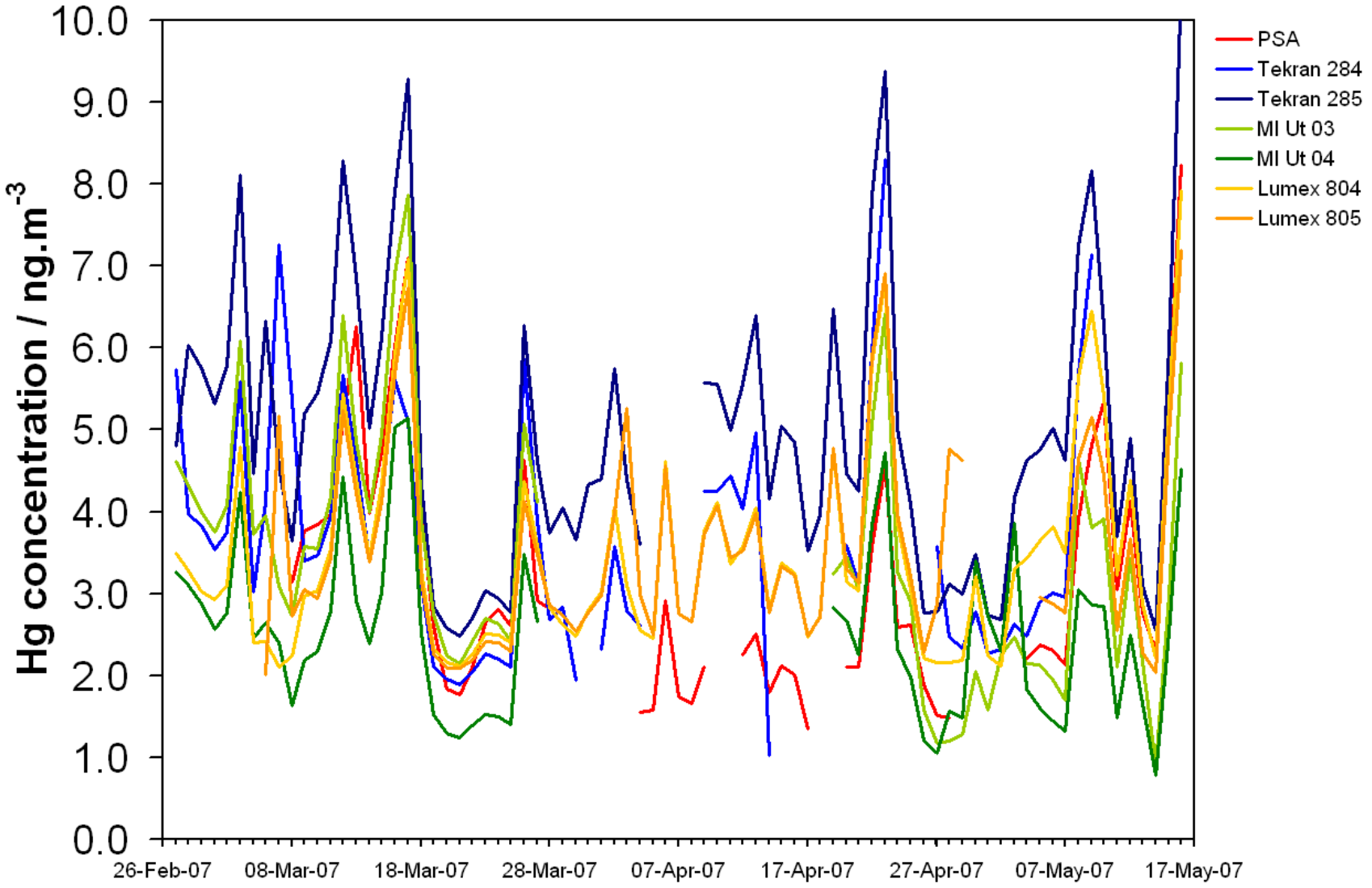

Figure 2. Daily mass concentration data from the Spanish TGM field trial.

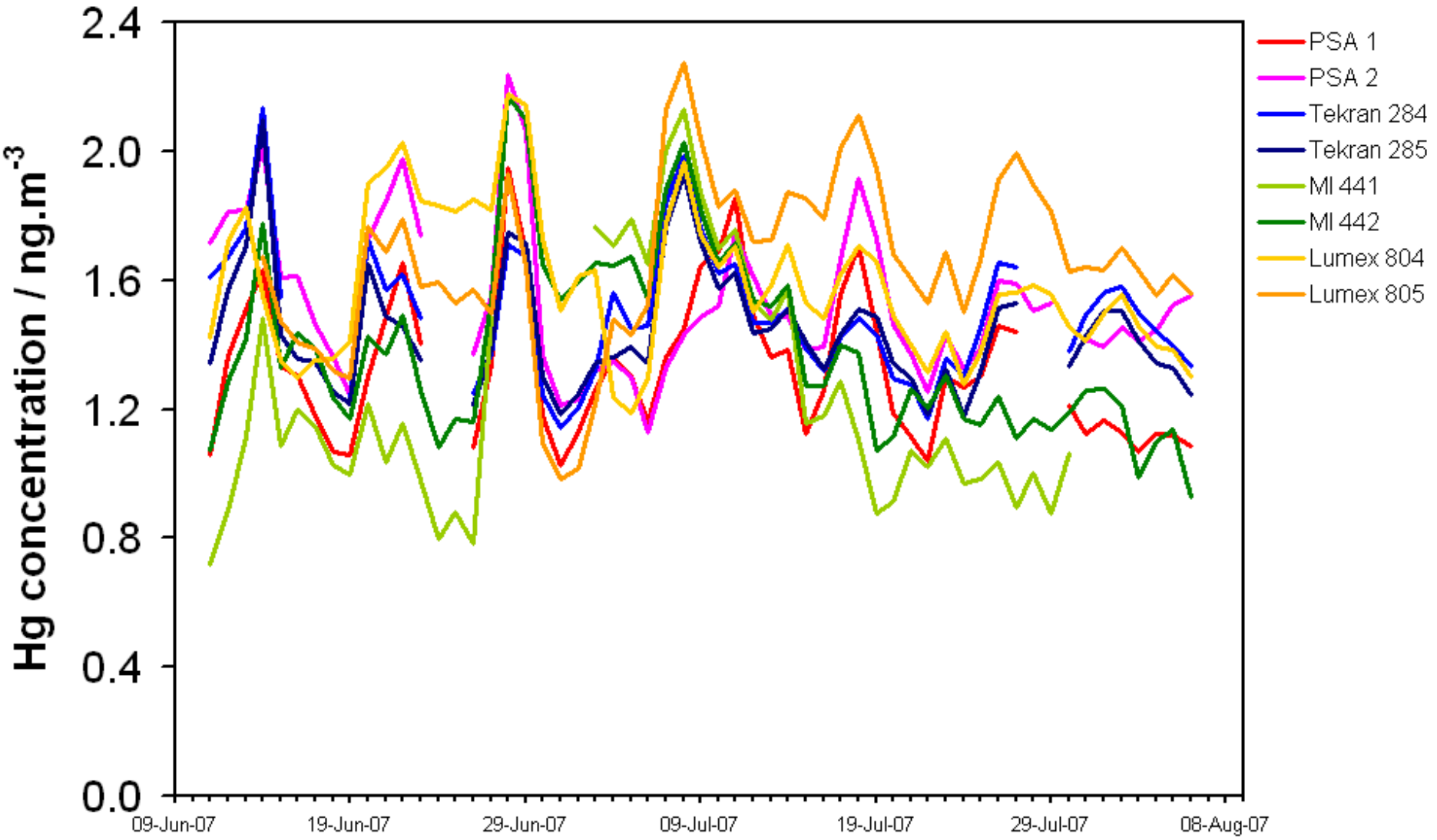

Figure 3. Daily mass concentration data from the Swedish TGM field trial.

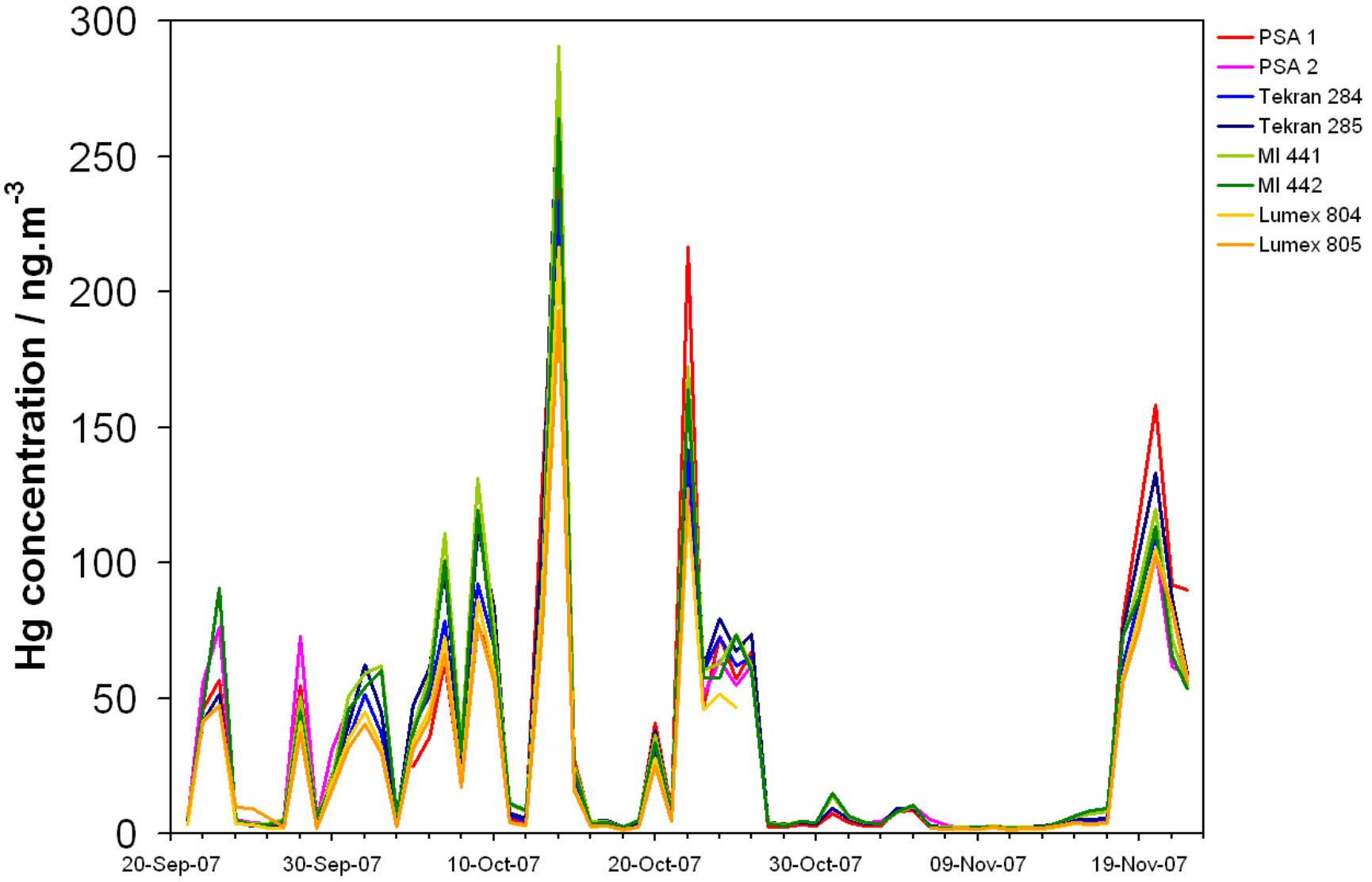

Figure 4. Daily mass concentration data from the Belgian TGM field trial.

3.3 Data analysis

Using the daily values displayed above, the random and non-random components of the uncertainty contributions from the field trial were estimated using the method outlined above. For the TGM measurements each instrument was assumed to be independent – even if two or more were present on the field trial that were from the same manufacturer. These results are presented in the table below.

Sampling location	Average deviation	
	Random	Non-random
Italy	2.3 %	26.9 %
Spain	2.3 %	13.1 %
Sweden	1.6 %	7.5 %
Belgium	3.3 %	9.9 %

Table 1. The average random and non-random deviations observed at each field trial location.

For completeness the average deviation between and within the different instrument types are also displayed in Tables 2 and 3 below – these are included for information only and are not used in the assessment of the measurement uncertainty from the field trials.

Manufacturer	Average deviation between instrument types	
	Random	Non-random
PSA	2.2 %	10.0 %
Tekran	1.5 %	14.2 %
Mercury Inst.	2.3 %	18.7 %
Lumex	2.1 %	11.8 %

Table 2. The average random and non-random deviations between the various instrument types tested at each field trial location. This shows how well instruments made by each manufacturer compare with all the other manufacturers.

Manufacturer	Average deviation within instrument types	
	Random	Non-random
PSA	2.3 %	6.8 %
Tekran	1.2 %	8.7 %
Mercury Inst.	2.2 %	6.1 %
Lumex	1.1 %	4.4 %

Table 3. The average random and non-random deviations within the various instrument types tested at each field trial location. This shows how well instruments made by the same manufacturer compare with each other.

It is clear from the results that non-random deviations are the most significant uncertainty component. In all cases the contribution from the random component is small. This is a clear indication that all the instruments tested are able to follow changes in ambient TGM concentration very effectively, hence the low random uncertainty, but there are significant systematic biases between the values produced by these instruments. This has been partly identified as being caused by the use of different calibration ranges and methodologies for different instruments. When more robust calibration procedures were employed as the field trials progressed, the non-random bias decreased significantly. Moreover, the presence of significant random and non-random uncertainties within instrument types, *i.e.* between those instruments made by the same manufacturer, highlights that the observed uncertainties are not simply due to the different types or make or instrument, but more to do with external factors, such as calibration protocol.

Using the methodology described above in 2.1, and the data from the table above, the four field trials yield expanded uncertainties at the 95% confidence interval (assuming a coverage factor of k=2) of:

- **Italy: 54.3 % at an average TGM concentration of 1.9 ng.m^{-3}**
- **Spain: 27.3 % at an average TGM concentration of 3.6 ng.m^{-3}**
- **Sweden: 16.6 % at an average TGM concentration of 1.5 ng.m^{-3}**
- **Belgium: 21.7 % at an average TGM concentration of 32 ng.m^{-3}**

There is no obvious trend in the uncertainty observed with concentration measured for the overall population of daily values at all the field trial locations. This is mainly due to the different calibration and operational methodologies used at each field trial site. However, the uncertainty for each daily value at each location may be plotted and examined separately. This is done in the figure below.

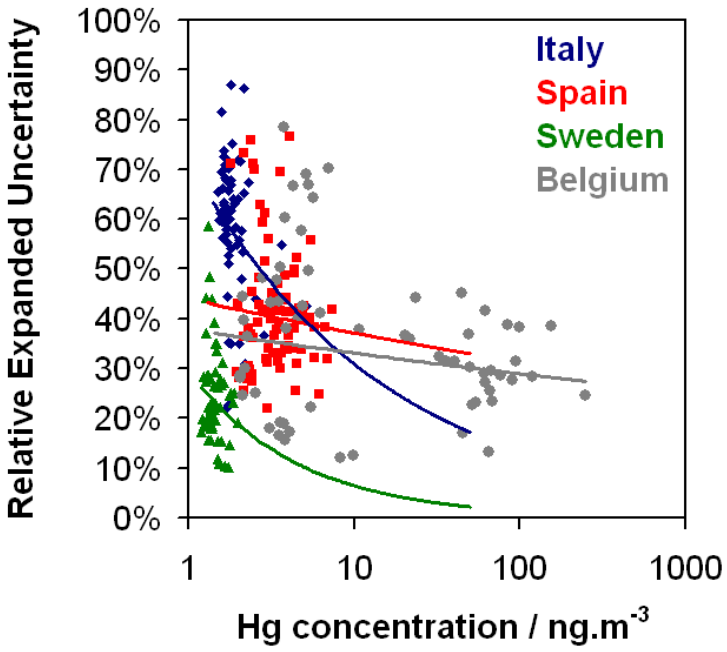

Figure 5. Expanded uncertainty against average measured daily concentration at the four field trial locations. A trend line of the form $y = ax^{-b}$ has been fitted to each set of field trial data.

In order to meet the data quality objectives of the Fourth Daughter Directive the expanded uncertainty of the method must not exceed 50%. Since no limit value is available at which to gauge this uncertainty requirement, we may instead determine the lowest concentration value at which the uncertainty requirement can be met. In turn this will yield the bottom of the applicable range of the standard. Since the overall field trial data cannot be assumed to belong to the same population, the most robust way to perform this calculation is to take an average of the trend lines for the individual field trials shown in Figure 5. The result of this analysis is shown in Figure 6.

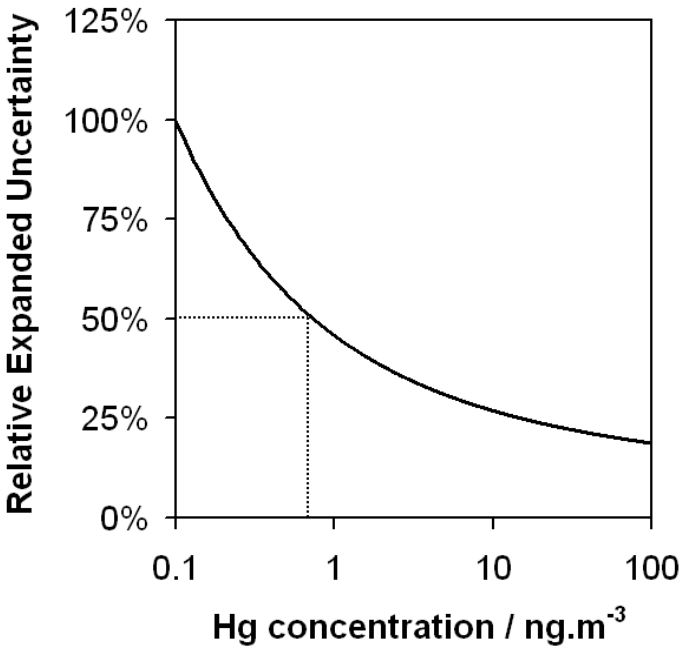

Figure 6. Expanded uncertainty against mercury concentration determined from the average of the trends exhibited by the four TGM field trials.

This operation yields a relative expanded uncertainty of 50% at a mercury mass concentration of approximately 0.75 ng.m^{-3}. Therefore, this can be proposed as the lower range of the method. This value represents the best estimate of the lower range of the method given the data available, but should only be treated as an estimate because of the relatively poor fit of the data extrapolations.

The maximum observed daily average concentration on any individual instrument was approximately 300 ng.m^{-3} and so this could be used as the upper limit of the range of the standard method, although there is no reason why the method should not be applicable to higher concentrations provided the performance characteristics of the method are not compromised, gold traps are not saturated and the mass of mercury collected is not greater than the dynamic range of the instrument. An additional important requirement is that the calibration range be very similar to the expected range of concentration values recorded. Over shorter collection periods, of approximately 5 minutes, concentrations as high at 4000 ng.m^{-3} were observed with no apparent impact on the instrumentation or measurement.

4 Deposition

4.1 Deposition field trial locations and sampling periods

Sweden
Site operator: IVL Swedish Environmental Research Institute, Göteborg
Site: Background site (coastal). EMEP site SE 14.
Coordinates: 57.394°N, 11.914°E
Sampling period: December 2006 – July 2007

Slovenia
Site Operator: IJS Institut Jožef Stefan, Ljubljana
Site: The sampling site was located approximately 2 km NE-E from a power plant and between a coal ash landfill expanding towards NW, a coal mine on S and E, and freshwater Lake Velenje.
Coordinate: 46.369°N, 15.083°E.
Sampling period: January 2007- September 2007

4.2 Deposition Results

The number of samplers at each field trial location, and the total number of samples collected was as follows:

- **Sweden:** 3 Bulk (59 samples), 2 Wet-only (38 samples), and 4 Bergerhoff (32 samples) samplers
- **Slovenia:** 2 Bulk (37 samples), 2 Wet-only (36 samples), and 4 Bergerhoff (40 samples) samplers

Weekly samples were taken, apart from the Bergerhoff samplers where approximately half the samples were taken monthly. The approximate data capture rates at each site were as follows:

- **Sweden:** 96%
- **Slovenia:** 94%

The vast majority of the lost data was due to mechanical failure of the wet-only samplers, or problems during the analysis step.

The results of the weekly sampling at each site, in chronological order of samples are detailed below.

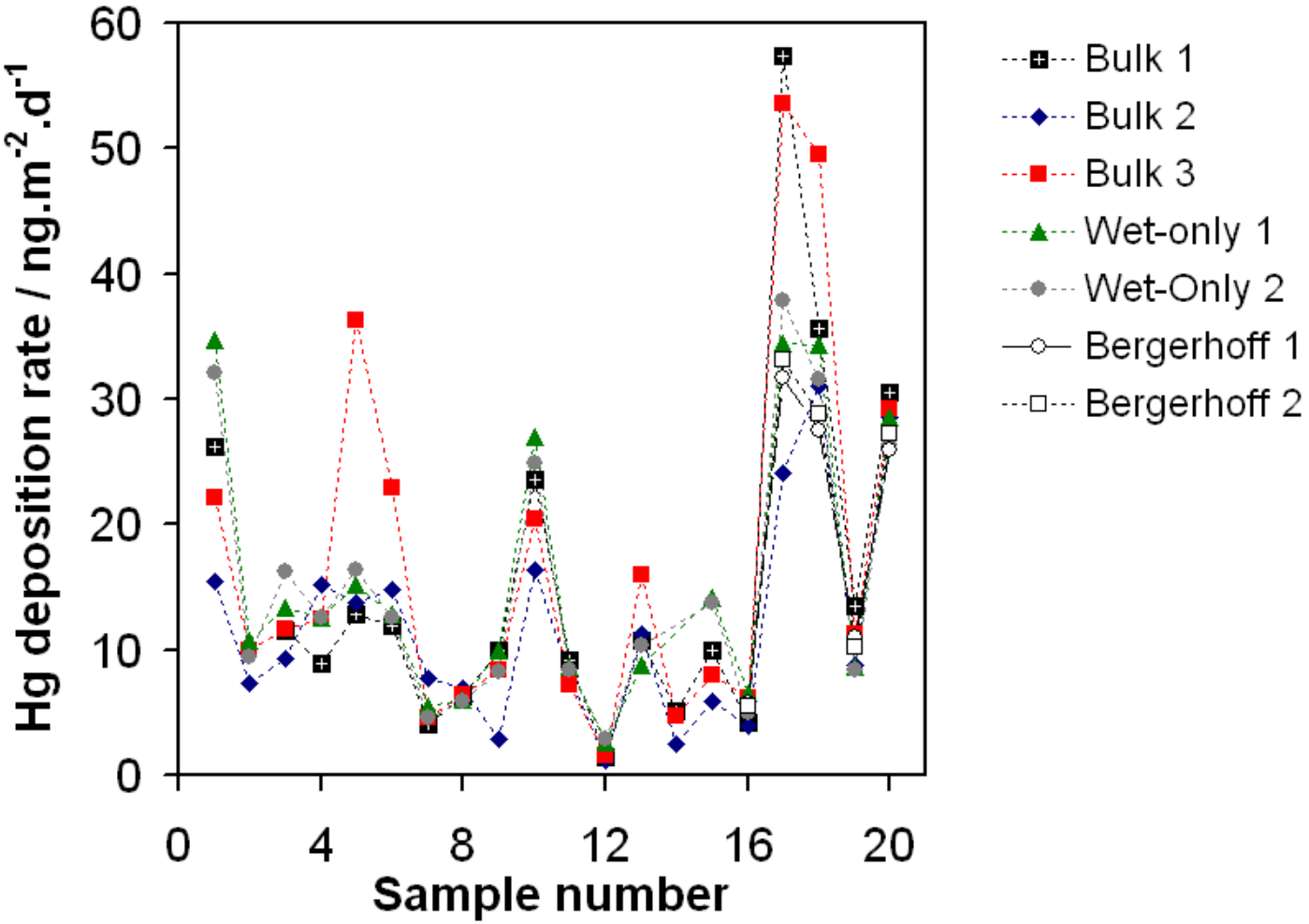

Figure 6. Weekly deposition rate results from the Swedish deposition field trial.

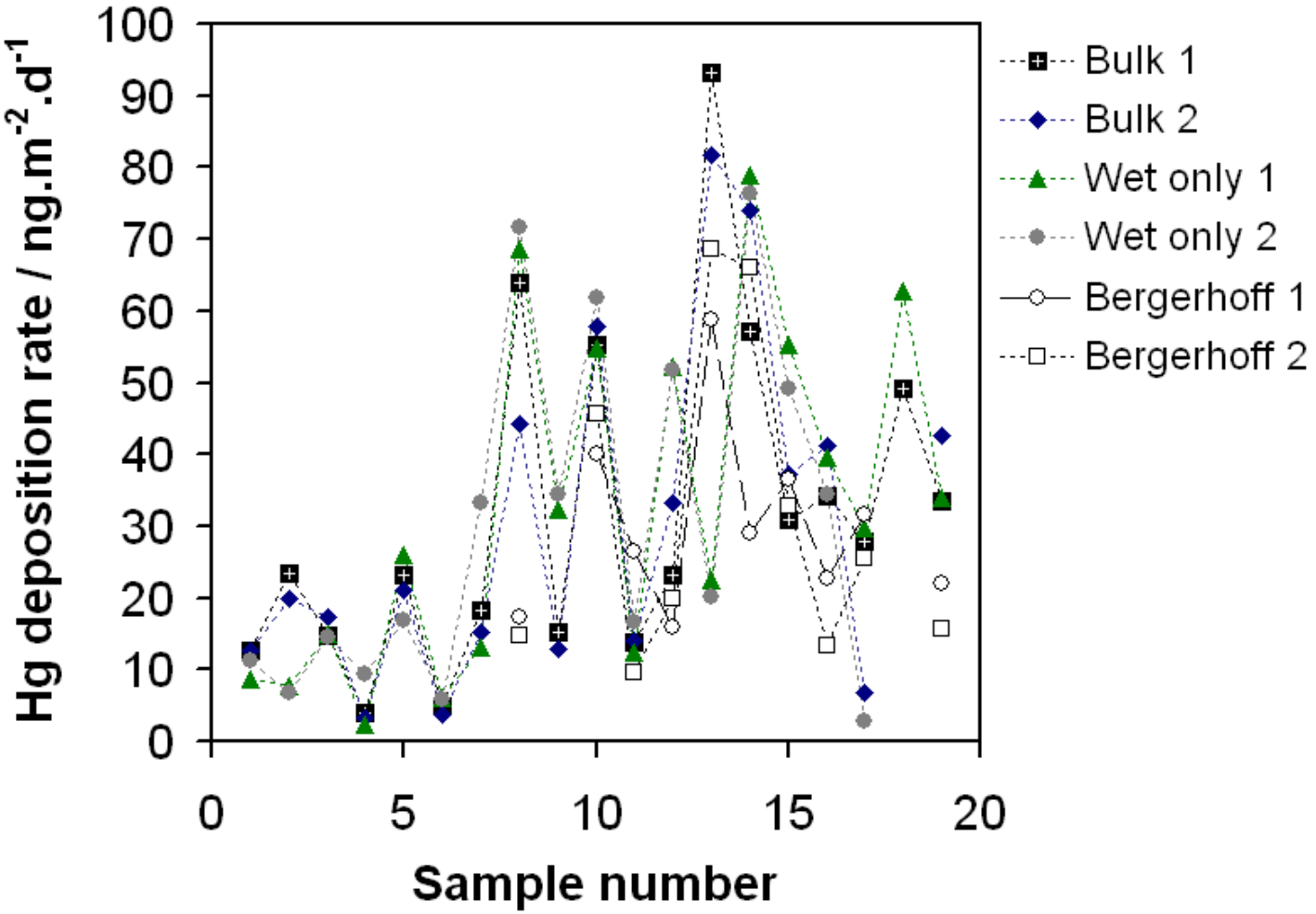

Figure 7. Weekly deposition rate results from the Slovenian deposition field trial.

4.3 Data Analysis

During the analysis of the data from the deposition trial, variation both within and between sampler types has been examined. When variation between sampler types has been examined, the average value produced by samplers of the same type has been considered in the analysis (unlike for TGM where each instrument was considered individually). Whilst the majority of samples collected were analysed by the co-ordinating laboratory, a subset was sent to a second laboratory so that an indication of the uncertainty associated with the analysis process could be estimated, since these data are not explicitly included in the EN13506.

The random and non-random bias within groups of samplers during the field trials is given in the tables below.

Sampler type	Average deviation between sampler type	
	Random	Non-random
Wet-only	1.2 %	4.0 %
Bulk	6.1 %	5.0 %
Bergerhoff	6.0 %	1.4 %
Sampler type	Average deviation within sampler type	
	Random	Non-random
Wet-only	1.8 %	1.7 %
Bulk	7.0 %	13.2 %
Bergerhoff	9.2 %	8.4 %

Table 4. The average random and non-random bias between and within groups of samplers during the field trial in Sweden

Sampler type	Average deviation between sampler type	
	Random	Non-random
Wet-only	12.2 %	9.6 %
Bulk	7.7 %	9.4 %
Bergerhoff	9.0 %	19.0 %
Sampler type	Average deviation within sampler type	
	Random	Non-random
Wet-only	3.5 %	4.2 %
Bulk	3.6 %	0.4 %
Bergerhoff	7.2 %	1.7 %

Table 5. The average random and non-random bias between and within groups of samplers during the field trial in Slovenia.

It is clear from the data presented that the largest contribution to the uncertainty of the measurement is the deviation between different types, although the contribution from the variability within the same sampler type cannot be neglected. Therefore, the random and non-random average deviations within sampler types are added in quadrature to the average deviation between sampler types to produce overall random and non-random deviations for each sampler type, to ensure that all the variability captured by the field trial has been included.

There is some evidence that the Bergerhoff sampler gave lower values than the other sampler types during the Slovenian trial, but this observation was not replicated during the Swedish campaign. Where it was possible to directly compare monthly Bergerhoff samples with four-week averages from bulk and wet-only samples these also gave lower values, but not enough comparisons were possible to make these observations statistically significant.

The exchange of samples between analytical laboratories result produced results that were in good agreement, considering the low concentrations being measured. Using the same process as described above, analysis of the results between laboratories where comparative analysis had been attempted yielded the following uncertainty characteristics:

- **Sweden:** samples exchanged between IVL and UBA showed a random uncertainty of 6.5% and a non-random uncertainty of 4.4%;
- **Slovenia:** samples exchanges between PSA and IJS showed a random uncertainty of 10.4% and a non-random uncertainty of 0.7%.

These values have been added in quadrature to the average random and non-random components for the sampler types determined at the individual field trial locations to provide an overall uncertainty estimate. This results in some double counting of uncertainty since a proportion of the random uncertainty in the analysis results will already be included in the random uncertainty within and between samplers. However this methodology errs on the conservative side.

For the two field trials, this procedure yielded expanded uncertainties at the 95% confidence interval of:

- **Sweden: 44.2% at and average deposition value of 17 ng.m^{-2}.d^{-1}**
- **Slovenia: 39.8% at and average deposition value of 30 ng.m^{-2}.d^{-1}**

The expanded uncertainty for each sampling period, averaged across all samplers, at each site is shown in Figure 8. Uncertainties are quoted at the 95% confidence interval (assuming a coverage factor of k=2). Because there is no significant difference in calibration and operation between the two sites, and the non-random differences in analysis are small, the results from both of the field trials can be assumed to be from the same population for the purposes of extrapolation.

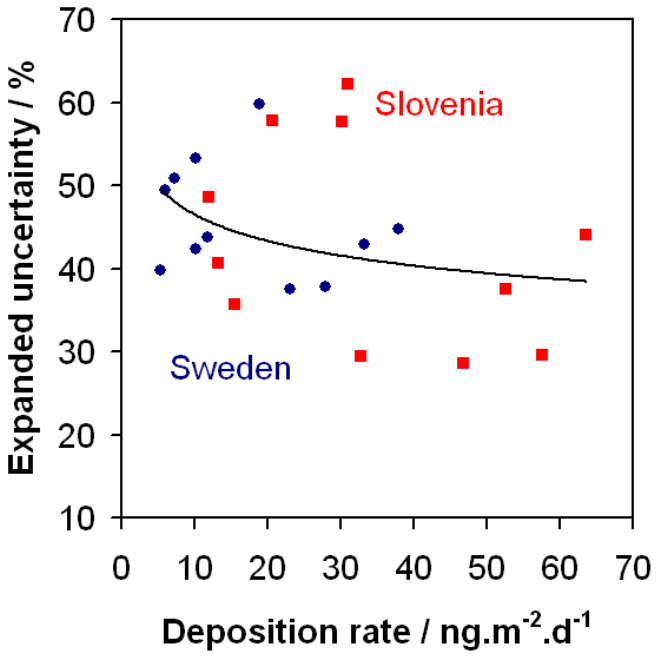

Figure 8. The standard uncertainty for each sampling periods, averaged over all samplers, at each site. A trend-line of the form $y = ax^{-b}$ is shown which excludes two outlying points from the Swedish field trial.

In order to meet the data quality objectives of the Fourth Daughter Directive a maximum expanded uncertainty of 70% for the measurement method is permitted. This value occurs at approximately 0.2 ng.m^{-2}.d^{-1} for extrapolation performed in Figure 8. Therefore this value is proposed as the lower end of the applicable range of the standard method although this is much lower than any individual samples

measured during the field trials. This value represents the best estimate of the lower range of the method given the data available, but should only be treated as an estimate because of the relatively poor fit of the data extrapolation. The maximum observed deposition rate on any individual sampler was approximately 1100 $ng.m^{-2}.d^{-1}$ and so this could be used as the upper limit of the range of the standard method, although there is no reason why the method should not be applicable to higher deposition rates provided the performance characteristics of the method are not compromised.

This discussion has so far focussed on the determination of whether the proposed standard method meets the uncertainty requirements of the Fourth Daughter Directive. However, as discussed above, for the deposition field trial, the sign of the non-random bias is also important as this gives an indication of the bias of any particular design of sampler. Therefore the normalised relative deposition rates for each sampler type have been calculated. This analysis of the relative performance of the deposition gauges has made the assumption that, unlike for the overall uncertainty calculation, the highest measured value is taken to be nearest to the true value. This is because, ignoring the small bias owing to analysis, there is no possibility for a deposition gauge to exhibit a positive bias (excluding the possibility of repeated and consistent contamination from external sources). The normalised relative deposition rates for each sampler type were as follows:

Location	Normalised Relative Deposition Rate		
	Bergerhoff	Wet only	Bulk
Sweden	1.00	0.94	0.97
Slovenia	0.77	1.00	0.97
Overall	0.90	1.00	1.00

Table 6. Normalised relative deposition rate measured by each collecting device at each of the two field trial locations, and in the field trials overall.

The data in Table 6 shows that all three samplers agreed well in Sweden. In Slovenia the wet-only and bulk samplers agreed well, but the Bergerhoff samplers showed a large negative bias. Overall the wet-only and bulk samplers agreed very well, and the Bergerhoff showed a 10% negative bias. The bias of the Bergerhoff sampler compared to the average of the other two designs of sampler for each individual sample is displayed in Figure 9.

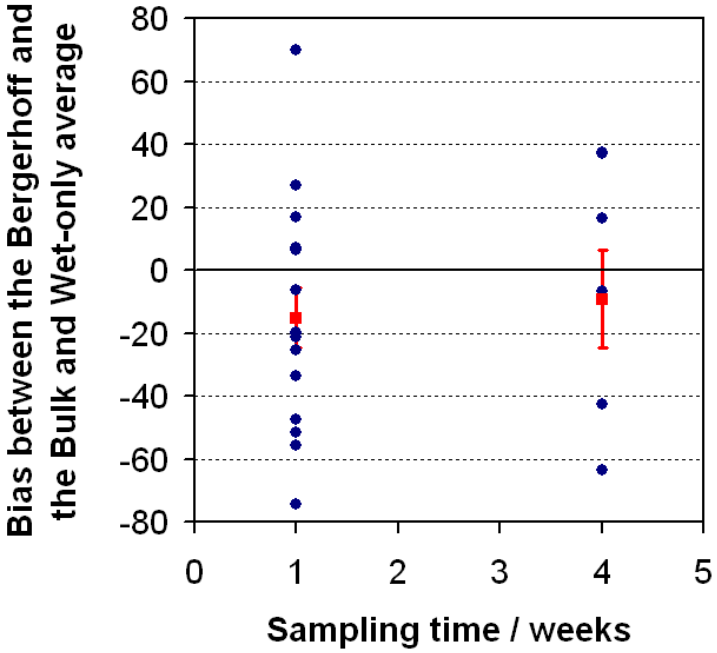

Figure 9. The average bias of the Bergerhoff sampler compared to the average of the other two designs of samplers, against sampling time, for the individual samples from the two field trials (blue circles), and the average bias for each sampling time (red squares). The error bars for the average bias points represent the standard error of the mean.

Figure 9 confirms that the Bergerhoff sampler shows a negative bias compared to the other two sampler designs although there is a large variability in the individual results. However there is no evidence that there is a significant change in this bias with a weekly or four-weekly sampling time. Therefore it is possible that the bias exhibited by the Bergerhoff sampler is related to blow-out of sampled dust, which would not necessarily be expected to increase with longer sampling times. If the bias was due to degradation of the sample within the sampling vessel this might be expected to show some correlation with sampling time. Indeed, it is known that the sampling efficiency of Bergerhoff gauges may be compromised by windy conditions causing blow-out[1]. The difference in observed performance of the Bergerhoff sampler at the two field trials may in part be due to different weather conditions at the two locations. Despite these observations there is not enough evidence to exclude the Bergerhoff sampler from the standard method; moreover, any sampler specific bias should be included in the estimation of the measurement uncertainty anyway. It may be worth noting in the proposed standard method that the collection efficiency of the Bergerhoff sampler can be affected by windy weather conditions, and that an increased uncertainty component for sampling efficiency should be employed when using this sampler.

[1] D. J. Hall, S. L. Upton, G. W. Marsland, Designs for a deposition gauge and flux gauge for monitoring ambient dust, *Atmospheric Environment*, 1994, **28**, 2963-2979.

5 Conclusions

This report provides statistical analysis of all TGM and mercury deposition data obtained at each CEN TC264 WG25 European field trial site. The report develops a methodology to estimate the overall expanded uncertainty of the methods for TGM and mercury deposition by calculating the random and non-random components of uncertainty from the field trial data. For the deposition field trial, an additional component of uncertainty has been added to account for variability within the sampler types, and the uncertainty of the analysis process.

In the absence of a limit value for TGM or deposition at which to assess compliance with the uncertainty requirements of the Fourth Daughter Directive the calculated uncertainty against concentration relationships for the field trial results have been extrapolated to determine the lowest concentration, or deposition rate, at which the method meets the uncertainty requirements. This also then serves at the lower range of validity of the method. The upper limit of validity of the method has been nominally given by the highest daily average concentration for TGM, or highest deposition rate for deposition measurement. However is has been noted there is no reason why the method should not be applicable to higher concentrations provided the performance characteristics of the method are not compromised. Therefore the proposed ranges of the standard methods are as follows:

TGM measurement range / $ng.m^{-3}$		
Lower limit	**Upper limit**	***Max. Measured Value***
0.75	**300**	***4000***

Table 7. The suggested measurement range for the TGM standard, and the maximum measured value during the field trials.

Mercury deposition measurement range / $ng.m^{-2}.d^{-1}$		
Lower limit	**Upper limit**	***Max. Measured Value***
0.2	**1100**	***1100***

Table 8. The suggested measurement range for the mercury deposition standard, and the maximum measured value during the field trials.

In the case of TGM the maximum measured value was recorded from an individual instrument over an individual sampling period (in this case a five minute average). For deposition, the maximum measured value during the field trials was the same as the upper limit since each deposition sample represented an individual datum.

This report has also discussed the observation that the Bergerhoff sampler exhibited a significant negative bias at one location during the deposition field trials. It was

speculated that this may have been due to windy conditions at the field trial location causing blow-out of the sample. There is not enough data to recommend that the Bergerhoff sampler be excluded from the standard method, and any sampler specific bias will be included in the estimation of the measurement uncertainty anyway. However, it may be worth noting in the proposed standard method that the collection efficiency of the Bergerhoff sampler can be affected by windy weather conditions, and that an increased uncertainty component for sampling efficiency should be employed when using this sampler.

6 Annex 1: Daily average mass concentrations measured at the four TGM field trial locations

6.1 Italy

Date	Daily average mass concentration / ng.m^{-3}							
	PSA	Tekran 171	Tekran 284	Tekran 285	MI 441	MI 442	Lumex 804	Lumex 805
6-Nov-06	2.37	2.32	2.58	3.07	1.11	0.43	1.57	0.97
7-Nov-06	2.08	2.02	2.02	2.74	0.92	0.32	1.45	1.05
8-Nov-06	2.02	1.90	2.06	2.55	0.81	0.87	1.43	1.20
9-Nov-06	2.17	1.90	2.22	2.74	1.03	0.66	1.52	1.11
10-Nov-06	4.03	4.37	4.30	5.16	2.17	1.38	4.15	3.37
11-Nov-06	2.54	2.50	2.60	3.15	1.47	0.93	2.08	1.81
12-Nov-06	1.92	1.77	1.90	2.31	1.15	0.70	1.35	1.08
13-Nov-06	1.92	1.92	1.97	2.47	1.15	0.74	1.51	1.27
14-Nov-06	2.23		2.26	2.78	1.33	0.85	1.66	1.18
15-Nov-06	2.13	1.45	2.15	2.65	1.17	0.75	1.57	1.15
16-Nov-06	1.95	1.89	1.92	2.39	1.06	0.70	1.45	1.14
17-Nov-06	2.40	2.46	2.27	3.00	1.29	0.81	1.43	1.09
18-Nov-06	2.35	2.55	2.40	2.73	1.71	0.91	1.48	1.13
19-Nov-06		2.84	2.49	2.98	2.09	0.82	1.52	1.12
20-Nov-06	2.66	2.47	2.26	2.72	1.26		1.41	1.07
21-Nov-06	2.43	2.27	2.23	2.64	1.25		1.41	1.13
22-Nov-06	2.15	1.99	2.04	2.39	1.12		1.34	1.25
23-Nov-06	2.15	2.13	2.08	2.46	1.14	0.72	1.57	1.31
24-Nov-06	2.28	2.28	2.23	2.62	1.18	0.72	1.55	1.08
25-Nov-06	2.07	2.08	2.01	2.35	1.10	0.66	1.39	0.99
26-Nov-06	2.04	1.94	1.97	2.26	1.05	0.95	1.40	1.06
27-Nov-06	2.09	2.05	2.05	2.44	1.07		1.50	1.09
28-Nov-06	2.13	2.05	1.81	2.49	1.01		1.43	0.99
29-Nov-06	2.29	2.59	2.45	2.77	1.13	3.49	1.56	0.99
30-Nov-06	2.99	2.86	3.02	3.50	1.31	0.80	1.82	1.01
1-Dec-06	2.27	2.08	2.46	2.87	1.15	0.81	1.80	1.03
2-Dec-06	2.19	2.04	2.33	2.75	1.08	0.69	1.79	1.01
3-Dec-06	2.09	1.98	2.23	2.64	1.03	0.66	1.62	0.89
4-Dec-06	2.05	2.17	2.21	2.64	1.08	0.65	1.80	1.35
5-Dec-06	2.55	2.91	3.20	3.69	1.43	0.83	2.09	1.81
6-Dec-06	2.08	2.23	2.39	3.00	1.10	0.68	1.63	1.39
7-Dec-06	1.94	2.06	2.16	2.70	1.08	0.65	1.55	1.09
8-Dec-06	1.96	2.11	2.14	2.71	1.10	0.68	1.47	0.88
9-Dec-06	1.78	1.86	1.94	2.43	1.00	0.61	1.47	0.99
10-Dec-06	2.03	2.17	2.16	2.71	1.16	0.67	1.63	1.04
11-Dec-06	1.99	2.37	2.23	2.80	1.18	0.70	1.61	0.95
12-Dec-06	1.80	2.23	2.11	2.64	1.17	1.13	1.65	1.05
13-Dec-06	1.97	1.92	1.93	2.40	1.07		1.65	1.14
14-Dec-06	2.48	2.60	2.41	2.99	1.17		2.60	1.99
15-Dec-06	2.32	2.06	2.04	2.52	1.04		1.57	1.12
16-Dec-06	2.37	2.14	2.05	2.55	1.02		1.47	0.98
17-Dec-06	2.28	2.08	2.00	2.49	1.02		1.45	0.97
18-Dec-06	2.30	2.12	2.03	2.47	1.02		1.48	0.96
19-Dec-06	2.36	2.14	2.10	4.26	1.12		1.56	0.95
20-Dec-06	2.28	2.34	2.06	3.41	1.15		1.77	1.21
21-Dec-06	2.71	3.46	2.88	3.58	1.43		3.29	2.62
22-Dec-06	4.60	6.02	4.78	6.03	2.38	7.30	5.33	4.36
23-Dec-06	2.41	2.66	2.48	3.05	1.18	4.16	2.50	1.98
24-Dec-06	2.22	2.23	2.25	2.75	1.12	2.53	2.40	1.93
25-Dec-06	2.17	2.16	2.14	2.61	0.97	2.26	2.16	1.69
26-Dec-06	2.05	1.94	1.96	2.39	1.01	1.71	1.86	1.43
27-Dec-06	3.53	1.91	1.93	2.26	0.95	1.14	1.59	1.15
28-Dec-06	3.69	1.92	1.94	2.28	0.92	1.47	1.61	1.09
29-Dec-06	2.43	2.41	2.32	2.72	1.13	1.56	1.86	1.11
30-Dec-06	2.24	2.05	2.03	2.40	1.01	1.05	1.73	1.10
31-Dec-06	2.17	1.94	1.96	2.30	0.89	0.86	1.68	1.12
1-Jan-07	2.17	1.85	1.98	2.32	0.96	0.82	1.77	1.15
2-Jan-07	2.53	2.36	2.45	2.88	1.15	0.79	2.63	1.94
3-Jan-07	2.08	1.98	1.90	2.27	1.04	0.60	1.80	1.32
4-Jan-07	2.19	2.07	1.92	2.31	1.05	0.73	1.70	1.08
5-Jan-07	2.44	2.55	2.32	2.80	1.53	1.04	2.41	1.75
6-Jan-07	2.06	1.94	1.86	2.23	1.49	1.32	1.41	
7-Jan-07	1.97	1.84	1.79	2.06	1.45	1.76	1.40	
8-Jan-07	1.83	1.79	1.64	1.93	1.42	1.76	1.36	

6.2 Spain

Date	Daily average mass concentration / ng.m^{-3}						
	PSA	Tekran 284	Tekran 285	MI 03	MI 04	Lumex 804	Lumex 805
27-Feb-07		5.74	4.80	4.62	3.26	3.50	
28-Feb-07		3.96	6.03	4.32	3.10	3.28	
1-Mar-07		3.83	5.76	3.99	2.87	3.03	
2-Mar-07		3.54	5.32	3.75	2.56	2.92	
3-Mar-07		3.75	5.79	4.08	2.76	3.11	
4-Mar-07		5.59	8.12	6.08	4.24	4.78	
5-Mar-07		3.02	4.46	3.73	2.45	2.40	
6-Mar-07		4.11	6.33	3.96	2.65	2.42	2.00
7-Mar-07		7.26	4.55	3.09	2.40	2.11	5.17
8-Mar-07	3.15	5.36	3.64	2.73	1.63	2.24	2.73
9-Mar-07	3.77	3.40	5.20	3.57	2.19	2.97	3.05
10-Mar-07	3.84	3.47	5.45	3.55	2.30	3.03	2.94
11-Mar-07	3.97	3.94	6.09	4.18	2.79	3.55	3.45
12-Mar-07	5.09	5.67	8.28	6.40	4.42	5.44	5.23
13-Mar-07	6.26	4.63	6.88	4.86	2.91	4.41	4.24
14-Mar-07	3.99	3.40	5.02	3.99	2.39	3.44	3.39
15-Mar-07	4.73	4.21	6.13	4.94	3.01	4.33	4.12
16-Mar-07	6.02	5.61	7.90	6.91	5.04	5.92	5.69
17-Mar-07	7.10	5.11	9.28	7.87	5.14	7.09	6.73
18-Mar-07	3.98	3.11	4.33	3.89	2.51	3.28	3.15
19-Mar-07	2.60	2.12	2.85	2.75	1.52	2.34	2.27
20-Mar-07	1.83	1.96	2.58	2.24	1.29	2.16	2.09
21-Mar-07	1.77	1.89	2.49	2.15	1.24	2.12	2.09
22-Mar-07	2.09	2.04	2.70	2.41	1.39	2.25	2.18
23-Mar-07	2.64	2.26	3.04	2.70	1.52	2.51	2.42
24-Mar-07	2.80	2.20	2.95	2.63	1.50	2.50	2.41
25-Mar-07	2.61	2.11	2.77	2.42	1.40	2.41	2.29
26-Mar-07	4.63	5.87	6.28	5.08	3.48	4.38	4.14
27-Mar-07	2.92	3.88	4.62	4.12	2.66	3.59	3.49
28-Mar-07	2.83	2.68	3.74			2.83	2.86
29-Mar-07		2.84	4.05			2.62	2.75
30-Mar-07		1.95	3.66			2.49	2.54
31-Mar-07			4.33			2.80	2.76
1-Apr-07		2.32	4.40			3.03	2.98
2-Apr-07		3.57	5.75			4.06	3.99
3-Apr-07		2.80	4.38			3.10	5.26
4-Apr-07	1.55	2.61	3.61			2.55	3.00
5-Apr-07	1.58					2.46	2.49
6-Apr-07	2.92					4.62	4.57
7-Apr-07	1.75					2.76	2.75
8-Apr-07	1.66					2.65	2.65
9-Apr-07	2.10	4.25	5.58			3.77	3.73
10-Apr-07		4.25	5.56			4.11	4.07
11-Apr-07		4.44	4.99			3.36	3.44
12-Apr-07	2.26	4.03	5.57			3.58	3.53
13-Apr-07	2.51	4.97	6.39			4.05	3.98
14-Apr-07	1.79	1.02	4.16			2.79	2.76
15-Apr-07	2.13		5.04			3.37	3.33
16-Apr-07	2.01	2.79	4.84			3.25	3.22
17-Apr-07	1.35		3.52			2.47	2.48
18-Apr-07		1.89	3.95			2.72	2.71
19-Apr-07			6.47	3.24	2.83	4.77	4.77
20-Apr-07	2.11	3.59	4.47	3.46	2.67	3.14	3.31
21-Apr-07	2.11	3.11	4.25	3.05	2.26	3.04	3.13
22-Apr-07	3.57	5.96	7.86	5.07	3.83	5.81	5.90
23-Apr-07	4.58	8.30	9.38	6.42	4.72	6.83	6.91
24-Apr-07	2.60		5.02	3.27	2.32	3.88	3.96
25-Apr-07	2.62		4.09	2.90	1.99	3.05	3.21
26-Apr-07	1.89		2.76	1.58	1.21	2.21	2.28
27-Apr-07	1.51	3.58	2.78	1.17	1.05	2.16	2.88
28-Apr-07	1.48	2.47	3.12	1.20	1.57	2.16	4.77
29-Apr-07		2.34	3.00	1.28	1.49	2.19	4.63
30-Apr-07		2.77	3.48	2.05	3.40	3.21	
1-May-07		2.27	2.73	1.58	2.72	2.24	
2-May-07		2.31	2.68	2.25	2.30	2.11	4.37
3-May-07		2.63	4.17	2.47	3.86	3.31	
4-May-07	2.21	2.49	4.63	2.14	1.84	3.43	
5-May-07	2.38	2.91	4.75	2.13	1.60	3.64	2.95
6-May-07	2.31	3.01	5.02	1.94	1.45	3.82	2.87
7-May-07	2.13	2.96	4.63	1.70	1.32	3.50	2.77
8-May-07	3.92	5.68	7.25	4.64	3.05	5.64	4.64
9-May-07	4.82	7.15	8.17	3.80	2.86	6.45	5.16
10-May-07	5.34		6.27	3.91	2.85	5.43	4.46
11-May-07	3.05		3.69	2.10	1.49	3.23	2.55
12-May-07	4.12		4.90	3.43	2.49	4.39	3.67
13-May-07	2.76		3.11	2.17	1.66	2.88	2.29
14-May-07	2.30		2.55	0.90	0.78	2.22	2.04
15-May-07	5.35		6.03	2.97	2.53	5.30	4.94
16-May-07	8.24		10.42	5.81	4.52	7.93	7.20

6.3 Sweden

Date	Daily average mass concentration / ng.m^{-3}							
	PSA 1	PSA 2	Tekran 284	Tekran 285	MI 441	MI 442	Lumex 804	Lumex 805
11-Jun-07	1.06	1.72	1.61	1.34	0.72	1.07	1.42	
12-Jun-07	1.37	1.81	1.67	1.57	0.89	1.29	1.72	
13-Jun-07	1.51	1.82	1.76	1.71	1.11	1.42	1.83	
14-Jun-07	1.63	2.02	2.14	2.10	1.48	1.77	1.55	1.67
15-Jun-07	1.33	1.61	1.55	1.43	1.09	1.33	1.35	1.47
16-Jun-07	1.31	1.61		1.35	1.20	1.44	1.30	1.41
17-Jun-07	1.18	1.46		1.35	1.15	1.39	1.35	1.39
18-Jun-07	1.07	1.36		1.25	1.02	1.23	1.36	1.32
19-Jun-07	1.06	1.24	1.23	1.22	1.00	1.17	1.41	1.30
20-Jun-07	1.30	1.73	1.72	1.65	1.22	1.43	1.90	1.77
21-Jun-07	1.49	1.85	1.57	1.49	1.04	1.37	1.95	1.69
22-Jun-07	1.65	1.98	1.62	1.46	1.16	1.49	2.03	1.79
23-Jun-07	1.40	1.74	1.48	1.35	0.98	1.26	1.85	1.58
24-Jun-07					0.80	1.08	1.83	1.59
25-Jun-07					0.88	1.17	1.81	1.53
26-Jun-07	1.08	1.37	1.25	1.21	0.78	1.16	1.85	1.57
27-Jun-07	1.34	1.55	1.37	1.39	1.49	1.54	1.82	1.50
28-Jun-07	1.95	2.24	1.71	1.75		2.17	2.18	1.93
29-Jun-07	1.68	2.06	1.67	1.72		2.10	2.14	1.64
30-Jun-07	1.18	1.37	1.25	1.30		1.65	1.73	1.10
1-Jul-07	1.02	1.21	1.14	1.18		1.54	1.51	0.98
2-Jul-07	1.13	1.23	1.21	1.25		1.60	1.61	1.02
3-Jul-07	1.26	1.32	1.32	1.34	1.77	1.65	1.63	1.22
4-Jul-07	1.36	1.35	1.56	1.36	1.71	1.65	1.24	1.48
5-Jul-07	1.30	1.30	1.45	1.39	1.79	1.67	1.19	1.43
6-Jul-07	1.16	1.13	1.46	1.34	1.65	1.54	1.30	1.53
7-Jul-07	1.36	1.33	1.84	1.76	2.00	1.88	1.78	2.13
8-Jul-07	1.45	1.43	1.99	1.93	2.13	2.03	1.97	2.27
9-Jul-07	1.65	1.49	1.76	1.72	1.87	1.82	1.74	2.04
10-Jul-07	1.69	1.52	1.62	1.57	1.70	1.66	1.64	1.83
11-Jul-07	1.85	1.74	1.65	1.62	1.76	1.72	1.71	1.88
12-Jul-07	1.49	1.61	1.47	1.44	1.53	1.54	1.50	1.72
13-Jul-07	1.36	1.49	1.47	1.45	1.48	1.52	1.58	1.72
14-Jul-07	1.39	1.49	1.51	1.51	1.57	1.58	1.71	1.87
15-Jul-07	1.12	1.38	1.39	1.41	1.16	1.27	1.53	1.85
16-Jul-07	1.26	1.39	1.32	1.33	1.18	1.27	1.48	1.79
17-Jul-07	1.56	1.67	1.42	1.43	1.29	1.40	1.62	2.01
18-Jul-07	1.70	1.92	1.48	1.51	1.11	1.38	1.70	2.11
19-Jul-07	1.45	1.73	1.43	1.49	0.88	1.07	1.66	1.95
20-Jul-07	1.19	1.46	1.30	1.34	0.92	1.12	1.49	1.68
21-Jul-07	1.11	1.37	1.28	1.30	1.07	1.27	1.40	1.60
22-Jul-07	1.04	1.26	1.17	1.18	1.02	1.20	1.31	1.53
23-Jul-07	1.30	1.43	1.36	1.32	1.11	1.31	1.44	1.69
24-Jul-07	1.27	1.32	1.31	1.18	0.97	1.17	1.28	1.50
25-Jul-07	1.30	1.39	1.45	1.32	0.99	1.15	1.38	1.66
26-Jul-07	1.46	1.60	1.66	1.51	1.03	1.24	1.56	1.91
27-Jul-07	1.44	1.59	1.64	1.53	0.90	1.11	1.56	1.99
28-Jul-07		1.50			1.00	1.17	1.58	1.90
29-Jul-07		1.53			0.88	1.14	1.56	1.81
30-Jul-07	1.21		1.38	1.33	1.06	1.19	1.45	1.63
31-Jul-07	1.12	1.42	1.49	1.43		1.26	1.41	1.64
1-Aug-07	1.16	1.39	1.56	1.51		1.26	1.50	1.63
2-Aug-07	1.13	1.46	1.58	1.51		1.21	1.56	1.70
3-Aug-07	1.07	1.41	1.50	1.41		0.99	1.46	1.63
4-Aug-07	1.12	1.45	1.44	1.34		1.10	1.39	1.55
5-Aug-07	1.12	1.52	1.40	1.33		1.14	1.38	1.62
6-Aug-07	1.09	1.55	1.33	1.24		0.93	1.30	1.56

6.4 Belgium

Date	Daily average mass concentration / ng.m^{-3}							
	PSA 1	PSA 2	Tekran 284	Tekran 285	MI 441	MI 442	Lumex 804	Lumex 805
21-Sep-07	3.58	4.50		4.40		5.80	3.08	6.48
22-Sep-07	45.60	55.40		44.40		46.10	41.17	40.76
23-Sep-07	56.70	76.10		55.30		90.70	46.79	46.28
24-Sep-07	4.50	5.40		4.50	4.80	4.80	3.52	9.46
25-Sep-07	3.40	4.00		3.10	3.80	3.40	3.32	9.12
26-Sep-07	2.90	3.50		2.60	3.70	3.40	2.18	5.83
27-Sep-07	4.40	5.10	3.30	3.90	5.20	4.50	2.13	2.35
28-Sep-07	54.80	72.70	47.20	50.70	50.60	44.80	40.18	36.26
29-Sep-07	3.70	5.30	3.40	3.50	5.60	5.50	1.59	1.87
30-Sep-07	22.00	31.00	18.80	19.90	20.70	18.30	18.34	16.03
1-Oct-07	39.70	46.40	37.30	43.00	50.70	45.60	34.31	31.35
2-Oct-07			55.40	67.00	59.00	53.80	44.49	40.02
3-Oct-07			39.60	48.20	62.00	60.50	31.67	29.03
4-Oct-07			5.20	5.80	6.90	6.90	2.30	2.47
5-Oct-07	24.50		42.50	51.00	39.40	37.40	33.57	30.79
6-Oct-07	35.80		54.60	65.50	58.60	54.10	45.36	42.07
7-Oct-07	63.60		84.40	104.10	110.80	100.70	71.77	65.78
8-Oct-07	18.10		23.90	29.10	32.10	29.10	18.46	16.94
9-Oct-07	77.10		98.90	121.30	131.20	119.50	85.57	77.08
10-Oct-07	61.40		74.20	89.70	75.60	68.20	59.48	55.35
11-Oct-07	5.20		6.80	8.10	10.90	11.14	3.89	4.02
12-Oct-07	4.20		5.10	6.10	8.10	8.39	2.93	3.19
13-Oct-07	129.10		97.70	118.80	90.80	81.71	84.36	75.46
14-Oct-07	433.70		250.80	308.10	290.60	264.10	214.24	191.02
15-Oct-07	27.40		20.30	24.80	25.70	23.34	16.67	15.50
16-Oct-07	4.20	2.70	4.00	4.70	4.30	3.72	2.49	2.69
17-Oct-07	4.60	3.60	4.30	5.00	4.62	4.10	2.63	2.82
18-Oct-07	2.40	2.00	2.40	2.80	2.61	2.32	1.24	1.48
19-Oct-07	4.00	3.20	3.70	4.40	4.76	4.72	2.23	2.44
20-Oct-07	40.70	28.80	33.50	40.80	36.34	33.78	27.95	25.24
21-Oct-07	8.20	5.70	6.20	7.30	7.34	7.00	4.60	4.46
22-Oct-07	216.50	128.30	152.20	181.00	172.33	164.10	120.16	126.55
23-Oct-07	46.60	51.10	64.20	65.90	60.35	57.41	45.46	
24-Oct-07	72.80	63.80	77.60	85.20	62.63	57.60	50.90	
25-Oct-07	57.20	54.70	66.50	72.10	73.63	73.45	46.20	
26-Oct-07	67.10	61.80	70.00	78.90	61.77	59.73		
27-Oct-07	2.50	3.60		4.20	4.12	3.71		
28-Oct-07	2.40	3.30		3.80	3.35	2.97		
29-Oct-07	3.10	4.20		4.30	4.59	4.54		
30-Oct-07	3.00	4.10		4.10	4.17	4.12		
31-Oct-07	7.30	8.90		9.90	13.63	14.90		
1-Nov-07	3.90	5.70		5.50	6.22	6.48		
2-Nov-07	2.80	4.20		3.90	4.08	4.15		
3-Nov-07	2.70	4.40		3.80	3.58	3.54		
4-Nov-07	7.90	8.50		10.00	7.81	8.05		
5-Nov-07	8.60	10.10		10.20	10.27	10.61		
6-Nov-07	2.20	5.10	2.50	2.90	2.52	2.44		2.21
7-Nov-07	2.30	3.40	2.30	2.70	2.28	2.06	1.72	1.73
8-Nov-07	2.30	2.10	2.40	2.70	2.25	2.05	1.57	1.82
9-Nov-07	2.30	2.10	2.30	2.70	2.54	2.48	1.56	1.77
10-Nov-07	2.80	2.40	2.70	3.10	2.85	2.62	1.81	2.29
11-Nov-07	2.30	2.00	2.20	2.60	2.32	2.10	1.37	1.72
12-Nov-07	2.20	1.90	2.30	2.70	2.30	2.14	1.40	1.89
13-Nov-07	1.80	1.80	2.50	3.00	2.52	2.41	1.57	1.89
14-Nov-07	2.50	2.60	3.40	4.10	3.90	4.02	2.27	2.78
15-Nov-07	4.00	4.10	5.30	6.20	6.10	6.44	3.81	4.12
16-Nov-07	3.90	3.90	4.70	5.70	7.39	8.70	3.37	3.80
17-Nov-07	4.70	4.60	5.10	6.20	8.12	9.51	3.77	4.22
18-Nov-07	78.80	58.40	66.30	80.30	72.66	72.98	56.14	54.79
19-Nov-07	117.10	81.00	92.80	111.60	91.90	86.94	79.02	73.59
20-Nov-07	158.20	105.40	118.70	143.10	119.78	113.55	102.33	99.56
21-Nov-07	92.00	61.40	77.00	92.80	71.90	65.64	80.55	80.20
22-Nov-07	90.00	58.60	59.80	63.60	54.58	53.29	56.06	54.44

The daily average mass concentrations recorded on each day for each instrument at each field trial site are given in the tables above. The absence of a value indicates the loss of data; mostly because of instrument or power failures, or sometimes owing to removal as an outlier.

7 Annex 2: Deposition rates recorded from samples taken at the two deposition field trial locations

7.1 Sweden

Sampling start	Sampling finish	Depostion rate / ng.m^{-2}.d^{-1}								
		Bulk 1	Bulk 2	Bulk 3	Wet-only 1	Wet-only 2	Bergerhoff 1	Bergerhoff 2	Bergerhoff 3	Bergerhoff 4
4-Dec-06	11-Dec-06	26.2	15.5	22.2	34.7	32.1	27.1	25.3	22.5	27.5
11-Dec-06	18-Dec-06		7.3	9.9	10.8	9.5				
18-Dec-06	1-Jan-07	11.6	9.3	11.7	13.4	16.2				
1-Jan-07	8-Jan-07	8.9	15.2	12.5	12.6	12.6	16.5	8.8	6.0	8.2
8-Jan-07	15-Jan-07	12.8	13.8	36.4	15.2	16.3				
15-Jan-07	22-Jan-07	11.9	14.8	23.0	12.8	12.6				
22-Jan-07	29-Jan-07	4.0	7.7	4.6	5.5	4.6				
29-Jan-07	26-Feb-07	6.3	7.0	6.4	6.0	5.9	4.2	4.8	4.7	4.6
26-Feb-07	5-Mar-07	10.0	2.9	8.4	10.0	8.3	12.1	12.0	14.8	13.5
5-Mar-07	12-Mar-07	23.5	16.4	20.5	27.0	24.9				
12-Mar-07	19-Mar-07	9.2	7.9	7.3	8.6	8.4				
19-Mar-07	2-Apr-07	1.4	1.1	1.6	2.6	2.9				
2-Apr-07	10-Apr-07	10.7	11.2	16.0	8.8	10.3	4.2	3.8	3.7	3.9
10-Apr-07	20-Apr-07	5.1	2.5	4.8						
20-Apr-07	30-Apr-07	10.0	6.0	7.9	14.2	13.8			23.6	22.0
30-Apr-07	7-May-07	4.2	4.0	6.2	6.6	5.0	5.8	5.5		
7-May-07	14-May-07	57.3	24.1	53.6	34.5	37.9	31.7	33.2		
14-May-07	21-May-07	35.6	31.0	49.5	34.3	31.5	27.5	28.8		
21-May-07	28-May-07	13.5	8.8	11.3	8.7	8.4	11.0	10.2		
28-May-07	4-Jun-07	30.5	28.5	29.2	28.6	26.3	25.9	27.3		

7.2 Slovenia

Sampling start	Sampling finish	Deposition rate / ng.m^{-2}.d^{-1}							
		Bulk 1	Bulk 2	Wet-only 1	Wet-only 2	Bergerhoff 1	Bergerhoff 2	Bergerhoff 3	Bergerhoff 4
18-Jan-07	25-Jan-07					21	18.5	17.9	19.1
25-Jan-07	2-Feb-07					6.7	6.7	10.5	6.4
2-Feb-07	9-Feb-07								
9-Feb-07	16-Feb-07	12.6	12.6	8.6	11.3				
16-Feb-07	23-Feb-07					20	24.2	22.6	23.5
23-Feb-07	2-Mar-07	23.4	20	7.7	6.9				
2-Mar-07	9-Mar-07	14.7	17.4	15	14.4	17.2	17.1	15.8	14.4
9-Mar-07	16-Mar-07	3.9	3.4	2.4	9.3				
16-Mar-07	23-Mar-07	23.2	21	26.1	16.9				
23-Mar-07	30-Mar-07	5	3.8	6	5.9				
30-Mar-07	6-Apr-07	18.2	15.2	13.2	33.2			4.9	4.3
04-May-07	11-May-07	64	44.3	68.7	71.6	17.3	14.7		
11-May-07	18-May-07	15.1	12.9	32.4	34.4			5.6	5.5
18-May-07	25-May-07	55.3	57.7	54.9	61.8	40	45.6		
25-May-07	1-Jun-07	13.8	14	12.3	16.7	26.4	9.6		
08-Jun-07	15-Jun-07	23.3	33.4	52.2	51.8	15.9	19.8		
15-Jun-07	22-Jun-07							19.4	12.3
22-Jun-07	29-Jun-07								
29-Jun-07	6-Jul-07	93.3	81.8	22.6	20.3	58.8	68.7		
6-Jul-07	13-Jul-07	57	74	79	76.4	29	66		
13-Jul-07	20-Jul-07							11.4	19.2
20-Jul-07	27-Jul-07								
27-Jul-07	3-Aug-07	30.9	37.2	55.3	49.2	36.5	32.8		
10-Aug-07	17-Aug-07	34.2	41.2	39.6	34.4	22.8	13.4		
17-Aug-07	24-Aug-07	27.9	6.8	29.7	2.7	31.5	25.5	21	20
24-Aug-07	31-Aug-07	49.2		62.8					
31-Aug-07	7-Sep-07	33.5	42.6	33.8		22	15.7		

The deposition rates recorded from samples taken during the deposition field trials are given in the tables above. The absence of a value usually indicates that a sample was not exposed during this period, although a small proportion of the missing data was lost owing to power failure (wet-only samplers), or analytical errors post-sampling.