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DEMONSTRATION OF THE EQUIVALENCE OF $PM_{2.5}$ AND PM_{10} MEASUREMENT METHODS IN HELSINKI 2007–2008

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Demonstration of the equivalence of $PM_{2.5}$ and PM_{10} measurement methods in Helsinki 2007-2008

Abstract

The European Directive for Ambient Air Quality and Cleaner Air for Europe (2008/50/EC) set the limit values for various different pollutants, i.e., the maximum concentrations of pollutants in the air to avoid, prevent or reduce harmful effects on human health and/or the environment as a whole. In addition to the limit values themselves, the data quality objectives and the reference methods (RM) are defined. A Member State (MS) can, however, use another method if this can be shown to be equivalent to the RM. The process of demonstration of equivalence of the candidate methods (non-reference methods) against the reference method for measurements of the concentration of particulate matter (PM) for the size classes of $PM_{2.5}$ and PM_{10}, i.e., particle sizes of less than 2.5 μm and 10 μm in aerodynamic diameter, respectively was conducted in Helsinki, Finland.

The Dekati PM10 impactor, FH 62 I-R, Grimm model 180, MP101 CLS, Osiris, SHARP model 5030, TEOM 1400ab and Verewa F-701-20, referred as the candidate methods (CM), took part in the tests. The Dekati PM10 impactor only took part in the $PM_{2.5}$ tests, while the others took part in both the $PM_{2.5}$ and PM_{10} measurements. The test program was not fully in accordance with the Guide for Demonstration of Equivalence of Ambient Air Monitoring Methods by the European Commission, and therefore actual approval of the CMs has not been presented in the report. However, based on the analysis of the results, the calibration function against the RM has been presented for each of the CMs as well as the results if non-compliance with criteria on any of the CMs has occurred. The results showed that the Dekati PM10 impactor and the Osiris failed to meet the criteria for equivalence for fixed measurements of $PM_{2.5}$. In the case of the PM_{10} tests, the suitability of the data was not acceptable and therefore no decisive rejection of any of the CMs has been made. Instead, based on the evidence of the results, a lower concentration range of PM_{10} in the air is set for some of the CMs.

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$PM_{2.5}$- ja PM_{10}-vertailumittaukset ekvivalenttisuuden osoittamiseksi

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Nimeke
$PM_{2.5}$- ja PM_{10}-mittausmenetelmien yhdenmukaisuuden osoittaminen vertailumenetelmää vastaan Helsingissä 2007–2008

Tiivistelmä

Euroopan parlamentin ja neuvoston direktiivi ilman laadusta ja sen parantamisesta (2008/50/EY) määrittää mm. raja-arvot tiettyjen epäpuhtauksien suurimmille sallituille pitoisuuksille ulkoilmassa. Direktiivin tavoitteena on myös välttää, ehkäistä tai vähentää epäpuhtauksien haitallisia vaikutuksia ihmisen terveyteen ja ympäristöön. Raja-arvojen ohella direktiivi määrittää havaintoaineiston laatutavoitteet ja epäpuhtauksien mittaamiseen käytettävät vertailumenetelmät. Euroopan Yhteisön jäsenmaa voi kuitenkin käyttää muuta kuin vertailumenetelmää, jos tämän voidaan osoittaa olevan yhdenmukainen vertailumenetelmän kanssa. Tässä tutkimuksessa on testattu Helsingissä hiukkasmittalaitteiden yhdenmukaisuutta vertailumenetelmää vastaan hiukkasten kokoluokassa $PM_{2.5}$ ja $PM_{10,}$ so. hiukkasten aerodynaamisen koon ollessa alle 2,5 µm ja vastaavasti alle 10 µm.

Vertailtavina hiukkasmittalaitteina olivat Dekati PM10 impactor, FH 62 I-R, Grimm model 180, MP101 CLS, Osiris, SHARP model 5030, TEOM 1400ab ja Verewa F-701-20. Dekati PM10 impactor otti osaa vain $PM_{2.5}$-vertailuun, kun taas muut laitteet osallistuivat sekä $PM_{2.5}$- että PM_{10}-vertailuihin. Testausohjelma ei kaikilta osin noudattanut Euroopan komission laatimaa ohjetta ”Guide for Demonstration of Equivalence of Ambient Air Monitoring Methods” (GDE). Tämän vuoksi ehdotonta hyväksyntää vertailtavien hiukkasmittalaitteiden yhdenmukaisuudesta vertailumenetelmää vastaan ei voitu suorittaa. Analysoitujen tulosten perusteella voitiin kuitenkin määrittää jokaiselle laitteelle kalibrointiyhtälöt vertailumenetelmää vastaan sekä osoittaa ne tilanteet, joissa tulokset poikkesivat yli sallittujen rajojen. Näiden tulosten perusteella Dekati PM10 impactor ja Osiris eivät läpäisseet direktiivissä määritellyille kiinteille mittauksille asetettuja laatuvaatimuksia $PM_{2.5}$-mittausten osalta. PM_{10}-mittausten osalta ulkoilmapitoisuudet eivät olleet riittävän korkeita täyttämään GDE:n asettamia vaatimuksia testausolosuhteiden pitoisuustasoille. Tämän vuoksi mitään mittalaitetta ei voitu hylätä, mutta tietyille mittalaitteille asetettiin alin pitoisuusraja, jota alhaisemmissa pitoisuuksissa laitetta ei voida direktiivin mukaisiin seurantamittauksiin käyttää.

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List of abbreviations

AQD	Air Quality Directive
CM	Candidate Method
DQO	Data Quality Objectives
EC	European Commission
EU	European Union
EMEP	Programme for Monitoring and Evaluation of long range transmission of air Pollutants in Europe
FMI	Finnish Meteorological Institute
GDE	Guidance for Demonstration of Equivalence
HSY	Helsinki Region Environmental Services Authority (previously Helsinki Metropolitan Area Council, YTV)
LV	Limit Value
MS	Member States
PM	Particulate Matter
PTFE	Polytetrafluoroethylene
RM	Reference Method
SMEAR	Station for Measuring forest Ecosystem and Atmospheric Relations
TSP	Total Suspended Particles
UAT	Upper Assessment Threshold
WG	Working Group

1. Introduction

Particulate matter (PM) in ambient air is considered one of the most hazardous pollutants to human health (WHO, 2006). PM is responsible for a significant reduction in life expectancy. With respect to the health effects, European legislation on air quality has made directives to define the limit values for the maximum concentrations of PM in ambient air. The most recent directive, the Air Quality Directive 2008/50/EC (AQD), defines the limit values for PM_{10} and for $PM_{2.5}$, i.e., for particles with sizes less than 10 µm and 2.5 µm in aerodynamic diameter, respectively. As well as the limit values themselves, the reference method (RM), data quality objectives (DQO) and the number of measurement stations in member states (MS) were also defined in the AQD. The MS are not, however, obliged to employ the reference method but can use another method if this can be shown to give results equivalent to the reference method. To harmonize the process of demonstrating the equivalency of the candidate method (CM) with the reference method, the EC working group on Guidance for the Demonstration of Equivalence has prepared a guide. As a result of the work of this group, the test criteria set out in the EC Guidance for the Demonstration of Equivalence of Ambient Air Monitoring Methods (GDE) was first published in 2005 and then reviewed in 2009. The meaning of the term 'equivalent method' was not defined in the AQD, but in the GDE instead as '*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'* (GDE, 2009). This definition is used also in this report.

In Finland, the municipal authorities are responsible for air quality measurements. There are 38 local networks and 124 measurement stations (www.ilmanlaatu.fi). PM_{10} is measured at 77 measurement stations and $PM_{2.5}$ at 34 stations. A large variety of automated measurement methods are used for PM measurements, which has made it an urgent matter to conduct equivalence studies for the variety of methods used in Finland as well as in Europe.

Several equivalence tests have been conducted for PM by different member states in the EU (Harrison et al. 2006; Beijk et al. 2007; de Jonge 2008; Bertrand, et al. 2009). At the moment there are planned or ongoing test programmes for demonstration of the equivalency of PM measurement methods in several member states.

This report provides test results of the comparisons of eight candidate methods against the reference methods for $PM_{2.5}$ measurements and seven comparisons for PM_{10} measurements. The comparisons conducted were not complete according to the GDE and therefore acceptance of the candidate methods can not be conclusive. However, the analysis of the comparison results follows the GDE. If the candidate method does not meet the DQO of the reference method during the comparisons, the conclusion can be drawn that the CM will not be equivalent with the reference method. If the candidate method fails to meet the DQO for fixed measurements, a check is made whether the DQO is met for indicative measurements.

2. PM equivalence procedure

2.1 Requirements of Directive 2008/50/EC

The Air Quality Directive 2008/50/EC (AQD) state that member states shall apply the reference measurement methods and criteria specified in the Directive. Other measurement methods may be used, subject to the conditions also set out in the Directive. The reference measurement method for the sampling and measurement of PM_{10} as well as $PM_{2.5}$ is that prescribed in standards EN 12341 (EN 12341, 1999) and EN 14907 (EN 14907, 2005), respectively. The Directive and the standards for PM_{10} and $PM_{2.5}$ refer to particulate matter that penetrates a size-selective inlet with 50 % efficiency at 10 µm and 2.5 µm aerodynamic diameters, respectively. The reference methods for PM_{10} and $PM_{2.5}$ are gravimetric. The standards prescribe not only the methods themselves, but also the inlet design criteria for both of the size classes as well as the storage and weighing procedures for the filters. The approved filter types to be used for collection of the PM fraction are also defined. In addition to the reference methods, the AQD lays down that the mass concentration for PM results shall be referred to at the prevailing ambient conditions in terms of temperature and atmospheric pressure. The DQO defined for the PM measurements in the AQD are listed in Table 2.1.

Table 2.1. The Data Quality Objective for the $PM_{2.5}$ and PM_{10} measurements for fixed and indicative measurements according to the AQD.

	$PM_{2.5}$ and PM_{10}
Fixed measurements	
uncertainty (1	25 %
minimum data capture	90 %
Indicative measurements	
uncertainty (1	50 %
minimum data capture	90 %
minimum time coverage	14 % (2

(1 Describes the relative expanded measurement uncertainty at the 95 % confidence level.

(2 One measurement a week at random, evenly distributed over the year, or eight weeks evenly distributed over the year.

Although the reference method defined for PM_{10} and $PM_{2.5}$ is a manual one, automated measurement methods have been manufactured and used for the PM measurements. The automated methods can be less expensive for routine air quality monitoring as well as provide data at much shorter intervals, e.g., hourly values for use in the calculation of air quality indexes and to trace sudden changes in the PM concentrations in the air.

As stated previously, in 2005 the EC working group on Guidance for the Demonstration of Equivalence prepared a document called the Guide to the Demonstration of Equivalence of Ambient Air Monitoring Methods, GDE. To facilitate the use of the GDE for checking the equivalence of the candidate methods for PM monitoring, an Excel macro was made available on the Commission web page (http://ec.europa.eu/environment/air/index_en.htm). The macro allows the testing of the equivalency for input pairs of data values of the CM and the RM. The GDE document was revised in 2008, and the Air quality committee in its advisory role under Directive 2008/50/EC agreed with the Commission to endorse this in July, 2009 as new guidance for the implementation of Directive 2008/50/EC. Some editorial corrections have also been made to the version 2009 which was released in January 2010.

In this report use is primarily made of the latest version of the GDE. Where needed, reference to the versions of 2005 and 2009 is made using the abbreviations GDE(05) and GDE(09) respectively.

2.2 The reference method

The reference method used during the PM equivalence tests in Helsinki (PM_{10} and $PM_{2.5}$) was a manual method equipped with the Digitel inlet for PM_{10} and $PM_{2.5}$ and a sample flow-controlling unit, Micro PNS S7 by MCZ Umwelttechnik, Germany. The MCZ unit controlled the flow rate and the total flow over the sampling period. The filter types used in the tests were polytetrafluoroethylene (PTFE) filters, Millipore Fluoropore FSLW047

3 µm, by Millipore. Two identical units of the reference methods were used both for the PM_{10} and the $PM_{2.5}$ tests. The layout of the reference method is shown in Figure 2.1.

Figure 2.1. The layout of the reference method, the flow-controlling units by MCZ and the PM inlets by Digitel, used for the PM_{10} and the $PM_{2.5}$ equivalence tests.

2.3 Candidate methods

The candidate instruments that took part in the PM equivalence tests were:

1. Dekati PM10 impactor by Dekati Ltd, Finland (Dekati PM10);
2. FH 62 I-R by Thermo Electron Corporation, USA (FH 62 I-R);
3. Grimm Environmental Dust Monitor, model 180, Germany (Grimm 180);
4. MP101 CLS by Environnement SA, France (MP101);
5. Osiris by Turnkey Instruments Ltd, England (Osiris);
6. Synchronized Hybrid Ambient Real-time Particulate Monitor, model 5030 by Thermo Electron Corporation, USA (SHARP);

7. Thermo Scientific Ambient Particulate Monitor, TEOM 1400ab by Thermo Electron Corporation, USA (TEOM 1400ab)
8. Ambient Beta Gauge Particulate Monitor, model F-701-20 by Verewa, Germany (Verewa).

In addition to these instruments, TEOM 1405-DF was also included in the original test configuration, but due to problems associated with the temperature of the sampling tube at certain ambient temperatures, the diagnostic software halted the operation of the device. Both of the devices were returned to the manufacturer for repair. Unfortunately, they were not repaired in time, and the TEOM 1405-DF did not participate the final tests. The Institute of Air and Water in Sweden (IVL) also took part in the tests with a PM-sampler made in-house. The PM-sampler by IVL is in use within the EMEP programme for the collection of PM samples for heavy metal analysis. The inlet design of the IVL sampler was not made according to EN 12341 or EN 14907, which was the reason for seeking equivalency for the sampler. Due to the problems found during the $PM_{2.5}$ tests with regulating the flow rates as well as in installing the $PM_{2.5}$ filters in the filter holder at the inlet, the IVL PM-sampler was recalled from the tests. It is worth mentioning that the Dekati PM10 impactor only took part in the $PM_{2.5}$ tests.

Short descriptions of the CMs are given below. The set-up and the sample equipment of each of the CMs are described. The type of sampling inlets, sampling flow rates, sampling period and the condition of the sample tube (heated/not heated) are reported. As a general rule, correction coefficients, if used or installed in the operational software by the manufacturer, were removed. This means that the CMs were tested against the RM with the basic measurement signal, sampling equipment and sampling tube conditions during the test campaigns. When deviations in the set-up of the CMs from the equivalence tests occurred in routine use, the test results may not be valid. Examples of such deviations are deviations from the sampling tube temperature, a different sample flow rate or sample inlet. In these circumstances more evidence is needed. If the deviation of the CM from the test condition is associated with the measurement signal and can be transformed to the test conditions mathematically, the test results obtained in the equivalence tests are then valid.

Dekati PM10 impactor

The Dekati PM10 impactor, shown in Figure 2.2, is a three-stage cascade impactor for determining particle gravimetric mass size distribution. The impactor size classifies the particles into four different size fractions; in each size fraction the particles are collected on a filter that is analyzed gravimetrically or chemically after the measurement. The impactor cut-off points are 10, 2.5 and 1 µm; if necessary, some of the stages can be removed from the assembly to make a simpler setup. The PM10 impactor is available with two different sample flow rates, 10 or 30 l/min. The particles are collected on Ø 47 mm substrates on the impactor stages (> 10 µm, > 2.5 µm and > 1 µm). Particles of less than 1 µm are collected on a back filter located in the lower part of the impactor. During the PM equivalence tests for $PM_{2.5}$, the other two stages, for PM_{10} and PM_1, were removed, and only the $PM_{2.5}$ stage and the back filter were in place. The filter type used in the tests was the Millipore Fluoropore FSLW047 # 3 µm, and the weighing procedure of the filter was the same as for the reference method. The TSP inlet by Digitel was installed at the top of the sample tube and a sampling flow rate of 30 l/min was used during the test. The sampling period was 24 h, and the sampling filter was changed at the same time as that of the RM.

Figure 2.2. Dekati PM10 impactor

FH 62 I-R

The ESM FH 62 I-R monitor by Thermo Fisher, USA, shown in Figure 2.3, uses the technique of β-attenuation (Kr-85 source). The attenuation of β-rays by a filter is directly related to the amount of mass on the filter. The sample filter tape is removed from the measurement/sample point once a day if not overloaded with the PM. The analysis of the sample, however, takes place cumulatively over the 24 h. To avoid condensation of water on the filter, the sampling tube is heated (35 °C). This process not only leads to the loss of water, but also to the loss of certain semi-volatile compounds such as ammonium nitrate. By changing the sample inlet, the device is capable of making measurements of PM_{10} and $PM_{2.5}$ at a sample flow of 1 m^3/h. The sample inlet was one of the commercial types designed according to the EN standards for $PM_{2.5}$ and PM_{10}. The measurement range for normal operation is from 0 to 5000 $\mu g/m^3$. The manufacturer provides a calibration kit, i.e., a zero plate and a plate of known amount of mass concentration on a film foil to calibrate the instrument. The calibration kit was used for calibration of the instrument during the equivalence test. The manufacturer of the instrument installed a correction factor with a default value of 1.3 in the operational software of the instrument to correct the measurement signal according to the guideline by the EC (EC WG on PM, 2001). In these tests, the correction factor was set to 1.0 according to the policy mentioned in the previous chapter.

Figure 2.3. FH 62 I-R monitor

Grimm Environmental Dust Monitor, model 180

The Grimm Ambient dust monitor 180 is a stationary continuous fine dust measuring system for the simultaneous and continuous measurement of PM_{10}, $PM_{2.5}$ and PM_1. The Grimm 180, shown in Figure 2.4, does not have $PM_{2.5}$ or PM_{10} sampling heads according to EN standards. The sample inlet of the Grimm is the manufacturer's own design, but it has been tested against the PM_{10} reference method according to EN 12341 (LUBW, 2005). The sample flow rate of the Grimm was 1.2 l/min as stated by the manual and the sampling tube was inside the shield tube at ambient temperature. The concentration range for dust particles is from 0.1 to 1500 $\mu g/m^3$. The instrument uses an optical technique, based on light scattering, to divide particles into different sizes in diameter. The value of the refraction index of the particles, i.e., how much the velocity of light is reduced due to the reflection from the surface of the particles, has been programmed into the software. Specific algorithms are used to transfer the number of particles of certain size into mass. The calculated cut-off point curves are then applied to define the mass concentration for $PM_{2.5}$ and PM_{10}. To decrease the effect of moisture to influence on the refraction index, a Nafion dryer is installed inside the sampling tube. The pump of the Nafion dryer starts at relative humidity of 75 % reducing the relative humidity down to 35 %. The software version 1.177 was used for both of the instruments. No changes were made to the software in these tests.

Figure 2.4. Grimm Environmental Dust Monitor, model 180

Environnement MP101 CLS

The MP101 CLS, shown in Figure 2.5, measures particulate concentration by measuring the amount of radiation a sample absorbs when exposed to a radioactive source. Low-energy β-rays (C-14 source) are absorbed by electron collisions, whose number is proportional to density (β-attenuation). By changing the sample inlet, the device is capable of measurements of PM_{10} and $PM_{2.5}$ at a sample flow of 1 m^3/h. The sample inlets for $PM_{2.5}$ and PM_{10} were designed according to the EN standards by the manufacturer. The sampling tube is not heated but instead is equipped with shielded flow to avoid condensation in the sample air when entering the analyser. The measurement ranges of the instrument are selectable up to 10 000 µg/m^3. The sampling time was set to 24 h in the operational software of the instrument by the manufacturer. No correction factors used in the software of the device have been made available by the manufacturer.

Figure 2.5. Environnement MP101 CLS monitor

Osiris

The Osiris is one of Turnkey's families of direct-reading airborne particle monitors, which can be used as a portable instrument or deployed in a semi-permanent installation. The Osiris, shown in Figure 2.6, indicates continuously the concentration of total suspended particles (TSP), PM_{10}, $PM_{2.5}$ and PM_1 at a range of up to 6000 µg/m^3 based on an optical method. The sample flow rate of the Osiris is 0.6 l/min. The sample tube was heated (35 °C) to avoid condensation. The sample inlet was designed by the manufacturer; no test report for the sample inlet against the reference method was available. No software correction factors were made available by the manufacturer.

Figure 2.6. Osiris optical dust monitor

Synchronized Hybrid Ambient Real-time Particulate Monitor, SHARP, model 5030

The SHARP monitor by Thermo Fisher combines light-scattering photometry and beta radiation attenuation (C-14 source) in one instrument, shown in Figure 2.7. The instrument combines nephelometry and the beta attenuation method to provide a continuous reading of the PM concentration. Control of relative humidity and frequent filter changes eliminate water vapour without loss of volatile organic compounds. By changing the sample inlet, the device is capable of measurements of PM_{10} and $PM_{2.5}$ at a sample flow of 1 m^3/h. The commercial sample inlet was used during the tests. The concentration ranges can be from 0 to 1000 $\mu g/m^3$ or from 0 to 10 000 $\mu g/m^3$. For calibration of the instrument the same calibration kit as in the FH 62 I-R was used. To avoid condensation, the sample tube was heated (35 °C). The software of the instrument was similar to that of the FH 62 I-R, and a similar correction factor in the software was installed by the manufacturer. During the comparison tests the correction factor was set to 1.0.

Figure 2.7. Synchronized Hybrid Ambient Real-time Particulate Monitor, SHARP, model 5030

Tapered Element Oscillating Microbalance, TEOM 1400ab

The TEOM 1400ab, shown in Figure 2.8, uses the tapered element oscillating microbalance technique to measure the concentration of the particulate matter in the air. It is a direct mass measurement technique on a filter with real-time data output. The sample filter was changed at regular intervals as recommended by the manufacturer. By changing the sample inlet, the device is capable of making measurements of PM_{10} and $PM_{2.5}$ at a sample flow of 1 m^3/h. The sample inlet provided by the manufacturer was used during the equivalence measurements. In the case of the $PM_{2.5}$ test, the cyclone (cut to size for $PM_{2.5}$) was installed in the sampling tube to remove particles larger than $PM_{2.5}$. The measurement concentration range of the particles for the TEOM 1400ab can be up to 5 g/m^3. To avoid condensation, the sample tube was heated (50 °C). The correction equation used in the software of the device by the manufacturer was of the form: $y = a + b \cdot C$, where $a = 3$ µg/m^3, $b = 1.03$ and C is the measurement signal. During the equivalence tests the factors were set to $a = 0$ and $b = 1.0$.

Figure 2.8. Thermo Scientific Ambient Particulate Monitor, TEOM 1400ab

Verewa model F-701-20

The F-701-20 ambient dust monitor, shown in Figure 2.9, is based on the attenuation of beta rays (electrons) emitted by a radioactive emitter through particles collected from an ambient air flow. The sample analysis took place after a one-hour integration time. By changing the sample inlet, the device is capable of making measurements of PM_{10} and $PM_{2.5}$ at a sample flow of 1 m^3/h. The sample inlets for $PM_{2.5}$ and PM_{10} were designed according to the EN standards by the manufacturer. The measuring ranges of the concentration of dust particles can be from 0 to 0.1 mg/m^3 or from 0 to 10 mg/m^3. To avoid condensation the sample tube was heated (40 °C). No correction factors were installed in the software by the manufacturer.

Figure 2.9. Verewa Ambient Beta Gauge Particulate Monitor, model F-701-20

In Table 2.2 are presented the participating CMs, the manufacturers or their Finnish representatives, the measurement methods and type of sampling inlets and the temperature of the sampling tube for both the $PM_{2.5}$ and for PM_{10} comparisons. It should be kept in mind that all the adjustment factors affecting the measurement signals by the software have been omitted during the tests.

Table 2.2. List of CMs, manufacturers/Finnish representatives, measurement methods and type of sampling inlets, sample flow rate and sampling tube temperature for the $PM_{2.5}$ and PM_{10} comparisons. The last column indicates the participation in the $PM_{2.5}$ and/or PM_{10} comparison.

INSTRUMENTS	REPRESENTATIVE / MANUFACTURER	Method	PM2.5/PM10 inlet	Sample flow rate (m^3/h)	Sample tube	Comparisons: PM2.5/PM10
REFERENCE SAMPLER (KFG	FMI + MCZ (Germany)	Manual sampler, gravimetric	Digitel / EN	2.3 m^3/h		PM2.5/PM10
ELPI-impactor	DEKATI (Finland)	Impactor, gravimetric	Digitel TSP	1.8 m^3/h		PM2.5
Environnement MP-101	ENVIRONNEMENT SA (France	β-attenuation	Environment EN	1.0 m^3/h	Shield tube, ambient temperature	PM2.5/PM10
GRIMM-180	EKONIA (Finland) / Grimm Aerosol Technique, GmbH&Co (Germany)	Optical (light scattering)	Grimm	0.072 m^3/h	Shield tube, ambient temperature	PM2.5/PM10
SHARP	FMI / THERMO Electron Co, (U	Light scattering photometer	Digitel /EN	1.0 m^3/h	Heated 35 °C	PM2.5/PM10
FH-62-IR	FMI / Estonian Environmental Research Centre (Estonia)	β-attenuation	Digitel /EN	1.0 m^3/h	Heated 35 °C	PM2.5/PM10
VEREWA	PPM-Systems (Finland)	β-attenuation	Verewa EN	1.0 m^3/h	Heated 40 °C	PM2.5/PM10
TEOM-1400A	Helsinki Region Environmental Services Authority, HSY (Finland), City of Turku (Finland) & University of Lund Sweden	Tapered Element Oscillating Microbalance	TEOM PM + 2.5 cyclone/EN ; TEOM PM10/EN	1.0 m^3/h	Heated 50 °C	PM2.5/PM10
OSIRIS	Hnu-Nordion (Finland) / Turnkey Instruments	Optical (nephelometer)	Osiris	0.036 m^3/h	Heated 35 °C	PM2.5/PM10
TEOM FD 1405	Kontram (Finland) / THERMO Electron Co (USA)	Tapered Element Oscillating Microbalance	TEOM PM 2.5 cyclone/EN	1.0 m^3/h	Shield tube, ambient temperature	
IVL-SAMPLER	Institute for Water and Air (Sweden)	Gravimetric	IVL-inlet	1.0 m^3/h		

The manufacturers provided their instruments for the tests for free. However, there was only limited space for the instruments in the measurement cabins, and some restrictions were made. The companies of Environnement SA (France), Ekonia/Grimm Aerosol Technique GmbH (Germany), PPM-Systems/Durag GmbH (Germany) and Hnu-Nordion/Turnkey Instruments (USA) each provided two CMs for the tests. The Finnish Meteorological Institute (FMI) provided two SHARPs and one FH 62 I-R. The Estonian Environmental Research Centre provided one FH 62 I-R. One TEOM 1400ab was provided by the Helsinki Region Environmental Services Authority, HSY, (formerly the Helsinki Metropolitan Council (YTV)), while the City of Turku (Finland) and the University of Lund (Sweden) jointly provided one TEOM 1400ab.

2.4. Equivalence procedure

As stated earlier, GDE(09) is followed in the data analysis. However, certain criteria used in GDE(05) are also used here in order to allow better comparability with the existing equivalence comparison in Europe.

Before actually performing the equivalence tests on the CMs, a preliminary assessment of the candidate method needs to be made in order to ensure that it (GDE(09)):

- fulfils the requirements of data capture and time coverage set for continuous/fixed measurements; and

- has the potential to meet the uncertainty criteria of the data quality objective at the limit or target value concentration for continuous or fixed measurements of the specified pollutant.

After the candidate method has passed this preliminary assessment, the test and evaluation programme relevant to the candidate method can be selected. In the case of PM measurements, the tests are performed according to test programme 3 of GDE(09). It should also be pointed out that the limiting conditions for the claiming of PM equivalence are associated with site-specific conditions, ranges of fractions of the constituent as well as the size or shape of the particles. This means that even though the generalization of equivalence claims is valid for a wide range of conditions and compounds, this is not the case for PM. The performance characteristics of the CM are influenced by the fraction of the semi-volatile constituent, which is site-specific and depends also on geographic location. Equivalence claims for a specific CM may thus not be applicable in general, but the CM may still be useable in specific conditions or at certain locations.

According to GDE(09), test programme 3, Methods for Particulate Matter, is suitable to evaluate a CM for monitoring the $PM_{2.5}$ and PM_{10} fractions of total suspended particulates in ambient air. The equivalence claims can be focused on the sample inlets and/or the measurement method (e.g., β-ray attenuation, optical method, oscillating balance). Basically the procedure for claiming the equivalence of the CM against an RM is a method involving calibration. The term "correction factor" has been omitted from GDE(09). Field campaigns were performed with the CMs that took part in the tests. Field tests were performed in such a way that the candidate and the reference methods were compared side-by-side. Two CMs of the same model, as well as two RMs, were included in the tests. The measurements were designed to assess:

- 'between-sampler/instrument' uncertainty of the candidate method through the use of two samplers or instruments

- 'comparability' of the candidate and reference methods.

The evaluation of the data collected included the following steps:

A *Suitability of datasets*

According to GDE(09), data may only be removed from the dataset when sound technical reasons can be found for doing so. However, when suspicious data are found, as discovered by, e.g., Grubb's test, it is permitted to remove up to 2.5 % of data pairs, as long as the number of valid data pairs per comparison is ≥ 40.

Of the <u>full dataset</u>:

1. ≥ 20 % of the results obtained using the reference method ≥ UAT, GDE(09)
2. ≥ 20 % of the results obtained using the reference method ≥ 50 % LV, GDE(05)

where UAT is the Upper Assessment Threshold for the annual limit value. For PM_{10}, the UAT is 28 µg/m^3, while for $PM_{2.5}$ it is 17 µg/m^3. In the case of GDE(05), the criteria were 50 % of the annual limit value, i.e., 20 µg/m^3 for PM_{10} and 12.5 µg/m^3 for $PM_{2.5}$.

B *Between-sampler/instrument uncertainty*

The between-sampler/instrument uncertainty, GDE(09), is determined:

- for the complete dataset
- PM_{10} concentrations ≥ 30 µg/m^3
- $PM_{2.5}$ concentrations ≥ 18 µg/m^3.

A between-sampler/instrument uncertainty u_{bs} > 2.5 µg/m^3 is an indication of the unsuitable performance of either one or both samplers and instruments, and equivalence shall not be declared for the candidate method when this criterion is not satisfied. For the reference method the between-sampler/instrument uncertainty, u_{bs}, shall fulfill the criterion, $u_{bs} \leq 2.0$ µg/m^3.

C *Comparison with the reference method*

Evaluation of the uncertainty due to the 'lack of comparability' between candidate and reference methods is established as the average of both of the CMs (GDE(05)) and that of each of the candidate instruments individually (GDE(09)) using a regression technique that leads to the symmetrical treatment of both variables. The relationship between the measurement results of both methods can be described by a linear relation of the form:

$$y_i = a + bx_i \tag{2.1}$$

where a is the intercept and b is the slope of the linear line. The procedure is applied to the full dataset obtained and to a number of subsets:

- *datasets representing PM concentrations ≥ 30 µg/m^3 for PM_{10}, or concentrations ≥ 18 µg/m^3 for $PM_{2.5}$, provided that the subset contains 40 or more valid data pairs*

- *datasets for each individual site.*

The tests of equivalence for each of the full data and for the subsets' data were performed with the Excel macro prepared for the data analysis. Among other things the macro includes calculations of the combined standard measurement uncertainty, u_{CR}. The relative combined standard uncertainty, $w_{c,CM}$, is then calculated as:

$$w_{c,CM}^2 = \frac{u_{CR}^2}{y_i^2} \qquad (2.2)$$

where y_i is the limit value of $PM_{2.5}$ or PM_{10} used for the calculation. The limit values used are 30 µg/m^3 for $PM_{2.5}$ and 50 µg/m^3 for PM_{10} (GDE(09)). The calculated relative expanded measurement uncertainty, W_{CM}, can be expressed as $W_{CM} = k \cdot w_{c,CM}$, where the coverage factor k = 2. When comparing W_{CM} with the data quality objective (DQO) of the AQD (see in Table 2.1), the following cases are possible:

1. $W_{CM} \leq W_{DQO}$: the CM is accepted as an equivalence method to the RM (2.3a)
2. $W_{CM} > W_{DQO}$: the CM is not accepted as an equivalence method to the RM. (2.3b)

In case 2, the results of the CM can be corrected using the results from the regression equation, Eq. (2.1), obtained for the full dataset. The term calibration is used here for correcting the data. After applying the calibrated values, the recalculated relative expanded measurement uncertainty, $W_{CM,cal}$ of the CM needs to satisfy requirement 1 (see above) for the full dataset as well as for each of the subsets. If this is not met, the CM shall not claim to be a method equivalent to the reference method. It may still turn out that even after applying the calibration to the CM, either the slope *b* (in Eq. (2.1)) may differ significantly from 1, or the intercept *a* (in Eq. (2.1)) may differ significantly from 0, or *both*. If any of these cases occur, it means that the calibration function is still not adequate and needs further modification in order to pass the significance test. The test of significance is related to the standard measurement uncertainty, *u(b)* for the slope *b,* and *u(a)* for the intercept *a* according to the three possibilities below:

$$|b-1| > 2 \cdot u(b) \tag{2.4}$$

$$|a| > 2 \cdot u(a) \tag{2.5}$$

$$|b-1| > 2 \cdot u(b) \text{ and } |a| > 2 \cdot u(a) \tag{2.6}$$

The algorithms for calculation of the standard measurement uncertainties of *u(a)* and *u(b)* are related to the results of the individual CM against the results of the RM (see Annex b in GDE(09)). From Eq. (2.4) to (2.6) one can see that there is no general requirement regarding how much *a* can deviate from zero and *b* deviate from 1. Instead, the smaller *u(a)* and *u(b)* are, the smaller deviation is allowed in the significance test for the intercept (= 0 ± *a*) and for the slope (= 1 ± *b*), respectively. Therefore no rejection of the CM has been made based on the values of *a* and *b*.

3. Experimental set up

3.1 Field campaigns and the measurement site

The equivalence tests for the candidate measurement methods against the reference method for $PM_{2.5}$ and PM_{10} were conducted at the air quality measurement station of Kumpula, in the city of Helsinki. The test started with two $PM_{2.5}$ comparison campaigns in series followed by two campaigns for PM_{10}; the CMs tested are listed in Table 2.2. The $PM_{2.5}$ tests started with a winter campaign during the period from December 9, 2007 to February 13, 2008. The spring campaign continued from February 14 to May 15, 2008. The PM_{10} campaigns started with summer tests from June 9 to August 11, 2008, while the autumn campaign started on August 12 and ended on October 12, 2008. The dates of the test campaigns are presented in Figure 3.1.

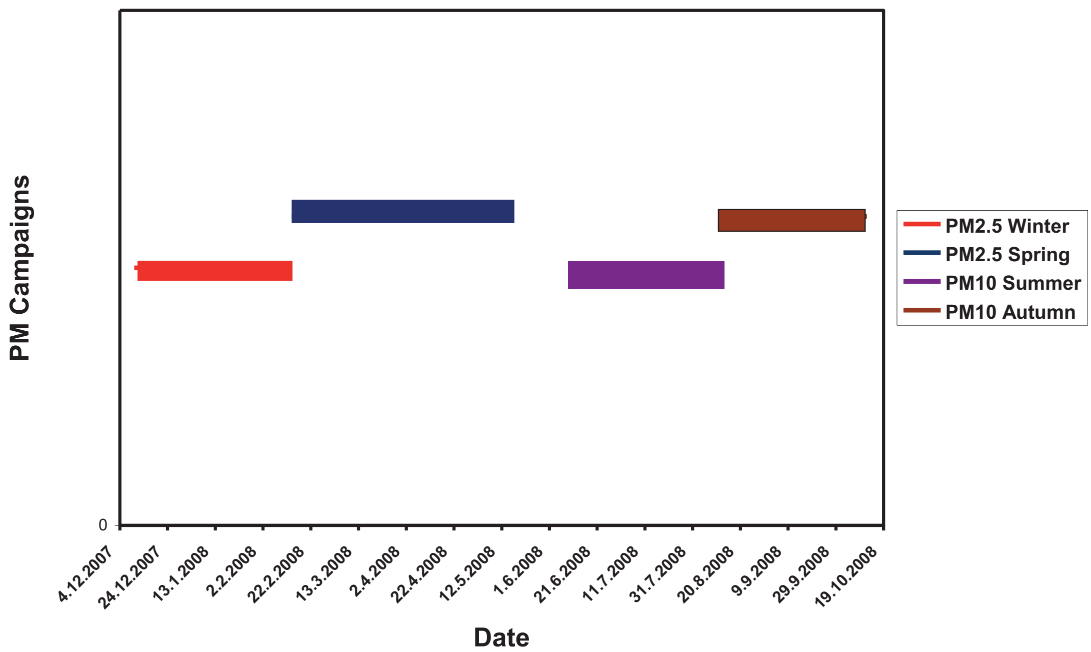

Figure 3.1. The dates of the equivalence test campaigns for $PM_{2.5}$ and PM_{10}.

The measurement station is located in the vicinity of the main building of the Finnish Meteorological Institute surrounded by the campus area of the University of Helsinki and a residential area. The station was classified as an urban background station according to the AQD. The distance to a major source of pollutant, the Kustaa Vaasa road, having a traffic density of close to 50 000 cars/day, is 200 m. The station is mainly influenced by traffic emissions and cross-boarder pollution, and as one of the SMEAR stations (Järvi et al., 2009) includes sophisticated aerosol measurement facilities for research purposes.

The location of the site was very convenient for the maintenance of the instruments; this was especially necessary for the filter changes of the reference methods and for the Dekati PM10 impactor, which needed to be performed on a daily basis. The measurement site, where all the instruments were arbitrarily installed into three cabins, is shown in Figure 3.2. The sampling inlets of the CMs were installed at heights of between 0.8 to 1.5 m from the surface of the roof; the sampling heights were from 3.5 to 4.2 m above ground level. The minimum distance between the adjacent sampling tubes was 0.5 m.

A meteorological observation station run by the FMI was located beside the measurement cabins. Its observations of air temperature, air pressure, relative humidity, and wind speed and wind direction were used to define the weather conditions during the measurement campaigns. The meteorological observation station was located 26 m above sea level, about 1.5 m lower than the floor level of the PM measurement cabins. The air temperature and relative humidity were measured at a height of 2.5 m, the air pressure at a height of 1.7 m and the wind speed and direction at a height of 32 m above the ground.

Figure 3.2. The equipment in the equivalence tests was installed in three cabins located in the vicinity of the FMI.

3.2 Filter weighing procedure

As stated in the previous chapter, two identical samplers were used as the reference method. During the $PM_{2.5}$ campaigns the comparison tests were conducted through the weekends with the RMs and the CMs while in case of PM_{10} campaigns the comparison tests were conducted only during the week days. The continuous CMs were measuring PM concentrations continuously. The sample inlets for PM_{10} and $PM_{2.5}$ were equipped with a filter holder for a 47 mm diameter filter. The filter change was made every day between 9 and 10 am (local time). The unloaded filters were conditioned in the weighing facility for 72 h at a temperature of (20 ± 1) ºC and a relative humidity of (50 ± 5) %, fulfilling the standards for the weighing room conditions. Two blank filters were stored and weighed with the same procedure as the PM filters in order to monitor any change in the environmental conditions in the weighing facility. No blank filters were used at the measurement site, since it was located right next to the FMI building and no storage of the filters took place at the station. The weighing of the filters was made with a Mettler ultra micro balance with a resolution of 1 µg at time intervals of 1, 48 and 72 h after installing the filters in the glove box. The calibration of the laboratory balance is carried out on a regular basis by an expert laboratory through which the traceability of the weighing results is linked to the national standard. In addition, the tare of the balance was checked on a daily basis by an automated function of the balance. The filter weighing facility was made in-house, and is shown in Figure 3.3.

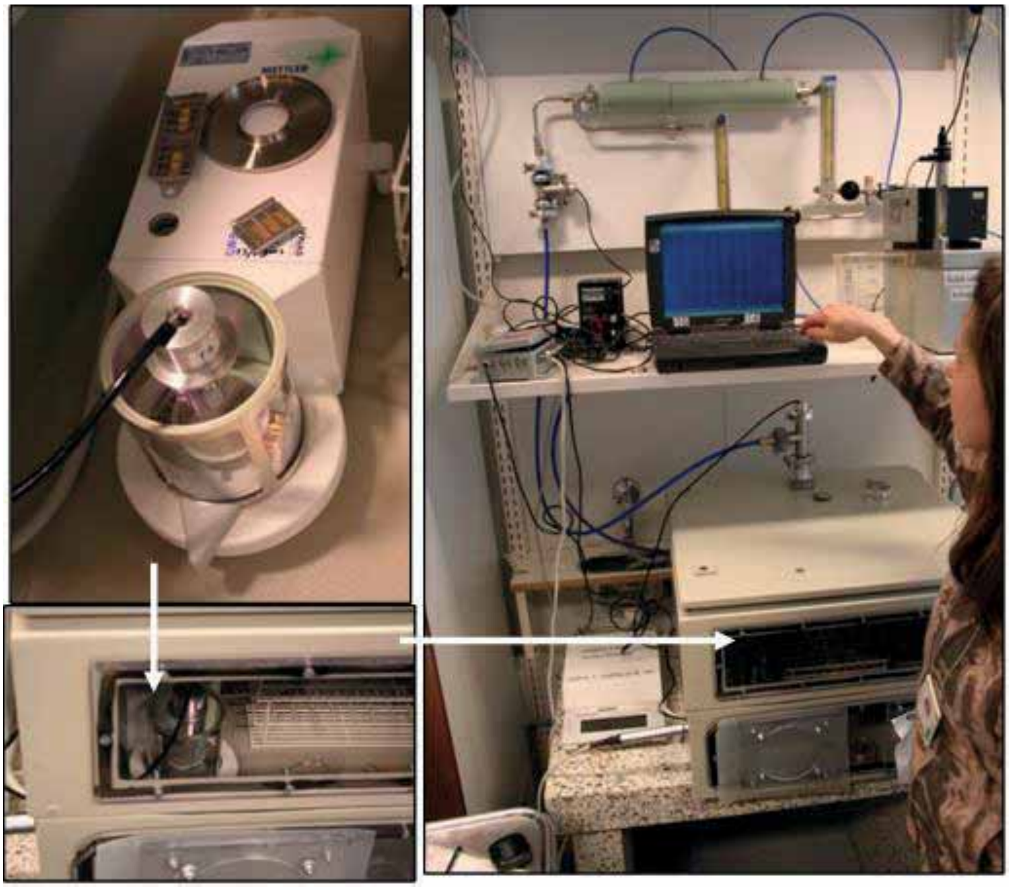

Figure 3.3. The weighing box for the filters and the control units for temperature and humidity (on the right) with the balance (on the top left) and the filter tray (on the lower left).

3.3 Data acquisition system

The data acquisition system used for the PM equivalence comparisons was a commercial EnviDas2000 for Windows (EnviDas, 2003). The data was collected as an average of 15 s values once a minute from every CM. The data protocols for each of the CMs were installed in the software with the help of the manufacturers. Two identical data acquisition systems were used so as to have all the CMs continuously connected. The station micros were connected through a direct line with the server micro where the data management software, Enview 2000 (Enview, 2004), was installed. Enview software stored the data in the database of the FMI for further analysis. From the Enview programme a secure www-link was made available to each manufacturer or representative to enable on-line surveillance of the recordings of the mass concentration by their instruments during the tests.

3.4 Operation of the instruments

The operation of the instruments was the responsibility of the manufacturers or their representatives, listed in Table 2.2. This also included the installation of the device and the sampling tube. If this was not able to be done by the representative of the CMs, the personnel of the FMI made the installation according to the manufacturer's instructions. However, connection of the CMs to the data acquisition system and a check that the data flow from each of the CMs was correct was made by the personnel of the FMI. The calibration of each CM was the responsibility of the representative. The sample flow rates for each of the CM and the RM were measured at the beginning and the end of each of the measurement campaigns. In case of the Osiris, the representative made more frequent checks of the sample flow rate. The flow rate was measured with a mass flow meter, the TSI model 3063, which was calibrated regularly against the reference flow measurement system, DHI Molbloc, model 1E5-VCR-V-Q, at the calibration laboratory of the FMI.

The calibration laboratory maintains the traceability of the flow measurement system by regular calibration against the primary flow measurement system at the Centre for Metrology and Accreditation, Finland. Cleaning of the inlets and changing the grease at the impactor plate was carried out every two weeks on the CMs as well as on the RMs employing the PM inlet described in the EN standards (see Table 2.2). The FH 62 I-R and the SHARP were calibrated at the beginning of the first $PM_{2.5}$ and at the end of the second $PM_{2.5}$ campaign and correspondingly with the first and second PM_{10} campaigns using the manufacturer's calibration kit.

During the measurement campaigns, several problems regarding the operation of the CMs occurred. In addition, a failure of the main electrical supply to one of the measurement cabins occurred once. As mentioned earlier, neither of the TEOM 1405-DF units operated correctly and had to be withdrawn from the tests. One of the Grimm 180 units needed maintenance for a short period during the PM_{10} tests. One of the Osiris units faced problems with the data acquisition system, causing a lack of data for several days during the $PM_{2.5}$ campaign. One of the instruments, Verewa, had problems with the sample tape, causing an erroneous sample analysis for several days during the PM_{10} campaign. The Dekati PM10 impactor, FH 62 I-R, MP101 CLS, SHARP and TEOM 1400ab all worked without technical problems during both tests. The malfunctioning of a CM has an influence on the DQO for data capture, which should be better than 90 % (AQD).

4. Data analysis

4.1 Description of the database

The minute readings from the CMs collected by the EnviDas data acquisition system were stored in the memory of the station PC and transmitted over a direct data line to the data server at the FMI. A few exceptions from the minute values occurred. In the case of the MP101, the manufacturer set the sampling time for both of the devices to 24 h. In the case of the Verewa, the sampling time was set to one hour. In both cases the CM sampling started at the same time as the RM sampling. The other instruments provided continuous readings of the prevailing mass concentrations of the PM. The Enview software stored the data in the database of the FMI. In the case of the RM, the results of each of the filter weighing and the data from the flow control units were stored on the local database of the FMI.

The data base of the equivalence tests for $PM_{2.5}$ and PM_{10} includes the minute values, hourly values and 24-hourly values for the CMs, 24-hourly values for RMs as well as the hourly values and 24-hourly values for the meteorological data, which were obtained from the meteorological database of the FMI.

4.2 Data processing

During the process of calculating the hourly and 24 h averages, the data were inspected at every step of the calculation, starting from the minute values to see the response of each of the CM. The averages for the different time intervals were performed provided that 75 % of the data were available over each of the calculation period. The notes and observations made in the logbooks of the RMs or CMs at both of the measurement cabins were studied. If technical reasons for the malfunctioning of any of the RMs or CMs were observed, the data was flagged. In case of the RMs, the malfunctioning that took place were the operation of the flow control units, the operation of the sampling pumps and the power failures. In the case of the CMs, several of the reasons resulted in incorrect behavior of the CMs. The 24 h means for each of the CM were calculated for the same period as that of the RMs.

The following data treatments were performed for PM_{10} and $PM_{2.5}$ (see in Ch. 2.4):

- Data capture, (AQD)	Pass/Fail
- Test of suitability of the data, GDE(09)	Pass/Fail
- Test of between-sampler for each pair of CMs, GDE(09)	Pass/Fail
- Test of between-sampler for RMs, GDE(09)	Pass/Fail
- Test of comparability, GDE(09)	
- uncorrected data	
- all data (averages of RMs and CMs over whole test campaigns)	Pass: OK Fail: Calibration
- subsets	Pass/Fail
- each of the CMs individually	Pass/Fail
- calibrated data (if 'all data' failed)	
- all data	Pass/Fail
- subsets	Pass/Fail
- each of the CMs individually	Pass/Fail

The tests of comparability were made with reference to the concentration value of 30 $\mu g/m^3$ for $PM_{2.5}$ and that of 50 $\mu g/m^3$ (the daily limit value) for PM_{10}, according to GDE(09). If another value is used as the limit value, the relative combined standard uncertainty will be changed accordingly. If the test failed to meet the DQO criteria for fixed measurements (see Eq. 2.3b), a check was made for the CM as to whether the test value, $W_{,CM}$, fulfilled the DQO for indicative measurements (see Table 2.1). It also occurred that some of the points did not seem to fit with rest of the data, and therefore Grubb's test or the judgment of an expert was used to remove some of the data points. As stated in GDE(09), no more than 2.5 % of the data could be removed based on this method.

5. Results

5.1 $PM_{2.5}$ comparisons

5.1.1 Meteorological conditions during the $PM_{2.5}$ comparisons

The winter 2007-2008 was exceptionally warm compared to the meteorological period 1971-2000. The monthly mean temperatures from December 2007 to February 2008 as well as in April 2008 were close to the upper range of the long-term means, while for the other months of the measurement campaigns the monthly mean temperatures were close to the long-term means. At the beginning of the measurements the snow cover was zero, being at its greatest depth, 15 cm, in March. The 24 h mean temperatures and relative humidity during the $PM_{2.5}$ comparison tests are presented in Figure 5.1. The wind rose of the hourly mean is shown in Figure 5.2. The wind speed is classified into five categories identified with different colors, according to the scale on the right of Figure 5.2.a. The wind direction is divided into sectors of 45º. The percentual scale with 10 % intervals is shown in the figure by the dashed lines. In addition to the wind rose, the $PM_{2.5}$ rose was also generated from the hourly values of the CM, and is shown in Figure 5.2.b. The $PM_{2.5}$ concentration is shown in two wind speed categories: no wind (≤ 1 m/s) and a wind speed larger than the detection limit of the anemometer (> 1 m/s). The wind directions are divided into sectors of 45º. The scale of the mass concentration of $PM_{2.5}$ is shown in the figure by dashed lines.

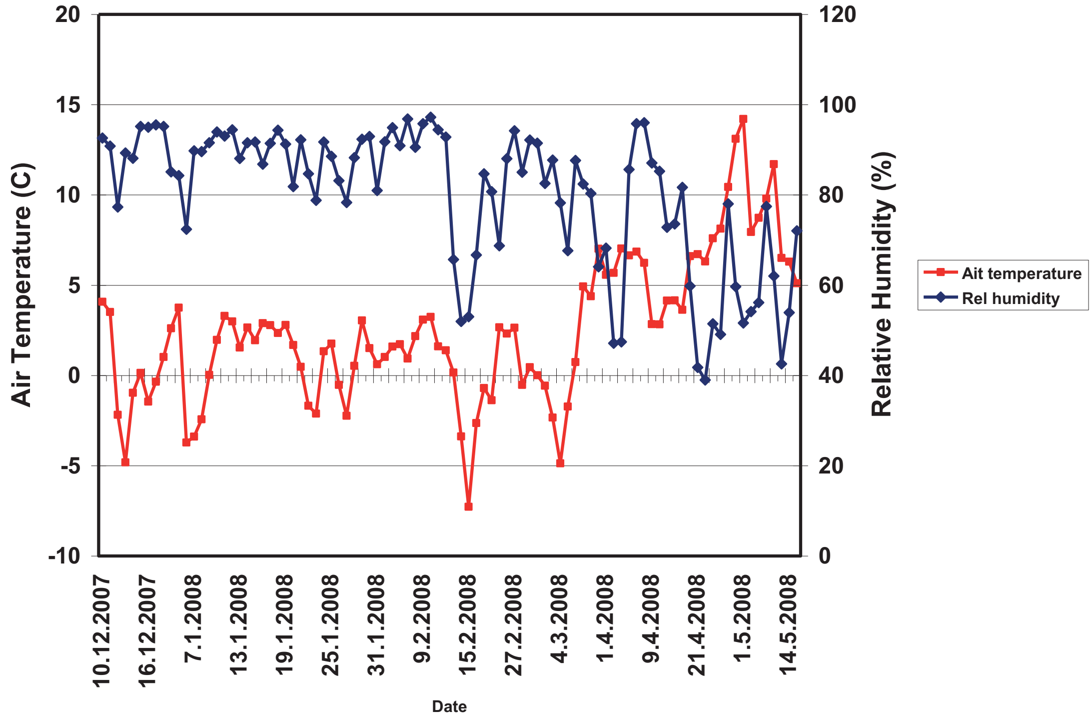

Figure 5.1. The 24 h mean values of temperature (scale on the left) and relative humidity (scale on the right) during the equivalence campaigns for $PM_{2.5}$ measurements.

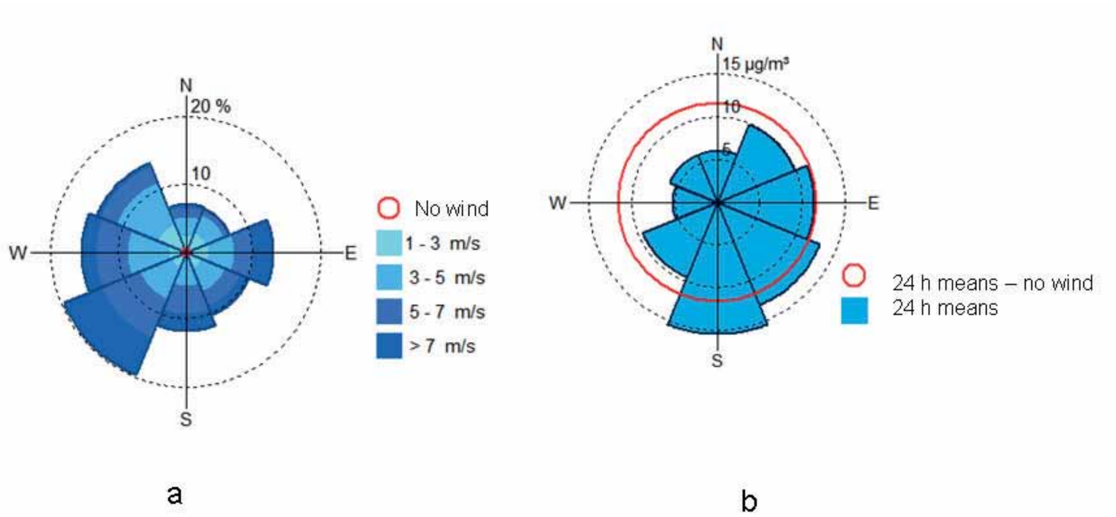

Figure 5.2.a and b. Wind speed (a) from daily values and $PM_{2.5}$ concentration (b) as a function of wind direction during the equivalence campaigns for $PM_{2.5}$ measurements.

5.1.2 Results of the reference method for $PM_{2.5}$

The equivalence tests of candidate measurement methods against the reference method started with the field campaigns for the $PM_{2.5}$ size class. The winter campaign started on December 9, 2007 and ended on February 13, 2008. Altogether 47 samples were included in this period. The spring campaign continued from February 14 to May 15, 2008, including 42 samples with the reference methods. In Figure 5.3 the time series of daily concentrations of the RMs for $PM_{2.5}$ are shown.

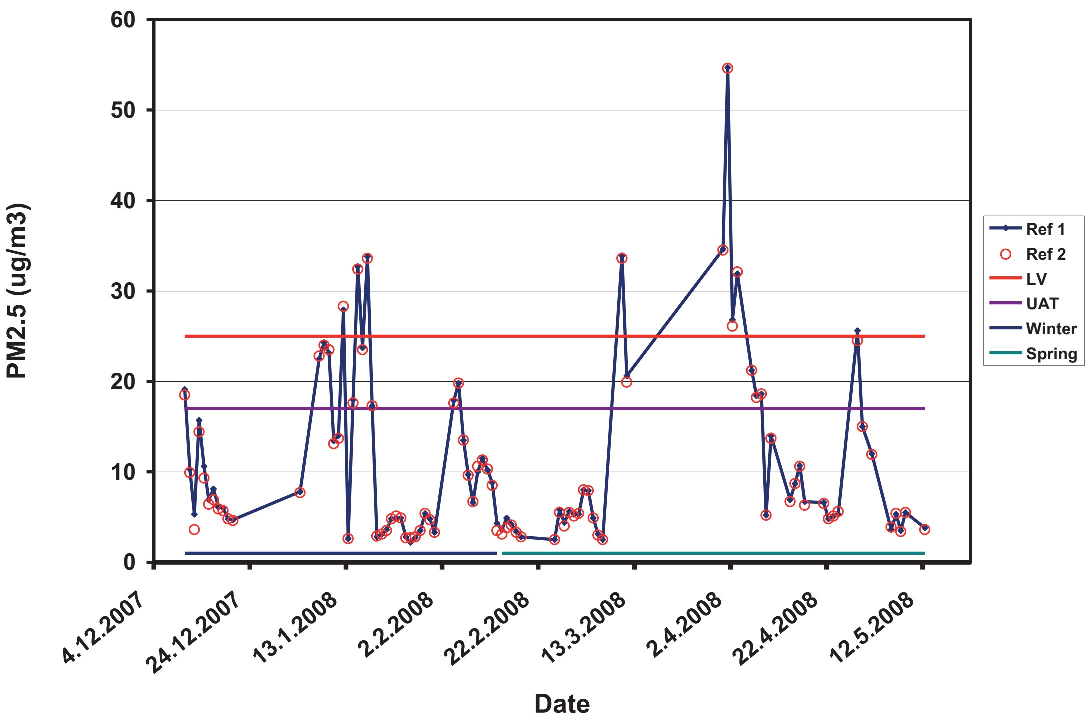

Figure 5.3. The time series of the two RMs for the $PM_{2.5}$ comparisons.

In Figure 5.3 the Upper Assessment Threshold value, 17 $\mu g/m^3$, and the annual limit value for $PM_{2.5}$, 25 $\mu g/m^3$ are shown. The concentration range was large enough to fulfill the criteria for the suitability of the data. 23 % of all data exceeded the UAT value. The subsets of winter campaign and spring campaign are also shown in the figure.

The scatter plot of RM2 against RM1 is shown in Figure 5.4.

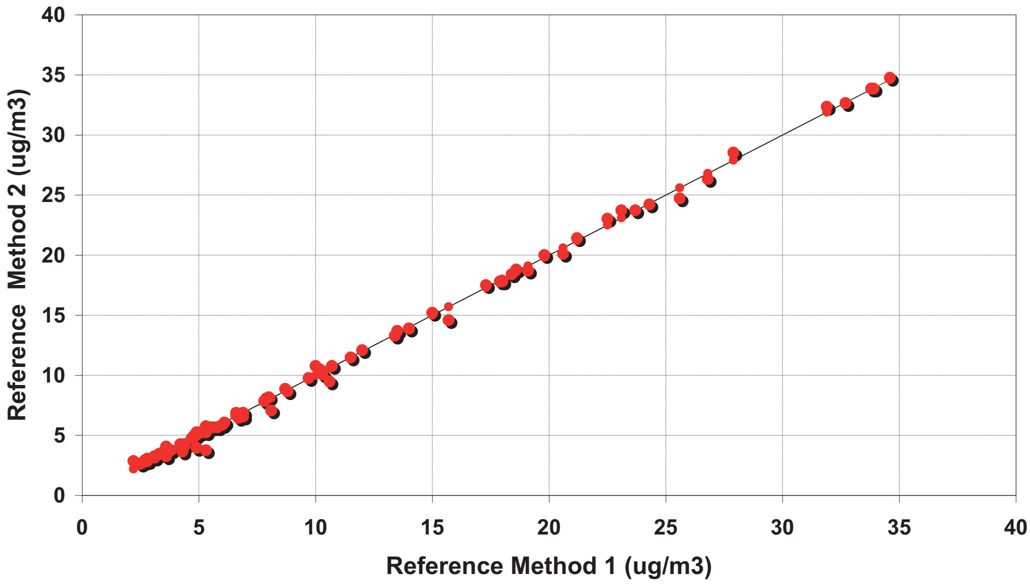

Figure 5.4. The scatter plot of RM2 against RM1 for $PM_{2.5}$.

The between-sampler uncertainty, (see Ch. 2.4) for the reference method was calculated to be 0.3 µg/m^3 both for all data and for data ≥ 18 µg/m^3. In addition, the combined standard uncertainty between both of the reference methods was 1.3 %.

5.1.3. Results of the candidate methods for $PM_{2.5}$

In the following Tables 5.1 to 5.8, the results for each of the CMs are presented. The results are presented in different colors depending on whether the criteria, shown in column 2 of each of the tables, are fulfilled (in black) or not (in red). The statement criterion Pass/Fail is made based only on the criterion that the relative combined standard uncertainty, $u_{CR} \leq 12.5$ % (Pass) or $u_{CR} > 12.5$ % (Fail) for the combined result of both of the CMs. The significance tests for the slope and the intercept are made with respect to the standard uncertainty of the slope and intercept of each of the CMs.

If a CM failed with the comparability test after the calibration correction, a check was made whether the CM would pass the test for indicative measurements (see 2008/50/EC Annex 1).

Table 5.1. The test results for the Dekati PM10 impactor in all the tests for demonstration of equivalence for $PM_{2.5}$ measurements.

Test	Criterion	Dekati PM10	Dekati PM10-A	Dekati PM10-B	Pass/Fail
Data capture	≥ 90 %		96.7 %	96.7 %	Pass
Suitability of data	20 % ≥ 18 µg/m^3	Pass	Pass	Pass	Pass
Between sampler test					
All data	u_{bs} < 2.5 µg/m^3	0.84			Pass
≥ 18 µg/m^3	u_{bs} < 2.5 µg/m^3	1.3			Pass
Test of comparability					
All data					
Number of Datapairs		89			
Slope	Not significant ≠ 1	1.12			
Intercept	Not significant ≠ 0	1.1			
Rel comb std un	≤ 12.5 %	19.3			Fail
Calibration equation					
Slope		0.89			
Intercept		-0.95			
Calibrated data					
All data					
Number of Data		89	89	89	
Slope	Not significant ≠ 1	0.99	1.02	0.96	
Intercept	Not significant ≠ 0	1.0	0.8	1.2	
Rel comb std un	≤ 12.5 %	10.8	11.9	10.4	Pass
Winter data					
Number of Data		47	47	47	
Slope	Not significant ≠ 1	0.83	0.86	0.80	
Intercept	Not significant ≠ 0	1.0	0.8	1.3	
Rel comb std un	≤ 12.5 %	13.6	11.5	15.7	Fail
Spring data					
Number of Data		42	42	42	
Slope	Not significant ≠ 1	1.10	1.13	1.07	
Intercept	Not significant ≠ 0	1.7	1.6	1.9	
Rel comb std un	≤ 12.5 %	19.8	22.2	17.8	Fail
≥ 18 µg/m^3					
Number of Data		20	20	20	Fail
Slope	Not significant ≠ 1	1.48	1.57	1.39	
Intercept	Not significant ≠ 0	-12.2	-14.2	-10.4	
Rel comb std un	≤ 12.5 %	17.2	18.8	16.2	Fail

Table 5.2. The test results for the FH 62 I-R in all the tests for demonstration of equivalence for $PM_{2.5}$ measurements.

Test	Criterion	FH 62 I-R	FH 62 I-R - A	FH 62 I-R - B	Pass/Fail
Data capture	≥ 90 %		**96.7 %**	**97.8 %**	**Pass**
Suitability of data	20 % ≥ 18 µg/m^3	**Pass**	**Pass**	**Pass**	**Pass**
Between sampler test					
All data	u_{bs} < 2.5 µg/m^3	**1.03**			**Pass**
≥ 18 µg/m^3	u_{bs} < 2.5 µg/m^3	**1.9**			**Pass**
Test of comparability					
All data					
Number of Data		**91**			
Slope	Not significant ≠ 1	**0.74**			
Intercept	Not significant ≠ 0	**0.5**			
Rel comb std un	≤ 12.5 %	**24.4**			**Fail**
Calibration equation					
Slope		**1.35**			
Intercept		**-0.73**			
Calibrated data					
All data					
Number of Data		**91**	**89**	**90**	
Slope	Not significant ≠ 1	**1.00**	**0.92**	**1.07**	
Intercept	Not significant ≠ 0	**0.0**	**0.2**	**-0.2**	
Rel comb std un	≤ 12.5 %	**3.1**	**8.5**	**6.7**	**Pass**
Winter data					
Number of Data		**47**	**45**	**47**	
Slope	Not significant ≠ 1	**0.98**	**0.86**	**1.07**	
Intercept	Not significant ≠ 0	**-0.1**	**0.3**	**-0.2**	
Rel comb std un	≤ 12.5 %	**3.4**	**13.0**	**7.1**	**Pass**
Spring data					
Number of Data		**44**	**44**	**43**	
Slope	Not significant ≠ 1	**1.02**	**0.98**	**1.07**	
Intercept	Not significant ≠ 0	**0.1**	**0.2**	**-0.1**	
Rel comb std un	≤ 12.5 %	**3.9**	**5.3**	**6.3**	**Pass**
≥ 18 µg/m^3					
Number of Data		**19**	**17**	**19**	**Fail**
Slope	Not significant ≠ 1	**1.08**	**1.06**	**1.12**	
Intercept	Not significant ≠ 0	**-2.0**	**-3.4**	**-1.7**	
Rel comb std un	≤ 12.5 %	**4.7**	**9.9**	**6.6**	**Pass**

Table 5.3. The test results for the Grimm 180 in all the tests for demonstration of equivalence for $PM_{2.5}$ measurements.

Test	Criterion	GRIMM-180	GRIMM-180 - A	GRIMM-180 - B	Pass/Fail
Data capture	≥ 90 %		93.5 %	96.7 %	Pass
Suitability of data	20 % ≥ 18 μg/m^3	Pass	Pass	Pass	Pass
Between sampler test					
All data	u_{bs} < 2.5 μg/m^3	0.69			Pass
≥ 18 μg/m^3	u_{bs} < 2.5 μg/m^3	1.2			Pass
Test of comparability					
All data					
Number of Data		89			
Slope	Not significant ≠ 1	1.34			
Intercept	Not significant ≠ 0	0.4			
Rel comb std un	≤ 12.5 %	36.2			Fail
Calibration equation					
Slope		0.75			
Intercept		-0.31			
Calibrated data					
All data					
Number of Data		89	86	89	
Slope	Not significant ≠ 1	1.00	1.02	0.99	
Intercept	Not significant ≠ 0	0.3	0.2	0.6	
Rel comb std un	≤ 12.5 %	3.8	4.1	4.2	Pass
Winter data					
Number of Data		47	44	47	
Slope	Not significant ≠ 1	0.97	0.98	0.97	
Intercept	Not significant ≠ 0	0.6	0.5	0.7	
Rel comb std un	≤ 12.5 %	4.7	4.4	5.3	Pass
Spring data					
Number of Data		42	42	42	
Slope	Not significant ≠ 1	1.04	1.06	1.01	
Intercept	Not significant ≠ 0	0.1	-0.2	0.4	
Rel comb std un	≤ 12.5 %	4.5	5.9	3.4	Pass
≥ 18 μg/m^3					
Number of Data		18	17	18	Fail
Slope	Not significant ≠ 1	0.99	0.95	1.02	
Intercept	Not significant ≠ 0	0.3	1.7	-0.4	
Rel comb std un	≤ 12.5 %	6.5	5.4	7.9	Pass

Table 5.4. The test results for the MP101 in all the tests for demonstration of equivalence for $PM_{2.5}$ measurements.

Test	Criterion	MP-101	MP-101 - A	MP-101 - B	Pass/Fail
Data capture	≥ 90 %		96.7 %	97.8 %	Pass
Suitability of data	20 % ≥ 17 μg/m³	Pass	Pass	Pass	Pass
Between sampler test					
All data	u_{bs} < 2.5 μg/m³	1.07			Pass
≥ 18 μg/m³	u_{bs} < 2.5 μg/m³	2.2			Pass
Test of comparability					
All data					
Number of Data		90			
Slope	Not significant ≠ 1	0.51			
Intercept	Not significant ≠ 0	-0.4			
Rel comb std un	≤ 12.5 %	50.8			Fail
Calibration equation					
Slope		1.97			
Intercept		0.85			
Calibrated data					
All data					
Number of Data		90	89	90	
Slope	Not significant ≠ 1	1.01	1.06	0.98	
Intercept	Not significant ≠ 0	-0.2	-0.8	0.4	
Rel comb std un	≤ 12.5 %	5.1	5.9	7.0	Pass
Winter data					
Number of Data		46	45	46	
Slope	Not significant ≠ 1	1.03	1.08	0.99	
Intercept	Not significant ≠ 0	-0.5	-1.1	0.0	
Rel comb std un	≤ 12.5 %	4.6	6.0	6.7	Pass
Spring data					
Number of Data		44	44	44	
Slope	Not significant ≠ 1	1.01	1.05	0.97	
Intercept	Not significant ≠ 0	0.2	-0.5	0.7	
Rel comb std un	≤ 12.5 %	5.6	6.0	7.4	Pass
≥ 18 μg/m³					
Number of Data		16	15	16	Fail
Slope	Not significant ≠ 1	1.16	1.25	1.11	
Intercept	Not significant ≠ 0	-4.2	-6.0	-3.7	
Rel comb std un	≤ 12.5 %	1.7	5.1	0.8	Pass

Table 5.5. The test results for the Osiris in all the tests for demonstration of equivalence for $PM_{2.5}$ measurements.

Test	Criterion	Osiris	Osiris - A	Osiris - B	Pass/Fail
Data capture	≥ 90 %		98.9 %	87.0 %	Pass
Suitability of data	20 % ≥ 17 μg/m³	Pass	Pass	Pass	Pass
Between sampler test					
All data	u_{bs} < 2.5 μg/m³	0.37			Pass
≥ 18 μg/m³	u_{bs} < 2.5 μg/m³	0.7			Pass
Test of comparability					
All data					
Number of Data		91			
Slope	Not significant ≠ 1	0.56			
Intercept	Not significant ≠ 0	0.1			
Rel comb std un	≤ 12.5 %	45.0			Fail
Calibration equation					
Slope		1.79			
Intercept		-0.11			
Calibrated data					
All data					
Number of Data		91	91	80	
Slope	Not significant ≠ 1	1.08	1.10	1.05	
Intercept	Not significant ≠ 0	-0.8	-1.0	-0.3	
Rel comb std un	≤ 12.5 %	16.8	17.9	12.7	Fail
Winter data					
Number of Data		47	47	40	
Slope	Not significant ≠ 1	1.28	1.31	1.14	
Intercept	Not significant ≠ 0	-1.6	-1.9	-0.2	
Rel comb std un	≤ 12.5 %	27.4	29.3	18.1	Fail
Spring data					
Number of Data		44	44	40	
Slope	Not significant ≠ 1	0.70	0.70	0.84	
Intercept	Not significant ≠ 0	1.3	1.2	0.5	
Rel comb std un	≤ 12.5 %	27.3	28.1	16.5	Fail
≥ 18 μg/m³					
Number of Data		19	19	13	
Slope	Not significant ≠ 1	2.63	2.80	2.00	
Intercept	Not significant ≠ 0	-40.3	-44.4	-24.1	
Rel comb std un	≤ 12.5 %	52.6	56.7	33.2	Fail

Table 5.6. The test results for the SHARP in all the tests for demonstration of equivalence for $PM_{2.5}$ measurements.

Test	Criterion	SHARP	SHARP - A	SHARP - B	Pass/Fail
Data capture	≥ 90 %		88.0 %	98.9 %	Pass
Suitability of data	20 % ≥ 17 μg/m³	Pass	Pass	Pass	Pass
Between sampler test					
All data	u_{bs} < 2.5 μg/m³	1.59			Pass
≥ 18 μg/m³	u_{bs} < 2.5 μg/m³	2.4			Pass
Test of comparability					
All data					
Number of Data		91			
Slope	Not significant ≠ 1	0.92			
Intercept	Not significant ≠ 0	0.3			
Rel comb std un	≤ 12.5 %	7.4			Pass
Calibration equation					
Slope		1.09			
Intercept					
Calibrated data					
All data					
Number of Data		91	81	91	
Slope	Not significant ≠ 1	1.00	1.10	0.91	
Intercept	Not significant ≠ 0	0.3	-0.5	0.9	
Rel comb std un	≤ 12.5 %	0.7	9.0	6.1	Pass
Winter data					
Number of Data		47	37	47	Fail
Slope	Not significant ≠ 1	1.03	1.15	0.94	
Intercept	Not significant ≠ 0	0.1	-1.0	0.7	
Rel comb std un	≤ 12.5 %	3.4	12.2	3.4	Pass
Spring data					
Number of Data		44	44	44	
Slope	Not significant ≠ 1	0.95	1.05	0.86	
Intercept	Not significant ≠ 0	0.6	-0.1	1.2	
Rel comb std un	≤ 12.5 %	2.8	5.3	9.8	Pass
≥ 18 μg/m³					
Number of Data		19	19	19	Fail
Slope	Not significant ≠ 1	1.02	1.12	0.94	
Intercept	Not significant ≠ 0	-0.3	-1.2	0.0	
Rel comb std un	≤ 12.5 %	0.7	8.3	5.8	Pass

Table 5.7. The test results for the TEOM 1400ab in all the tests for demonstration of equivalence for $PM_{2.5}$ measurements.

Test	Criterion	TEOM 1400ab	TEOM 1400ab - A	TEOM 1400ab - B	Pass/Fail
Data capture	≥ 90 %		88.0 %	97.8 %	Pass
Suitability of data	20 % ≥ 17 µg/m^3	Pass	Pass	Pass	Pass
Between sampler test					
All data	u_{bs} < 2.5 µg/m^3	0.64			Pass
≥ 18 µg/m^3	u_{bs} < 2.5 µg/m^3	1.2			Pass
Test of comparability					
All data					
Number of Data		90			
Slope	Not significant ≠ 1	0.80			
Intercept	Not significant ≠ 0	-1.2			
Rel comb std un	≤ 12.5 %	25.3			Fail
Calibration equation					
Slope		1.25			
Intercept		1.56			
Calibrated data					
All data					
Number of Data		90	81	90	
Slope	Not significant ≠ 1	1.01	0.97	1.03	
Intercept	Not significant ≠ 0	-0.1	0.0	-0.3	
Rel comb std un	≤ 12.5 %	8.2	6.6	9.1	Pass
Winter data					
Number of Data		46	37	46	Fail
Slope	Not significant ≠ 1	0.96	0.90	0.98	
Intercept	Not significant ≠ 0	0.5	0.5	0.5	
Rel comb std un	≤ 12.5 %	9.8	9.4	10.0	Pass
Spring data					
Number of Data		44	44	44	
Slope	Not significant ≠ 1	1.05	1.03	1.07	
Intercept	Not significant ≠ 0	-0.6	-0.4	-0.9	
Rel comb std un	≤ 12.5 %	6.9	6.5	8.3	Pass
≥ 18 µg/m^3					
Number of Data		19	18	19	Fail
Slope	Not significant ≠ 1	1.19	1.19	1.24	
Intercept	Not significant ≠ 0	-5.1	-5.8	-6.3	
Rel comb std un	≤ 12.5 %	11.4	9.8	13.2	Pass

Table 5.8. The test results for the Verewa in all the tests for demonstration of equivalence for $PM_{2.5}$ measurements.

Test	Criterion	Verewa	Verewa - A	Verewa - B	Pass/Fail
Data capture	≥ 90 %		98.9 %	95.7 %	Pass
Suitability of data	20 % ≥ 17 $\mu g/m^3$	Pass	Pass	Pass	Pass
Between sampler test					
All data	$u_{bs} < 2.5\ \mu g/m^3$	1.02			Pass
≥ 18 $\mu g/m^3$	$u_{bs} < 2.5\ \mu g/m^3$	0.2			Pass
Test of comparability					
All data					
Number of Data		91			
Slope	Not significant ≠ 1	0.72			
Intercept	Not significant ≠ 0	0.9			
Rel comb std un	≤ 12.5 %	25.0			Fail
Calibration equation					
Slope		1.39			
Intercept		-1.20			
Calibrated data					
All data					
Number of Data		91	91	88	
Slope	Not significant ≠ 1	1.02	1.04	1.01	
Intercept	Not significant ≠ 0	-0.1	-0.1	-0.3	
Rel comb std un	≤ 12.5 %	6.9	7.3	8.3	Pass
Winter data					
Number of Data		47	47	44	
Slope	Not significant ≠ 1	0.98	1.02	0.96	
Intercept	Not significant ≠ 0	-0.1	0.0	-0.4	
Rel comb std un	≤ 12.5 %	7.6	7.3	10.4	Pass
Spring data					
Number of Data		44	44	44	
Slope	Not significant ≠ 1	1.06	1.06	1.08	
Intercept	Not significant ≠ 0	-0.1	-0.2	-0.3	
Rel comb std un	≤ 12.5 %	7.9	8.1	9.6	Pass
≥ 18 $\mu g/m^3$					
Number of Data		19	19	19	Fail
Slope	Not significant ≠ 1	1.40	1.39	1.45	
Intercept	Not significant ≠ 0	-10.0	-9.5	-11.6	
Rel comb std un	≤ 12.5 %	14.1	13.9	16.1	Fail

5.1.4 Summary of $PM_{2.5}$ comparisons

The winter 2007-2008 was an exceptionally warm, with no snow until February 2008. In Figure 5.1 one can see that the 24 h means of air temperature were between -4 ºC to -7 ºC until the beginning of April, and after that above +5 ºC. For comparison, the long-term monthly mean temperature (meteorological period from 1971-2000) is from -2.2 ºC (December) to -5 ºC (March). The relative humidity varied from 40 % to almost 100 %. In the winter campaign there was a long period with the relative humidity above 90 %, which is also quite exceptional. The wind rose figure (Fig. 5.2.a.) shows clearly that the prevailing wind was from the south-west, which is normal. From the $PM_{2.5}$ rose (Fig. 5.2.b.), the highest concentrations are from the southerly sector, i.e., the sector of central Helsinki. The south-easterly sector is responsible for the second highest concentrations of $PM_{2.5}$. The lowest concentrations are measured in the wind sectors from west to north, i.e., from outside Helsinki.

The results of the reference methods for $PM_{2.5}$ show very good agreement between the two RMs, as can be seen from Figure 5.3. The concentration range of $PM_{2.5}$ reasonably well covers both high values and low values. For comparison, the monthly mean concentration of $PM_{2.5}$ is presented in Figure 5.5 for two other stations: a traffic station in Helsinki where concentrations have been at their highest and a rural background station (Virolahti), representing low concentrations. The standard deviation of the mean is also shown in the figure as error bars. The mean concentrations of $PM_{2.5}$ from the equivalence tests are also presented in Figure 5.5 together with their standard deviation. The $PM_{2.5}$ concentrations from the equivalence tests represent fairly well the concentration ranges met with in Finland.

The standard uncertainty for the between-sampler tests was 0.3 $\mu g/m^3$. The Teflon filters used in the RMs turned out to be a good choice, as the deviation of the parallel results was very small. In addition the content of water in the sampled filters was not dominant, as could be the case for quartz filters. The differences in the weighing results between the

48 h and 72 h stabilization times with the sampled filters were not significantly different. Based on the weighing results, the average water content in the sampled filters was 10 %.

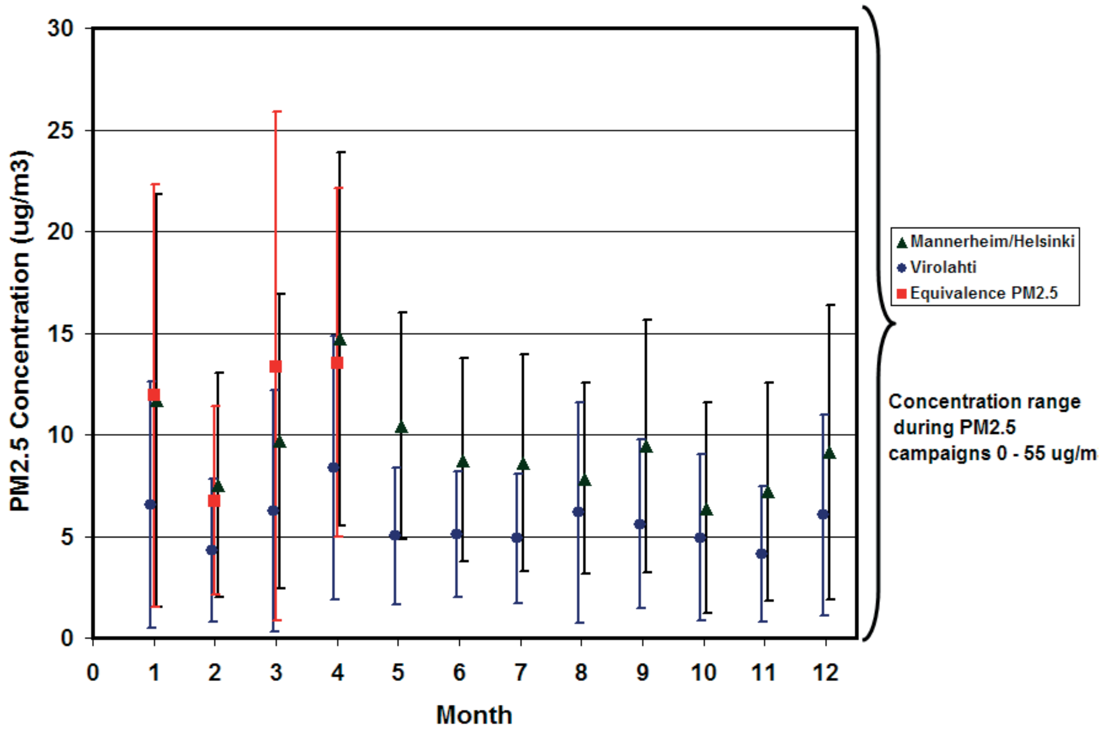

Figure 5.5. The monthly mean concentration of $PM_{2.5}$ in 2008 from the traffic station in Helsinki (triangles), from the background station at Virolahti (round dots) and from the $PM_{2.5}$ equivalence tests (squares).

The data capture for the Dekati PM10 was 96.7 % for both of the instruments. The results from the Dekati PM10 impactor were acceptable for the between-sampler test, but for the test of comparability with the reference method the results were not satisfactory. The calibration equation (Table 5.1) shows that the results of the Dekati PM10 show a slight overestimation. The Dekati PM10 impactor passed the comparability test for the whole dataset with calibrated values, but failed with the individual campaigns. In case of concentrations $\geq$ 18 $\mu g/m^3$, the number of data pairs was not adequate to make a conclusive judgment of the failure of the analyser. The test results of Dekati PM10 impactor show that it can be applicable for indicative measurements of $PM_{2.5}$ concentration (see Table 2.1), but not for fixed measurements.

The data capture for the FH 62 I-R was good, 96.7 % and 97.8 % see Table 5.2. The between-sampler test was also acceptable for both of the datasets. The test for comparability failed with the uncorrected results. After applying the calibration equation to the results, the comparability test was passed for all data and for each of the subsets of data. The results of the comparability test for the individual analysers (FH 62 I-R A and B) differ considerably from each other in the all-data tests, in the winter tests and in the spring tests.

In the case of the Grimm 180, the data capture, 93.5 % and 96.7 % for the devices A and B, was acceptable, as can be seen in Table 5.3. The between-sampler test was also acceptable for both of the datasets (all data and concentrations $\geq$ 18 $\mu g/m^3$). The test of comparability failed with the uncorrected results, but on applying the calibration equation, the comparability test was acceptable for all data and for each of the data subsets. Both of the analysers (Grimm 180 A and B) show mutually consistent results for all data and for each of the individual sub-tests.

Data capture, 96.7 % and 97.8 % with the MP101 A and B respectively, was acceptable for both of the devices (see Table 5.4). Also the between-sampler test was acceptable for both of the datasets. The test of comparability failed with the uncorrected data, but after applying the calibration equation, the MP101 passed the tests. However, from Table 5.4 one can see that the slope of the calibration equation (1.97) is exceptionally high compared to comparisons made to the MP101 analyser previously, where a calibration equation slope of 1.2 was achieved (Bertrand et al, 2009). No clear reason for this can be given. The sampling time of the analyser was set to 24 h in this comparison, which would lead one to expect that the slope would be closer to one. There was a systematic difference between the two analysers (MP101 A and B) throughout the individual tests of each sub-test.

In Table 5.5 the results from the Osiris show that the data capture was 98.9 % for one of the analysers but 87.0 % for the other. The Osiris passed the between-sampler test, but failed the comparability test for the uncorrected data. After applying the calibration equation to the data the Osiris still failed with the comparability test for fixed measurements. The test result after correction was acceptable for indicative measurements in the case of all data, but not with sub-sets of the data. Therefore the Osiris does not fulfill requirements of Table 2.1 for fixed measurements nor for indicative measurements.

The SHARP passed the data capture (88.0 % and 98.9 % for devices A and B) and between-sampler tests, as shown in Table 5.6. The test of comparability was acceptable in the case of combined standard uncertainty, but the slope of the regression line was significantly different from one. The calibration factor (slope) was therefore applied to the results. As a result of this the SHARP passed all the subsets for comparability. By applying the calibration factor the combined standard uncertainty was lower than without any correction. There was, however, a clear difference between the results of the individual analysers (SHARP A and B) within each of the sub-tests.

In Table 5.7 the results from the TEOM 1400ab show that the data capture was 88.0 % for one of the analysers but 97.8 % for the other. The between-sampler tests were acceptable. The test of comparability failed with the uncorrected data, but after applying the calibration equation, the results were acceptable for all data and for each of the subsets. There were no notable differences between the results of the individual analysers (TEOM 1400ab A and B) in the results of each of the sub-tests.

In case of the Verewa (see Table 5.8) the data capture was 98.9 % for one of the analysers but 95.7 % for the other. The between-sampler tests were acceptable. The comparability test failed with the uncorrected data, but after applying the calibration equation, the comparability test was acceptable for all data and for the winter and spring subsets. In the case of the ≥ 18 $\mu g/m^3$ subset the analyser failed to meet the criteria for uncertainty, but the number of data pairs was not adequate to make a conclusive judgment of the failure of the analyser. There were no notable differences between the results of the individual analysers (Verewa A and B) in the results of each of the sub-tests.

5.2. PM_{10} comparisons

5.2.1 Meteorological conditions during the PM_{10} comparisons

The summer of 2008 was exceptionally rainy and cold. Only twice did the daily mean temperature exceed +20 ºC. The 24 h mean temperature and relative humidity during the equivalence campaigns for PM_{10} are shown in Figure 5.6.

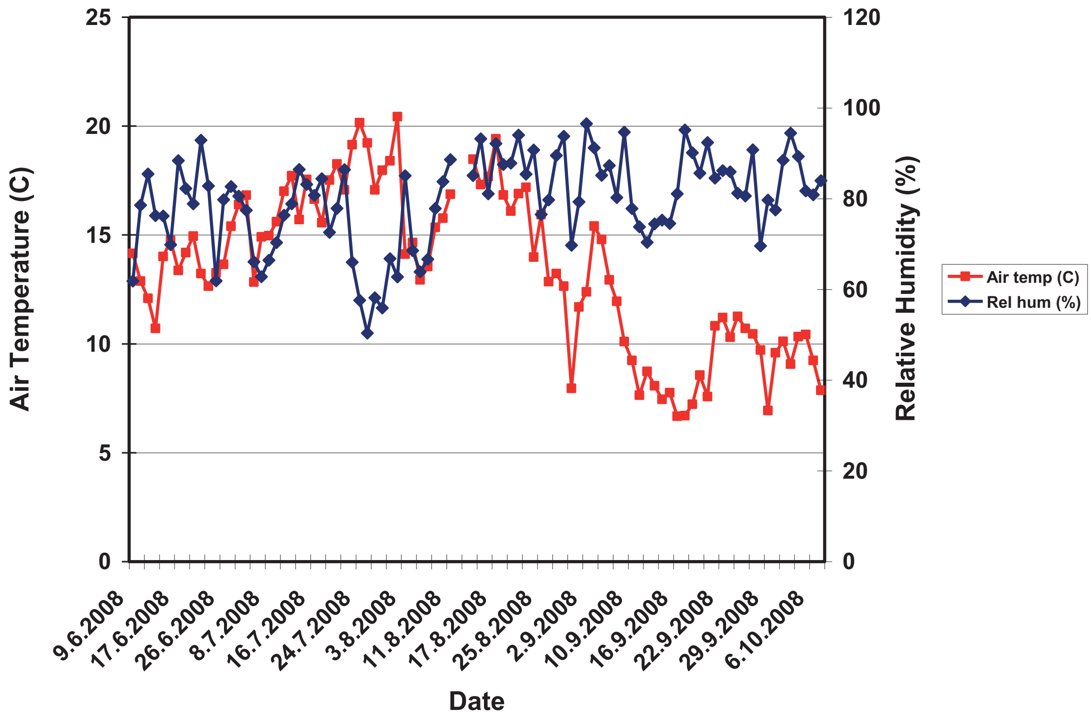

Figure 5.6. The 24 h mean values of temperature (scale on the left) and the relative humidity (scale on the right) during the equivalence campaigns for PM_{10} measurements.

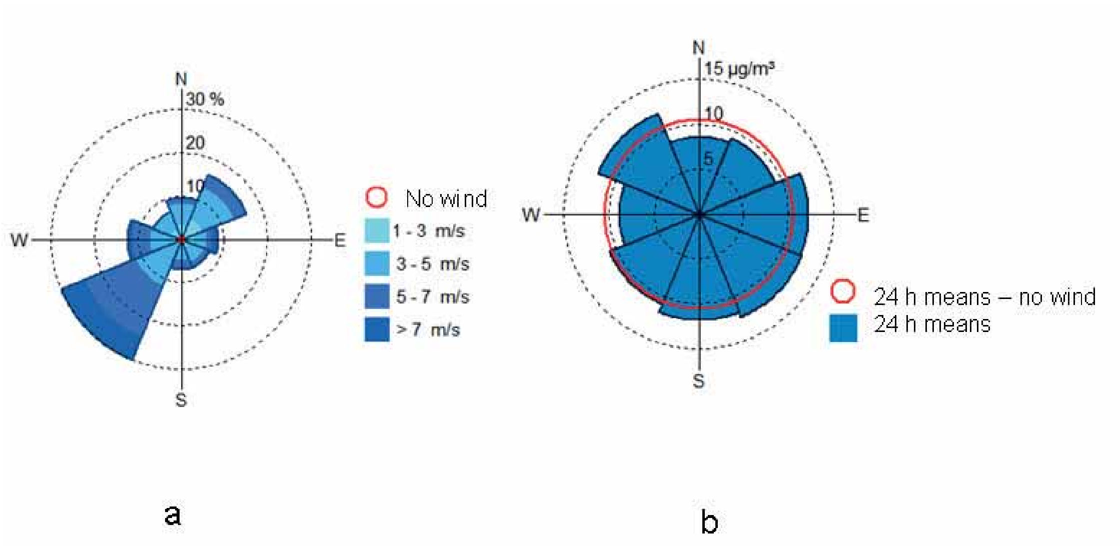

Figure 5.7. Wind speeds from 24 h mean values (a) and PM_{10} concentration (b) as a function of wind direction during the equivalence campaigns for PM_{10} measurements.

5.2.2 Results of the reference method for PM_{10}

The field campaigns of the equivalence tests of candidate measurement methods against the reference method for the size class of PM_{10} started on June 9, 2008 with the summer campaign, which was followed by the autumn campaign. The summer campaign ended on August 11, 2008, while the autumn campaign started on August 12 and ended on October 7, 2008. Altogether 90 samples were included for the period of the PM_{10} campaigns, of which 43 were taken in the summer campaign and 47 in the autumn campaign. In Figure 5.8 the time series of daily concentrations of the RMs for PM_{10} are shown.

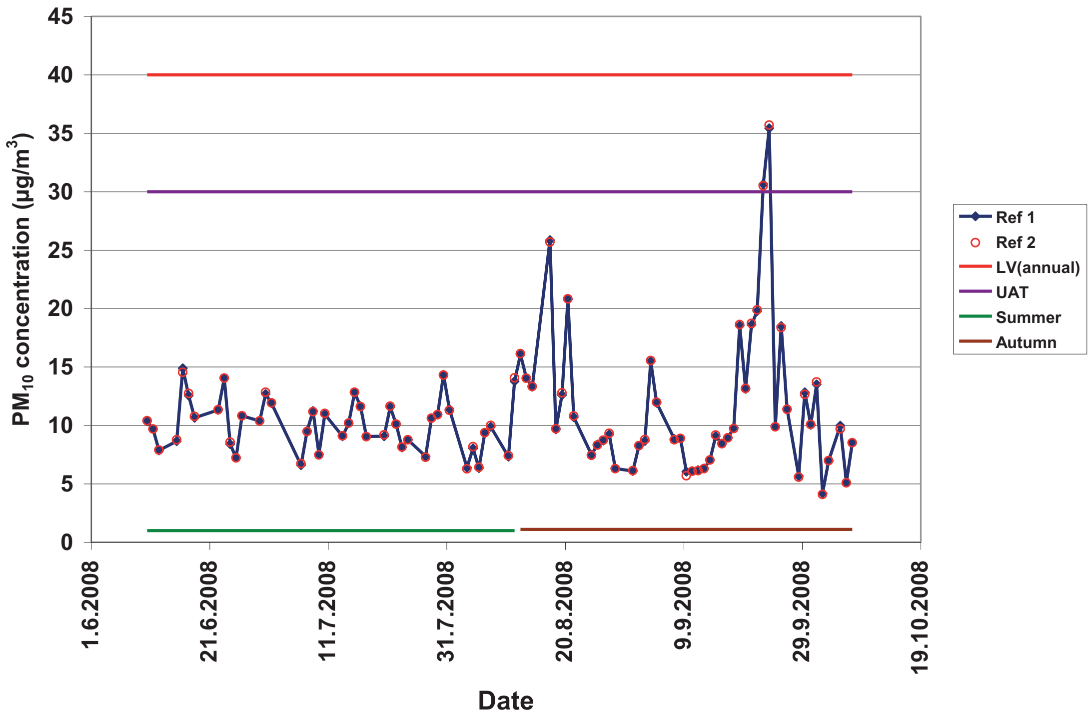

Figure 5.8. The time series of the two RMs for PM_{10} comparisons.

As can be seen from Figure 5.8, the concentration values of PM_{10} were very low throughout the whole campaign. This had no practical influence on the results, since, based on the results of the continuous methods, only during one week-end was a value exceeding that of the UAT observed. In 2008 the main reason for the low PM_{10} concentrations, especially during the summer campaign, was the very rainy weather. As a consequence of this, the particles were washed out (and washed in) by the water droplets. Secondly, the forest fires, in particular those across the Russian border, which had been quite a regular phenomenon in previous years, did not recur. The scatter plot of the RM2 against the RM1 is shown in Figure 5.9 for the full data.

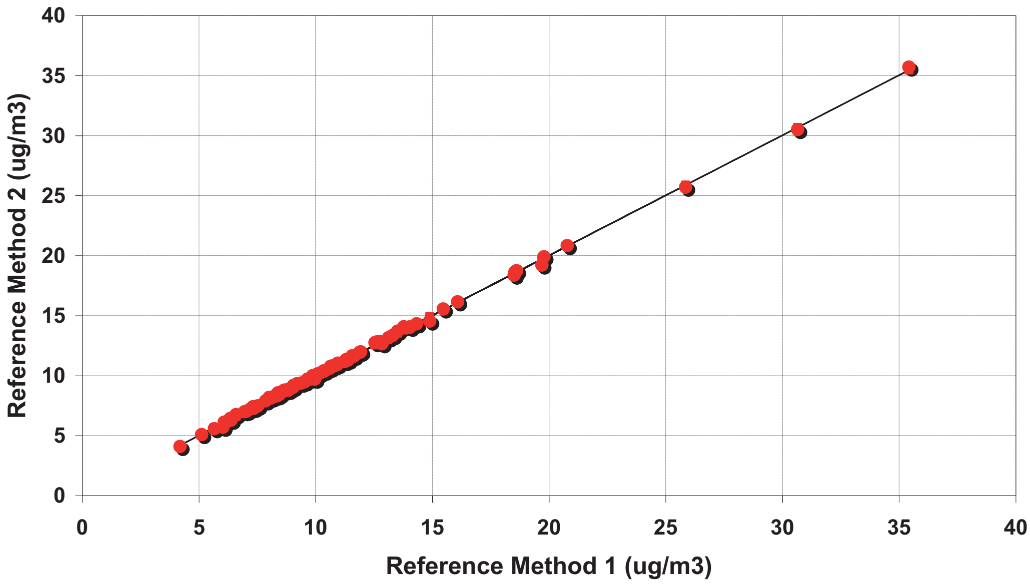

Figure 5.9. The scatter plot of the RM2 against the RM1 for PM_{10}.

The between-sampler uncertainty, (see Ch. 2.4) for the reference method was calculated to be 0.1 µg/m^3 for all data. In addition, the combined standard uncertainty between both of the reference methods was 0.2 %.

5.2.3. Results of the candidate methods for PM_{10}

Even though the PM_{10} concentrations were low, the test procedures were conducted according to GDE(09). In the following Tables 5.9 to 5.15 the results of the tests according to GDE(09) are shown. The analysis of the data is the same as in the case of the $PM_{2.5}$ comparison.

Table 5.9. The test results of the FH 62 I-R for all the tests for demonstration of equivalence for PM_{10} measurements.

Test PM_{10}	Criterion	FH 62 I-R	FH 62 I-R - A	FH 62 I-R - B	Pass/Fail
Data capture	≥ 90 %		**100.0 %**	**100.0 %**	**Pass**
Suitability of data	20 % > 30 μg/m^3	**Fail**	**Fail**	**Fail**	**Fail**
Between-sampler test					
All data	u_{bs} < 2.5 μg/m^3	**1.14**			**Pass**
≥ 30 μg/m3	u_{bs} < 2.5 μg/m^3				
Test of comparability					
All data					
Number of Data		**90**			
Slope	Not significant ≠ 1	**0.80**			
Intercept	Not significant ≠ 0	**0.4**			
Rel comb std un	≤ 12.5 %	**19.4**			**Fail**
Calibration equation					
Slope		**1.25**			
Intercept		**-0.50**			
Calibrated data					
All data					
Number of Data		**90**	**90**	**90**	
Slope	Not significant ≠ 1	**1.00**	**0.90**	**1.12**	
Intercept	Not significant ≠ 0	**0.0**	**0.4**	**-0.8**	
Rel comb std un	≤ 12.5 %	**1.2**	**9.7**	**10.8**	**Pass**
Summer data					
		43	**43**	**43**	
Slope	Not significant ≠ 1	**1.11**	**1.06**	**1.17**	
Intercept	Not significant ≠ 0	**-0.9**	**-0.6**	**-1.3**	
Rel comb std un	≤ 12.5 %	**9.2**	**4.4**	**14.9**	**Pass**
Autumn data					
Number of Data		**47**	**47**	**47**	
Slope	Not significant ≠ 1	**0.99**	**0.88**	**1.11**	
Intercept	Not significant ≠ 0	**-0.2**	**0.1**	**-0.6**	
Rel comb std un	≤ 12.5 %	**2.3**	**11.6**	**10.3**	**Pass**

Table 5.10. The test results of the Grimm 180 for all the tests for demonstration of equivalence for PM_{10} measurements.

Test PM_{10}	Criterion	Grimm 180	Grimm 180 - A	Grimm 180 - B	Pass/Fail
Data capture	≥ 90 %		**96.7 %**	**90.0 %**	**Pass**
Suitability of data	20 % > 30 µg/m^3	**Fail**	**Fail**	**Fail**	**Fail**
Between-sampler test					
All data	u_{bs} < 2.5 µg/m^3	**1.79**			**Pass**
≥ 30 µg/m3	u_{bs} < 2.5 µg/m^3				
Test of comparability					
All data					
Number of Data		**88**			
Slope	Not significant ≠ 1	**1.37**			
Intercept	Not significant ≠ 0	**-1.7**			
Rel comb std un	≤ 12.5 %	**33.2**			**Fail**
Calibration equation					
Slope		**0.71**			
Intercept		**1.45**			
Calibrated data					
All data					
Number of Data		**88**	**87**	**81**	
Slope	Not significant ≠ 1	**0.98**	**1.03**	**0.86**	
Intercept	Not significant ≠ 0	**0.2**	**0.4**	**0.6**	
Rel comb std un	≤ 12.5 %	**1.2**	**3.9**	**13.1**	**Pass**
Summer data					
Number of Data		**42**	**42**	**42**	
Slope	Not significant ≠ 1	**1.00**	**1.10**	**0.94**	
Intercept	Not significant ≠ 0	**0.1**	**-0.3**	**0.0**	
Rel comb std un	≤ 12.5 %	**0.1**	**9.0**	**5.8**	**Pass**
Autumn data					
Number of Data		**46**	**45**	**39**	
Slope	Not significant ≠ 1	**0.98**	**1.02**	**0.85**	
Intercept	Not significant ≠ 0	**0.1**	**0.5**	**0.3**	
Rel comb std un	≤ 12.5 %	**1.3**	**3.2**	**14.7**	**Pass**

Table 5.11. The test results of the MP101 for all the tests for demonstration of equivalence for PM_{10} measurements.

Test PM_{10}	Criterion	MP 101	MP 101 - A	MP 101 - B	Pass/Fail
Data capture	≥ 90 %		97.8 %	98.9 %	Pass
Suitability of data	20 % > 30 µg/m^3	Fail	Fail	Fail	Fail
Between-sampler test					
All data	u_{bs} < 2.5 µg/m^3	0.76			Pass
≥ 30 µg/m3	u_{bs} < 2.5 µg/m^3				
Test of comparability					
All data					
Number of Data		89			
Slope	Not significant ≠ 1	0.54			
Intercept	Not significant ≠ 0	-0.5			
Rel comb std un	≤ 12.5 %	47.2			Fail
Calibration equation					
Slope		1.85			
Intercept		1.10			
Calibrated data					
All data					
Number of Data		89	88	89	
Slope	Not significant ≠ 1	1.02	1.13	0.94	
Intercept	Not significant ≠ 0	-0.3	-1.0	0.2	
Rel comb std un	≤ 12.5 %	3.2	11.9	6.5	Pass
Summer data					
Number of Data		43	42	43	
Slope	Not significant ≠ 1	1.15	1.30	1.08	
Intercept	Not significant ≠ 0	-1.5	-2.9	-1.0	
Rel comb std un	≤ 12.5 %	12.2	24.1	6.5	Pass
Autumn data					
Number of Data		46	46	46	
Slope	Not significant ≠ 1	1.01	1.10	0.92	
Intercept	Not significant ≠ 0	-0.2	-0.6	0.1	
Rel comb std un	≤ 12.5 %	2.9	9.9	7.9	Pass

Table 5.12. The test results of the Osiris for all the tests for demonstration of equivalence for PM_{10} measurements.

Test PM_{10}	Criterion	Osiris	Osiris - A	Osiris - B	Pass/Fail
Data capture	≥ 90 %		98.9 %	98.9 %	Pass
Suitability of data	20 % > 30 µg/m^3	Fail	Fail	Fail	Fail
Between-sampler test					
All data	u_{bs} < 2.5 µg/m^3	1.76			Pass
≥ 30 µg/m3	u_{bs} < 2.5 µg/m^3				
Test of comparability					
All data					
Number of Data		89			
Slope	Not significant ≠ 1	0.70			
Intercept	Not significant ≠ 0	0.9			
Rel comb std un	≤ 12.5 %	28.5			Fail
Calibration equation					
Slope		1.42			
Intercept		-1.10			
Calibrated data					
All data					
Number of Data		89	89	89	
Slope	Not significant ≠ 1	1.03	1.21	0.86	
Intercept	Not significant ≠ 0	-0.2	-0.4	-0.2	
Rel comb std un	≤ 12.5 %	3.4	20.1	14.3	Pass
Summer data					
Number of Data		42	42	42	
Slope	Not significant ≠ 1	1.33	1.57	1.15	
Intercept	Not significant ≠ 0	-3.4	-4.3	-3.0	
Rel comb std un	≤ 12.5 %	26.7	48.3	8.6	Fail
Autumn data					
Number of Data		47	47	47	
Slope	Not significant ≠ 1	0.99	1.16	0.83	
Intercept	Not significant ≠ 0	0.3	0.4	0.1	
Rel comb std un	≤ 12.5 %	4.0	17.2	16.6	Pass

Table 5.13. The test results of the SHARP for all the tests for demonstration of equivalence for PM_{10} measurements.

Test PM_{10}	Criterion	SHARP	SHARP - A	SHARP - B	Pass/Fail
Data capture	≥ 90 %		**100.0 %**	**100.0 %**	**Pass**
Suitability of data	20 % > 30 μg/m^3	**Fail**	**Fail**	**Fail**	**Fail**
Between-sampler test					
All data	u_{bs} < 2.5 μg/m^3	**0.72**			**Pass**
≥ 30 μg/m3	u_{bs} < 2.5 μg/m^3				
Test of comparability					
All data					
Number of Data		**90**	**90**	**90**	
Slope	Not significant ≠ 1	**0.97**	**0.96**	**0.98**	
Intercept	Not significant ≠ 0	**-0.2**	**-0.2**	**-0.2**	
Rel comb std un	≤ 12.5 %	**4.0**	**5.2**	**3.9**	**Pass**
Calibration equation					
Slope		**Not needed**			
Intercept		**Not needed**			
Calibrated data					
All data					
Number of Data					
Slope	Not significant ≠ 1				
Intercept	Not significant ≠ 0				
Rel comb std un	≤ 12.5 %				
Summer data					
Number of Data		**43**	**43**	**43**	
Slope	Not significant ≠ 1	**0.97**	**0.92**	**1.06**	
Intercept	Not significant ≠ 0	**-0.4**	**0.1**	**-1.2**	
Rel comb std un	≤ 12.5 %	**3.8**	**8.4**	**3.8**	**Pass**
Autumn data					
Number of Data		**47**	**47**	**47**	
Slope	Not significant ≠ 1	**0.96**	**0.96**	**0.96**	
Intercept	Not significant ≠ 0	**0.1**	**0.0**	**0.1**	
Rel comb std un	≤ 12.5 %	**5.3**	**5.5**	**5.0**	**Pass**

Table 5.14. The test results of the TEOM 1400ab for all the tests for demonstration of equivalence for PM_{10} measurements.

Test PM_{10}	Criterion	TEOM1400ab	TEOM1400ab - A	TEOM1400ab - B	Pass/Fail
Data capture	≥ 90 %		97.8 %	98.9 %	Pass
Suitability of data	20 % > 30 μg/m^3	Fail	Fail	Fail	Fail
Between-sampler test					
All data	u_{bs} < 2.5 μg/m^3	0.55			Pass
≥ 30 μg/m3	u_{bs} < 2.5 μg/m^3				
Test of comparability					
All data					
Number of Data		89			
Slope	Not significant ≠ 1	0.90			
Intercept	Not significant ≠ 0	-1.1			
Rel comb std un	≤ 12.5 %	13.1			Fail
Calibration equation					
Slope		1.12			
Intercept		1.26			
Calibrated data					
All data					
Number of Data		89	88	89	
Slope	Not significant ≠ 1	1.01	0.99	1.03	
Intercept	Not significant ≠ 0	-0.1	-0.1	-0.2	
Rel comb std un	≤ 12.5 %	3.4	3.4	4.7	Pass
Summer data					
Number of Data		42	42	42	
Slope	Not significant ≠ 1	1.21	1.12	1.33	
Intercept	Not significant ≠ 0	-2.1	-1.5	-3.0	
Rel comb std un	≤ 12.5 %	16.9	9.4	27.3	Fail
Autumn data					
Number of Data		47	46	47	
Slope	Not significant ≠ 1	0.99	0.97	1.01	
Intercept	Not significant ≠ 0	0.1	0.2	0.0	
Rel comb std un	≤ 12.5 %	5.1	4.5	4.4	Pass

Table 5.15. The test results of the Verewa for all the tests for demonstration of equivalence for PM_{10} measurements.

Test PM_{10}	Criterion	Verewa	Verewa - A	Verewa - B	Pass/Fail
Data capture	≥ 90 %		86.7 %	98. 9 %	Pass
Suitability of data	20 % > 30 μg/m^3	Fail	Fail	Fail	Fail
Between-sampler test					
All data	u_{bs} < 2.5 μg/m^3	1.40			Pass
≥ 30 μg/m3					
Test of comparability					
All data					
Number of Data		89			
Slope	Not significant ≠ 1	0.73			
Intercept	Not significant ≠ 0	0.8			
Rel comb std un	≤ 12.5 %	25.2			Fail
Calibration equation					
Slope		1.30			
Intercept		-0.61			
Calibrated data					
All data					
Number of Data		89	78	89	
Slope	Not significant ≠ 1	0.99	1.09	1.05	
Intercept	Not significant ≠ 0	0.0	-1.0	-0.4	
Rel comb std un	≤ 12.5 %	4.4	9.0	6.2	Pass
Summer data					
Number of Data		42	42	42	
Slope	Not significant ≠ 1	1.56	2.04	1.59	
Intercept	Not significant ≠ 0	-5.5	-10.3	-5.7	
Rel comb std un	≤ 12.5 %	45.3	83.6	48.2	Fail
Autumn data					
Number of Data		47	36	47	
Slope	Not significant ≠ 1	0.95	1.01	0.94	
Intercept	Not significant ≠ 0	0.2	0.0	0.1	
Rel comb std un	≤ 12.5 %	6.4	6.1	7.1	Pass

5.2.4 Summary of PM_{10} comparisons

The weather conditions during the PM_{10} campaigns were different from the long-term means (meteorological period from 1971-2000) with respect to precipitation. The frequent rain showers throughout the whole summer caused very effective deposition of the particulate matter, especially in the case of the PM_{10} size fraction. The daily mean temperatures were between +6 ºC and +20 ºC during both of the campaigns, as can be seen from Figure 5.6. The relative humidity was above 50 % during both of the campaigns. The prevailing wind sector (30 % of the hourly wind speeds) is in the south-westerly sector where the maximum wind speed (> 7 m/s) also occurred, as shown in Figure 5.7.a. In the case of the concentration of PM_{10}, there is no clear wind sector where the concentrations are at their highest, as can be seen from Figure 5.7.b.

The result of the reference methods for PM_{10} shows very good agreement between the two RMs, as can be seen from Figure 5.9. The standard uncertainty for the between-sampler tests was 0.1 $\mu g/m^3$. The PM_{10} concentration range was exceptionally low, and does not reflect typical PM_{10} concentrations particularly well. To illustrate this, the monthly mean concentrations of PM_{10} from stations representing the traffic situation in Helsinki, Lahti, Vaasa and Kouvola, from the rural background station at Virolahti and from the PM_{10} equivalence tests are presented in Figure 5.10. The standard deviations of the mean are also shown in the figure as error bars. The PM_{10} concentrations in the equivalence tests represent urban background concentration ranges and concentrations at traffic stations in some Finnish cities. It will not, however, represent the high concentrations met in Finland during the spring time or during the episodes from cross boarder PM concentrations, e.g. forest fires. The concentrations measured in Helsinki at the traffic station were also higher than in the equivalence campaigns for PM_{10}.

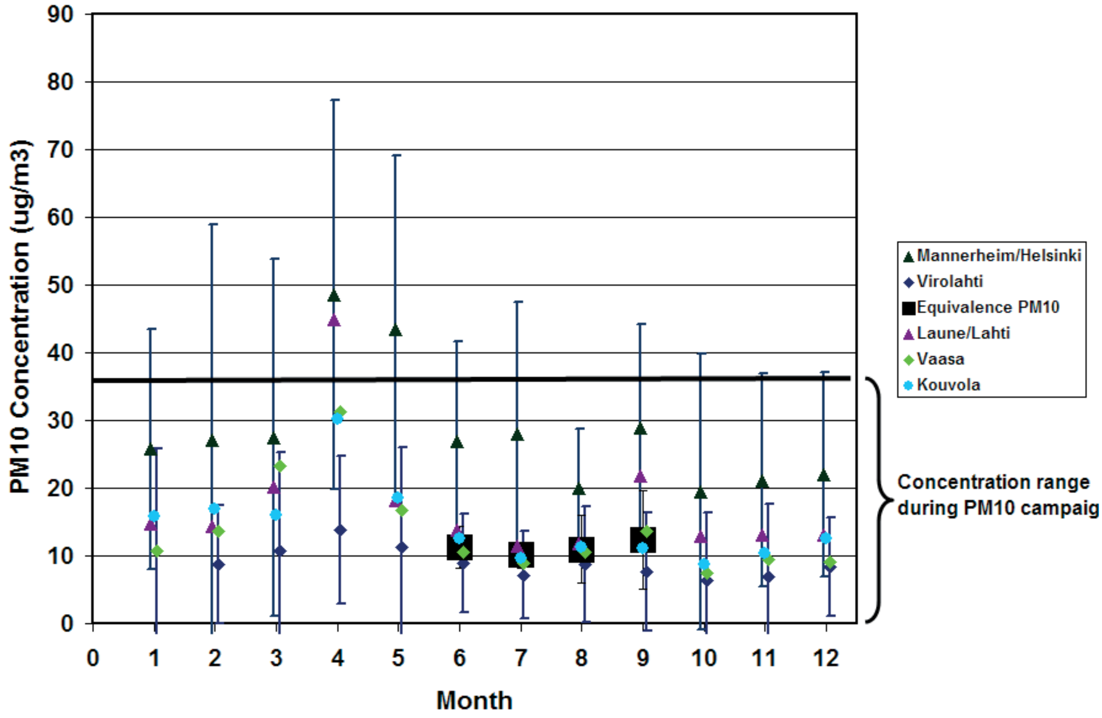

Figure 5.10. The monthly mean concentration of PM_{10} in 2008 at the traffic station in Helsinki (black triangle), at the background station at Virolahti (diamond), at Laune (purple triangle), at Vaasa (green diamond) at Kouvola (light blue dot), and in the $PM_{2.5}$ equivalence tests (square).

The data capture of the FH 62 I-R was 100 % for both of the instruments (see Table 5.9). The between-sampler uncertainty was also acceptable for the whole data set. The test for comparability failed with the uncorrected results. After applying the calibration equation to the results, the comparability test was passed for all the data and for each of the subsets of the data. The results of the comparability test for the individual analysers (FH 62 I-R A and B) differ considerably from each other, as they also did in the $PM_{2.5}$ tests.

In the case of the Grimm 180, the data capture, 96.7 % and 90.0 % for the A and B devices, respectively, was acceptable, as can be seen in Table 5.10. The between-sampler uncertainty was also acceptable for all the data. The test of comparability failed with the uncorrected results, but on applying the calibration equation, the comparability test was acceptable for all the data and for each of the subsets of the data. There was a considerable difference between the slope of the two analysers (Grimm 180 A and B), which was not met with in the $PM_{2.5}$ tests. Due to the repair of instrument B, the data from the autumn campaign were just too few.

The data capture with the MP101 was 97.8 % and 98.9 % for devices A and B (see Table 5.11). The between-sampler uncertainty was acceptable. The test of comparability failed with the uncorrected data, but after applying the calibration equation, the MP101 passed the tests. However, from Table 5.11 one can see that the slope of the calibration equation is exceptionally high, as was also the case in the $PM_{2.5}$ test. There was also a clear difference between the two analysers (MP101 A and B) throughout the individual tests of each sub-test.

The Osiris passed the data capture test with values of 98.9 % for both of the instruments, as seen in Table 5.12. The Osiris passed the between-sampler test, but failed the comparability test for the uncorrected data. After applying the calibration equation to the data, the Osiris passed the comparability test for all the data and for the autumn data, but failed with the summer data. This was mainly because of the operation of one of the units (Osiris A). The difference between the two instruments was significant, as can be seen from the values of the slope in each of the sub-sets.

The SHARP passed the data capture with 100 % for both of the instruments, as well as the between-sampler test, as shown in Table 5.13. The test of comparability was acceptable as an average and for both of the instruments individually. No calibration equation (slope or intercept) was therefore applied to the results. The SHARP also passed all the sub-set tests for comparability.

The TEOM 1400ab passed the data capture, 97.8 % and 98.9 % for the instruments TEOM 1400ab A and B, and also the between-sampler test, as can be seen from Table 5.14. The test of comparability failed with the uncorrected data, but after applying the calibration equation, the results were acceptable for all the data and for the autumn data. In the case of the summer data, the tests failed both with the instruments together and in the case of a single instrument (TEOM 1400ab B). There were no notable differences between the results of the individual analysers (TEOM 1400ab A and B) regarding the results from all the data and from the autumn data, but using the summer data the differences between the test results of the individual instruments were considerable.

In the case of the Verewa, see Table 5.15, the data capture was 86.7 % (Verewa A) and 98.9 % (Verewa B), which was not acceptable in the case of Verewa A. The between-sampler test was acceptable. The comparability test failed with the uncorrected data, but after applying the calibration equation, the comparability test was acceptable for all the data and for the autumn sub-set, but not for the summer data. There were no notable differences between the results of the individual analysers (Verewa A and B) in the autumn data, but in using the summer data the test results differed considerably between the two instruments.

5.3. Calibration equations for CMs

The calibration equations for each of the CMs are presented for both of the size categories (see Tables 5.1 to 5.15) in Table 5.16. The concentration range for the measurement campaigns was taken from the measurements by the RM. For $PM_{2.5}$ the overall measurement range was from 2 to 55 $\mu g/m^3$ for all data (2 to 34 $\mu g/m^3$ for winter data and 2 to 55 $\mu g/m^3$ for spring data). In the case of the PM_{10} campaigns, the overall range was from 4 to 36 $\mu g/m^3$ (6 to 15 $\mu g/m^3$ for summer data and 4 to 36 $\mu g/m^3$ for autumn data).

Table 5.16. The calibration range and the equations (see Eq. (2.1), b = slope and a = intercept) against the reference method for $PM_{2.5}$ and PM_{10} together with the relative combined standard uncertainty.

Test $PM_{2.5}$	Dekati PM10	FH 62 I-R	Grimm 180	MP 101	Osiris	SHARP	TEOM1400ab	Verewa
Calibration range ($\mu g/m^3$)		0 - 55	0 - 55	0 - 55		0 - 55	0 - 55	0 - 55
Calibration equation								
Slope	0.89	1.35	0.75	1.97	1.79	1.09	1.25	1.39
Intercept ($\mu g/m^3$)	-0.95	-0.73	-0.31	0.85	-0.11		1.56	-1.18
Relative combined standard uncertainty (%)	10.8	3.1	3.8	5.1	16.8	0.7	8.2	6.9
Test PM_{10}								
Calibration range ($\mu g/m^3$)		0 - 36	0 - 36	0 - 36	10 - 36	0 - 36	10 - 36	10 - 36
Calibration equation								
Slope		1.25	0.71	1.85	1.42	Not needed	1.12	1.30
Intercept ($\mu g/m^3$)		-0.50	1.45	1.10	-1.10	Not needed	1.26	-0.61
Relative combined standard uncertainty (%)		1.2	1.2	3.2	3.4	4.0	3.4	4.4

In Table 5.16 the ranges for the $PM_{2.5}$ tests are not indicated for the Dekati PM10 Impactor and for the Osiris, which did not pass the test for fixed measurements. The Dekati PM10 impactor passed the test for fixed measurements with corrected results for the whole data set but not for both of the campaigns and instruments individually. Sub-set results met the requirements for indicative measurements. Osiris failed the test for fixed and for indicative measurements. In the case of PM_{10}, the Osiris, the TEOM and the Verewa did not pass the summer test, and therefore the measurement range has been raised from the mean concentration of the summer campaign to the highest value from the autumn campaign.

In the case of the TEOM 1400ab, one should keep in mind that in this case the default equation has been removed from both of the analysers, and the calibration equation should be applied to the results using uncorrected data. If the default values are used, i.e., slope = 1.03 and intercept 3 $\mu g/m^3$, the calibration equations for both of the PM size fractions in Table 5.16 can be used if the results of the TEOM 1400ab are first transformed using the equation:

$$Y = (\text{TEOM 1400ab(default)}) - 3\ \mu g/m^3)/1.03$$

where TEOM 1400ab(default) means the result of the analyser with the default values used for the slope and the intercept in the software of the analyser.

6. Conclusions

Air quality has a high priority in European policy and legislation. Especial interest has been shown concerning the concentration of particulate matter in ambient air that causes serious health risks. To focus on this issue, the Commission has issued air quality directives to be followed to ensure reliable and comparable data regarding the concentrations of PM in the air. The directives define the reference methods to be used for the measurements, but have made it possible to use any other methods that a member state can prove fulfills the data quality objectives of the reference method. This process, the demonstration of equivalency, has been conducted for several candidate methods for $PM_{2.5}$ and PM_{10} measurement methods following the guidance report prepared by the EC Working Group.

The tests conducted were not fully compliant with GDE(09): only two campaigns instead of four per size class were performed, and only one site was employed instead of two. Furthermore, the concentrations during the PM_{10} campaigns did not meet the suitability criteria for the tests. In order to have a complete dataset, additional data would be needed from two campaigns performed at different sites having the same climatic conditions and aerosol content as met with in Finland, and with all the data fulfilling the criteria of suitability.

The test results from the $PM_{2.5}$ campaigns showed problems with two CMs, the Dekati PM10 impactor and the Osiris. The Dekati PM10 impactor passed the test for all data using the calibration equation, but it did not pass the subsets of individual campaigns (winter and spring campaigns) nor with data for $\geq$ 18 $\mu g/m^3$ (the method slightly overestimate the concentrations). As a result, the Dekati PM10 impactor can be used for indicative measurements for the $PM_{2.5}$ size class. In the case of the Osiris, the results showed that the instrument is not applicable for fixed measurements or for indicative measurements. In the case of the Verewa the test results for $\geq$ 18 $\mu g/m^3$ did not meet the criteria for uncertainty, but the number of data pairs was not adequate to make a conclusive judgment of the failure (see Table 5.8). All the other CMs passed the tests for fixed $PM_{2.5}$ measurements against the reference method using calibration equations. The calibration equations needed to correct the original data for each of the CMs are shown in Table 5.16.

In the case of the PM_{10} comparison, the most problematic issue was the low concentrations throughout the whole test period. Such low concentrations were rather exceptional, since cross-boarder episodes caused by forest fires, especially around St. Petersburg in Russia, are quite common during the summer time. In spring time, cleaning of the streets and the collection of winter sand from roads causes another concentration peak for PM_{10}. Since the PM concentrations were rather low during the PM_{10} test, it is more likely that most of that size class is due to $PM_{2.5}$. Nevertheless the test results were rather good for all of the CMs, and no clear failures were met with. The calibration equations are similar with those obtained from the $PM_{2.5}$ tests, as is shown in Table 5.16.

Because of the shortcomings of the data no proof of acceptance could be made. The site category, weather conditions, origin and mass concentration of the particles can be limiting factors for generalizing the test results. The results and functioning of the reference methods, however, have been very good for both of the size classes. In addition the use of Teflon filters appears to be a good choice.

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Appendices

A1 $PM_{2.5}$ equivalence tests for Dekati PM10 impactors

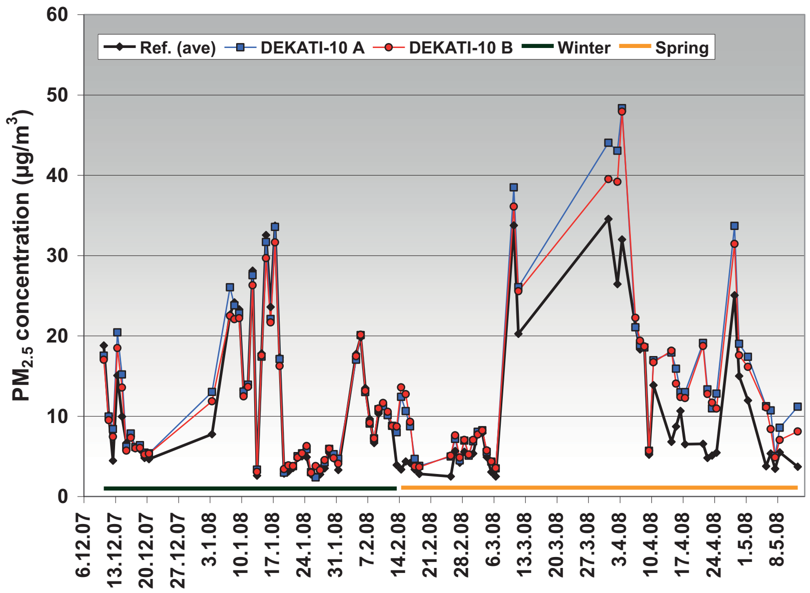

Figure A1.1. Time series of 24 h concentration values of Dekati PM10 impactors and the RMs during the $PM_{2.5}$ equivalence campaigns in Helsinki

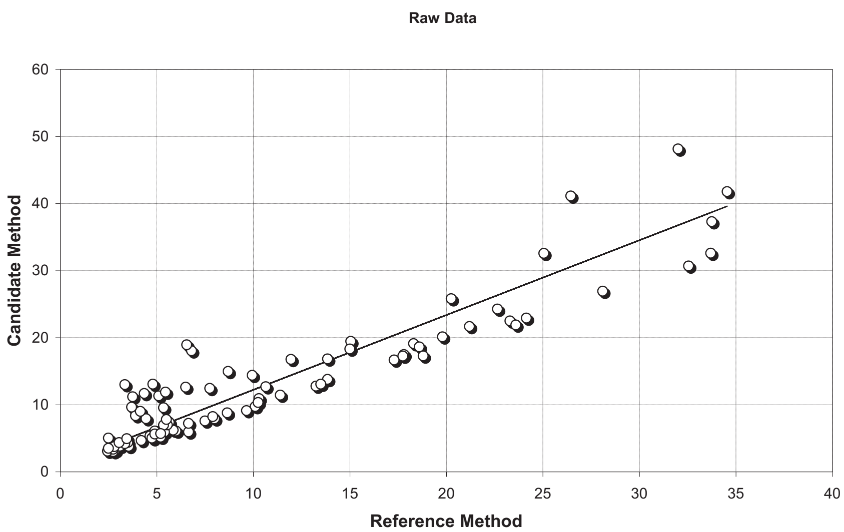

Figure A1.2. Scatter plot of Dekati PM10 impactor versus the RMs: Uncorrected data

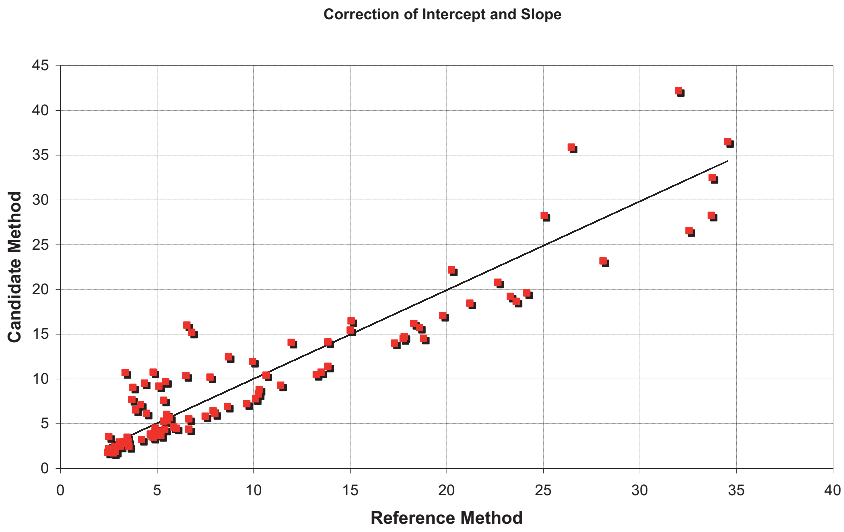

Figure A1.3. Scatter plot of Dekati PM10 impactor versus the RMs: Calibrated data

Table A1.1. Equivalence test results for Dekati PM10 impactor against the RMs for $PM_{2.5}$, all data

PM2.5	Equivalence field test		Number of data points:	89	
UNCORRECTED DATA			INTERCEPT CORRECTION		
REGRESSION OUTPUT			REGRESSION OUTPUT		
slope b	1.12	significant	slope b	1.12	significant
uncertainty of b	0.04		uncertainty of b	0.04	
intercept a	1.06	not significant	intercept a	0.00	not significant
uncertainty of a	0.60		uncertainty of a	0.60	
EQUIVALENCE TEST RESULTS			EQUIVALENCE TEST RESULTS		
random term	3.60	ug/m3	random term	3.65	ug/m3
bias at LV	4.53	ug/m3	bias at LV	3.47	ug/m3
combined uncertainty	5.78	ug/m3	combined uncertainty	5.04	ug/m3
relative uncertainty at the LV	19.28	fail	relative uncertainty at the LV	16.79	fail
RM between-sampler uncertainty	0.84	ug/m3	RM between-sampler uncertainty	0.84	ug/m3
SLOPE CORRECTION			INTERCEPT AND SLOPE CORRECTION		
REGRESSION OUTPUT			REGRESSION OUTPUT		
slope b	0.99	not significant	slope b	0.99	not significant
uncertainty of b	0.04		uncertainty of b	0.04	
intercept a	1.04	not significant	intercept a	0.09	not significant
uncertainty of a	0.54		uncertainty of a	0.54	
EQUIVALENCE TEST RESULTS			EQUIVALENCE TEST RESULTS		
random term	3.45	ug/m3	random term	3.51	ug/m3
bias at LV	0.78	ug/m3	bias at LV	-0.16	ug/m3
combined uncertainty	3.54	ug/m3	combined uncertainty	3.51	ug/m3
relative uncertainty at the LV	11.80	pass	relative uncertainty at the LV	11.70	pass
RM between-sampler uncertainty	0.84	ug/m3	RM between-sampler uncertainty	0.84	ug/m3

A2. $PM_{2.5}$ equivalence tests for FH 62 I-R analysers

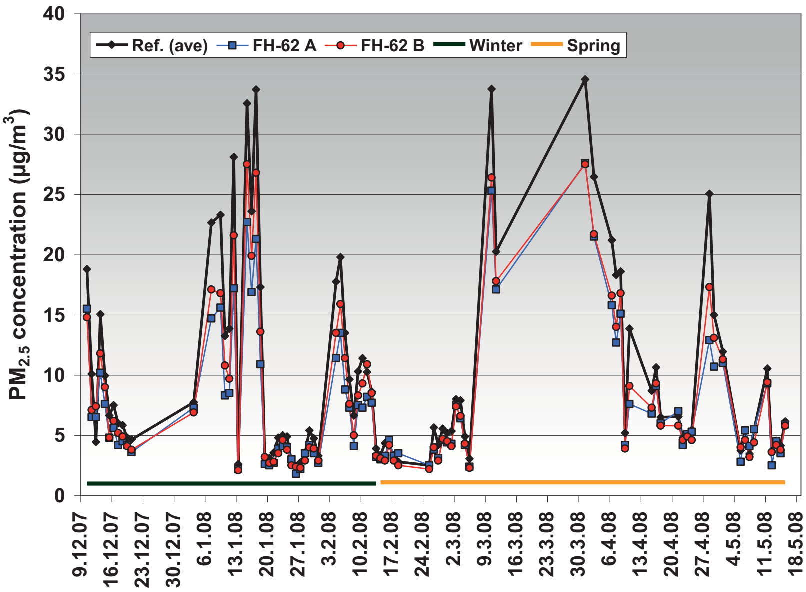

Figure A2.1. Time series of 24 h concentration values of FH 62 I-R and the RMs during the $PM_{2.5}$ equivalence campaigns in Helsinki

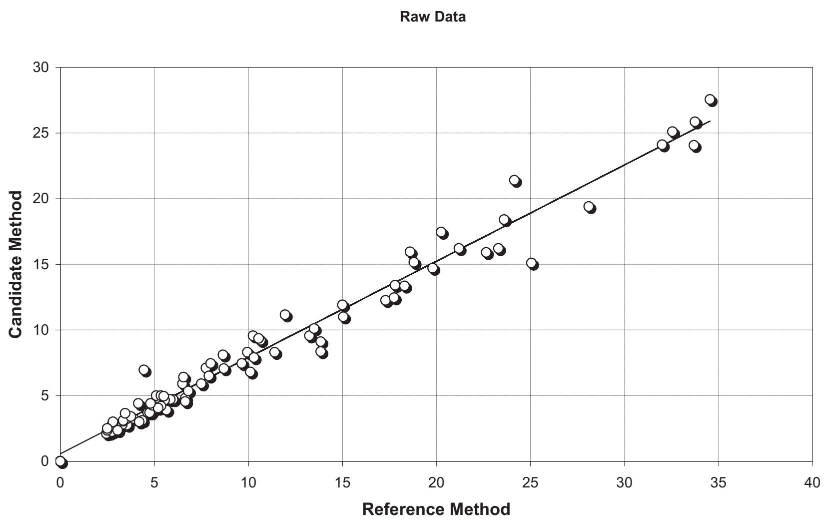

Figure A2.2. Scatter plot of FH 62 I-R versus the RMs: Uncorrected data

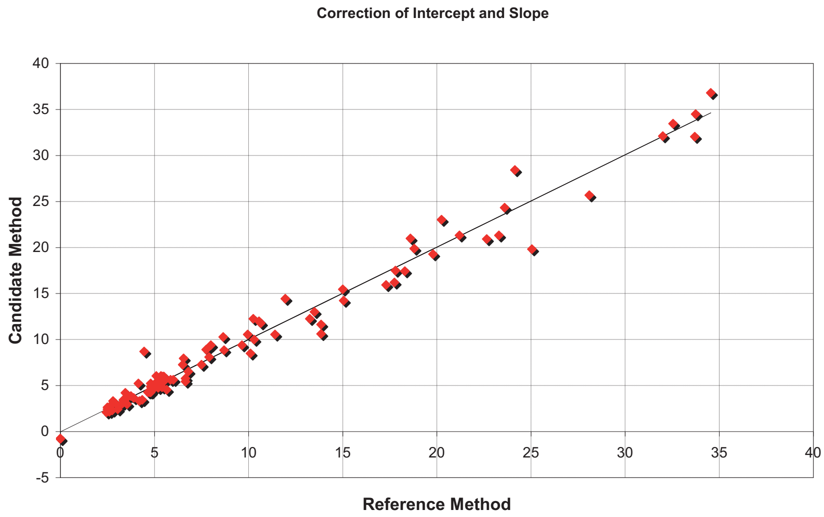

Figure A2.3. Scatter plot of FH 62 I-R versus the RMs: Calibrated data

Table A2.1. Equivalence test results for FH 62 I-R against the RMs for $PM_{2.5}$, all data.

PM2.5	Equivalence field test		Number of data points:	88	
UNCORRECTED DATA			INTERCEPT CORRECTION		
REGRESSION OUTPUT			REGRESSION OUTPUT		
slope b	0.74	significant	slope b	0.74	significant
uncertainty of b	0.01		uncertainty of b	0.01	
intercept a	0.54	significant	intercept a	0.02	not significant
uncertainty of a	0.17		uncertainty of a	0.17	
EQUIVALENCE TEST RESULTS			EQUIVALENCE TEST RESULTS		
random term	0.00	ug/m3	random term	0.00	ug/m3
bias at LV	-7.33	ug/m3	bias at LV	-7.88	ug/m3
combined uncertainty	7.33	ug/m3	combined uncertainty	7.88	ug/m3
relative uncertainty at the LV	24.44	**fail**	relative uncertainty at the LV	26.27	**fail**
RM between-sampler uncertainty	1.03	ug/m3	RM between-sampler uncertainty	1.03	ug/m3
SLOPE CORRECTION			INTERCEPT AND SLOPE CORRECTION		
REGRESSION OUTPUT			REGRESSION OUTPUT		
slope b	1.00	not significant	slope b	1.00	not significant
uncertainty of b	0.02		uncertainty of b	0.02	
intercept a	0.73	significant	intercept a	-0.01	not significant
uncertainty of a	0.23		uncertainty of a	0.23	
EQUIVALENCE TEST RESULTS			EQUIVALENCE TEST RESULTS		
random term	0.98	ug/m3	random term	1.00	ug/m3
bias at LV	0.81	ug/m3	bias at LV	0.07	ug/m3
combined uncertainty	1.27	ug/m3	combined uncertainty	1.00	ug/m3
relative uncertainty at the LV	4.24	**pass**	relative uncertainty at the LV	3.33	**pass**
RM between-sampler uncertainty	1.03	ug/m3	RM between-sampler uncertainty	1.03	ug/m3

A3. $PM_{2.5}$ equivalence tests for Grimm 180 analysers

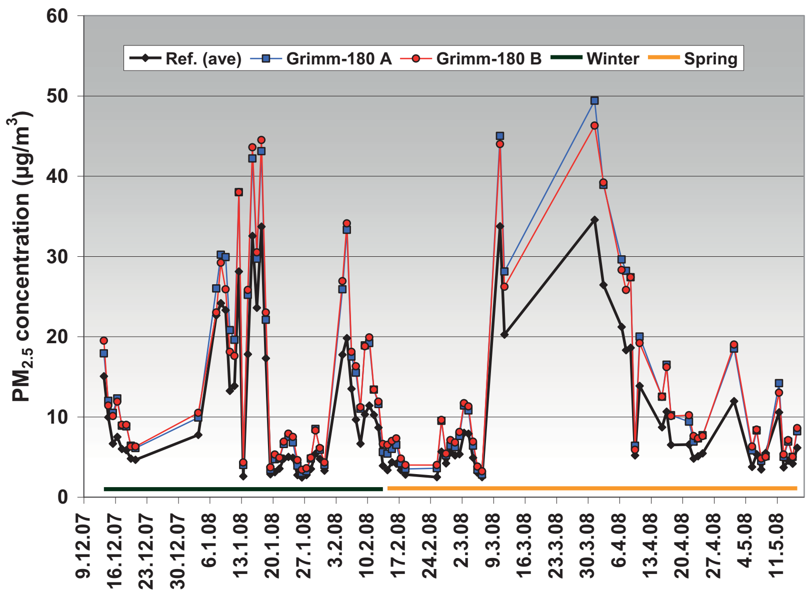

Figure A3.1. Time series of 24 h concentration values of Grimm 180 and the RMs during the $PM_{2.5}$ equivalence campaigns in Helsinki

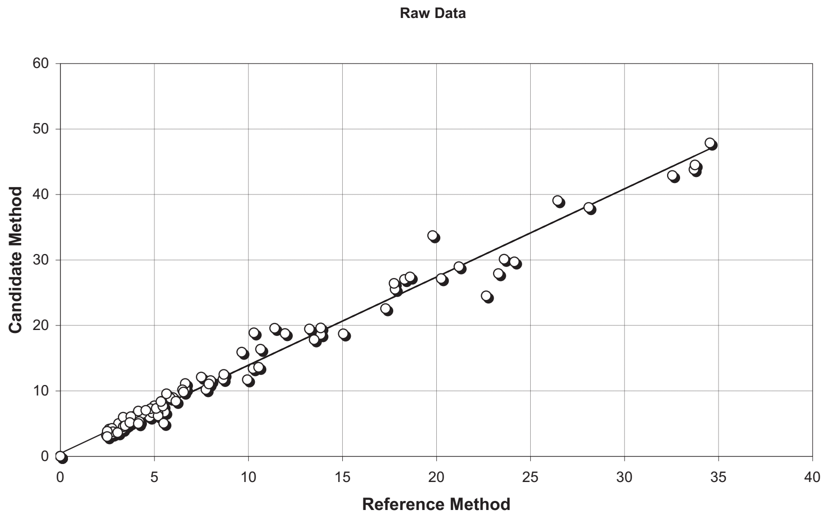

Figure A3.2. Scatter plot of Grimm 180 versus the RMs: Uncorrected data

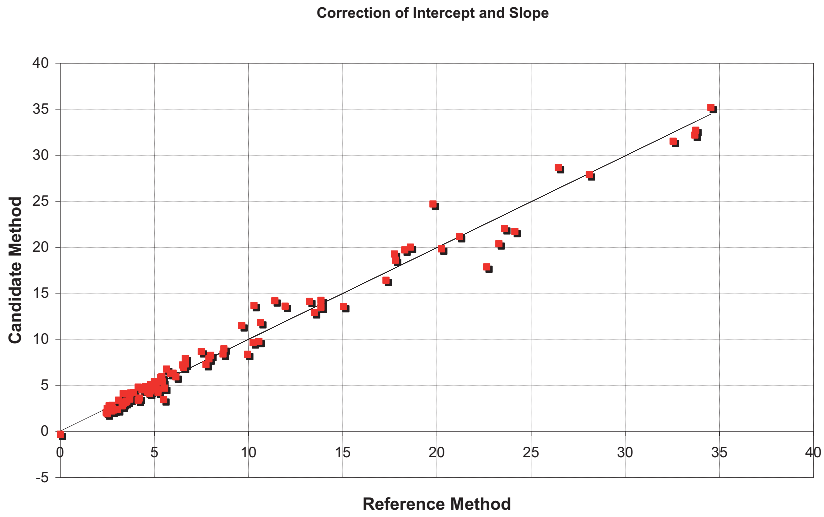

Figure A3.3. Scatter plot of Grimm 180 versus the RMs: Calibrated data

Table A3.1. Equivalence test results for Grimm 180 against the RMs for $PM_{2.5}$, all data.

PM2.5	Equivalence field test		Number of data points:	86	
UNCORRECTED DATA			INTERCEPT CORRECTION		
REGRESSION OUTPUT			REGRESSION OUTPUT		
slope b	*1.34*	significant	*slope b*	*1.34*	significant
uncertainty of b	*0.02*		*uncertainty of b*	*0.02*	
intercept a	*0.41*	not significant	*intercept a*	*-0.02*	not significant
uncertainty of a	*0.30*		*uncertainty of a*	*0.28*	
EQUIVALENCE TEST RESULTS			EQUIVALENCE TEST RESULTS		
random term	1.60	ug/m3	random term	1.60	ug/m3
bias at LV	10.73	ug/m3	bias at LV	10.33	ug/m3
combined uncertainty	10.85	ug/m3	combined uncertainty	10.45	ug/m3
relative uncertainty at the LV	36.17	**fail**	relative uncertainty at the LV	34.83	**fail**
RM between-sampler uncertainty	0.70	ug/m3	RM between-sampler uncertainty	0.70	ug/m3
SLOPE CORRECTION			INTERCEPT AND SLOPE CORRECTION		
REGRESSION OUTPUT			REGRESSION OUTPUT		
slope b	*1.00*	not significant	*slope b*	*1.00*	not significant
uncertainty of b	*0.02*		*uncertainty of b*	*0.02*	
intercept a	*0.33*	not significant	*intercept a*	*0.02*	not significant
uncertainty of a	*0.21*		*uncertainty of a*	*0.21*	
EQUIVALENCE TEST RESULTS			EQUIVALENCE TEST RESULTS		
random term	1.26	ug/m3	random term	1.30	ug/m3
bias at LV	0.24	ug/m3	bias at LV	-0.06	ug/m3
combined uncertainty	1.28	ug/m3	combined uncertainty	1.30	ug/m3
relative uncertainty at the LV	4.28	**pass**	relative uncertainty at the LV	4.32	**pass**
RM between-sampler uncertainty	0.70	ug/m3	RM between-sampler uncertainty	0.70	ug/m3

A4. $PM_{2.5}$ equivalence tests for Environnement MP101 CLS analysers

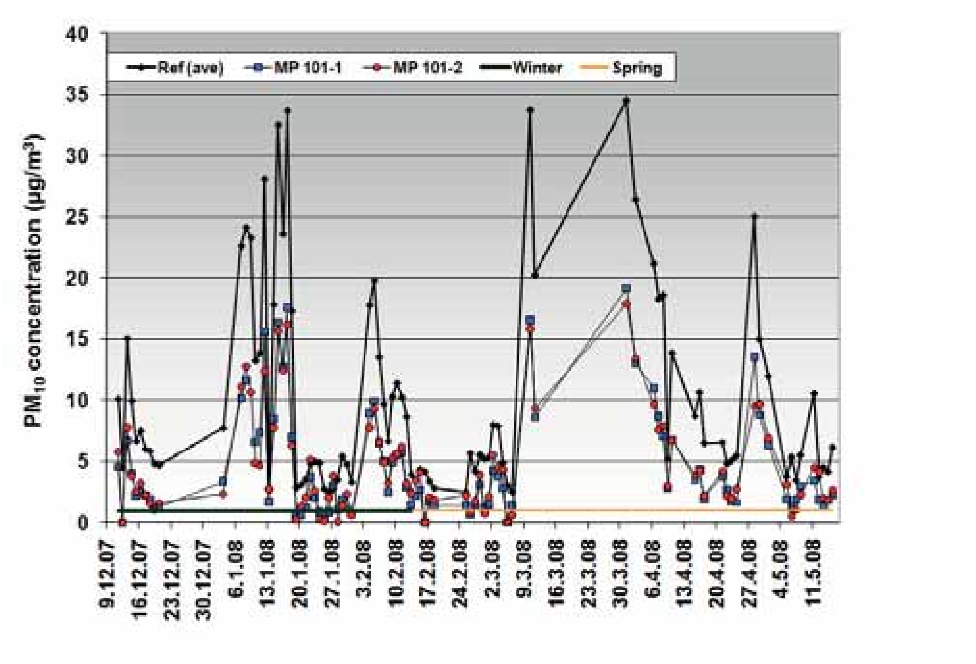

Figure A4.1. Time series of 24 h concentration values of MP101 and the RMs during the $PM_{2.5}$ equivalence campaigns in Helsinki

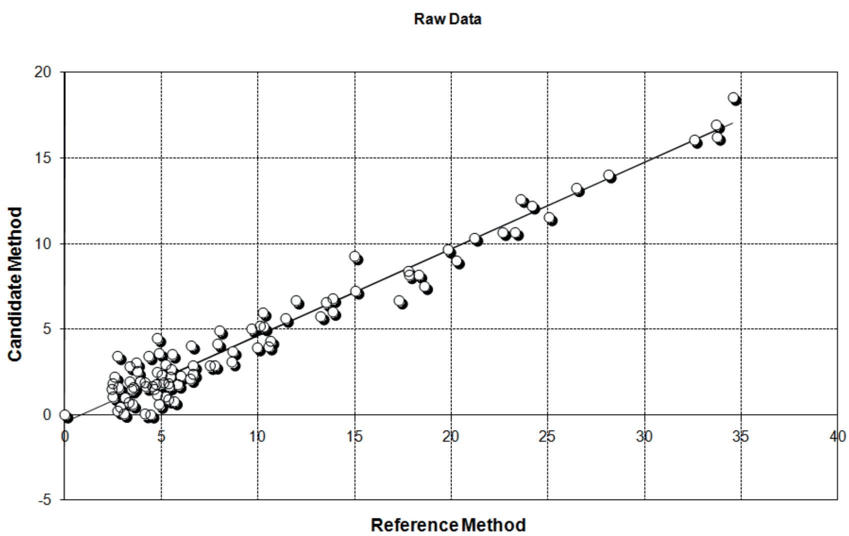

Figure A4.2. Scatter plot of MP101 versus the RMs: Uncorrected data

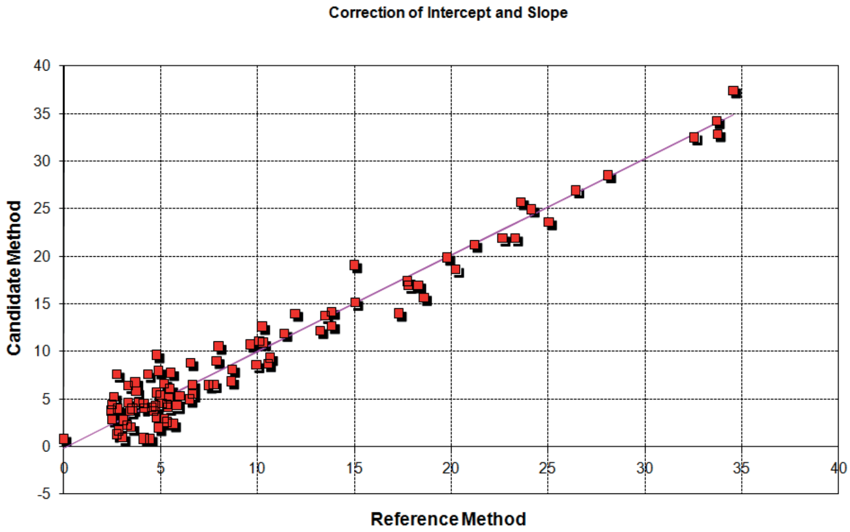

Figure A4.3. Scatter plot of MP101 versus the RMs: Calibrated data

Table A4.1. Equivalence test results for MP101 against the RMs for $PM_{2.5}$, all data

PM2.5	Equivalence field test		Number of data points:	89	
UNCORRECTED DATA			INTERCEPT CORRECTION		
REGRESSION OUTPUT			REGRESSION OUTPUT		
slope b	0.51	significant	slope b	0.51	significant
uncertainty of b	0.01		uncertainty of b	0.01	
intercept a	-0.43	significant	intercept a	0.00	not significant
uncertainty of a	0.16		uncertainty of a	0.15	
EQUIVALENCE TEST RESULTS			EQUIVALENCE TEST RESULTS		
random term	0.00	ug/m3	random term	0.00	ug/m3
bias at LV	-15.23	ug/m3	bias at LV	-14.80	ug/m3
combined uncertainty	15.23	ug/m3	combined uncertainty	14.80	ug/m3
relative uncertainty at the LV	50.77	fail	relative uncertainty at the LV	49.34	fail
RM between-sampler uncertainty	1.07	ug/m3	RM between-sampler uncertainty	1.07	ug/m3
SLOPE CORRECTION			INTERCEPT AND SLOPE CORRECTION		
REGRESSION OUTPUT			REGRESSION OUTPUT		
slope b	1.01	not significant	slope b	1.01	not significant
uncertainty of b	0.02		uncertainty of b	0.02	
intercept a	-1.00	significant	intercept a	-0.15	not significant
uncertainty of a	0.30		uncertainty of a	0.30	
EQUIVALENCE TEST RESULTS			EQUIVALENCE TEST RESULTS		
random term	1.54	ug/m3	random term	1.55	ug/m3
bias at LV	-0.56	ug/m3	bias at LV	0.29	ug/m3
combined uncertainty	1.64	ug/m3	combined uncertainty	1.58	ug/m3
relative uncertainty at the LV	5.48	pass	relative uncertainty at the LV	5.26	pass
RM between-sampler uncertainty	1.07	ug/m3	RM between-sampler uncertainty	1.07	ug/m3

A5. PM$_{2.5}$ equivalence tests for Osiris analysers

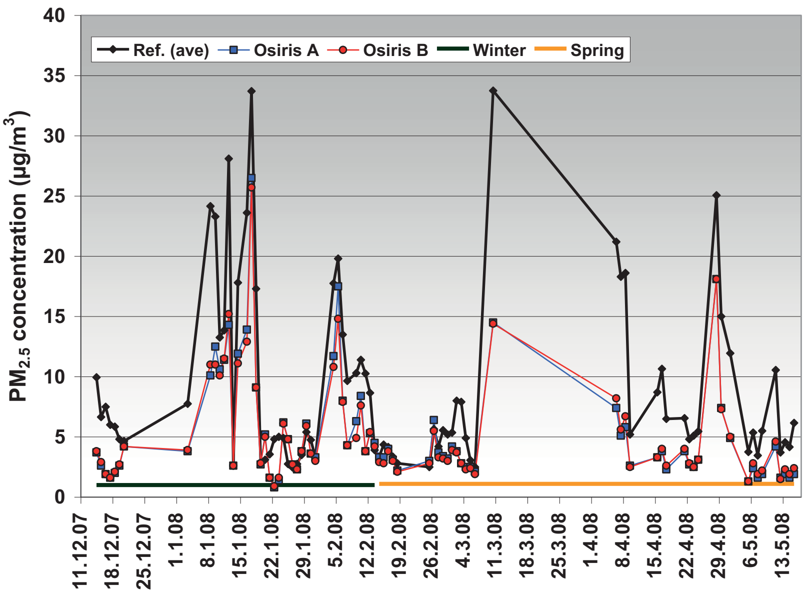

Figure A5.1. Time series of 24 h concentration values of Osiris and the RMs during the PM$_{2.5}$ equivalence campaigns in Helsinki

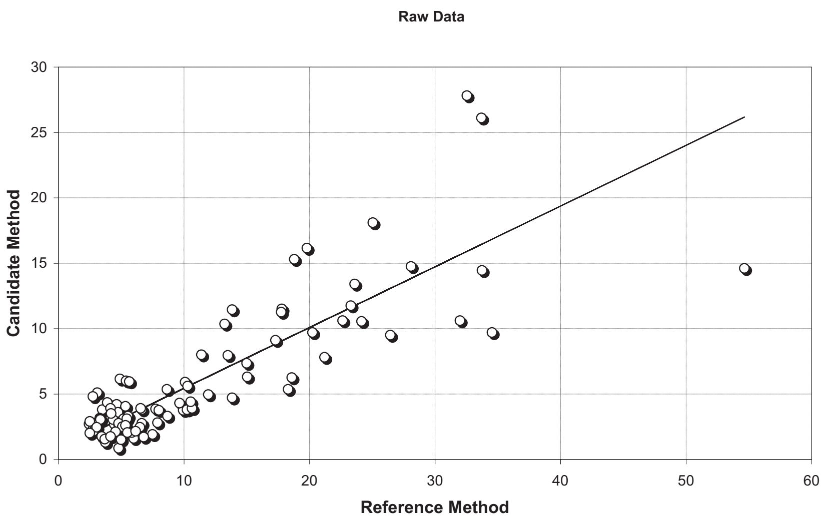

Figure A5.2. Scatter plot of Osiris versus the RMs: Uncorrected data

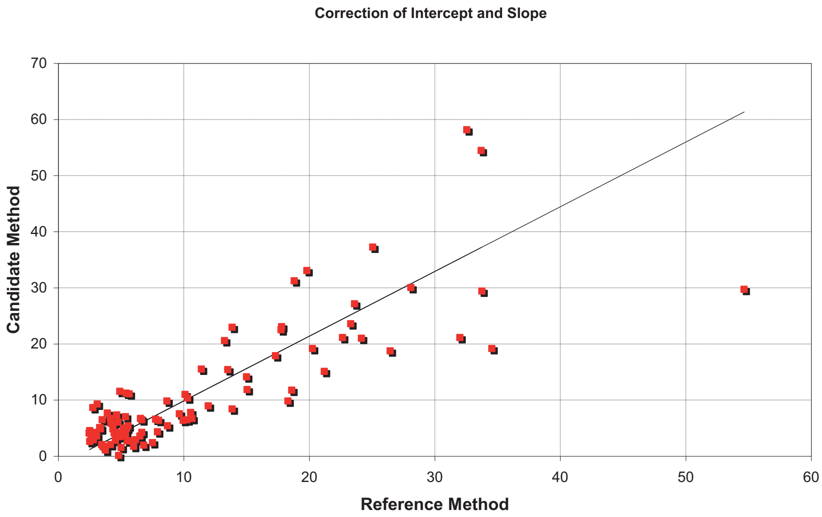

Figure A5.3. Scatter plot of Osiris versus the RMs: Calibrated data

Table A5.1. Equivalence test results for Osiris against the RMs for $PM_{2.5}$, all data.

PM2.5	Equivalence field test		Number of data points:	91	
UNCORRECTED DATA			INTERCEPT CORRECTION		
REGRESSION OUTPUT			REGRESSION OUTPUT		
slope b	*0.56*	significant	*slope b*	*0.56*	significant
uncertainty of b	*0.03*		*uncertainty of b*	*0.03*	
intercept a	*0.06*	not significant	*intercept a*	*0.00*	not significant
uncertainty of a	*0.43*		*uncertainty of a*	*0.43*	
EQUIVALENCE TEST RESULTS			EQUIVALENCE TEST RESULTS		
random term	2.56	ug/m3	random term	2.59	ug/m3
bias at LV	-13.25	ug/m3	bias at LV	-13.30	ug/m3
combined uncertainty	13.49	ug/m3	combined uncertainty	13.55	ug/m3
relative uncertainty at the LV	44.97	**fail**	relative uncertainty at the LV	45.18	**fail**
RM between-sampler uncertainty	0.37	ug/m3	RM between-sampler uncertainty	0.37	ug/m3
SLOPE CORRECTION			INTERCEPT AND SLOPE CORRECTION		
REGRESSION OUTPUT			REGRESSION OUTPUT		
slope b	*1.09*	not significant	*slope b*	*1.09*	not significant
uncertainty of b	*0.06*		*uncertainty of b*	*0.06*	
intercept a	*-0.83*	not significant	*intercept a*	*-0.93*	not significant
uncertainty of a	*0.77*		*uncertainty of a*	*0.77*	
EQUIVALENCE TEST RESULTS			EQUIVALENCE TEST RESULTS		
random term	4.89	ug/m3	random term	4.91	ug/m3
bias at LV	1.91	ug/m3	bias at LV	1.80	ug/m3
combined uncertainty	5.25	ug/m3	combined uncertainty	5.23	ug/m3
relative uncertainty at the LV	17.50	**fail**	relative uncertainty at the LV	17.44	**fail**
RM between-sampler uncertainty	0.37	ug/m3	RM between-sampler uncertainty	0.37	ug/m3

A6. $PM_{2.5}$ equivalence tests for SHARP analysers

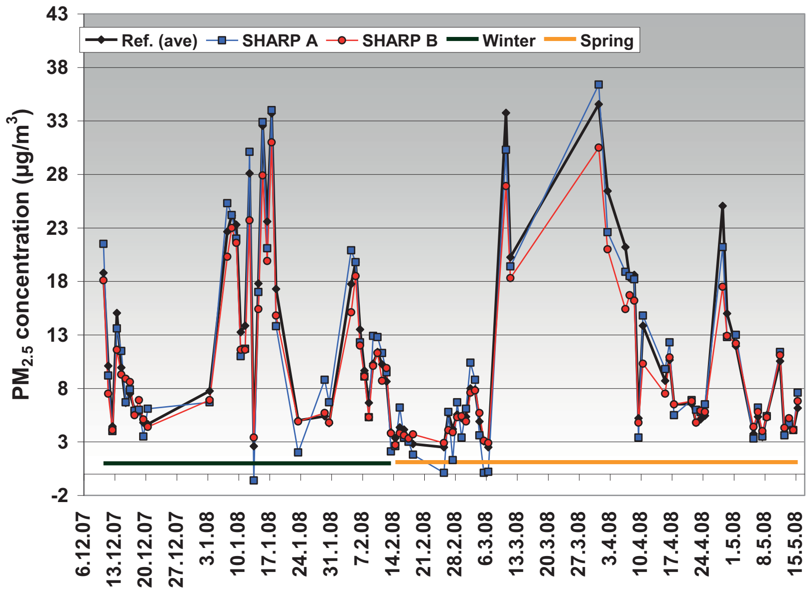

Figure A6.1. Time series of 24 h concentration values of SHARP and the RMs during the $PM_{2.5}$ equivalence campaigns in Helsinki

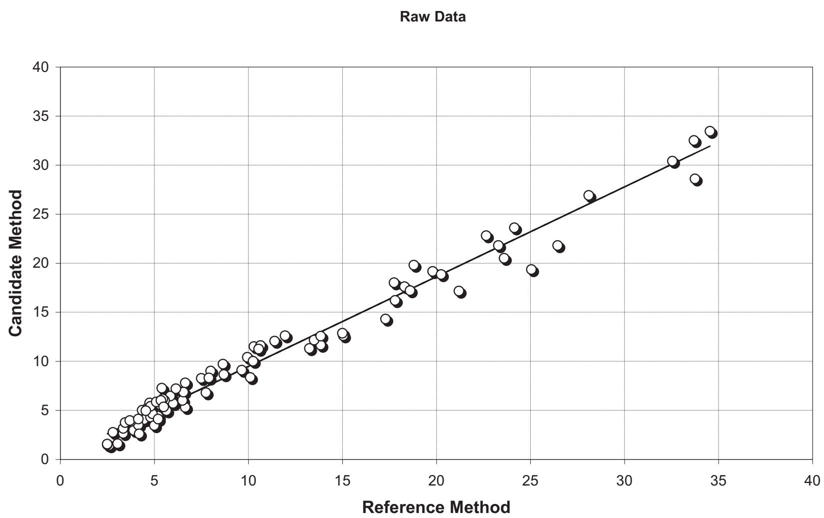

Figure A6.2. Scatter plot of SHARP versus the RMs: Uncorrected data

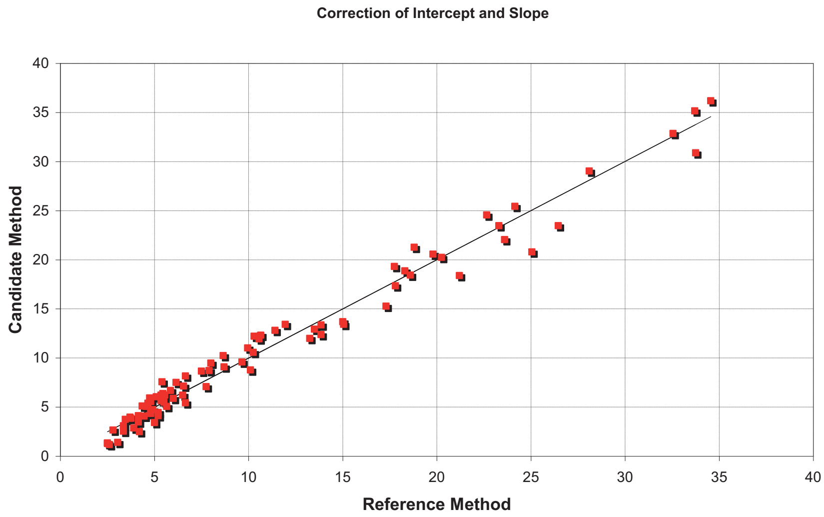

Figure A6.3. Scatter plot of SHARP versus the RMs: Calibrated data

Table A6.1. Equivalence test results for SHARP against the RMs for $PM_{2.5}$, all data

PM2.5	Equivalence field test		Number of data points:	91	
UNCORRECTED DATA			INTERCEPT CORRECTION		
REGRESSION OUTPUT			*REGRESSION OUTPUT*		
slope b	*0.92*	significant	*slope b*	*0.92*	significant
uncertainty of b	*0.01*		*uncertainty of b*	*0.01*	
intercept a	*0.29*	not significant	*intercept a*	*0.00*	not significant
uncertainty of a	*0.19*		*uncertainty of a*	*0.19*	
EQUIVALENCE TEST RESULTS			*EQUIVALENCE TEST RESULTS*		
random term	0.00	ug/m3	random term	0.00	ug/m3
bias at LV	-2.21	ug/m3	bias at LV	-2.51	ug/m3
combined uncertainty	2.21	ug/m3	combined uncertainty	2.51	ug/m3
relative uncertainty at the LV	7.37	**pass**	relative uncertainty at the LV	8.36	**pass**
RM between-sampler uncertainty	1.61	ug/m3	RM between-sampler uncertainty	1.61	ug/m3
SLOPE CORRECTION			INTERCEPT AND SLOPE CORRECTION		
REGRESSION OUTPUT			*REGRESSION OUTPUT*		
slope b	*1.00*	not significant	*slope b*	*1.00*	not significant
uncertainty of b	*0.02*		*uncertainty of b*	*0.02*	
intercept a	*0.31*	not significant	*intercept a*	*-0.01*	not significant
uncertainty of a	*0.21*		*uncertainty of a*	*0.21*	
EQUIVALENCE TEST RESULTS			*EQUIVALENCE TEST RESULTS*		
random term	0.00	ug/m3	random term	0.00	ug/m3
bias at LV	0.34	ug/m3	bias at LV	0.02	ug/m3
combined uncertainty	0.34	ug/m3	combined uncertainty	0.02	ug/m3
relative uncertainty at the LV	1.14	**pass**	relative uncertainty at the LV	0.06	**pass**
RM between-sampler uncertainty	1.61	ug/m3	RM between-sampler uncertainty	1.61	ug/m3

A7. $PM_{2.5}$ equivalence tests for TEOM 1400ab analysers

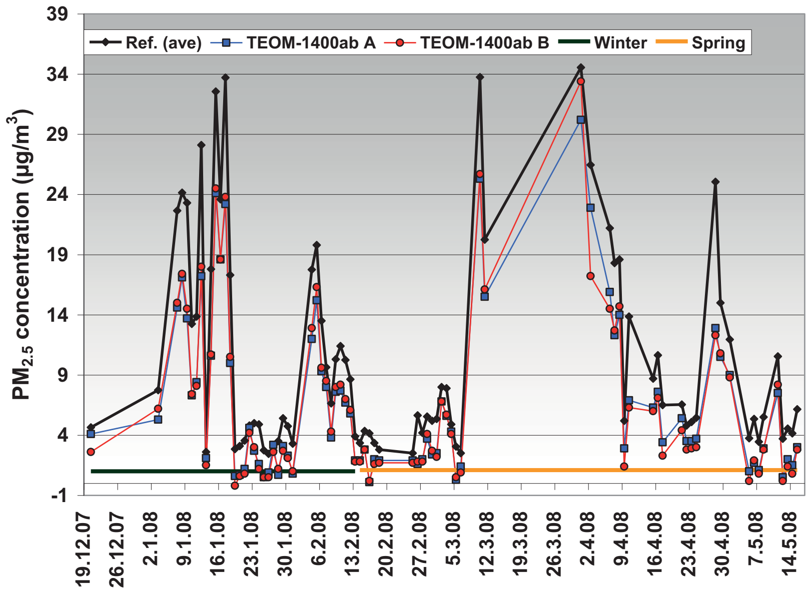

Figure A7.1. Time series of 24 h concentration values of TEOM 1400ab and the RMs during the $PM_{2.5}$ equivalence campaigns in Helsinki

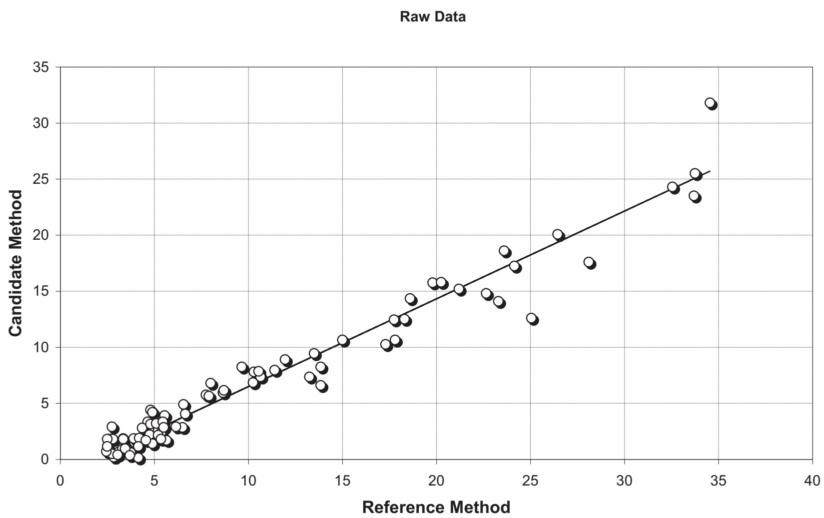

Figure A7.2. Scatter plot of TEOM 1400ab versus the RMs: Uncorrected data

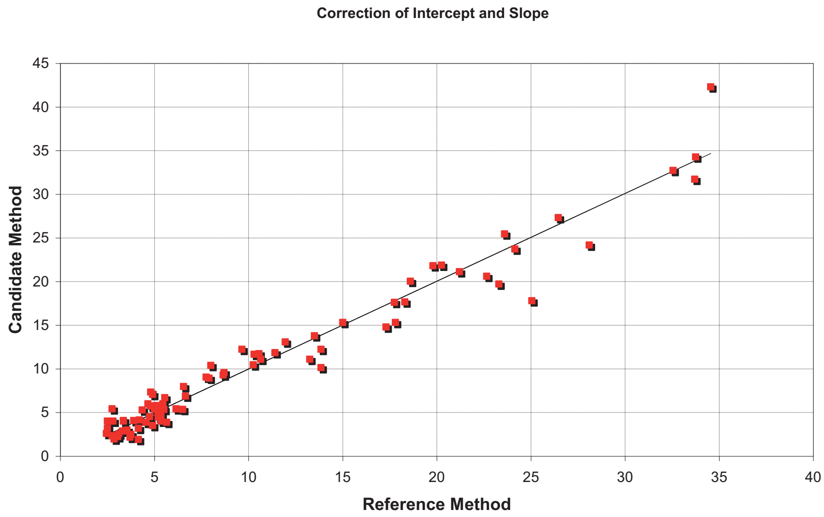

Figure A7.3. Scatter plot of TEOM 1400ab versus the RMs: Calibrated data

Table A7.1. Equivalence test results for TEOM 1400ab against the RMs for $PM_{2.5}$, all data

PM2.5	Equivalence field test		Number of data points:	90	
UNCORRECTED DATA			INTERCEPT CORRECTION		
REGRESSION OUTPUT			REGRESSION OUTPUT		
slope b	0.80	significant	slope b	0.80	significant
uncertainty of b	0.03		uncertainty of b	0.03	
intercept a	-1.25	significant	intercept a	0.00	not significant
uncertainty of a	0.33		uncertainty of a	0.33	
EQUIVALENCE TEST RESULTS			EQUIVALENCE TEST RESULTS		
random term	1.92	ug/m3	random term	1.95	ug/m3
bias at LV	-7.33	ug/m3	bias at LV	-6.08	ug/m3
combined uncertainty	7.58	ug/m3	combined uncertainty	6.39	ug/m3
relative uncertainty at the LV	25.26	fail	relative uncertainty at the LV	21.30	fail
RM between-sampler uncertainty	0.64	ug/m3	RM between-sampler uncertainty	0.64	ug/m3
SLOPE CORRECTION			INTERCEPT AND SLOPE CORRECTION		
REGRESSION OUTPUT			REGRESSION OUTPUT		
slope b	1.01	not significant	slope b	1.01	not significant
uncertainty of b	0.03		uncertainty of b	0.03	
intercept a	-1.67	significant	intercept a	-0.11	not significant
uncertainty of a	0.42		uncertainty of a	0.42	
EQUIVALENCE TEST RESULTS			EQUIVALENCE TEST RESULTS		
random term	2.58	ug/m3	random term	2.60	ug/m3
bias at LV	-1.35	ug/m3	bias at LV	0.21	ug/m3
combined uncertainty	2.92	ug/m3	combined uncertainty	2.61	ug/m3
relative uncertainty at the LV	9.72	pass	relative uncertainty at the LV	8.71	pass
RM between-sampler uncertainty	0.64	ug/m3	RM between-sampler uncertainty	0.64	ug/m3

A8. $PM_{2.5}$ equivalence tests for Verewa analysers

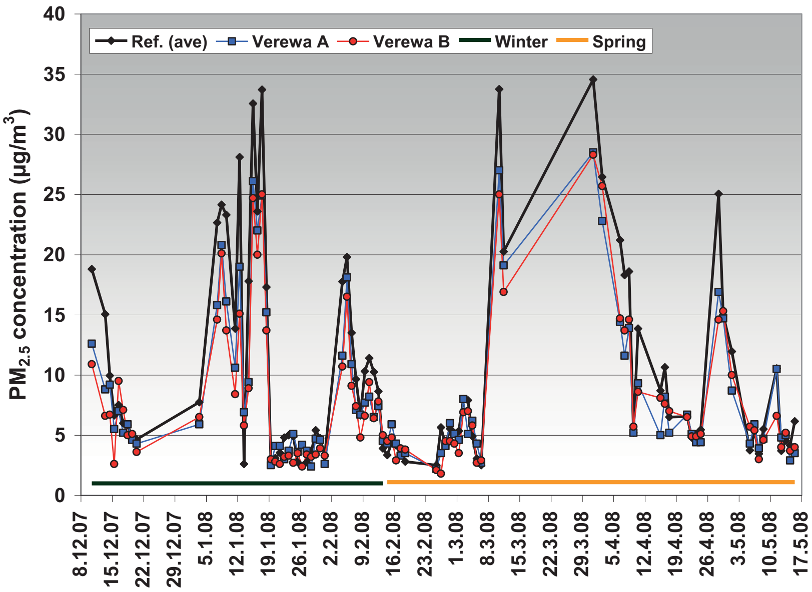

Figure A8.1. Time series of 24 h concentration values of Verewa and the RMs during the $PM_{2.5}$ equivalence campaigns in Helsinki

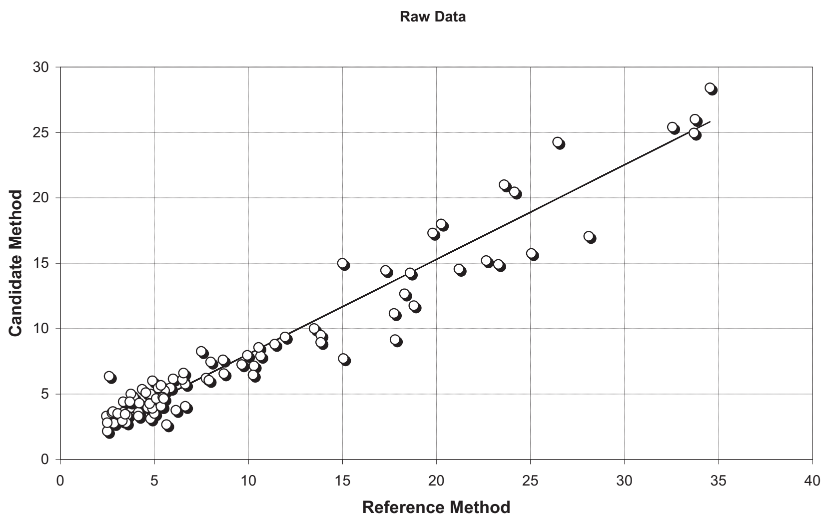

Figure A8.2. Scatter plot of Verewa versus the RMs: Uncorrected data

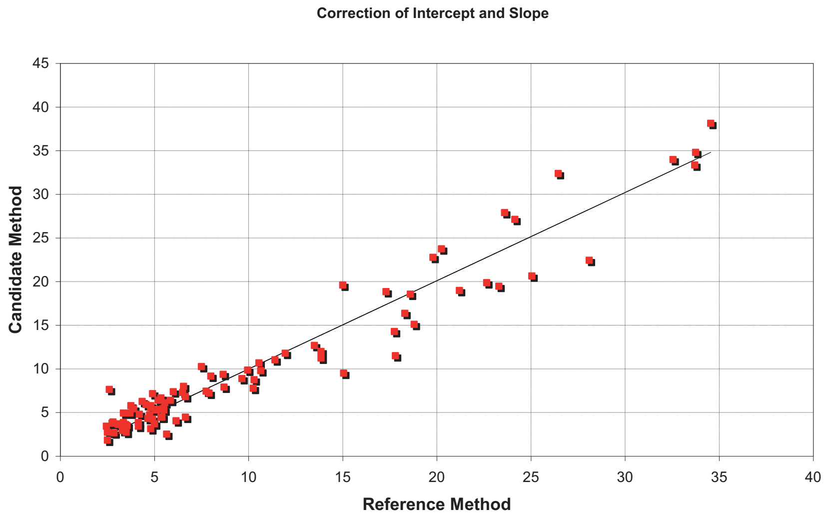

Figure A8.3. Scatter plot of Verewa versus the RMs: Calibrated data

Table A8.1. Equivalence test results for Verewa against the RMs for $PM_{2.5}$, all data

PM2.5	Equivalence field test		Number of data points:	91	
UNCORRECTED DATA			INTERCEPT CORRECTION		
REGRESSION OUTPUT			*REGRESSION OUTPUT*		
slope b	*0.72*	significant	*slope b*	*0.72*	significant
uncertainty of b	*0.02*		*uncertainty of b*	*0.02*	
intercept a	*0.85*	significant	*intercept a*	*0.00*	not significant
uncertainty of a	*0.27*		*uncertainty of a*	*0.27*	
EQUIVALENCE TEST RESULTS			*EQUIVALENCE TEST RESULTS*		
random term	1.24	ug/m3	random term	1.27	ug/m3
bias at LV	-7.40	ug/m3	bias at LV	-8.25	ug/m3
combined uncertainty	7.50	ug/m3	combined uncertainty	8.35	ug/m3
relative uncertainty at the LV	25.01	**fail**	relative uncertainty at the LV	27.83	**fail**
RM between-sampler uncertainty	1.02	ug/m3	RM between-sampler uncertainty	1.02	ug/m3
SLOPE CORRECTION			INTERCEPT AND SLOPE CORRECTION		
REGRESSION OUTPUT			*REGRESSION OUTPUT*		
slope b	*1.01*	not significant	*slope b*	*1.01*	not significant
uncertainty of b	*0.03*		*uncertainty of b*	*0.03*	
intercept a	*1.06*	significant	*intercept a*	*-0.11*	not significant
uncertainty of a	*0.37*		*uncertainty of a*	*0.37*	
EQUIVALENCE TEST RESULTS			*EQUIVALENCE TEST RESULTS*		
random term	2.07	ug/m3	random term	2.09	ug/m3
bias at LV	1.40	ug/m3	bias at LV	0.22	ug/m3
combined uncertainty	2.50	ug/m3	combined uncertainty	2.10	ug/m3
relative uncertainty at the LV	8.33	**pass**	relative uncertainty at the LV	7.00	**pass**
RM between-sampler uncertainty	1.02	ug/m3	RM between-sampler uncertainty	1.02	ug/m3

A9. PM$_{10}$ equivalence tests for FH 62 I-R analysers

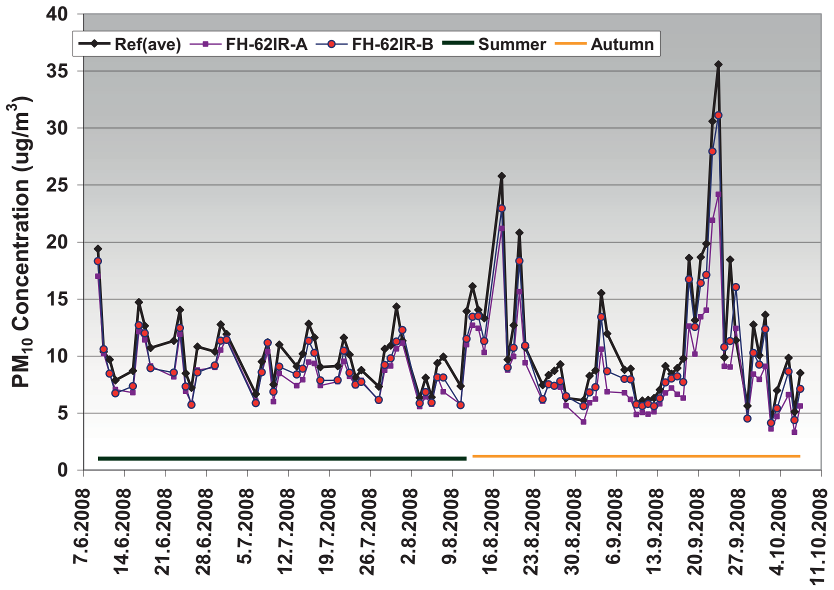

Figure A9.1. Time series of 24 h concentration values of FH 62 I-R and the RMs during the PM$_{10}$ equivalence campaigns in Helsinki

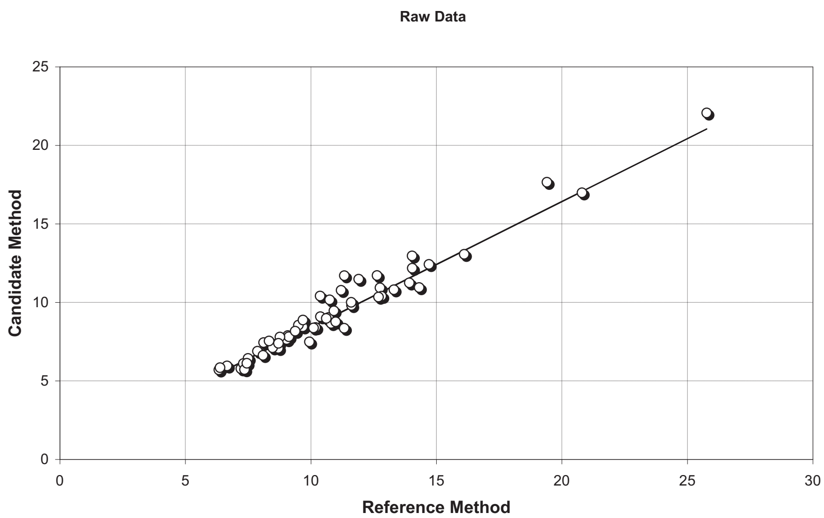

Figure A9.2. Scatter plot of FH 62 I-R versus the RMs: Uncorrected data

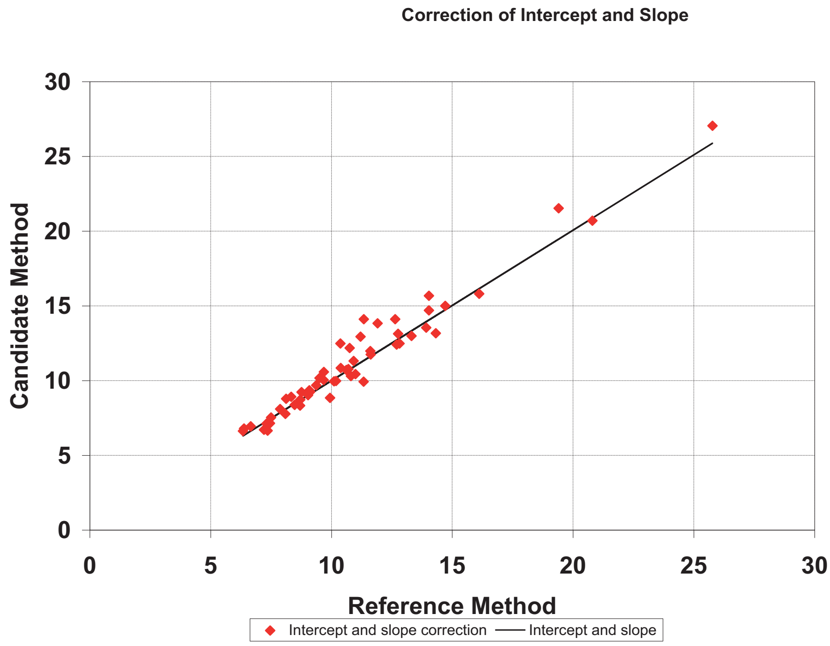

Figure A9.3. Scatter plot of FH 62 I-R versus the RMs: Calibrated data

Table A9.1. Equivalence test results for FH 62 I-R against the RMs for PM_{10}, all data.

PM 10	Equivalence field test		Number of data points:	90	
UNCORRECTED DATA			INTERCEPT CORRECTION		
REGRESSION OUTPUT			REGRESSION OUTPUT		
slope b	0.80	significant	slope b	0.80	significant
uncertainty of b	0.02		uncertainty of b	0.02	
intercept a	0.43	not significant	intercept a	0.00	not significant
uncertainty of a	0.26		uncertainty of a	0.26	
EQUIVALENCE TEST RESULTS			EQUIVALENCE TEST RESULTS		
random term	0.00	ug/m3	random term	0.00	ug/m3
bias at LV	-9.69	ug/m3	bias at LV	-10.11	ug/m3
combined uncertainty	9.69	ug/m3	combined uncertainty	10.11	ug/m3
relative uncertainty at the LV	19.38	fail	relative uncertainty at the LV	20.23	fail
RM between-sampler uncertainty	1.14	ug/m3	RM between-sampler uncertainty	1.14	ug/m3
SLOPE CORRECTION			INTERCEPT AND SLOPE CORRECTION		
REGRESSION OUTPUT			REGRESSION OUTPUT		
slope b	1.01	not significant	slope b	1.01	not significant
uncertainty of b	0.03		uncertainty of b	0.03	
intercept a	0.45	not significant	intercept a	-0.08	not significant
uncertainty of a	0.32		uncertainty of a	0.32	
EQUIVALENCE TEST RESULTS			EQUIVALENCE TEST RESULTS		
random term	1.21	ug/m3	random term	1.24	ug/m3
bias at LV	0.81	ug/m3	bias at LV	0.28	ug/m3
combined uncertainty	1.46	ug/m3	combined uncertainty	1.27	ug/m3
relative uncertainty at the LV	2.92	pass	relative uncertainty at the LV	2.54	pass
RM between-sampler uncertainty	1.14	ug/m3	RM between-sampler uncertainty	1.14	ug/m3

A10. PM$_{10}$ equivalence tests for Grimm 180 analysers

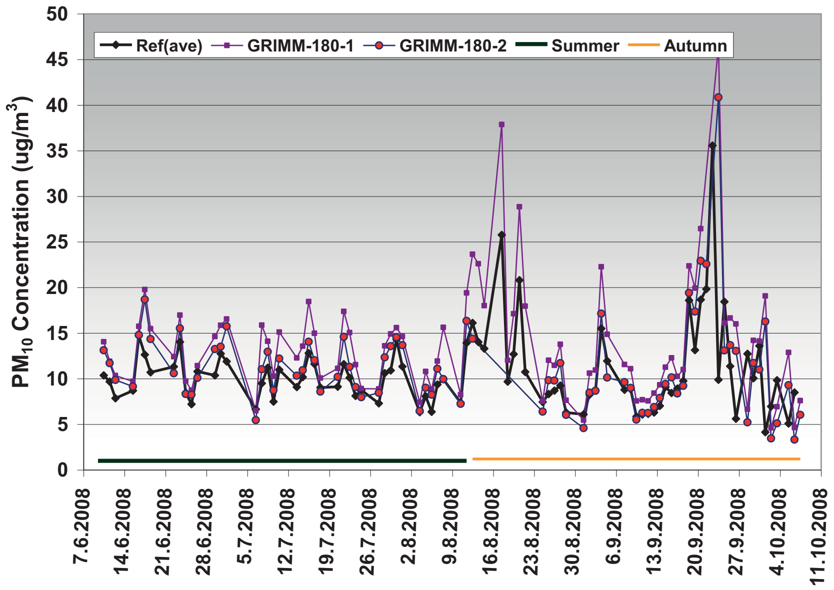

Figure A10.1. Time series of 24 h concentration values of Grimm 180 and the RMs during the PM$_{10}$ equivalence campaigns in Helsinki

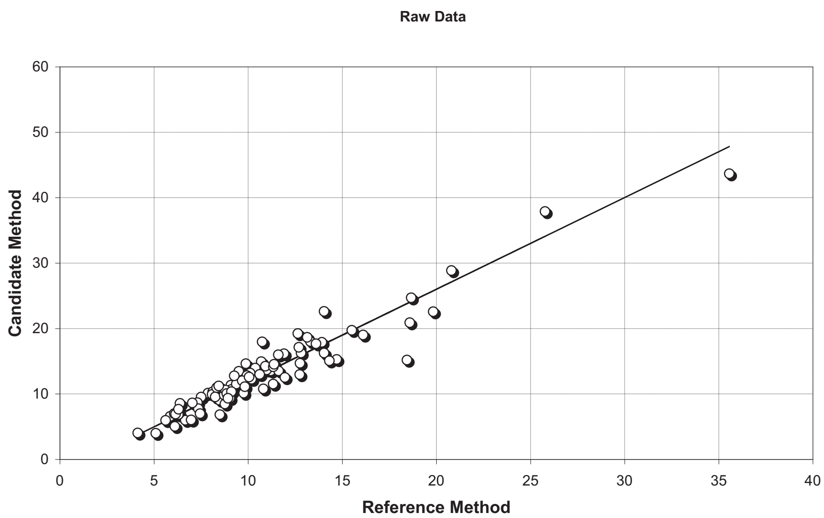

Figure A10.2. Scatter plot of Grimm 180 versus the RMs: Uncorrected data

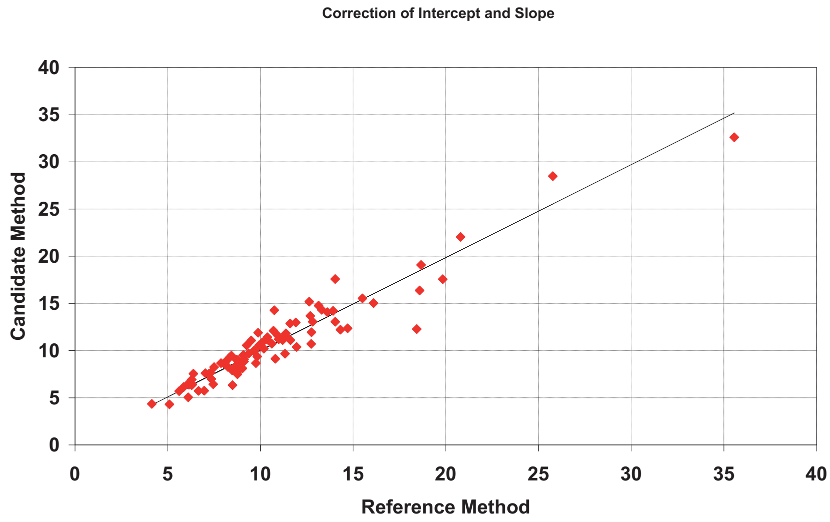

Figure A10.3. Scatter plot of Grimm 180 versus the RMs: Calibrated data

Table A10.1. Equivalence test results for Grimm 180 against the RMs for PM_{10}, all data.

PM 10	Equivalence field test		Number of data points:	89	
UNCORRECTED DATA			INTERCEPT CORRECTION		
REGRESSION OUTPUT			*REGRESSION OUTPUT*		
slope b	*1.37*	significant	*slope b*	*1.37*	significant
uncertainty of b	*0.04*		*uncertainty of b*	*0.04*	
intercept a	*-1.69*	significant	*intercept a*	*0.00*	not significant
uncertainty of a	*0.49*		*uncertainty of a*	*0.49*	
EQUIVALENCE TEST RESULTS			*EQUIVALENCE TEST RESULTS*		
random term	0.74	ug/m3	random term	0.89	ug/m3
bias at LV	16.60	ug/m3	bias at LV	18.29	ug/m3
combined uncertainty	16.61	ug/m3	combined uncertainty	18.31	ug/m3
relative uncertainty at the LV	33.23	**fail**	relative uncertainty at the LV	36.61	**fail**
RM between-sampler uncertainty	1.80	ug/m3	RM between-sampler uncertainty	1.80	ug/m3
SLOPE CORRECTION			INTERCEPT AND SLOPE CORRECTION		
REGRESSION OUTPUT			*REGRESSION OUTPUT*		
slope b	*0.99*	not significant	*slope b*	*0.99*	not significant
uncertainty of b	*0.03*		*uncertainty of b*	*0.03*	
intercept a	*-1.10*	significant	*intercept a*	*0.14*	not significant
uncertainty of a	*0.36*		*uncertainty of a*	*0.36*	
EQUIVALENCE TEST RESULTS			*EQUIVALENCE TEST RESULTS*		
random term	1.70	ug/m3	random term	1.77	ug/m3
bias at LV	-1.73	ug/m3	bias at LV	-0.49	ug/m3
combined uncertainty	2.42	ug/m3	combined uncertainty	1.83	ug/m3
relative uncertainty at the LV	4.84	**pass**	relative uncertainty at the LV	3.67	**pass**
RM between-sampler uncertainty	1.80	ug/m3	RM between-sampler uncertainty	1.80	ug/m3

A11. PM_{10} equivalence tests for Environnement MP101 CLS analysers

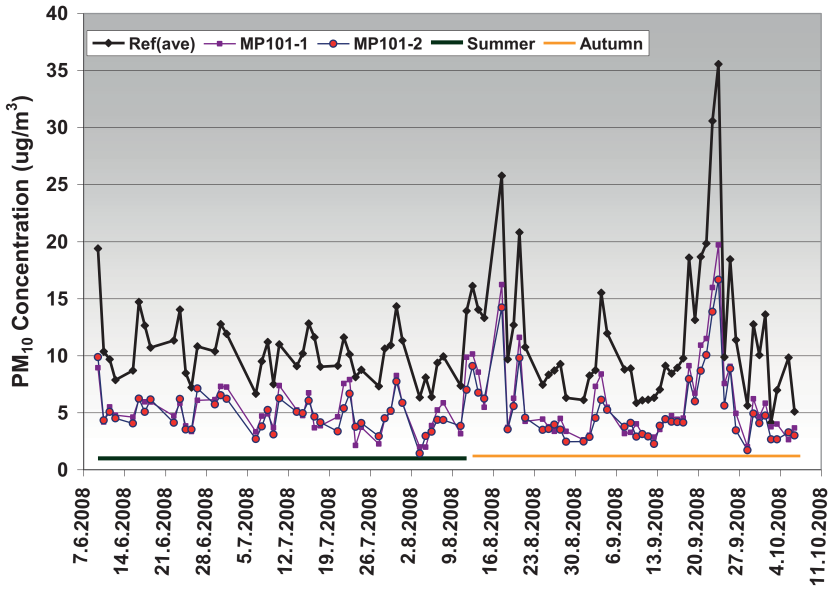

Figure A11.1. Time series of 24 h concentration values of MP101 and the RMs during the PM_{10} equivalence campaigns in Helsinki

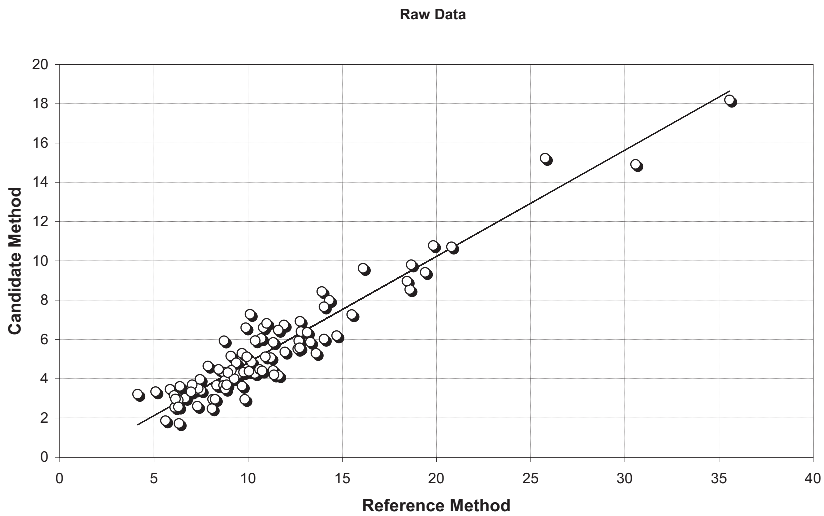

Figure A11.2. Scatter plot of MP101 versus the RMs: Uncorrected data

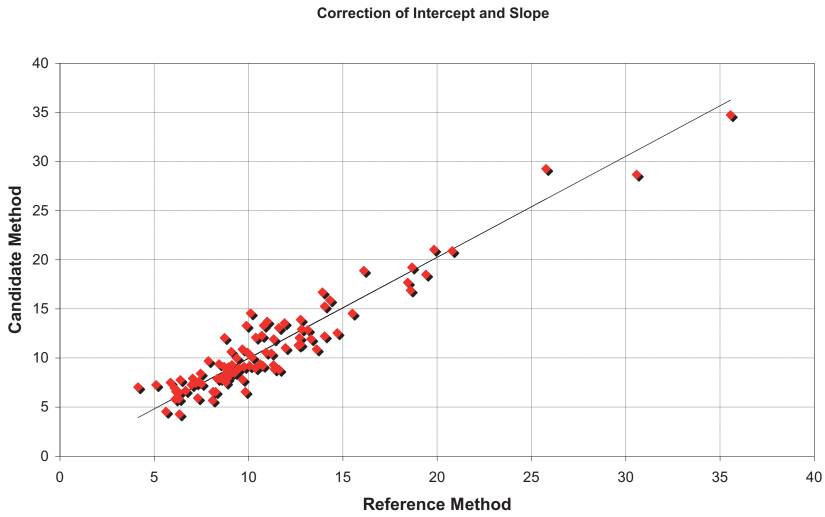

Figure A11.3. Scatter plot of MP101 versus the RMs: Calibrated data

Table A11.1. Equivalence test results for MP101 against the RMs for PM_{10}, all data.

PM 10	Equivalence field test		Number of data points:	88	
UNCORRECTED DATA			INTERCEPT CORRECTION		
REGRESSION OUTPUT			REGRESSION OUTPUT		
slope b	*0.54*	significant	*slope b*	*0.54*	significant
uncertainty of b	*0.02*		*uncertainty of b*	*0.02*	
intercept a	*-0.53*	significant	*intercept a*	*0.00*	not significant
uncertainty of a	*0.23*		*uncertainty of a*	*0.23*	
EQUIVALENCE TEST RESULTS			EQUIVALENCE TEST RESULTS		
random term	0.47	ug/m3	random term	0.52	ug/m3
bias at LV	-23.61	ug/m3	bias at LV	-23.07	ug/m3
combined uncertainty	23.61	ug/m3	combined uncertainty	23.08	ug/m3
relative uncertainty at the LV	47.22	**fail**	relative uncertainty at the LV	46.16	**fail**
RM between-sampler uncertainty	0.76	ug/m3	RM between-sampler uncertainty	0.76	ug/m3
SLOPE CORRECTION			INTERCEPT AND SLOPE CORRECTION		
REGRESSION OUTPUT			REGRESSION OUTPUT		
slope b	*1.03*	not significant	*slope b*	*1.03*	not significant
uncertainty of b	*0.03*		*uncertainty of b*	*0.03*	
intercept a	*-1.32*	significant	*intercept a*	*-0.33*	not significant
uncertainty of a	*0.42*		*uncertainty of a*	*0.42*	
EQUIVALENCE TEST RESULTS			EQUIVALENCE TEST RESULTS		
random term	1.77	ug/m3	random term	1.78	ug/m3
bias at LV	0.19	ug/m3	bias at LV	1.18	ug/m3
combined uncertainty	1.78	ug/m3	combined uncertainty	2.14	ug/m3
relative uncertainty at the LV	3.56	**pass**	relative uncertainty at the LV	4.27	**pass**
RM between-sampler uncertainty	0.76	ug/m3	RM between-sampler uncertainty	0.76	ug/m3

A12. PM_{10} equivalence tests for Osiris analysers

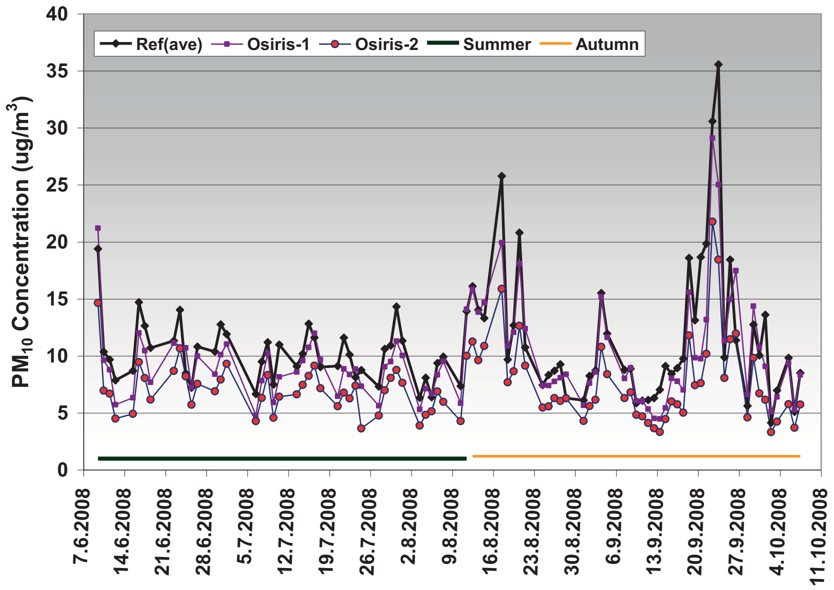

Figure A12.1. Time series of 24 h concentration values of Osiris and the RMs during the PM_{10} equivalence campaigns in Helsinki

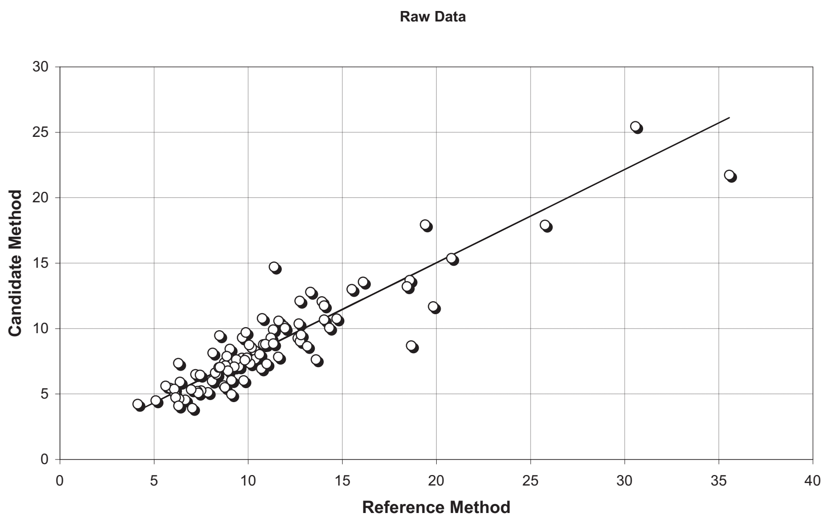

Figure A12.2. Scatter plot of Osiris versus the RMs: Uncorrected data

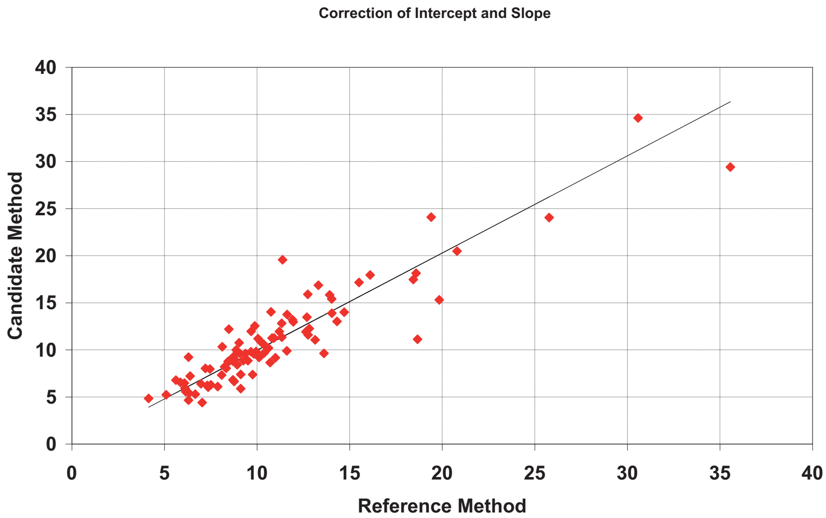

Figure A12.3. Scatter plot of Osiris versus the RMs: Calibrated data

Table A12.1. Equivalence test results for Osiris against the RMs for PM_{10}, all data.

PM 10	Equivalence field test		Number of data points:	89	
UNCORRECTED DATA			INTERCEPT CORRECTION		
REGRESSION OUTPUT			REGRESSION OUTPUT		
slope b	*0.70*	significant	*slope b*	*0.70*	significant
uncertainty of b	*0.03*		*uncertainty of b*	*0.03*	
intercept a	*0.91*	significant	*intercept a*	*0.00*	not significant
uncertainty of a	*0.38*		*uncertainty of a*	*0.38*	
EQUIVALENCE TEST RESULTS			EQUIVALENCE TEST RESULTS		
random term	0.00	ug/m3	random term	0.00	ug/m3
bias at LV	-14.26	ug/m3	bias at LV	-15.16	ug/m3
combined uncertainty	14.26	ug/m3	combined uncertainty	15.16	ug/m3
relative uncertainty at the LV	28.51	**fail**	relative uncertainty at the LV	30.33	**fail**
RM between-sampler uncertainty	3.00	ug/m3	RM between-sampler uncertainty	3.00	ug/m3
SLOPE CORRECTION			INTERCEPT AND SLOPE CORRECTION		
REGRESSION OUTPUT			REGRESSION OUTPUT		
slope b	*1.03*	not significant	*slope b*	*1.03*	not significant
uncertainty of b	*0.05*		*uncertainty of b*	*0.05*	
intercept a	*0.93*	not significant	*intercept a*	*-0.38*	not significant
uncertainty of a	*0.55*		*uncertainty of a*	*0.55*	
EQUIVALENCE TEST RESULTS			EQUIVALENCE TEST RESULTS		
random term	0.00	ug/m3	random term	0.00	ug/m3
bias at LV	2.64	ug/m3	bias at LV	1.34	ug/m3
combined uncertainty	2.64	ug/m3	combined uncertainty	1.34	ug/m3
relative uncertainty at the LV	5.28	**pass**	relative uncertainty at the LV	2.67	**pass**
RM between-sampler uncertainty	3.00	ug/m3	RM between-sampler uncertainty	3.00	ug/m3

A13. PM$_{10}$ equivalence tests for SHARP analysers

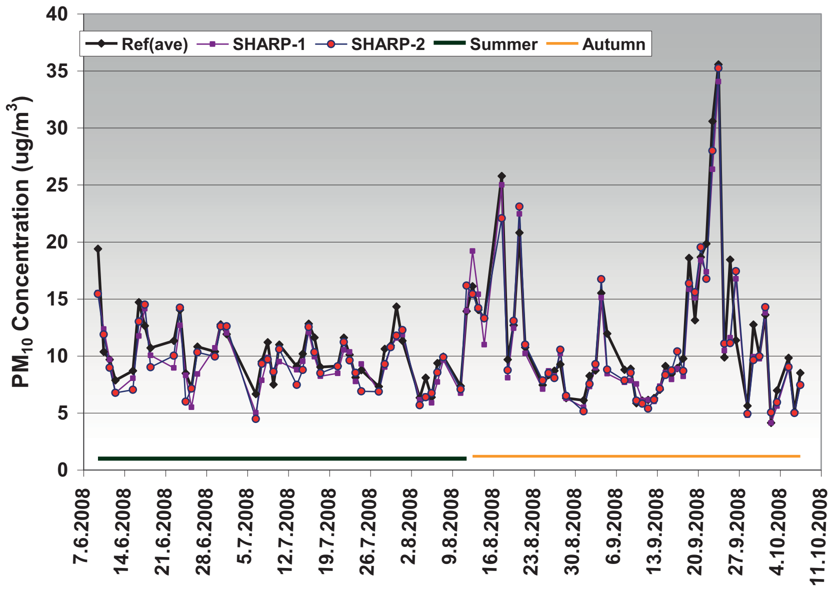

Figure A13.1. Time series of 24 h concentration values of SHARP and the RMs during the PM$_{10}$ equivalence campaigns in Helsinki

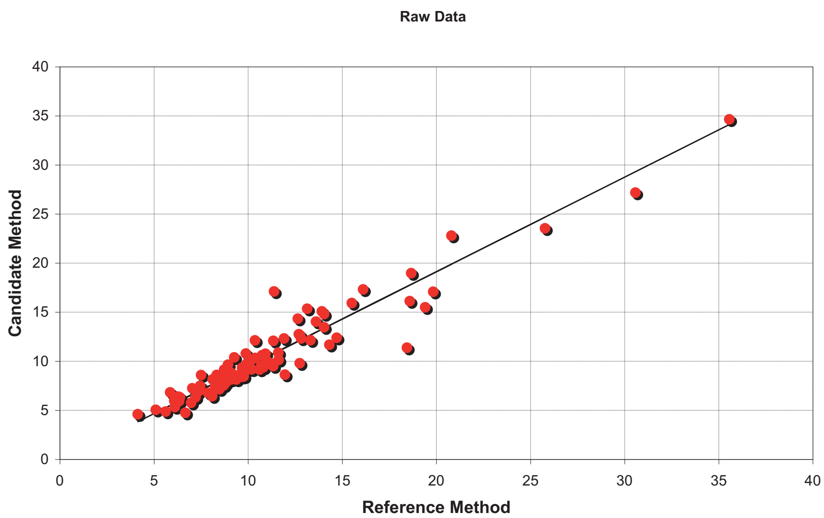

Figure A13.2. Scatter plot of SHARP versus the RMs: Uncorrected data

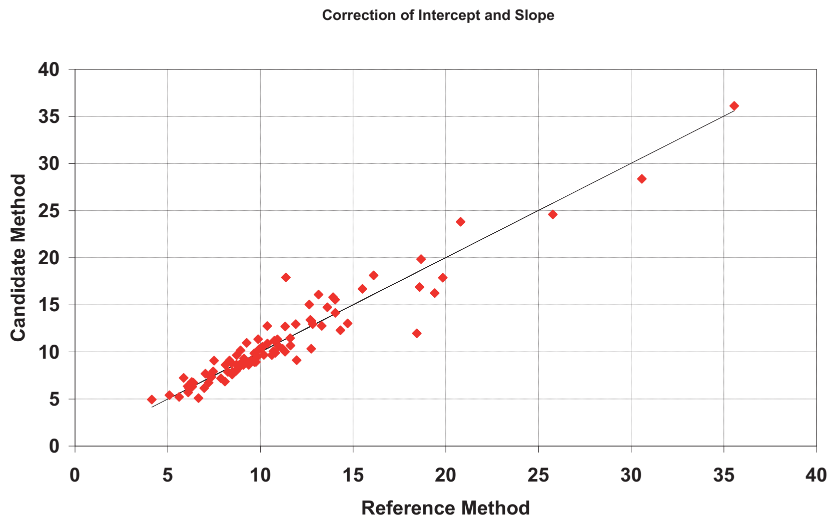

Figure A13.3. Scatter plot of SHARP versus the RMs: Calibrated data

Table A13.1. Equivalence test results for SHARP against the RMs for PM_{10}, all data.

PM 10	Equivalence field test		Number of data points:	89	
UNCORRECTED DATA			INTERCEPT CORRECTION		
REGRESSION OUTPUT			*REGRESSION OUTPUT*		
slope b	*0.97*	not significant	*slope b*	*0.97*	not significant
uncertainty of b	*0.03*		*uncertainty of b*	*0.03*	
intercept a	*-0.23*	not significant	*intercept a*	*0.00*	not significant
uncertainty of a	*0.37*		*uncertainty of a*	*0.37*	
EQUIVALENCE TEST RESULTS			*EQUIVALENCE TEST RESULTS*		
random term	1.27	ug/m3	random term	1.32	ug/m3
bias at LV	-1.55	ug/m3	bias at LV	-1.31	ug/m3
combined uncertainty	2.00	ug/m3	combined uncertainty	1.86	ug/m3
relative uncertainty at the LV	4.00	**pass**	relative uncertainty at the LV	3.73	**pass**
RM between-sampler uncertainty	0.72	ug/m3	RM between-sampler uncertainty	0.72	ug/m3
SLOPE CORRECTION			INTERCEPT AND SLOPE CORRECTION		
REGRESSION OUTPUT			*REGRESSION OUTPUT*		
slope b	*1.00*	not significant	*slope b*	*1.00*	not significant
uncertainty of b	*0.03*		*uncertainty of b*	*0.03*	
intercept a	*-0.25*	not significant	*intercept a*	*-0.01*	not significant
uncertainty of a	*0.38*		*uncertainty of a*	*0.38*	
EQUIVALENCE TEST RESULTS			*EQUIVALENCE TEST RESULTS*		
random term	2.02	ug/m3	random term	2.05	ug/m3
bias at LV	-0.19	ug/m3	bias at LV	0.05	ug/m3
combined uncertainty	2.03	ug/m3	combined uncertainty	2.05	ug/m3
relative uncertainty at the LV	4.06	**pass**	relative uncertainty at the LV	4.11	**pass**
RM between-sampler uncertainty	0.72	ug/m3	RM between-sampler uncertainty	0.72	ug/m3

A14. PM_{10} equivalence tests for TEOM 1400ab analysers

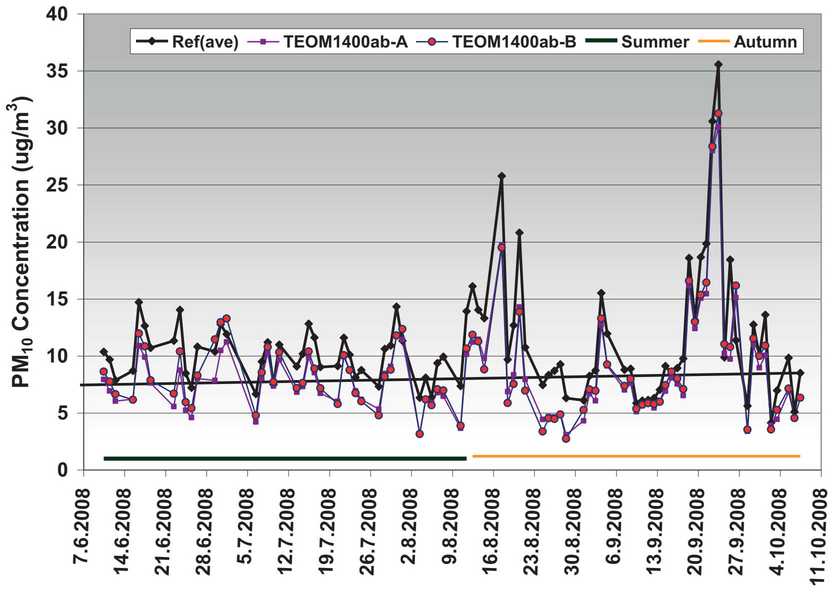

Figure A14.1. Time series of 24 h concentration values of TEOM 1400ab and the RMs during the PM_{10} equivalence campaigns in Helsinki

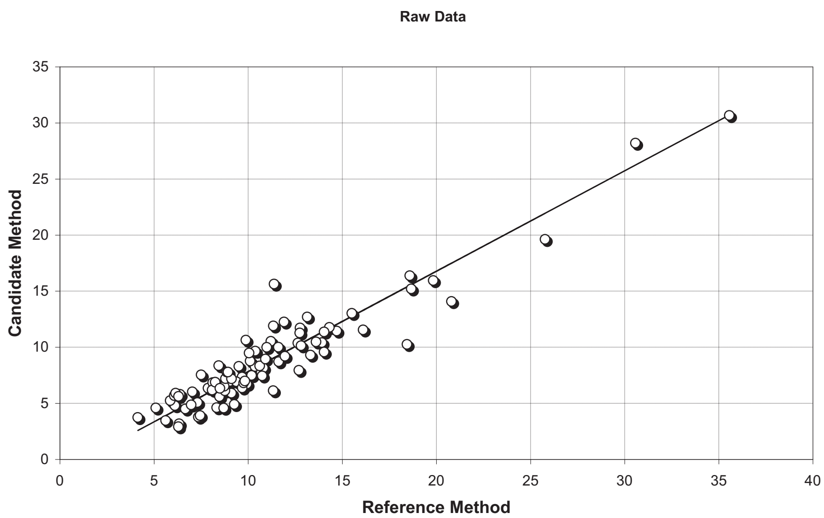

Figure A14.2. Scatter plot of TEOM 1400ab versus the RMs: Uncorrected data

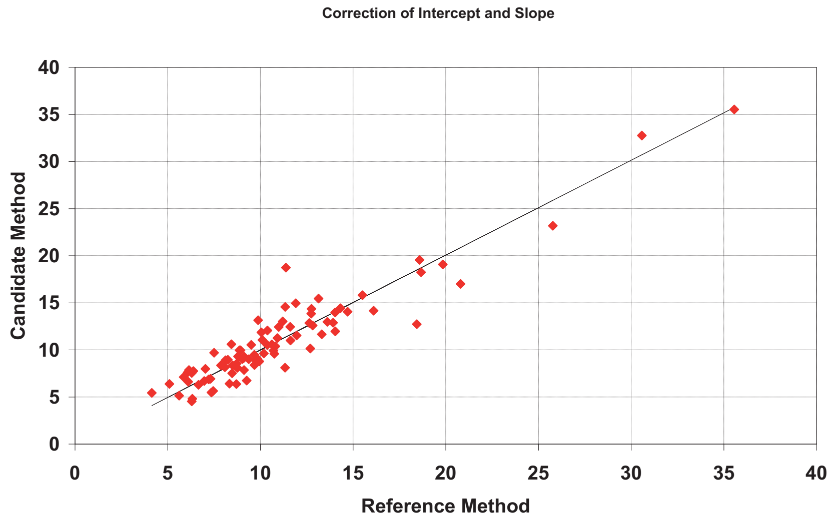

Figure A14.3. Scatter plot of TEOM 1400ab versus the RMs: Calibrated data

Table A14.1. Equivalence test results for TEOM 1400ab against the RMs for PM_{10}, all data

PM 10	Equivalence field test		Number of data points:	89	
UNCORRECTED DATA			INTERCEPT CORRECTION		
REGRESSION OUTPUT			*REGRESSION OUTPUT*		
slope b	*0.90*	significant	*slope b*	*0.90*	significant
uncertainty of b	*0.03*		*uncertainty of b*	*0.03*	
intercept a	*-1.13*	significant	*intercept a*	*0.00*	not significant
uncertainty of a	*0.39*		*uncertainty of a*	*0.39*	
EQUIVALENCE TEST RESULTS			*EQUIVALENCE TEST RESULTS*		
random term	1.46	ug/m3	random term	1.52	ug/m3
bias at LV	-6.37	ug/m3	bias at LV	-5.24	ug/m3
combined uncertainty	6.53	ug/m3	combined uncertainty	5.45	ug/m3
relative uncertainty at the LV	13.07	**fail**	relative uncertainty at the LV	10.90	**pass**
RM between-sampler uncertainty	0.55	ug/m3	RM between-sampler uncertainty	0.55	ug/m3
SLOPE CORRECTION			INTERCEPT AND SLOPE CORRECTION		
REGRESSION OUTPUT			*REGRESSION OUTPUT*		
slope b	*1.01*	not significant	*slope b*	*1.01*	not significant
uncertainty of b	*0.04*		*uncertainty of b*	*0.04*	
intercept a	*-1.34*	significant	*intercept a*	*-0.08*	not significant
uncertainty of a	*0.44*		*uncertainty of a*	*0.44*	
EQUIVALENCE TEST RESULTS			*EQUIVALENCE TEST RESULTS*		
random term	2.33	ug/m3	random term	2.37	ug/m3
bias at LV	-0.99	ug/m3	bias at LV	0.27	ug/m3
combined uncertainty	2.54	ug/m3	combined uncertainty	2.38	ug/m3
relative uncertainty at the LV	5.07	**pass**	relative uncertainty at the LV	4.77	**pass**
RM between-sampler uncertainty	0.55	ug/m3	RM between-sampler uncertainty	0.55	ug/m3

A15. PM$_{10}$ equivalence tests for Verewa analysers

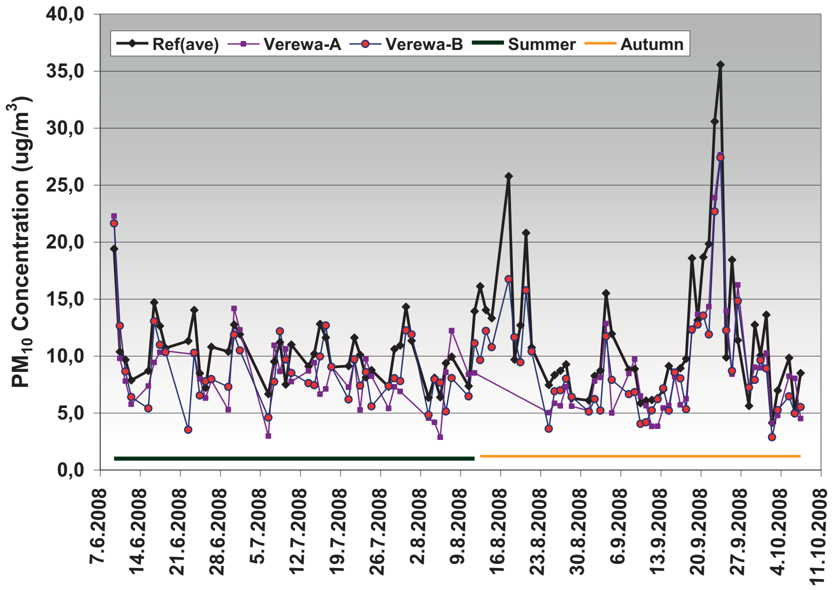

Figure A15.1. Time series of 24 h concentration values of Verewa and the RMs during the PM$_{10}$ equivalence campaigns in Helsinki

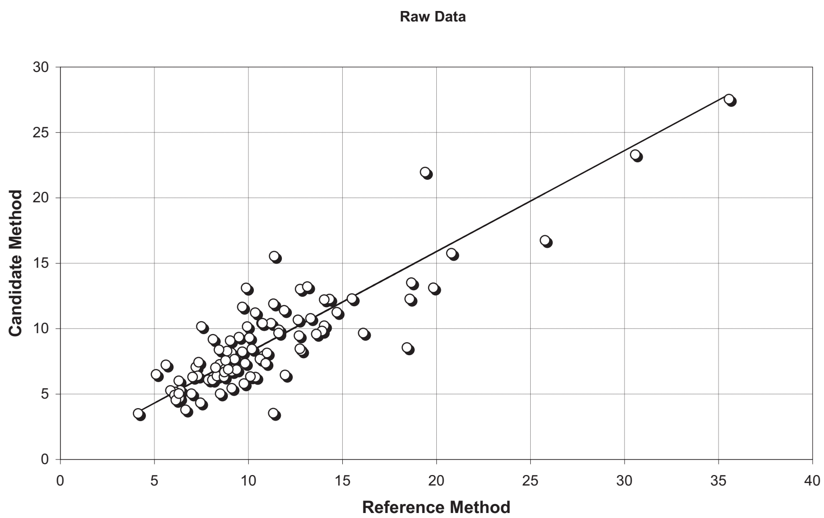

Figure A15.2. Scatter plot of Verewa versus the RMs: Uncorrected data

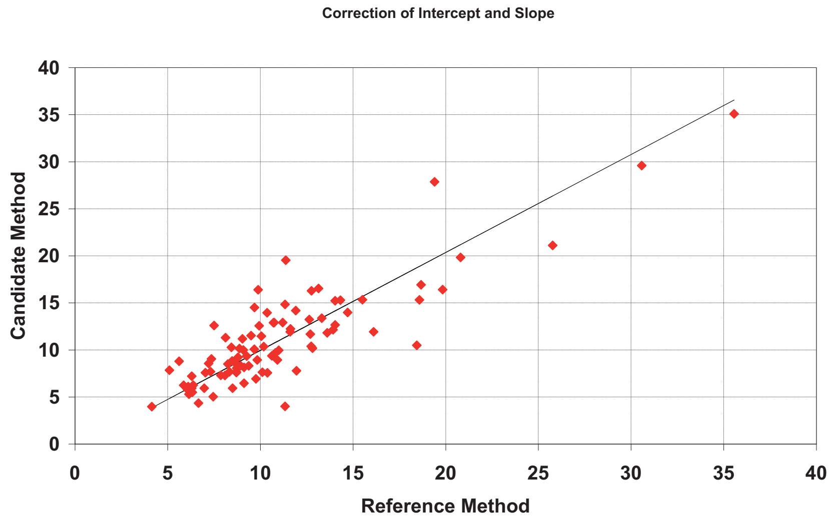

Figure A15.3. Scatter plot of Verewa versus the RMs: Calibrated data

Table A15.1. Equivalence test results for Verewa against the RMs for PM_{10}, all data

PM 10	Equivalence field test		Number of data points:	89	
UNCORRECTED DATA			INTERCEPT CORRECTION		
REGRESSION OUTPUT			REGRESSION OUTPUT		
slope b	*0.73*	significant	*slope b*	*0.73*	significant
uncertainty of b	*0.04*		*uncertainty of b*	*0.04*	
intercept a	*0.79*	not significant	*intercept a*	*0.00*	not significant
uncertainty of a	*0.49*		*uncertainty of a*	*0.49*	
EQUIVALENCE TEST RESULTS			EQUIVALENCE TEST RESULTS		
random term	1.34	ug/m3	random term	1.43	ug/m3
bias at LV	-12.52	ug/m3	bias at LV	-13.31	ug/m3
combined uncertainty	12.59	ug/m3	combined uncertainty	13.38	ug/m3
relative uncertainty at the LV	25.17	**fail**	relative uncertainty at the LV	26.76	**fail**
RM between-sampler uncertainty	1.40	ug/m3	RM between-sampler uncertainty	1.40	ug/m3
SLOPE CORRECTION			INTERCEPT AND SLOPE CORRECTION		
REGRESSION OUTPUT			REGRESSION OUTPUT		
slope b	*1.05*	not significant	*slope b*	*1.05*	not significant
uncertainty of b	*0.06*		*uncertainty of b*	*0.06*	
intercept a	*0.57*	not significant	*intercept a*	*-0.51*	not significant
uncertainty of a	*0.66*		*uncertainty of a*	*0.66*	
EQUIVALENCE TEST RESULTS			EQUIVALENCE TEST RESULTS		
random term	3.06	ug/m3	random term	3.10	ug/m3
bias at LV	2.88	ug/m3	bias at LV	1.80	ug/m3
combined uncertainty	4.20	ug/m3	combined uncertainty	3.59	ug/m3
relative uncertainty at the LV	8.41	**pass**	relative uncertainty at the LV	7.17	**pass**
RM between-sampler uncertainty	1.40	ug/m3	RM between-sampler uncertainty	1.40	ug/m3

Tutkimuksia – Undersökningar - Studies

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