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A Quality Assurance and Control Program for PM2.5 and PM10 measurements in European Air Quality Monitoring Networks

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Summary

For the purpose of harmonizing PM measurement methods, the European Commission's Joint Research Centre and the AQUILA Network of National Air Quality Reference Laboratories have organized a PM quality assurance/quality control program in Europe. From 2006 until 2009, 18 measurement campaigns have been organized in European Member States through carrying out parallel measurements with the JRC mobile laboratory next to the Member States National Reference Laboratories and routine monitoring networks. For the campaigns purpose the JRC mobile PM laboratory was equipped with reference samplers for PM10, PM2.5, PM1, a continuous PM10 instrument and a semi-continuous elemental and organic carbon analyzer.

The campaigns took place during spring and autumn in order to avoid extreme weather situations. Most of the campaigns were set up in urban background locations.

The primary objectives of the program were
- To provide information on the comparability of PM10 measurements as implemented by the NRLs with those of JRC (ERLAP)
- To investigate the comparability of routine PM10 measurements at network monitoring stations with those of JRC
- To assess, in the field, the comparability of reference and equivalent methods and the achievement of the data quality objectives (DQO)
- To assess the state of implementation and use of correction factors for automatic monitors in the monitoring networks that are used in reporting under Directive 2008/50/EC.

In addition, a considerable amount of "secondary" information was acquired throughout the implementation and evaluation of the program.

The primary conclusions of the evaluation of the results of the program were the following:

- When using all data supplied, National Reference Laboratories were found to underestimate the Reference Values for PM10 by 5.3% with a reproducibility standard deviation of 16%. Local Networks were found, on average, to almost exactly reproduce the Reference Values with a reproducibility standard deviation of 19%. For PM2.5 the underestimation of the Reference Values by National Reference Laboratories increased to about 11%, whereas the average of the Local Networks was 1.6% lower. However, the reproducibility of the Local Networks was considerably worse (50% vs. 15% for the National Reference Laboratories). On a whole, these findings indicate that – within the uncertainties associated with the measurements – the average results of National Reference Laboratories and Local Networks agree with the JRC Reference Values.

- For assessment of compliance with the uncertainty data quality objectives of Directive 2008/50/EC both uncertainties of individual results and uncertainties of grouped results have been considered. Of individual PM10 measurements, 7.1% did not comply with the Data Quality Objective at the limit value given in Directive 2008/50/EC; of individual PM2.5 measurements 23.8% did not comply with the Data Quality Objective at the target value given in EU Directive 2008/50/EC. Deviations could not be directly attributed to specific parameters like filter material, sampling temperature or instrumentation type as too many variables are influencing the measurement results. Around one third of the PM10 and half of the

PM2.5 measurements exceed the required uncertainty at the limit respectively target value, with automatic analyzers performing worse than the gravimetric methods. When considering relative uncertainties of grouped results based on reproducibility standard deviations after removal of outliers these are 28% (95% confidence) for PM10 and 33% (95% confidence) for PM2.5. For reference methodologies the uncertainties are lower than for automatic analyzers, which may partly be attributed to the use of default correction factors instead of factors derived from equivalence tests. However, the reasons for the high uncertainties require further investigation. For PM2.5 these findings will have consequences for the establishment of the reduction in the Average Exposure Indicator.

- Almost half of all users of automatic analyzers have used correction factors for the results obtained by the analyzers. The use of correction factors generally improves their results.

Furthermore, the following findings have been reported:

- When comparing low-volume sampling to high-volume sampling, results for low-volume sampling are generally found to be higher. For high-volume sampling, no difference can be found between results obtained using quartz-fibre or glass-fibre filters (the two mostly used filter types), however for low-volume sampling results obtained using quartz-fibre filters are higher.

- A considerable fraction of the field blanks examined during this study exceeds the criterion given in EN 14907, with levels of up to 6 µg/m^3. The reason for this phenomenon requires further investigation.

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Nomenclature and Abbreviations

AT	Austria
BE	Belgium
CZ	Czech Republic
DE	Germany
DK	Denmark
EE	Estonia
ES	Spain
FI	Finland
FR	France
GB	United Kingdom
HU	Hungary
IE	Ireland
IT	Italy
NL	Netherlands
PT	Portugal
SE	Sweden
SI	Slovenia
SK	Slovak Republic
EU	European Union
AEA	AEA (Atomic Energy Authority) Technology
AIRPARIF	Surveillance de la Qualité de l'Air en Ile-de-France
ARPA	Agenzia Regionale per la Protezione dell'Ambiente
AdM	Ayuntamiento de Madrid
BV	Bureau Veritas
CHMI	Czech Hydrometeorological Institute
DCC	Dublin City Council
EDM	École de mines (LCSQA – Mines de Douai)
EERC	Estonian Environmental Research Centre
EIMV	Elektroinstitut Milan Vidmar
EHAS	Environment and Health Administration, City of Stockholm
EPA	Environmental Protection Agency
ERLAP	European Reference Laboratory of Air Pollution
FMI	Finnish Metrological Institute
GGD	Municipal Health Service Amsterdam
HLUG	Hessisches Landesamt fuer Umwelt und Geologie
HMS	Hungarian Meteorological Service
ISCIII	Instituto de Salud Carlos III
IdA	Instituto do Ambiente
INERIS	Institut National de l'Environnement Industriel et de Risques
ISPRA	Istituto Superiore per la Protezione e la Ricerca Ambientale
ISSeP	Institut scientifique de service public
ITM	University of Stockholm
IVL	Swedish Environmental Research Institute
JRC	Joint Research Centre
LANUV	Landesamt fuer Natur, Umwelt und Verbraucherschutz
LR OOe	Amt der Oberösterreichischen Landesregierung
LR Stmk.	Amt der Steiermärkischen Landesregierung
MDV	Middle Danube Valley Network Hungary
NERI	National Environmental Research Institute
NPT	Neath Port Talbot County Borough Council
RIVM	National Institute for Public Health and the Environment
SHMU	Slovak Hydrometeorological Institute
UBA	Umweltbundesamt Ges.m.b.H.
VMM	Vlaamse Milieumaatschappij
AQUILA	Network of Air Quality Reference Laboratories
NRL	National Reference Laboratories
DQO	Data Quality Objective (of the European Directive)

LV   Limit Value
QA/QC   Quality Assurance / Quality Control

PM10   Particulate Matter in the size fraction ≤ 10 µm
PM2.5   Particulate Matter in the size fraction ≤ 2.5 µm
PM1   Particulate Matter in the size fraction ≤ 1 µm
OC/EC   Organic and Elemental Carbon

1.   Introduction

Legislation

Measurements of particulate matter have been carried out in Europe since many years. During the 80's total suspended particulates were measured, referring to the "Black Smoke OECD" method (Directive 80/779/EC). Studies on health impact assessment of particles have led to the revision of European air quality policy during the 90's. The PM10 and PM2.5 fraction of PM, considered as inhalable, were introduced with the publication of Directive 1999/30/EC [1]. In line with the 'Clean Air for Europe' strategy of the European Commission to minimize harmful effects of pollution on human health and the environment and to improve monitoring and assessment of air quality, the measurement of PM10 and PM2.5 has been updated by the recently adopted Air Quality Directive 2008/50/EC [2]. Member States now have to measure as well PM2.5 concentrations on the basis of "common methods and criteria". The Directive refers to the European Standards EN 12341 [3] and 14907 [4] for the measurement of fine particles in ambient air. Siting criteria are given for sampling locations. Quality objectives are set regarding the accuracy of the measured value and minimum data capture.

A need for quality control and harmonization derives from experience showing that even though common methods and criteria are applied, reported values on PM concentrations may differ considerably. To ensure compliance with the data quality objectives set in the Air Quality Directive, Member States have to establish a quality assurance and control system, as well as a traceability chain in accordance with international guidelines. In addition, institutions designated for QA/QC shall participate in the Community-wide quality assurance programs organised by the Commission.

Currently, under Directive 2008/50/EC, there are 3 different thresholds existing for fine particles:

- PM10 limit value calendar year average 40 µg/m^3
- PM10 limit value daily average 50 µg/m^3 not to be exceeded more than 35 times a year
- PM2.5 target value calendar year average 25 µg/m^3

Since 2009 Member States are obliged to evaluate as well an Average Exposure Indicator, a three-year average based upon PM2.5 measurements in urban background locations.

CEN standards

The CEN Technical Committee 'Air Quality' - Working Group 15 (PM10 and PM2.5) has been dealing with the set up of standardized measurement methods for PM10 resulting in EN 12341 [3] and PM2.5 resulting in EN 14907 [4]. Extensive validation measurement campaigns have been carried out in order to describe the best suitable consensus method for PM measurements for the purpose of Air Quality Directives 1999/30/EC [1] and 2008/50/EC [2].

EN 12341, published in 1998, is describing three reference methods for measuring PM10 and a field test procedure to demonstrate equivalence of "candidate" methods. The three reference methods, quartz fibre filter based, are a 2.3 m^3/h Low-Volume-System, a 68 m^3/h High-Volume-System and a 1966 m^3/h system (WRAC-Wide Range Aerosol Classifier) which has been used in the past for research purposes only.

EN 14907, published in 2005, included thus many refinements deriving from experience with the PM10 standard. The PM2.5 standard describes two sampling systems: a 2.3 m^3/h Low-Volume-system and a 30 m^3/h High-Volume-system. It includes more rigorous quality assurance requirements, but it allows for four different filter types namely glass fibre, quartz fibre, PTFE and PTFE coated filters.

The European PM standard methods are currently being revised by the Working Group, as the results achieved by applying the standard methods may vary considerably due to influencing factors like choice of Low-Volume or High-Volume Sampler, filter material, conditioning of filters, sampling duration, sampling time of the day, temperature, etc.

Scope and motivation of the project

The European Commission's Joint Research Centre carries out quality assurance programmes for gaseous air pollutants since many years. Gases are both generated and measured simultaneously by the participating laboratories on the spot at the ERLAP facility in Ispra (IT), or gas cylinders are sent around and measured by participants in their own laboratory.

The situation with particulate matter is slightly more complex since it is difficult to generate homogenous particle concentrations for several participants in one spot. For that reason, it was decided that ERLAP will visit Member States monitoring sites by means of a mobile laboratory equipped with reference instrumentation. This had the advantage, that both a routine monitoring network station and the National Reference Laboratory of each Member State could be involved, allowing on the one hand a comparison with the NRL, the body responsible for QA/QC in the Member State, and on the other hand to draw a statement on the quality level of routine monitoring. In particular correction factors for automated PM instrumentation could be investigated. The "Guidance on PM10 monitoring" prescribes the use of a correction factor of 1.3 in absence of self-investigated correction factors when measuring with an automated system (*http://ec.europa.eu/environment/air/quality/legislation/pdf/finalwgreporten.pdf*). The Guide to the Demonstration of Equivalence of Ambient Air Monitoring Methods (GDE - *http://ec.europa.eu/environment/air/quality/legislation/assessment.htm*) [5], first published in 2005, describes a practical approach to establish such factors. However, the level of implementation of correction factors was unclear so far.

The aims of the JRC-AQUILA QA/QC programme were
- To provide information on the comparability of PM10 measurements as implemented by the NRLs with those of JRC (ERLAP)
- To investigate the comparability of routine PM10 measurements at network monitoring stations with those of JRC
- To assess, in the field, the comparability of reference and equivalent methods and the achievement of the data quality objectives (DQO)
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In addition to PM10 a number of participants took advantage out of the possibility to compare as well measurements of PM2.5.

Further, it was expected that – as a spin-off of the programme – a considerable amount of "secondary" information would become available, e.g. comparability of different techniques and instruments and the effects of parameters such as filter types for gravimetric methods and heating of sampling lines for automatic monitors.

2. Measurement campaigns

During the period March 2006 to March 2009 a total of 18 measurement campaigns were conducted in 18 Member States of the European Union. Figure 1 shows the visited countries.

Figure 1: Visited countries
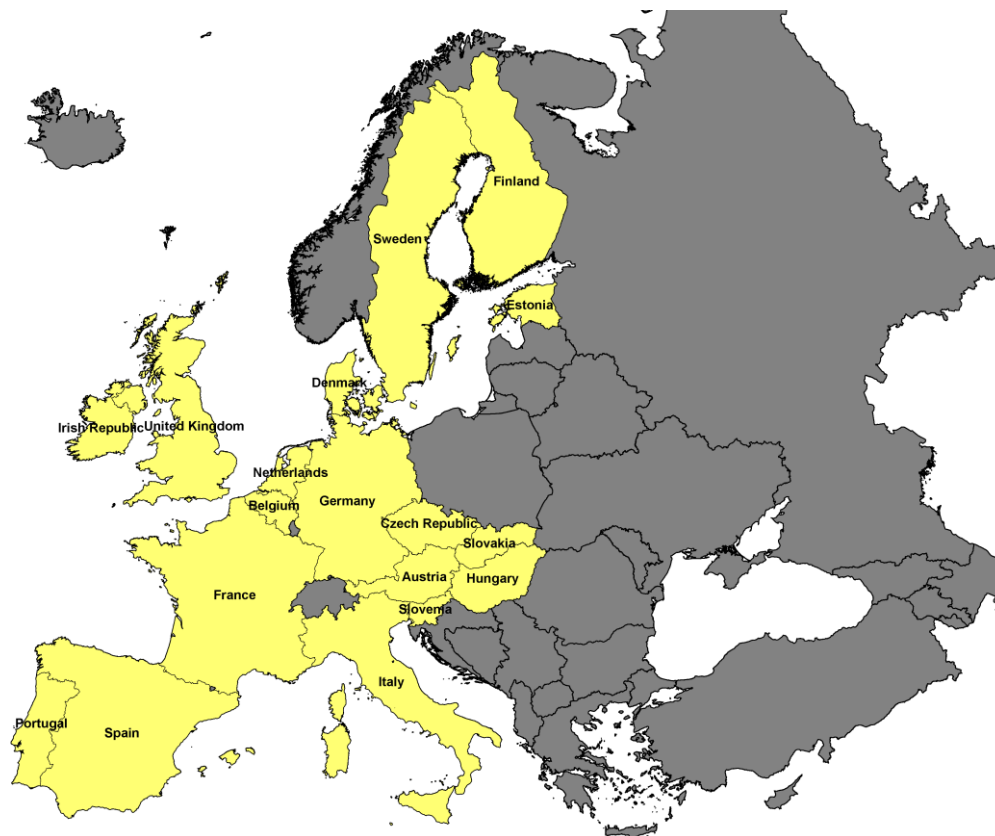
Each campaign had a duration of 14 measurement days resulting in 14 daily averages per instrument for PM10 and PM2.5 (where available) to be compared. Due to instrument malfunctions in some occasions less than 14 values were obtained. Wherever it was possible, the duration of a measurement campaign was extended to avoid scanty daily averages. In some occasions even more than 14 values were measured. To allow a better comparability of data it was foreseen to measure only in urban background sites and to avoid very cold and hot weather periods. In some countries suitable urban background sites could not be found and therefore a limited number of campaigns had to be performed in different locations. Three campaigns (ES, DK and SE) were carried out in sites with emissions dominated by traffic (see Annex 7) resulting partly in higher between sampler uncertainties. In Annex 1 a description of all measurement sites with photos and drawings showing the distance between the used measurement equipment can be found. Table 1 gives an overview of the visited sites.

Table 1: Visited measurement sites

Country	Measurement site	Address	Type	Period
ES	Escuelas Aguirre	Crossing of Alcala and O'Donnell Street, Madrid	traffic	March 2nd - 16th, 2006
PT	Instituto do Ambiente	Rua da Murgueira, 9/9A, Amadora	urban background	March 23rd - April 6th, 2006
SI	Environmental Agency	Vojkova 1b, 1000 Ljubljana	urban background	Sept. 20th - Oct. 4th, 2006
AT	Graz Süd	Tiergartenweg, 8020 Graz	urban background	Oct. 9th - 22nd, 2006
CZ	Czech Hydrometeorological Institute	Na Šabatce 17, 143 06 Praha 4, Komořany	urban background	Oct. 29th - Nov. 12th, 2006
DE	Hessisches Landesamt für Umwelt und Geologie	Rheingaustrasse 186, 65203 Wiesbaden	urban background	Nov. 25th - Dec. 8th, 2006
DK	H.C. Andersen Boulevard	H.C. Andersen Boulevard 23, Copenhagen	traffic	Feb. 19th - March 4th, 2007
SE	Hornsgatan	Hornsgatan 110, 117 26 Stockholm	traffic	March 9th - 22th, 2007
FI	Finnish Metrological Institute	Erik Palménin aukio 1, 00560 Helsinki	urban background	April 2nd - 16th, 2007
EE	Õismāe	Õismāe tee 28 a, Tallinn	urban background	April 19th - May 2nd, 2007
NL	Biest - Houtakker	Biestsestraat (next to channel), Biest-Houtakker	rural	Feb. 6th - 19th, 2008
BE	Borgerhout	Plantin en Moretuslei 165	urban background	Feb. 22nd - March 6th, 2008
FR	Bobigny	Chemin lateral, Parc de la Bergère, 93008 Bobigny	urban background	March 13th - 27th, 2008
IE	Phoenix Park	Ordonance survey, Ordonance Road, Dublin	urban background	April 4th - 20th, 2008
GB	Port Talbot	Central Road, Margam, Port Talbot	urban background/industrial	April 24th - May 23rd, 2008
IT	Parco Giuriati	Via Ponzio, Milan	urban background	Sept. 10th - 28th, 2008
HU	Meteorological Observatory	Gilice ter 39, Budapest 18	urban background	Feb. 19th - March 4th, 2009
SK	Salesiane Centre	Mamateyova road, Bratislava	urban background	March 12th - 25th, 2009

2.1 Participating laboratories

35 laboratories from the AQUILA Network, local and private air quality monitoring networks participated in the measurement campaigns. Members of the AQUILA Network are called "National Reference Laboratories", both local and private air quality monitoring networks are summarized as "local networks" in this report. Details of each participant can be found in Table 2.

Table 2: Participating laboratories

Country	Institution	Type of network
ES	Instituto de Salud Carlos III	NRL
ES	Ayuntamiento de Madrid	Local network
PT	Instituto do Ambiente	NRL
SI	Environmental Agency of the Republic of Slovenia	NRL
SI	Elektroinstitut Milan Vidmar EIMV - department ENV	Local network
SI	ANHOVO	Local network
AT	Umweltbundesamt Ges.m.b.H	NRL
AT	Amt der Oberösterreichischen Landesregierung	NRL
AT	Amt der Steiermärkischen Landesregierung	Local network
CZ	Czech Hydrometeorological Institute	NRL
DE	Landesamt für Natur, Umwelt und Verbraucherschutz	NRL
DE	Hessisches Landesamt für Umwelt und Geologie	Local network
DK	National Environmental Research Institute	NRL
SE	University of Stockholm ITM, Department of Applied Environmental Science	NRL
SE	City of Stockholm, Environment and Health Administration	Local network
SE	IVL Swedish Environmental Research Institute	Local network
FI	Finnish Metrological Institute	NRL
EE	Estonian Environmental Research Centre	NRL
NL	RIVM - National Institute for Public Health and the Environment Laboratory for Environmental Monitoring	NRL
NL	GGD - Municipal Health Service Amsterdam Department of Air Research, Environmental medicine	Local network
BE	VMM - Vlaamse Milieumaatschappij Afdeling Lucht, Milieu en Communicatie, cdvp Immissiemeetnetten Lucht	NRL
BE	ISSeP, Veille Technologique, Cellule qualitè de l'Air	NRL
FR	Ineris	NRL
FR	LCSQA - Mines de Douai, Département Chimie & Environnement	NRL
FR	AIRPARIF	Local network
IE	Environmental Protection Agency	NRL
IE	Dublin City Council	Local network
GB	AEA Technology	NRL
GB	Bureau Veritas	Local network
GB	Neath Port Talbot Borough Council and Air Monitors	Local network
IT	Istituto Superiore per la Protezione e Ricerca Ambientale	NRL
IT	Agenzia Regionale per la Protezione dell'Ambiente della Lombardia	Local network
HU	Hungarian Meteorological Service	NRL
HU	Middle Danube Valley Inspectorate of Environmental Protection, Nature Conservation and Water management	Local network
SK	Slovak Hydrometeorological Institute	NRL

2.2 Used equipment

Each participant was asked to provide information about the equipment used in the field and in the laboratory, maintenance procedures and details how data are expressed. Detailed information regarding the used equipment is given in this report, especially with respect to sampling (e.g. inlet, flow rate, sampling temperature).

PM10 and PM2.5 measurements were made using both manual samplers and automatic instruments. In this report, manual samplers are split into "Low Volume Samplers (LVS)" and "High Volume Samplers (HVS)".

Manual samplers are based on the gravimetric measurement of the particulate mass sampled on a filter. Samplers could either be a single filter device or equipped with an automatic filter changer. The used filter material and its manufacturer differ between the participants. The same is valid for the inlets and the flow rates of the samplers. Pictures and more details on the different types of sampling inlets can be found in Annex 2. A total of 29 LVS and 13 HVS were used by the participants during the measurement campaigns for PM10. Table 3 provides detailed information.

Table 3: PM10 manual samplers

Country	Institution	Sampler	Flow rate	Inlet	Filter manufacturer and material
EU	JRC	SEQ Leckel 47/50 A	2.3 m^3/h	Type 3	Whatman QMA
		SEQ Leckel 47/50 B	2.3 m^3/h	Type 3	Whatman QMA
ES	ISCIII	Derenda MVS 6.1 A	2.3 m^3/h	Type 1	Whatman QMA
		Derenda MVS 6.1 B	2.3 m^3/h	Type 1	Whatman QMA
PT	IdA	Andersen	68 m^3/h	Type 6	Whatman Glass fibre
		Tecora	1 m^3/h	Type 4	Schleicher & Schuell Quartz
SI	EPA SI	Derenda Seq PNS3.1-15	2.3 m^3/h	Type 1	Whatman QMA
SI	EIMV	Tecora	2.3 m^3/h	Type 5	Schleicher & Schuell Quartz
		Andersen	68 m^3/h	Type 6	Peckman environment Glass fibre
SI	ANHOVO	Tecora	2.3 m^3/h	Type 5	unknown
AT	UBA	Digitel	30 m^3/h	Type 8	Ederol Glass fibre
AT	LR OOe.	Digitel	30 m^3/h	Type 8	Whatman QMA
AT	LR Stmk.	Digitel	30 m^3/h	Type 8	Pall Quartz
CZ	CHMI	Thermo FH 95 KF	2.3 m^3/h	Type 14	Millipore RAWP Cellulose nitrate
		Thermo FH 95 KF	2.3 m^3/h	Type 14	Schleicher & Schuell Glass fibre
		MCZ / Andersen	68 m^3/h	Type 6	Whatman QMA
		Derenda SEQ High Vol A	30 m^3/h	Type 13	Whatman/Schleicher & Schuell Glass fibre

Country	Institution	Sampler	Flow rate	Inlet	Filter manufacturer and material
		Derenda SEQ High Vol B	30 m^3/h	Type 13	Whatman/Schleicher & Schuell Glass fibre
		Derenda SEQ Low Vol	2.3 m^3/h	Type 1	Schleicher & Schuell Glass fibre
DE	LANUV	Digitel A	30 m^3/h	Type 8	Whatman QMA
		Digitel B	30 m^3/h	Type 8	Whatman QMA
DE	HLUG	Leckel SEQ 47/50	2.3 m^3/h	Type 3	Schleicher und Schuell Glass fibre GF10
SE	ITM	Leckel SEQ 47/50	2.3 m^3/h	Type 3	Pall fibre film T60A20 / heat resistant borosilicate glass fibre coated with fluorocarbon (TFE)
SE	IVL	IVL homemade A	18 l/min	Type 16	unknown
		IVL homemade B	18 l/min	Type 16	unknown
EE	EERC	Digitel (container)	30 m^3/h	Type 8	Ederol Glass fibre
		Digitel (mob.lab)	30 m^3/h	Type 8	Ederol Glass fibre
NL	RIVM	Leckel SEQ 47/50	2.3 m^3/h	Type 11	Whatman QMA Quartz fibre
NL	GGD	Derenda SEQ Low Vol	2.3 m^3/h	Type 1	Whatman QMA (pre-conditioned at high humidity)
BE	VMM	Leckel SEQ 47/50	2.3 m^3/h	Type 3	Whatman QMA (pre - fired)
BE	ISSeP	FAI SW sn.126	2.3 m^3/h	Type 12	Whatman QMA
		FAI SW sn.129	2.3 m^3/h	Type 12	Whatman QMA
FR	INERIS	Partisol +	1 m^3/h	Type 9	Pallflex PTFE membrane 2 µm
IE	DCC	Partisol 2025	1 m^3/h	Type 9	Whatman Glass fibre
GB	AEA	Partisol 2025	1 m^3/h	Type 9	Emfab
GB	BV	Partisol 2025	1 m^3/h	Type 9	Emfab
		Partisol 2025	1 m^3/h	Type 9	Quartz
IT	ISPRA	Tecora	2.3 m^3/h	Type 20	Millipore AQFA quartz
IT	ARPA	Zambelli explorer plus	1 m^3/h	Type 22	Pall, PTFE with support ring
		Tecora	1 m^3/h	Type 9	Pall, T6020 fibre film, teflonated borosilicate glass
HU	HMS	Digitel	30 m^3/h	Type 8	Schleicher & Schuell Quartz

A total of 17 LVS and 3 HVS were used by the participants during the measurement campaigns for PM2.5. Table 4 provides detailed information.

Table 4: PM2.5 manual samplers

Country	Institution	Sampler	Flow rate	Inlet	Filter manufacturer and material
EU	JRC	SEQ Leckel 47/50	2.3 m^3/h	Type 3	Whatman QMA
ES	ISCIII	Derenda MVS 6.1	2.3 m^3/h	Type 1	Whatman QMA
PT	IdA	Tecora	1 m^3/h	Type 4	Schleicher & Schuell Quartz

SI	EPA SI	SEQ Leckel 47/50	2.3 m³/h	Type 3	Whatman QMA
AT	UBA	Digitel DAH 80	30 m³/h	Type 8	Ederol Glass fibre
AT	LR OOe.	Digitel DAH 80	30 m³/h	Type 8	Whatman QMA
CZ	CHMI	SEQ Leckel 47/50 Derenda SEQ LVS	2.3 m³/h 2.3 m³/h	Type 3 Type 1	Millipore RAWP Cellulose nitrate Schleicher & Schuell Glass Fibre
SE	IVL	IVL homemade A IVL homemade B	18 l/min 18 l/min	Type 16 Type 16	unknown unknown
NL	GGD	Derenda SEQ LVS	2.3 m³/h	Type 1	Whatman QMA (pre-conditioned at high humidity)
BE	VMM	SEQ Leckel 47/50 SEQ Leckel 47/50	2.3 m³/h 2.3 m³/h	Type 3 Type 3	Whatman QMA (pre-fired) Pall, Emfab (PTFE coated glass fibre)
BE	ISSeP	FAI SW sn. 126 FAI SW sn. 129	2.3 m³/h 2.3 m³/h	Type 12 Type 12	Whatman QMA Whatman QMA
GB	BV	Partisol 2025	1 m³/h	Type 9	Emfab
GB	NPT	Partisol 2025	1 m³/h	Type 9	Quartz
IT	ARPA	Zambelli explorer plus	1 m³/h	Type 21	Pall, PTFE with support ring
HU	MDV	Digitel DAH 80	30 m³/h	Type 8	Munktell, glass fibre

Automatic samplers used during the campaigns are based on the following principles:

- Tapered Element Oscillating Microbalance (TEOM)
- Filter Dynamics Measurement System (FDMS) combined with TEOM
- ß – radiation attenuation
- Light scattering

The used flow rates, sampling line temperatures and inlets differ between the participants. Pictures of the inlets can be found in Annex 2. A total of 5 TEOM, 12 FDMS, 19 ß – radiation and 1 light scattering instrument were used for PM10; 1 instrument used a combination of both the last techniques. Table 5 provides detailed information on the automatic PM10 instruments.

Table 5: PM10 automatic samplers

Country	Institution	Instrument	Flow rate	Sampling line / heating	Inlet
EU	JRC	Teom FDMS Vers. B	1 m³/h	straight / 30° C	Type 9
ES	AdM	Teom 1400 AB	1 m³/h	straight / 50° C	Type 9
PT	IdA	Environnement MP 101	1 m³/h	straight / 50° C	Type 9
SI	EPA SI	Teom 1400	1 m³/h	straight / 30° C	Type 9
AT	UBA	Teom FDMS	1 m³/h	straight / 30° C	Type 7
AT	LR OOe.	Teom FDMS	1 m³/h	straight / 40° C	Type 9
AT	LR Stmk.	Eberline FH 62 IR	1 m³/h	curved / 40° C	Type 7
CZ	CHMI	FH 62 IR	1 m³/h	curved / 30° C	Type 7
DE	HLUG	FH 62 IR FH 62 IR Sharp	1 m³/h 1 m³/h	curved / amb.T + 8° C curved / amb.T + 8° C	Type 7 Type 7
DK	NERI	Opsis SM 200 Teom 1400	1 m³/h 1 m³/h	straight / no heating straight / 50° C	Type 10 Type 10
SE	EHAS	Teom 1400 Teom FDMS	1 m³/h 1 m³/h	straight / 50° C straight / unknown	Type 10 Type 9

FI	FMI	Thermo FH 62 IR_632	1 m³/h	curved / 35° C	Type 9
		Thermo FH 62 IR_280	1 m³/h	curved / 35° C	Type 9
EE	EERC	Thermo FH 62 IR (container)	1 m³/h	curved / sheath air	Type 9
		Thermo FH 62 IR (mob.lab)	1 m³/h	curved, no heating	Type 9
NL	RIVM	Thermo FH 62 IR	1 m³/h	curved, amb. T + 10° C	Type 7
BE	VMM	ESM Andersen	1 m³/h	curved, dynamic heating	Type 9
		Teom 1400	1 m³/h	straight / 50° C	Type 9
		Teom FDMS	1 m³/h	straight / 30° C	Type 9
BE	ISSeP	FAI SW sn. 126	2.3 m³/h	straight / no heating	Type 12
		FAI SW sn. 129	2.3 m³/h	straight / no heating	Type 12
		Environnement MP 101 sn. 33	1 m³/h	straight / heating depending on r.h.	Type 7
		Environnement MP 101 sn 78	1 m³/h	straight / heating depending on r.h.	Type 7
		Grimm 180	72 l/h	straight / no heating	Type 15
FR	INERIS	Teom FDMS Vers. C, sn. 9032	1 m³/h	straight / 30° C	Type 9
		Teom FDMS Vers. C, sn. 15702	1 m³/h	straight / 30° C	Type 9
FR	EDM	Environnement MP 101M-RST	1 m³/h	straight / dynamic heating (depends on amb. T & r.h.)	Type 9
FR	AIRPARIF	Teom FDMS 1400 AB	1 m³/h	straight / 30° C	Type 9
IE	EPA IE	Teom FDMS	1 m³/h	straight / 30° C	Type 10
GB	NPT	Teom FDMS Vers. C	1 m³/h	straight / unknown	Type 9
IT	ARPA	Opsis SM 200	1 m³/h	straight / line not heated / 40° C only at input zone	Type 18
		Teom FDMS Vers. C	1 m³/h	straight / 40° C	Type 9
HU	HMS	FH 62 IR	1 m³/h	curved / 40° C	Type 23
HU	MDV	FH 62 IR	1 m³/h	curved / no heating	Type 9
SK	SHMU	Teom FDMS Vers. AB	1 m³/h	straight / 30° C	Type 9

A total of 2 TEOM, 2 FDMS, 7 ß – radiation and 1 light scattering instrument were used for PM2.5. Table 6 provides detailed information.

Table 6: PM2.5 automatic samplers

Country	Institution	Instrument	Flow rate	Sampling line	Inlet
CZ	CHMI	FH 62 IR	1 m³/h	curved / 30° C	Type 7
DK	NERI	Teom 1400	1 m³/h	straight / 50° C	Type 10, cyclone
SE	EHAS	Teom 1400	1 m³/h	straight / 50° C	Type 10, cyclone
EE	EERC	Thermo FH 62 IR	1 m³/h	curved / 40° C	Type 7
BE	VMM	ESM Andersen	1 m³/h	curved / dynamic heating	Type 9, cyclone
BE	ISSeP	FAI SW sn. 126	2.3 m³/h	straight / no heating	Type 12
		FAI SW sn. 129	2.3 m³/h	straight / no heating	Type 12
		Grimm 180	72 l/h	straight / no heating	Type 15
FR	AIRPARIF	Teom FDMS 1400 AB	1 m³/h	straight / 30° C	Type 9, cyclone
GB	BV	Teom FDMS Vers. C	1 m³/h	straight / 30° C	Type 9, cyclone
IT	ARPA	Opsis SM 200	1 m³/h	straight / line not heated / 40° only at input zone	Type 17
HU	MDV	FH 62 IR	1 m³/h	curved / 40° C	Type 23

2.3 The European Reference Laboratory of Air Pollution (ERLAP) and its equipment

Upon decision by the AQUILA Network and JRC, the ERLAP of the JRC in Ispra, Italy, took the responsibility to provide the Reference Values for the whole project. To perform the measurement campaigns, ERLAP prepared an air conditioned mobile laboratory with the following equipment on board:

> 2 Sequential Samplers SEQ 47/50 for PM10 gravimetric measurements
>
> 1 Sequential Sampler SEQ 47/50 for PM2.5 gravimetric measurements
>
> 1 Sequential Sampler SEQ 47/50 for PM1 gravimetric measurements
>
> 1 TEOM FDMS for online PM10 measurements
>
> 1 Sunset semi – continuous OC/EC analyzer
>
> Meteorological parameters (ambient temperature, ambient relative humidity, ambient pressure, 10m mast for wind speed and wind direction)

In addition to the equipment of the mobile laboratory, the following stationary equipment at the ERLAP laboratory in Ispra was used:

> 1 Balance room in conformity with EN standards [4] for weighing and conditioning of filters
>
> 1 Balance Mettler Toledo AX26, resolution 1 µg
>
> Reference mass pieces of 100 and 50 mg

Quality control of used equipment and material

The balance and the reference mass pieces are certified on a periodic time schedule by accredited companies, the climate conditions of the balance room are registered online and checked with certified thermo- and hygrometer.

The used filter material for the sequential samplers was 47 mm QMA (quartz with 5% borosilicate glass as a binder) filters from Whatman. Filters have been conditioned and weighed as described in EN 14907. Laboratory and travelling blanks have been used to evaluate possible changes in filter mass during the campaigns. To avoid contamination and loss of volatile material during transport, filters were always stored in petri dishes (Millipore, material of construction: molded polystyrene) inside a cool box or refrigerator. To minimize "dead time" between weighing and sampling, filters were transported in the hand luggage of airplanes to/from measurement sites, apart from a few occasions where transport was done with the mobile laboratory.

Twice a year all Sequential Samplers and the TEOM FDMS have been maintained at the Ispra site and their flow rate was recalibrated using a certified gas counter. At each measurement site, before the start of a measurement campaign, a verification of the flow rate took place. The same was done for the incorporated pressure and temperature sensors to verify if they were within their required limits (±1 K, ±10 hPa). Sequential Sampler inlets have been cleaned and greased before each campaign, regarding the campaign at the kerbside in Stockholm (SE) even once more during the campaign.

The OC/EC analyzer was maintained on an annual basis at the Ispra site. Its flow rate was as well verified before each campaign.

3.   The Reference Value

The Reference Values for PM10 were calculated as the average of both PM10 Sequential Samplers, exceptionally on three days one sampler was taken only. These samplers were placed inside the Mobile Laboratory keeping, by means of the air conditioning system of the measurement cabin, the filter temperature ≤ 20˚ C limiting in such a way losses of volatile material. Special care was taken in placing the outlet of the air conditioning system far away from the PM sampling points. The sampling height was ca. 3.5 m above ground.

The Reference Values for PM2.5 were taken from the PM2.5 Sequential Sampler. This sampler was placed outside next to the Mobile Laboratory. Exact distances and positions between samplers during each measurement campaign can be derived from the drawings in Annex 1. The sampling height was ca. 1.6 m above ground. The same applies to the PM1 Sequential Sampler.

Only values where the sampling took place for entire 24 hours were taken into account. In total 249 (PM10), 238 (PM2.5) and 242 (PM1) Reference Values were generated.

3.1 Equivalence test

Before the Sequential Samplers could be implemented in the measurement campaigns, they had to be compared in an Equivalence test to the Reference Method as described in EN 12341 and EN 14907, according to the "Guide to the Demonstration of Equivalence of Ambient Air Monitoring Methods" [5]. Three campaigns in three different measurement sites over the run of 41 days were conducted. The first campaign took place in Ispra (IT) during October and November 2005 for 22 days, the second in Marseille (FR) during November and December 2005 for 8 days, the third on a different site in Ispra in January 2006 for 11 days. Regarding PM10, two LVS Derenda 3.1 (Reference Method) were compared to two Leckel SEQ 47/50 (Candidate Method). The measured 24h average PM10 concentrations ranged from 17 to 131 $\mu g/m^3$.

For PM2.5 the measurement sites were the same, however only one LVS Derenda 3.1 was compared to one Leckel SEQ 47/50 over the run of 34 days. The measured 24h average PM2.5 concentrations ranged from 11 to 124 $\mu g/m^3$.

The equivalence test for PM10 was passed successfully; results and their acceptance criteria are presented in table 7.

Table 7: Results of the PM10 equivalence test for Leckel SEQ 47/50 samplers

	Orthogonal regression		expanded uncertainty at limit value	between sampler uncertainty	
	slope	intercept		Candidate Method	Reference Method
Acceptance criteria			≤25%	≤2.5 $\mu g/m^3$	≤2 $\mu g/m^3$
Site					
Ispra 1	1.02	-0.65	2.2	0.7	1.0
Marseille	0.98	0.91	5	0.6	0.4
Ispra 2	0.99	-0.08	9.9	1.0	1.7
All sites	**0.99**	**0.53**	**5.5**	**0.8**	**1.2**

The results of the PM2.5 comparison of one Leckel SEQ 47/50 to one Derenda LVS 3.1 (Reference Method) are given in Table 8.

Table 8: Results of the PM2.5 comparison of a Leckel SEQ 47/50

	Orthogonal regression slope	intercept	expanded uncertainty at target value
Acceptance criteria			≤25%
Site			
All sites	**1.03**	**-1.44**	**6.6**

3.2 Uncertainty calculation

The uncertainty calculation is based on EN 14907 using the following formula to calculate the combined uncertainty:

$$u_c = \sqrt{(u_{field}{}^2 + u_m{}^2/V^2 + C^2 * u_f{}^2/100^2)}\,\mu g/m^3$$

Where

V = the nominal sampled volume in cubic meters

C = the mass concentration of PM, specified as daily mean in $\mu g/m^3$

u_{field} = field uncertainty

u_m = mass uncertainty

u_f = flow uncertainty

3.2.1 Field uncertainty u_{field}:

As field uncertainty for PM10 the Between-Sampler Uncertainty of both Leckel Seq 47/50 samplers was taken. It was calculated individually for each measurement campaign according to the following formula:

$$u_{field}{}^2 = \frac{\sum(X_{i,1} - X_{i,2})^2}{2n}$$

Where

$X_{i,1}$ and $X_{i,2}$ are the simultaneous concentration data

n is the number of paired values

For PM2.5 and PM1 only one sampler each was operated, therefore the corresponding field uncertainty was calculated as follows:

PM10 Between-Sampler Uncertainty * ratio of PM2.5 on PM10

PM10 Between-Sampler Uncertainty * ratio of PM1 on PM10

However, due to the lack of a measured PM2.5 field uncertainty, a default value of u_{field} = 1 $\mu g/m^3$ (as proposed in [4]) was applied as uncertainty contribution of this size – fraction in the following calculations:

PM2.5 En-numbers (chapter 5.9.1, annex 5)

Calculation of uncertainty at the target value (chapter 5.4.2, annex 6)

PM2.5 uncertainties at low concentration level (chapter 5.9.3)

Table 9 shows the Between Sampler Uncertainties for PM10, the ratios of PM2.5/PM10 and PM1/PM10 are given later in figure 13 and 14.

Table 9: Number of Data pairs and Between-Sampler Uncertainties of both JRC Leckel Seq 47/50 samplers

Measurement site	Between sampler uncertainty u_{field} in µg/m^3	Data pairs
Madrid	0.8	14
Lisbon	0.8	14
Ljubljana	0.2	14
Graz	1.0	12
Prague	0.3	14
Wiesbaden	0.5	13
Copenhagen	2.0	12
Stockholm	1.6	12
Helsinki	1.3	14
Tallin	0.4	12
Biest H	0.6	14
Borgerhout	0.8	14
Paris	0.4	14
Dublin	0.4	17
Port Talbot	0.6	14
Milan	0.3	15
Budapest	1.0	14
Bratislava	0.3	13
Median:	0.6	
Min:	0.2	
Max:	2.0	
Sum:		246

3.2.2 Mass uncertainty u_m:

According to EN 14907 the following contributions have been taken into account to calculate the mass uncertainty for PM10, PM2.5 and PM1:

Uncertainty of the balance

Repeatability weighing blank filters

Repeatability weighing loaded filters

Buoyancy effect

The uncertainty of the balance is derived from its certificate issued by an accredited body. It accounts for linearity, repeatability, eccentricity and thermal drifts and is evaluated once a year. The contribution of the filter-weighing repeatability is expressed as the standard deviation of the differences between the first and second weighing. It is calculated individually for each campaign, separated into blank and loaded filters. The contribution of the buoyancy effect is taken from EN 14907 as $3/\sqrt{3}$ µg/m^3. Field blanks were collected in all campaigns with the exception of Madrid. They were generally not subtracted from the mass concentrations and not taken into account as a contribution to uncertainty.

However, the measurement campaigns in Budapest and Bratislava showed very high blank values (as described in chapter 5.10). Further investigations on the blank filters (measurements of OC/EC, etc) could not give a definitive answer on a possible source of contamination; yet one set of filter packages was identified to be associated with the mass gain. Hence, for Budapest and Bratislava the field blanks were subtracted from the measurement results. Further, for both campaigns the mass uncertainty accounts also for the repeatability of field blanks.

3.2.3 Flow uncertainty u_f:

The following contributions have been taken into account to calculate the flow uncertainty for PM10, PM2.5 and PM1:

        Uncertainty of the flow calibration device (gas counter)

        Calibration deviation

        Flow drift over time

        Temperature sensor

        Pressure sensor

The uncertainty of the gas counter, given as 0.15%, was taken from its certificate issued by an accredited body. The calibration deviation taken into account was estimated to be 2% maximum with a rectangular distribution. The flow drift over the run of 6 month was estimated to be 3% maximum, as well assuming a rectangular distribution. The accuracy and drift of the temperature sensor was estimated to be 1 K resulting in an uncertainty contribution of 0.3%; the accuracy and drift of the pressure sensor was estimated to be 10 hPa resulting in an uncertainty contribution of 1%.

3.3 Robustness of the Reference Values

In order to assess the validity of the reference values taken in these 18 measurement campaigns, a number of calculations were undertaken. The following paragraphs explain in detail the performed verifications:

3.3.1 Between-Sampler Uncertainty

The Between-Sampler Uncertainty, a measure of random components, reflects the precision of the Reference Values. It is used to demonstrate the agreement of both Leckel Seq 47/50 PM10 samplers. Table 9 gives an overview of all 18 measurement sites. To evaluate the quality of the encountered Between-Sampler Uncertainties, the criteria of the "Guide for the Demonstration of equivalence of Ambient Air Monitoring Methods" [5] for the reference method, u_{field} ≤2 µg/m^3, was taken. All values are lower than the criteria and hence demonstrating an acceptable performance. The highest values encountered were at traffic sites in Copenhagen and Stockholm (re-suspension of PM during winter period, see Annex 7). In the Stockholm dataset one daily average, identified as an outlier with the Grubbs test (ISO 5725-2 [6]), was removed to fulfil the criteria.

3.3.2 Combined uncertainties and E_n – numbers of both gravimetric PM10 samplers

Combined uncertainties, calculated separately for each Leckel Seq 47/50 as described in 3.2, are the estimated amount by which the calculated value may differ from the true one. It is expected, that ideally independent measurements of the same air mass show overlapping uncertainties. The two Leckel Seq 47/50 PM10 samplers measured 246 data-pairs of daily averages complying with the between-sampler uncertainty requirement (see table 9). Figures 2 to 5 give an overview of all data-pairs and their associated expanded uncertainties (k=2) which are overlapping in all cases.

Figure 2: JRC daily averages of PM10 gravimetric samplers and associated expanded uncertainties – Measurement campaigns Spain, Portugal, Slovenia, Austria and Czech Republic

Daily averages of JRC PM10 Seq I & II with expanded uncertainties
Spain, Portugal, Slovenia, Austria, Czech Republic
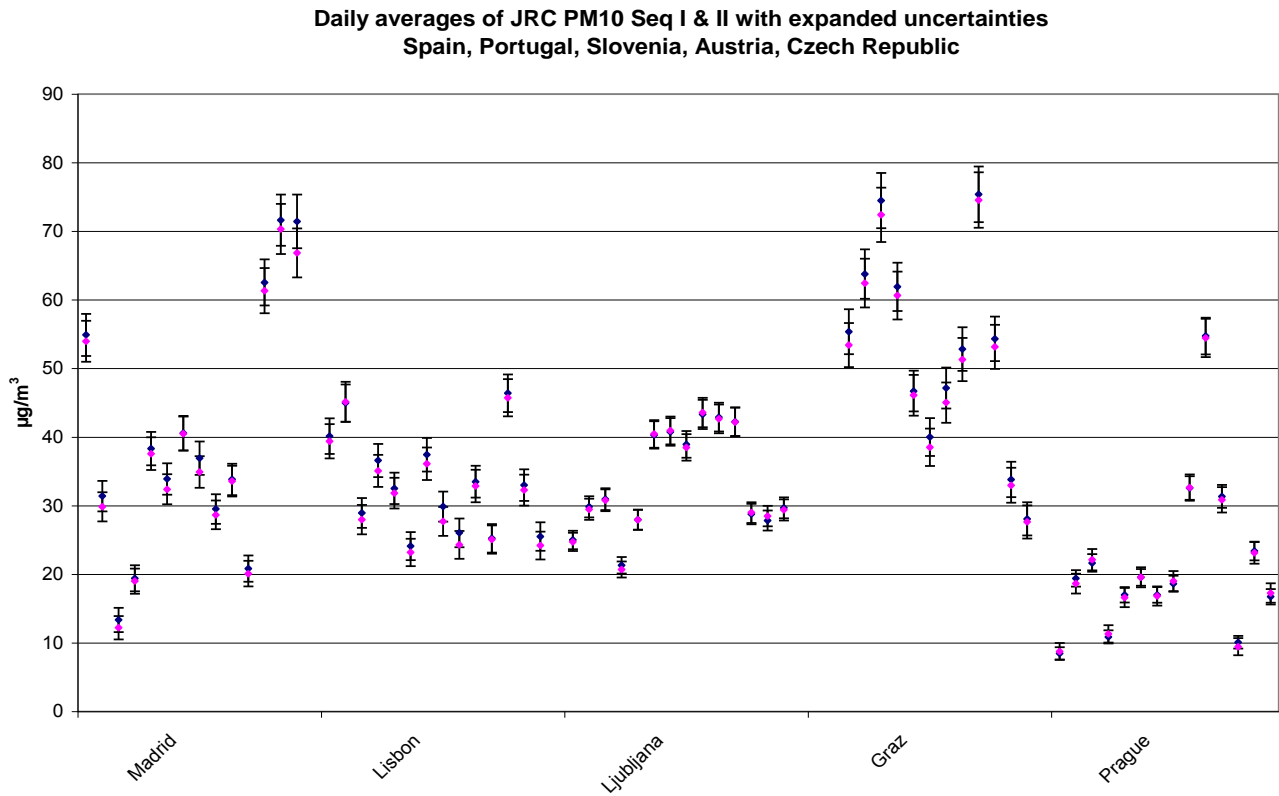
Figure 3: JRC daily averages of PM10 gravimetric samplers and associated expanded uncertainties – Measurement campaigns Germany, Denmark, Sweden, Finland and Estonia

Daily averages of JRC PM10 Seq I & II with expanded uncertainties
Germany, Denmark, Sweden, Finland, Estonia
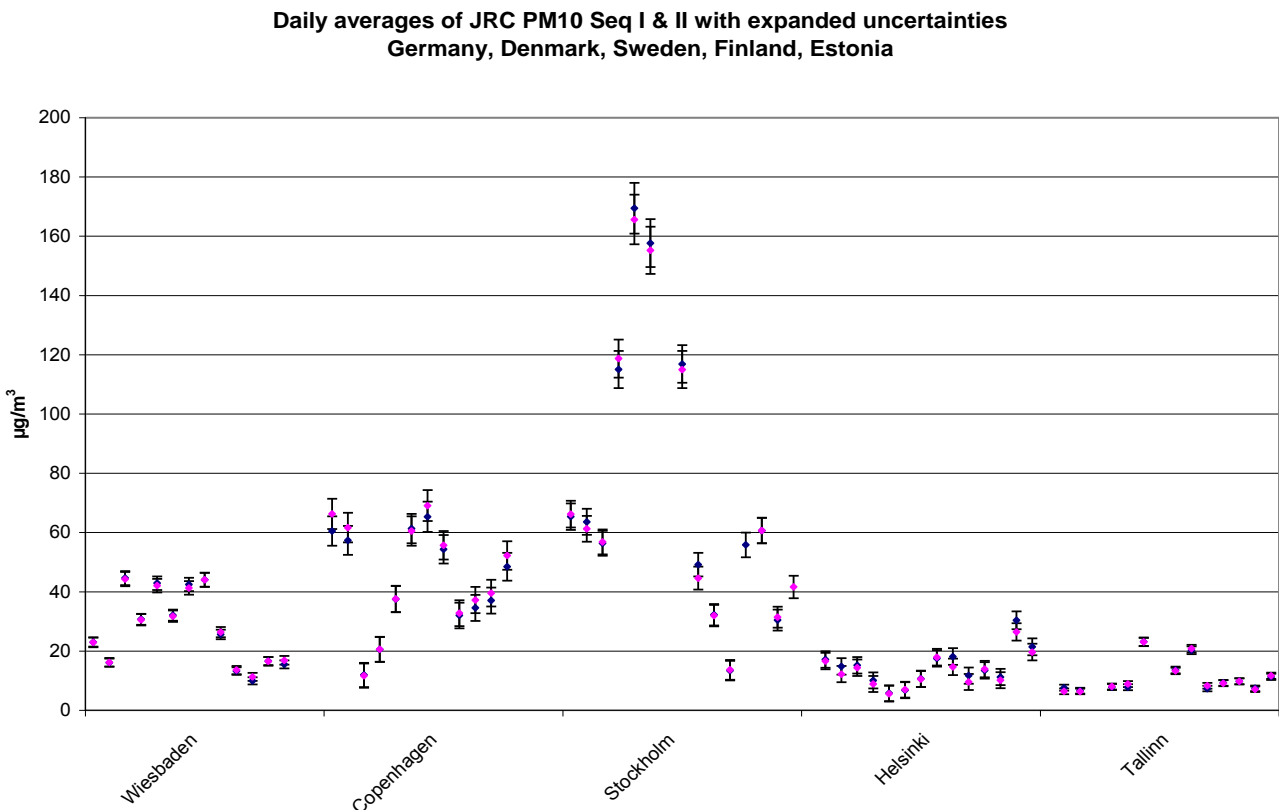
Figure 4: JRC daily averages of PM10 gravimetric samplers and associated expanded uncertainties –
Measurement campaigns Netherlands, Belgium, France, Ireland and United Kingdom

Daily average of JRC PM10 Seq I & II with expanded uncertainties
Netherlands, Belgium, France, Ireland, United Kingdom
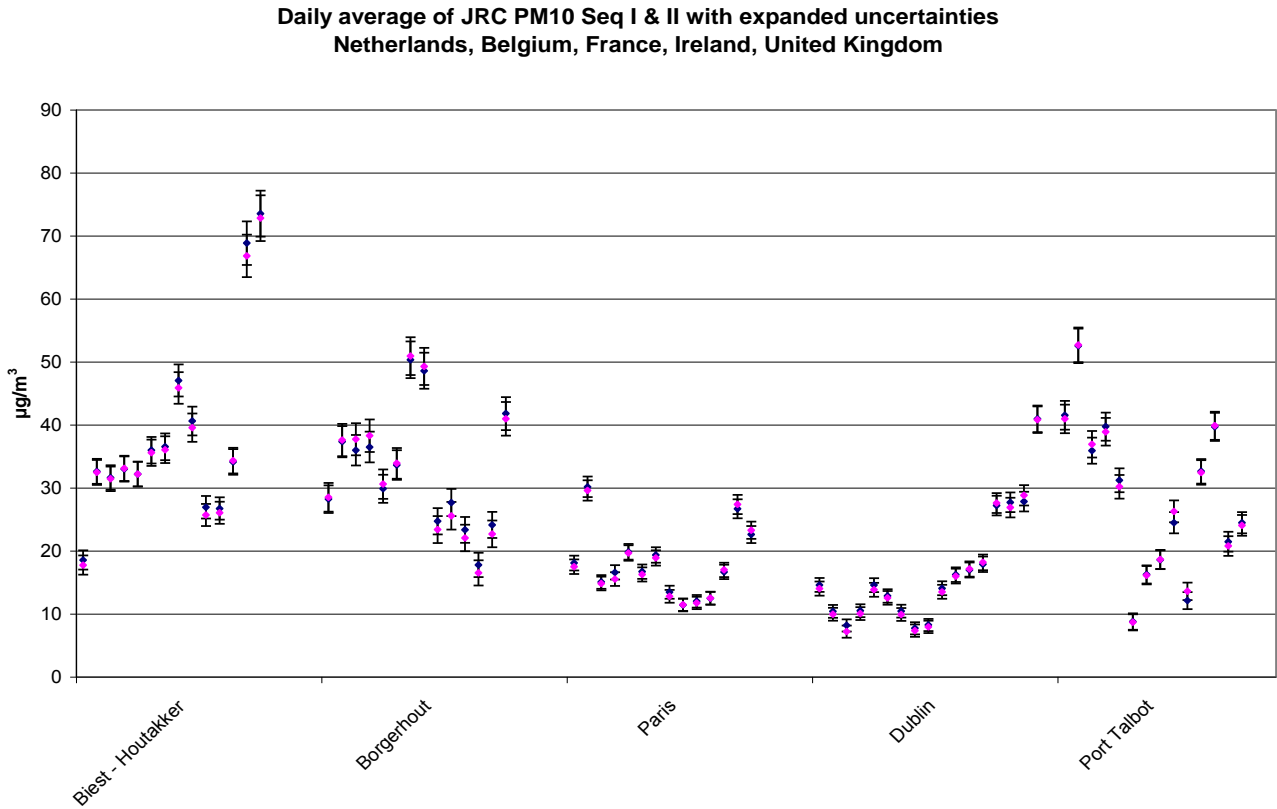
Figure 5: JRC daily averages of PM10 gravimetric samplers and associated expanded uncertainties –
Measurement campaigns Italy, Hungary and Slovak Republic

Daily average of JRC PM10 Seq I & II with expanded uncertainties
Italy, Hungary, Slovak Republic
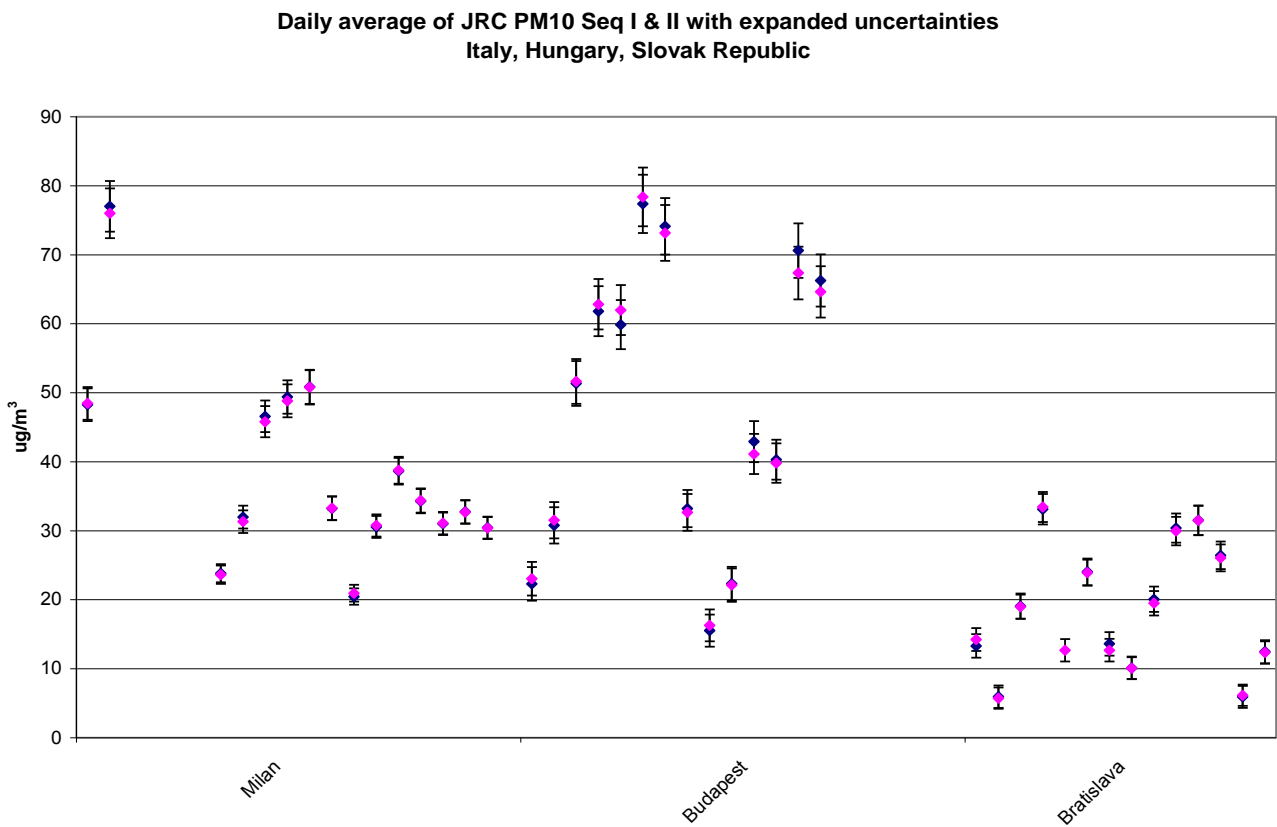
The calculation of E_n – numbers is commonly used in statistics to identify if a measurement and a reference value agree within their stated uncertainties. They are calculated according to the ISO/IEC guide 43-1 [7] using the formula

$$E_n = \frac{x - X}{\sqrt{U_{lab}^2 + U_{ref}^2}}$$

Where

x and X are the simultaneous concentration data

U_{lab} and U_{ref} are the simultaneous expanded uncertainties

One Seq 47/50 was used as "ref", the other one as "lab" to compare both results and uncertainties. The criteria given by the guide for a satisfactory result is $|E_n| \leq 1$, $|E_n| > 1$ is considered unsatisfactory. As it can be seen in Figure 6, all 246 daily averages used for further evaluations gave a satisfactory result; two data pairs with an En – number slightly >1 were removed before.

Figure 6: En – numbers of the Reference Values
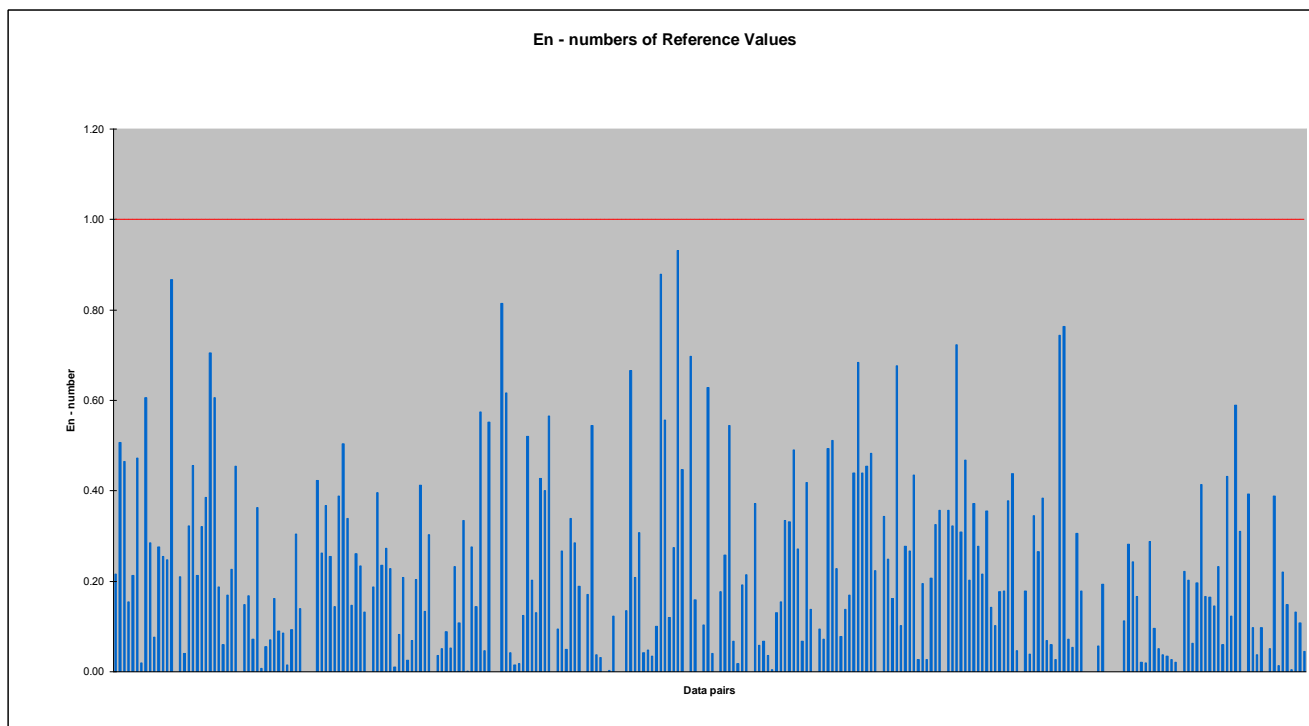
3.3.3 Bias of the Reference Values to the Grand Means – Determination of the Critical Difference

JRC values were produced in the capacity of Reference Values; this implies that biases between the grand means and the JRC values are implicit. However, to get an indication how close the Reference Values agree with the grand means of all participants, potential biases were calculated and compared to the critical differences as given in ISO 5725-6 [8]. To avoid an influence of different measurement techniques on the grand mean, these calculations were limited to LVS used during the campaigns. The bias δ of the Reference Value was calculated with the formula:

$$\delta = \mu - \overline{\overline{y}}$$

Where

$\overline{\overline{y}}$ is the grand mean of all participants using LVS

μ is the average Reference Value

The critical difference CD for $\left|\delta = \mu - \overline{\overline{y}}\right|$ was calculated with the formula:

$$CD = \frac{1}{\sqrt{2p}} * \sqrt{(2\sqrt{2} \cdot \sigma_R)^2 - (2\sqrt{2} \cdot \sigma_r)^2 (1 - \frac{1}{p}\sum\frac{1}{n_i})}$$

Where

p is the number of data-sets

n is the number of data pairs

σ_R is the estimate of the reproducibility standard deviation

σ_r is the estimate of the repeatability standard deviation

$2\sqrt{2}$ is a constant, see chapter 4.1.2 of the ISO standard

Note: As "data-set" is understood a series of daily averages measured by one participant with one instrument during one measurement campaign

To facilitate these calculations all data have been "normalized" dividing each daily average of a participant by the Reference Value of the same day. In an ideal case the result would be 1, in case of an underestimation of a participant the result is <1, in case of an overestimation it is >1. The bias and the CD were first calculated for all data of LVS and second for a limited number after eliminating suspect data. As suspect data was considered a data-set either identified as questionable by statistical means or with ≤10 daily averages. Further details about suspect data can be seen in chapter 5.1. The results for both the PM10 and PM2.5 Reference Values can be found in Table 10.

Table 10: Bias of the PM10 and PM2.5 Reference Values to the Grand Mean and Critical Difference

PM10 (p)	Bias of the Reference Value	Critical Difference
all LVS (29)	0.0142	0.0375
LVS after elimination of suspect data (18)	0.0336	0.0369

PM2.5 (p)	Bias of the Reference Value	Critical Difference
all LVS (16)	-0.0093	0.1641
LVS after elimination of suspect data (10)	0.0681	0.0762

In practice this means that for PM10 the average Reference Value is 1.42 % higher than the grand mean of all LVS, this is less than the critical difference of 3.75 %. After elimination of suspect data the difference rises to 3.36 % but stays still within the critical difference of 3.69 %.

For PM2.5 the average Reference Value is 0.01 % lower than the grand mean of all LVS, this is less than the critical difference of 16.41 %. After elimination of suspect data the average Reference Value becomes 6.8 %

higher than the grand mean but stays still within the critical difference of 7.62 %.

Concluding these calculations it can be stated that the Reference Values for PM10 and PM2.5 have sufficient accuracy and robustness to be used as such during further evaluations of all data in this report. Nevertheless the Reference Values show a tendency to be higher than the measurement results of the participating laboratories.

4. Overview of data measured by ERLAP during the measurement campaigns

The following chapter describes the data (Reference Values) measured by ERLAP during all measurement campaigns.

4.1 Concentration ranges

Due to different site characteristics (see Annex 7) and meteorological conditions the PM concentrations could differ significantly from one campaign to another. To see how often a certain concentration level occurred as Reference Value, a histogram of the three size fractions was drawn. PM10 presents two modes, one between 10 and 20 µg/m^3 and the other between 30 and 40 µg/m^3, while PM2.5 and PM1 present one distinct mode between 10 and 20 µg/m^3 and <10 µg/m^3 respectively. An overview is given in Figure 7.

Figure 7: Histogram of the Reference Values
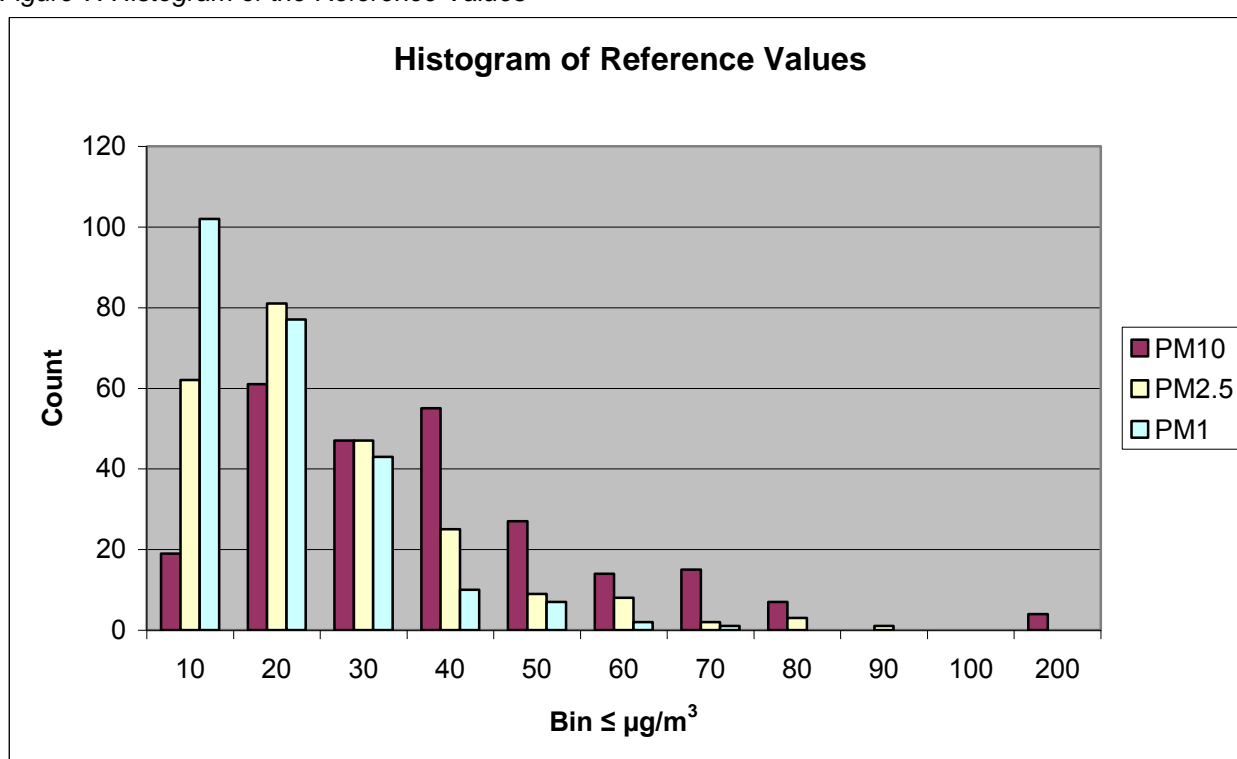
To summarize and compare the measurement campaigns, for each of them the minimum, maximum, median, the 25 and 75 percentiles of the Reference Value were calculated. The overall lowest values measured were in Finland with 5.7 µg/m^3 for PM10, 2.8 µg/m^3 for PM2.5 and 1.5 µg/m^3 for PM1; the overall highest values measured were 167.5 µg/m^3 for PM10 (Sweden), 81.4 µg/m^3 for PM2.5 (Sweden) and 61.0 µg/m^3 for PM1 (Hungary). Data measured in the kerbside in Stockholm have the biggest spread. On the other hand, due to constantly low concentration levels, comparisons between reference and participants particularly in Helsinki and Tallinn might result in large relative deviations, but the absolute differences approach the between-sampler uncertainty. Descriptive statistics of each campaign are illustrated in Figure 8 (PM10), Figure 9 (PM2.5) and Figure 10 (PM1).

Figure 8: Box and whisker diagram for the PM10 Reference Values

PM10 DESCRIPTIVE STATISTICS
Median; Box: 25%-75%; Whisker: Min-Max
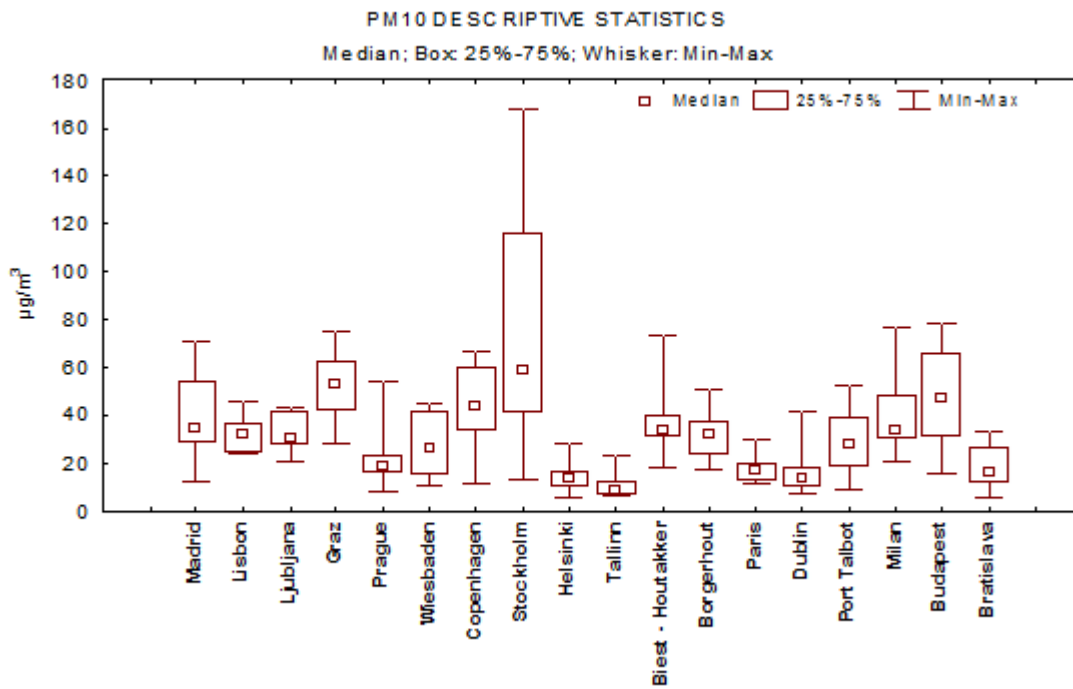
Figure 9: Box and whisker diagram for the PM2.5 Reference Values

PM2.5 DESCRIPTIVE STATISTICS
Median; Box: 25%-75%; Whisker: Min-Max
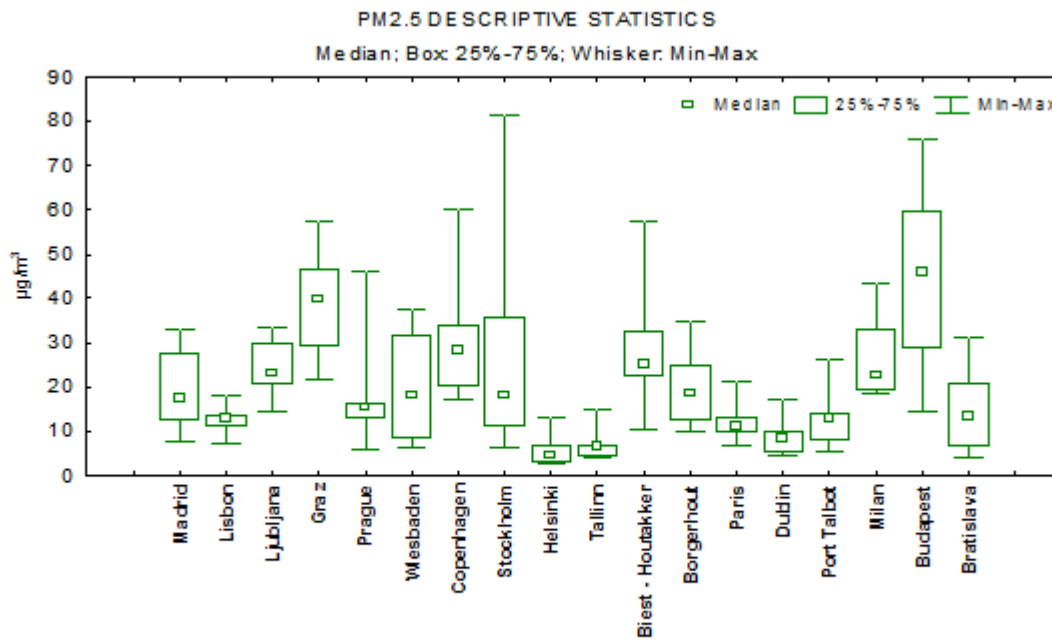
Figure 10: Box and whisker diagram for the PM1 Reference Values

PM1 DESCRIPTIVE STATISTICS
Median; Box 25%-75 %; Whisker: Min-Max
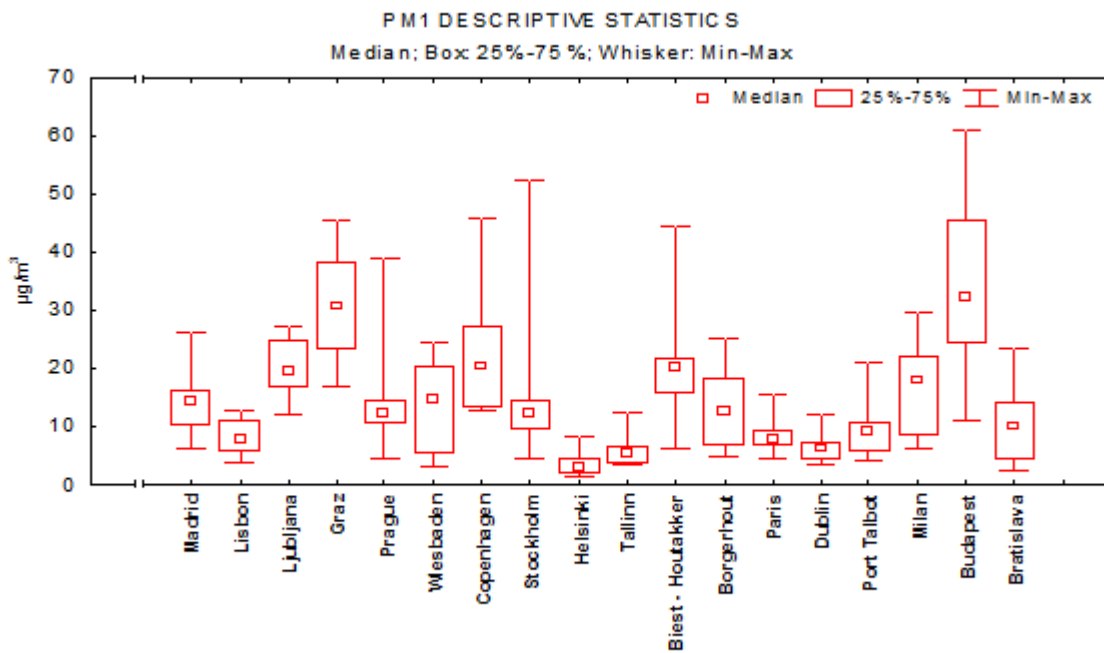
The assigned uncertainties to the PM10 and PM2.5 Reference Values are summarized in Figure 11 and 12 displaying the minimum, maximum and average combined uncertainty associated with each campaign.

Figure 11: Minimum, maximum and average combined uncertainty of the PM10 Reference Value for each measurement campaign

Combined uncertainty of PM10 Reference Value: Min, max and average
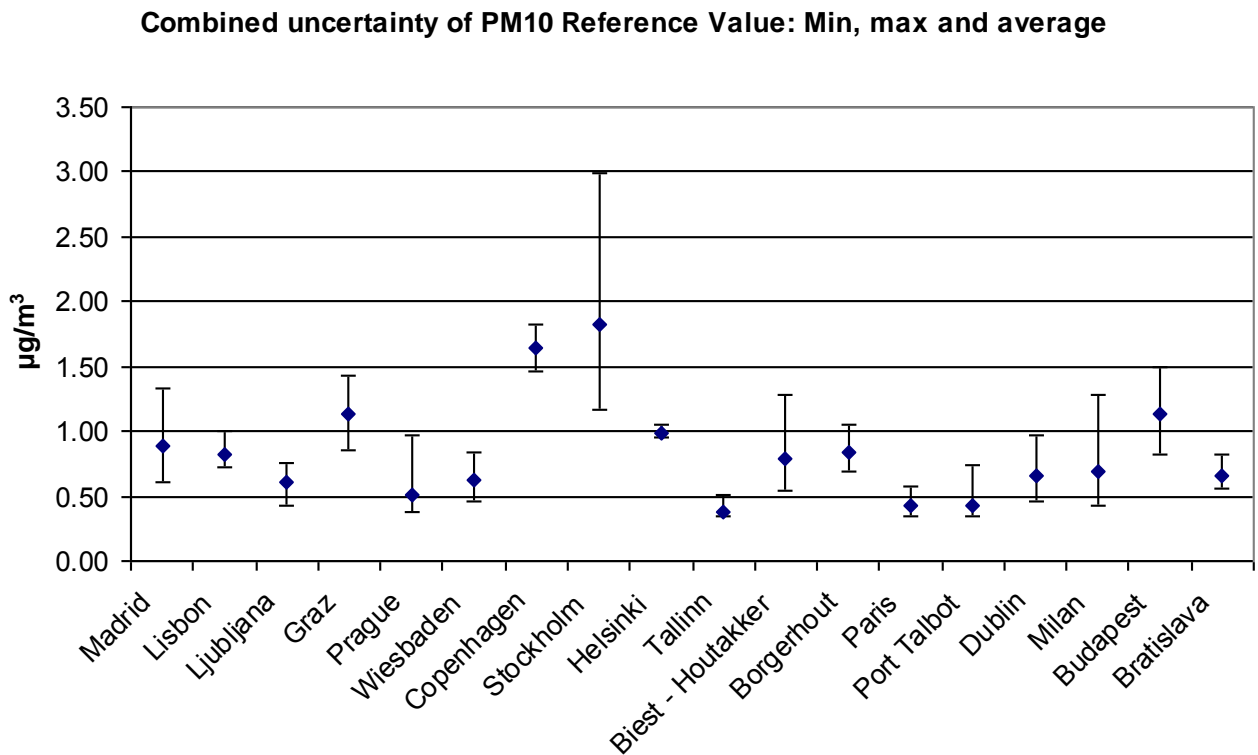
Figure 12: Minimum, maximum and average combined uncertainty of the PM2.5 Reference Value for each measurement campaign

Combined uncertainty of PM2.5 Reference Value: Min, max and average
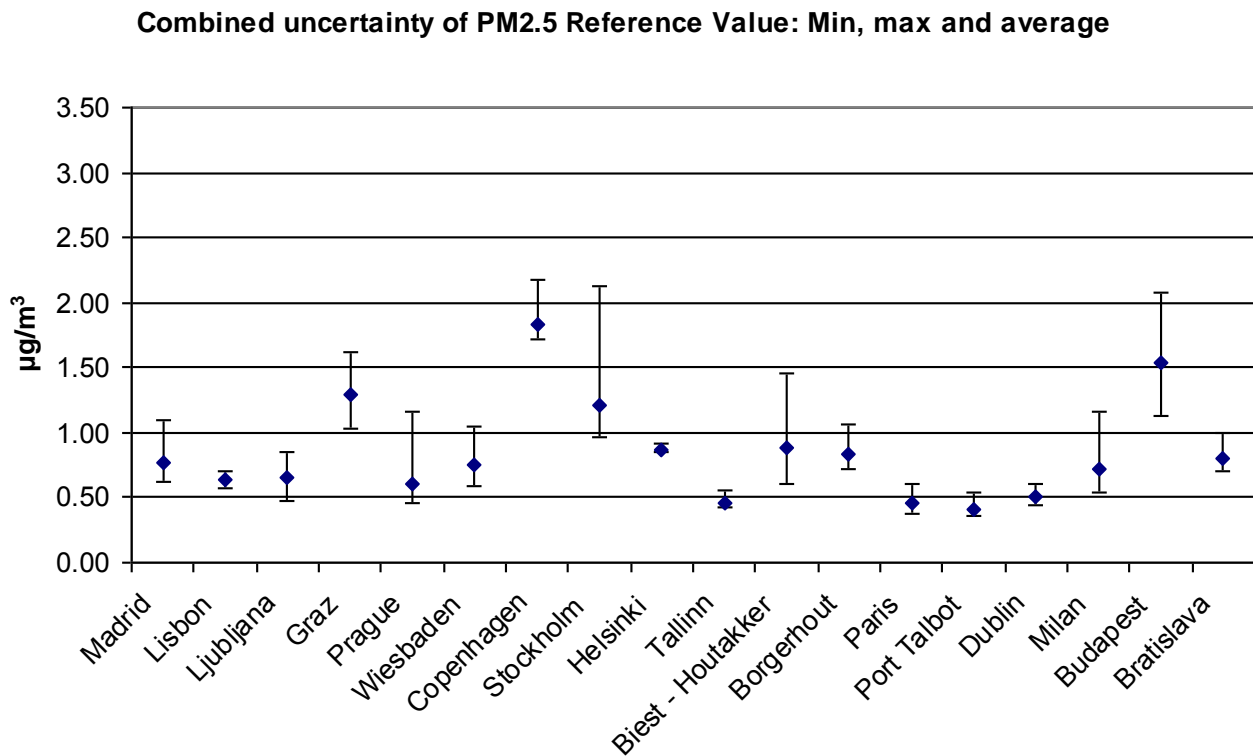
4.2 Ratios of PM2.5 and PM1 on PM10

The percentage of PM2.5 on PM10 was generally in line with other European results, as reported in the 2nd position paper on particulate matter [9] or recent results reported by Putaud et al [10]. In some situations close to traffic, the contribution of re-suspension was dominating the importance of the coarse fraction. In other cases natural contributions like sea salt decreased the ratio fine/coarse fraction (see Annex 7).

The minimum, maximum and average ratios for all campaigns can be found in Figure 13 (PM2.5 on PM10) and Figure 14 (PM1 on PM10).

Figure 13: Minimum, maximum and average ratios of PM2.5 on PM10

Percentage of PM2.5 on PM10 min, max and average
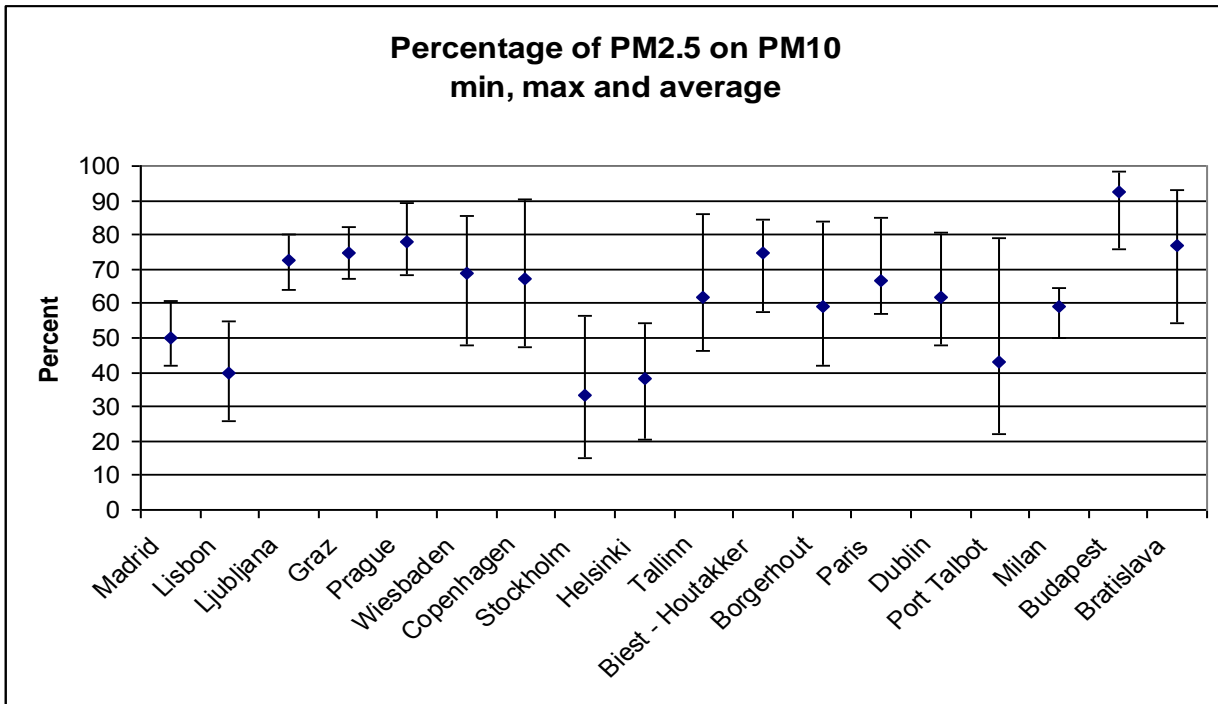
Figure 14: Minimum, maximum and average ratios of PM1 on PM10

Percentage of PM 1 on PM 10 min, max and average
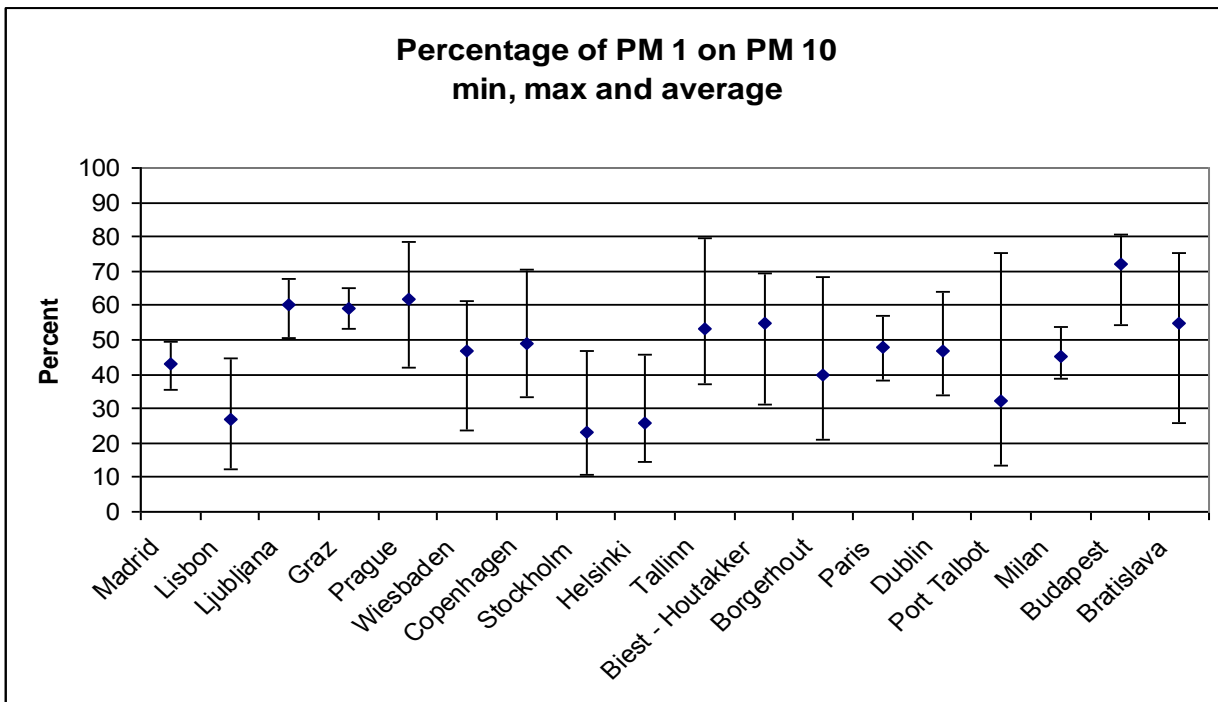
To investigate if the PM2.5 Reference Values are influenced by the coarse fraction, a scatter plot of the ratios PM2.5/PM10 and PM1/PM10 was drawn (Figure 15). The regression of this plot is showing ratios arranged along a straight line indicating that the contribution of PM2.5 to PM10 is proportional to the contribution of the sub-micrometric fraction to PM10. Considering that contribution from road dust re-suspension to PM1 is negligible (~3%, Amato et al., 2009) these findings underpin the assumption that the PM2.5 Reference Values are not influenced by local re-suspension.

Figure 15: Scatter plot of the ratios PM2.5 on PM10 and PM1 on PM10

Scatter plot ratios PM2.5 / PM1

$y = 0.8072x - 0.0337$
$R^2 = 0.9374$
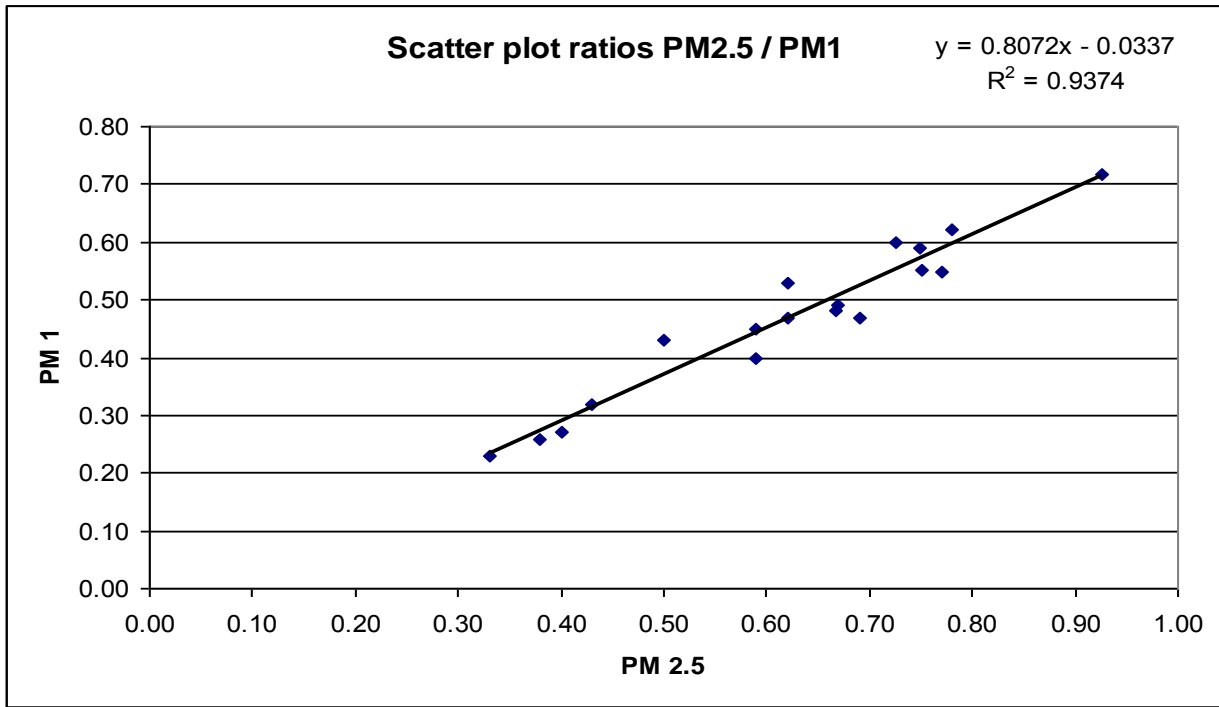
5. Evaluation of all data sets

5.1 Calculation of the "Grand mean" and identification of suspect data using "normalized" data-sets

This chapter presents the comparability of all measured data using ISO 5725-2 [6] to perform the necessary calculations. In a first step all data were "normalized" dividing each daily average of a participant by the Reference Value of the same day. In an ideal case the result would be 1, in case of an underestimation of a participant the result is <1, in case of an overestimation it is >1. Such a relative approach allows on the one hand calculation of statistical parameters like average, standard deviation and Mandel's h and k statistics for each participant, on the other hand identification of outliers and calculation of statistical parameters for the entire lot of data.

To verify the graphical consistency of data-sets, Mandel's h and k statistics were used. Mandel's h statistic describes the between-laboratory and Mandel's k statistic the within-laboratory consistency. Both statistics were plotted together with indicator lines serving to identify suspect data-sets. Cochran's and Grubb's test were applied on the entire lot of data to identify outliers with a numerical technique, their results were compared to their corresponding critical values.

A detailed numeric overview of all "normalized" data-sets and their corresponding codification (used in the following graphs) is given in Annex 4.

5.1.1 Calculations for PM10

5.1.1.1 Averages and standard deviation

For PM10, 79 data-sets were evaluated. The averages of the "normalized" data-sets range from 0.71 to 1.44, their standard deviations from 0.01 to 0.75; an overview is given in figure 16.

Figure 16: "Normalized" data-sets for PM10: Average and standard deviation of each participant
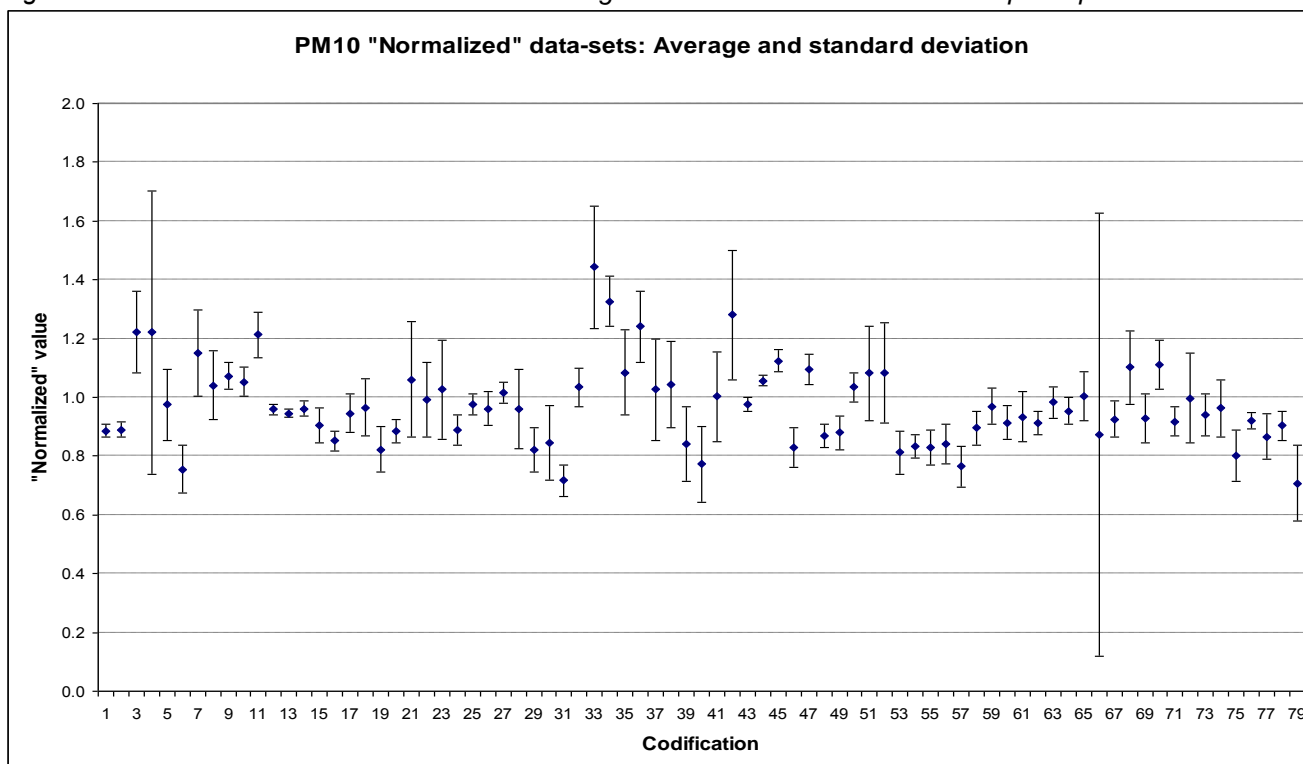
5.1.1.2 Mandel's h and k statistics

Mandel's *h* values can either be positive or negative, in an ideal case they should be evenly distributed around zero. The Critical Value at the 5% significance level is represented by a green line, at the 1% significance level by a red line. Critical Values taken are based on p = 30 (maximum number of reporting labs given in ISO 5725-2) assuming that they remain constant for a higher number of laboratories (p = 79). Two data-sets, code 33 and 34, exceed even the 1% significance level. A summary of h statistics is given in figure 17.

Figure 17: Mandel's h statistic for PM10 with Critical Values for the 5% (green) and 1% (red) significance level
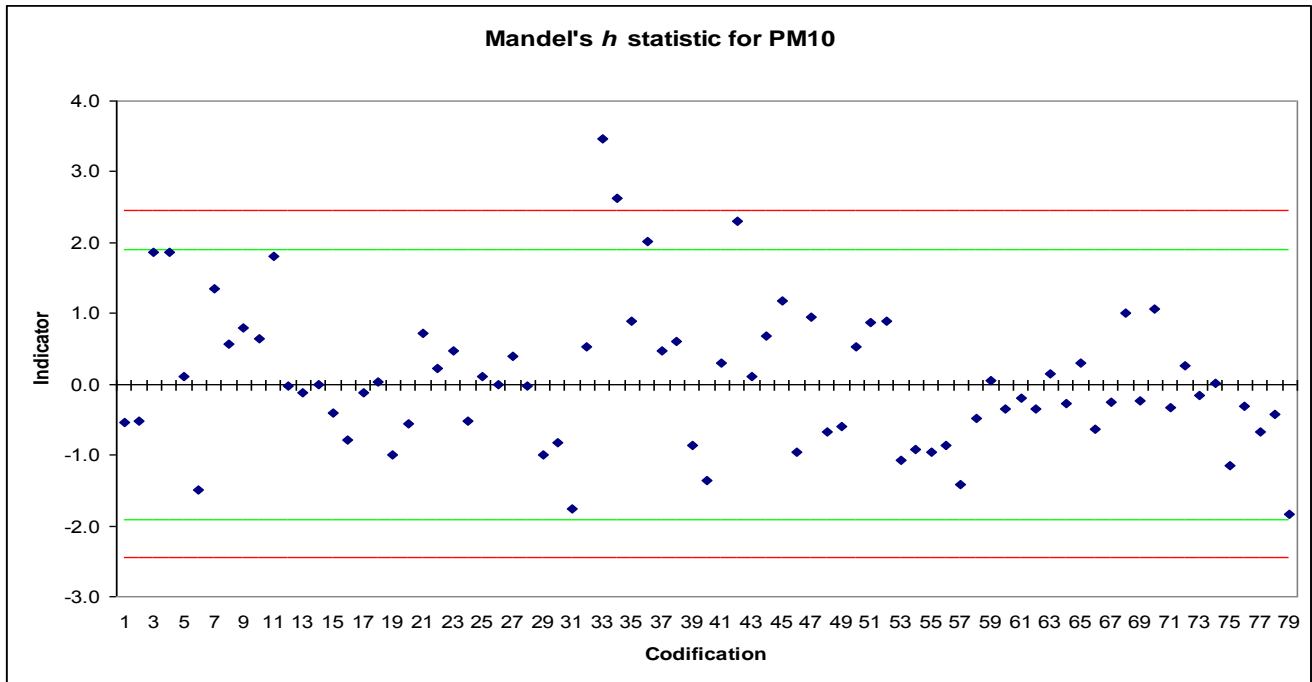
Mandel's *k* values are always positive, high values indicate a poor repeatability. The Critical Value at the 5% significance level is represented by a green line, at the 1% significance level by a red one. Critical Values taken are based on p = 30 and 10 replicates (maximum value given in ISO 5725-2) assuming that they remain constant for a higher number of laboratories and replicates (p = 79, 14 replicates usually). Three data-sets, code 4, 42 and 66, exceed even the 1% level while code 33 is exactly on the red line. A summary of k values is given in Figure 18.

Figure 18: Mandel's k statistic for PM10 with Critical Values for the 5% (green) and 1% (red) significance level
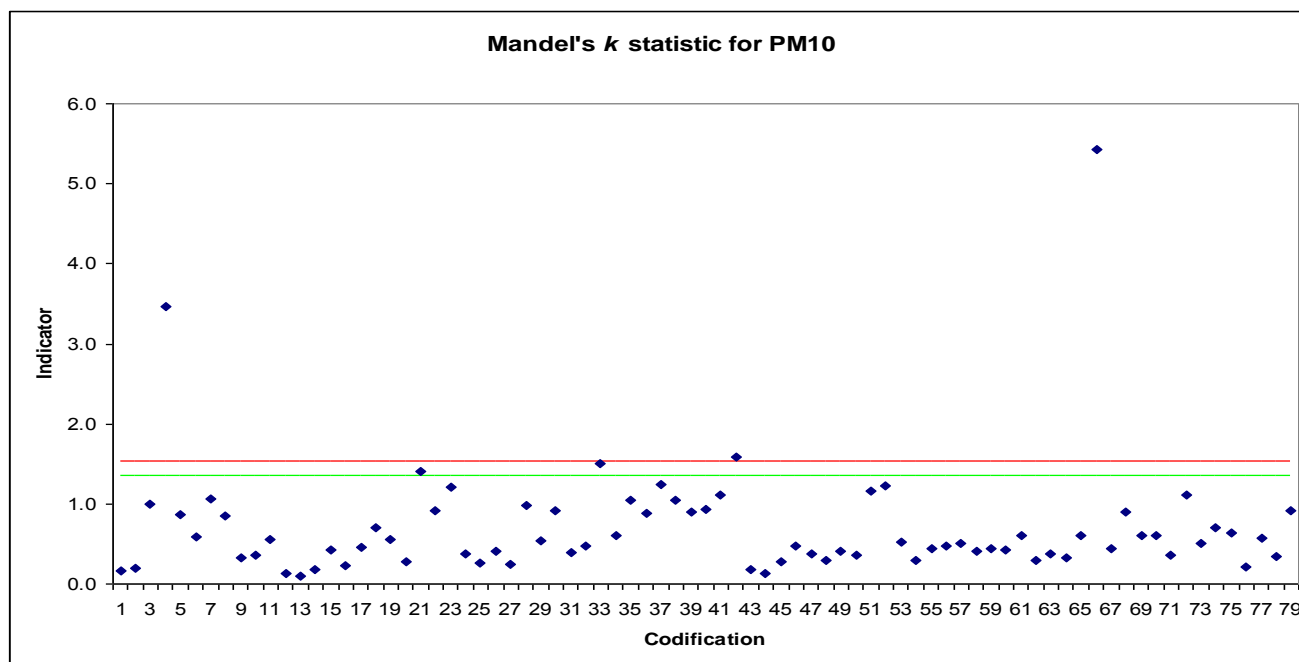
5.1.1.3 Grubbs outlier test

A Grubbs outlier test for one maximum or minimum observation was performed with all 79 data-sets. Starting G_{max} (3.4680) was between the 5% (3.3061) and 1% (3.6729) critical values [11] for Grubbs' test (p = 80), identifying data set 33 as a straggler.

5.1.1.4 Cochran test

In order to test the within laboratory variances, Cochran test was performed with all 79 data-sets (consisting of 12 data each on average). Eliminating five doubtful data-sets improved the result from an original value of 0.3718 to a lower value of 0.0501, but still higher than the critical value for the Cochran test interpolated from tables: 0.0475 at the 1% and 0.0415 at the 5% level of significance (p = 74 and n = 12) [12].

5.1.1.5 Summary of consistency and outlier tests

Mandel's *h* statistic identifies data-sets 33 and 34 as suspect. The examination of figure 16 confirms the lack of consistency of the two data-sets presenting the highest deviations from the reference value. On the other hand, Mandel's *k* statistic identifies data-sets 4, 42 and 66 as suspect which in figure 16 are those with the highest standard deviation. The Grubbs test identifies data-set 33 as a straggler as well.

In the Cochran test, critical value was exceeded even after the exclusion of suspect data-sets (4, 21, 33, 42 and 66). This demonstrates that differences in the within-laboratory variance are not negligible.

To summarize all PM10 measurements, the grand mean, median, repeatability and reproducibility (both expressed as standard deviation) were calculated for all data-sets (uncensored) and a reduced amount of data-sets (censored) with suspect data-sets 4, 21 33, 34, 42 and 66 excluded. Table 11 presents the consensus values in detail.

Table 11: PM10 consensus values for uncensored and censored data-sets

	uncensored	censored
number of data-sets	79	73
grand mean	0.962	0.950
median	0.94	0.94
repeatability	0.124	0.090
reproducibility	0.171	0.141

Based on the reproducibility standard deviation found after censoring, the relative uncertainty of PM10 measurement results from this study is estimated to be 14%. Using a coverage factor of 2, which for the number of datasets available represents a confidence interval of 95%, the relative expanded uncertainty is 28%. For an overall mean of reference values of 32.2 $\mu g/m^3$, this means an absolute expanded uncertainty of 9 $\mu g/m^3$.

5.1.2 Calculations for PM2.5

5.1.2.1 Averages and standard deviation

For PM2.5, 31 data-sets were evaluated. The averages of the "normalized" data-sets range from 0.43 to 2.17, their standard deviations from 0.01 to 0.94; an overview is given in figure 19.

Figure 19: "Normalized" data-sets for PM2.5: Average and standard deviation of each participant
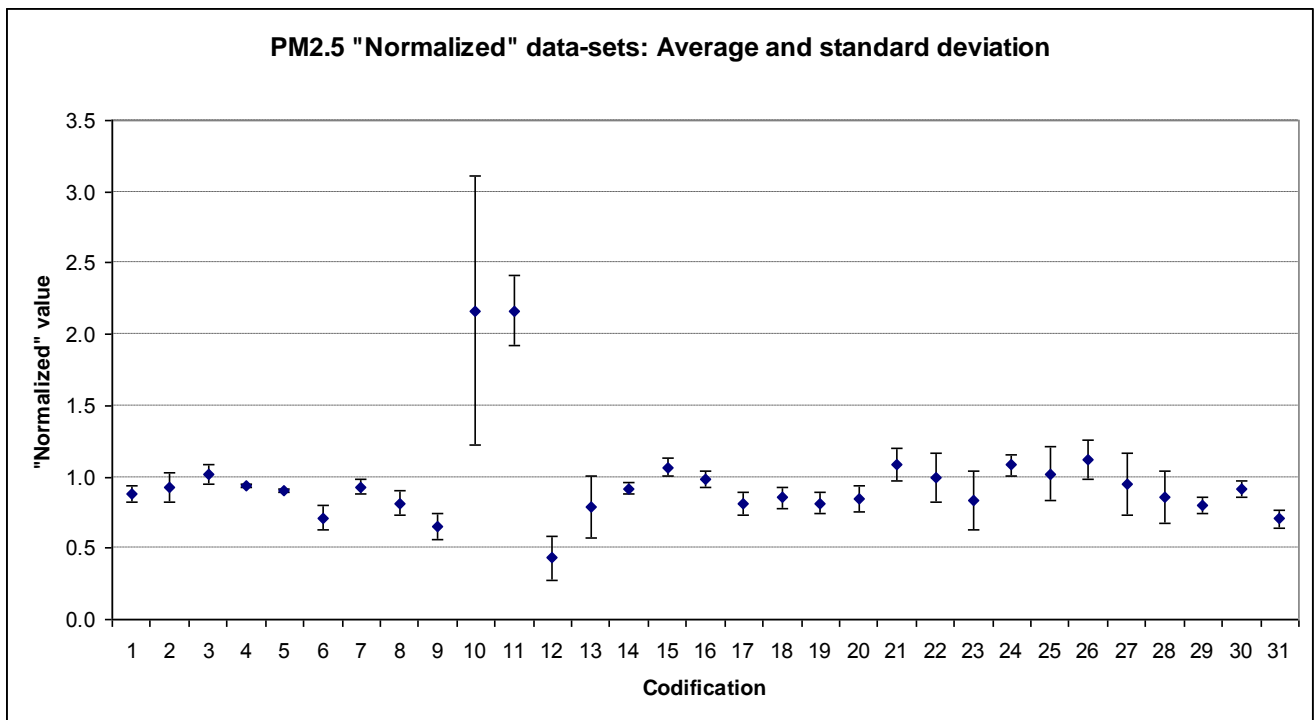
The majority of the averages fall within the interval 0.5-1.5. Data-sets 10 and 11 present an average well above the rest while data-set 12 is the only one below the mentioned interval. In addition to the anomalous average data-set 10 presents also a considerable data spread.

5.1.2.2 Mandel's h and k statistics

A description of the adopted methodology is given in chapter 5.1.1.2. Two data-sets, 10 and 11, exceed even the 1% level for Mandel's *h* statistic. An overview of the mentioned statistic for each data-set is given in figure 20.

Figure 20: Mandel's h statistic for PM2.5 with Critical Values for the 5% (green) and 1% (red) significance level
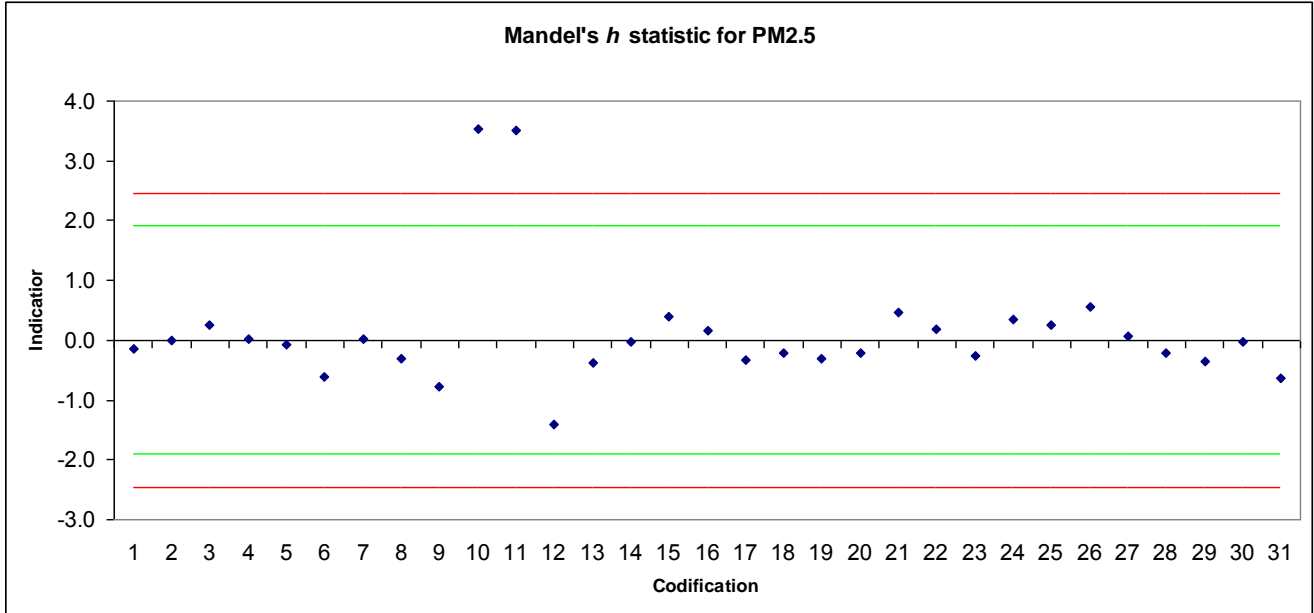
Data-set 10 exceeds even the 1% level of significance for the Mandel *k* test. An overview of the mentioned statistic for all PM2.5 data-sets is given in Figure 21.

Figure 21: Mandel's k statistic for PM2.5 with Critical Values for the 5% (green) and 1% (red) significance level
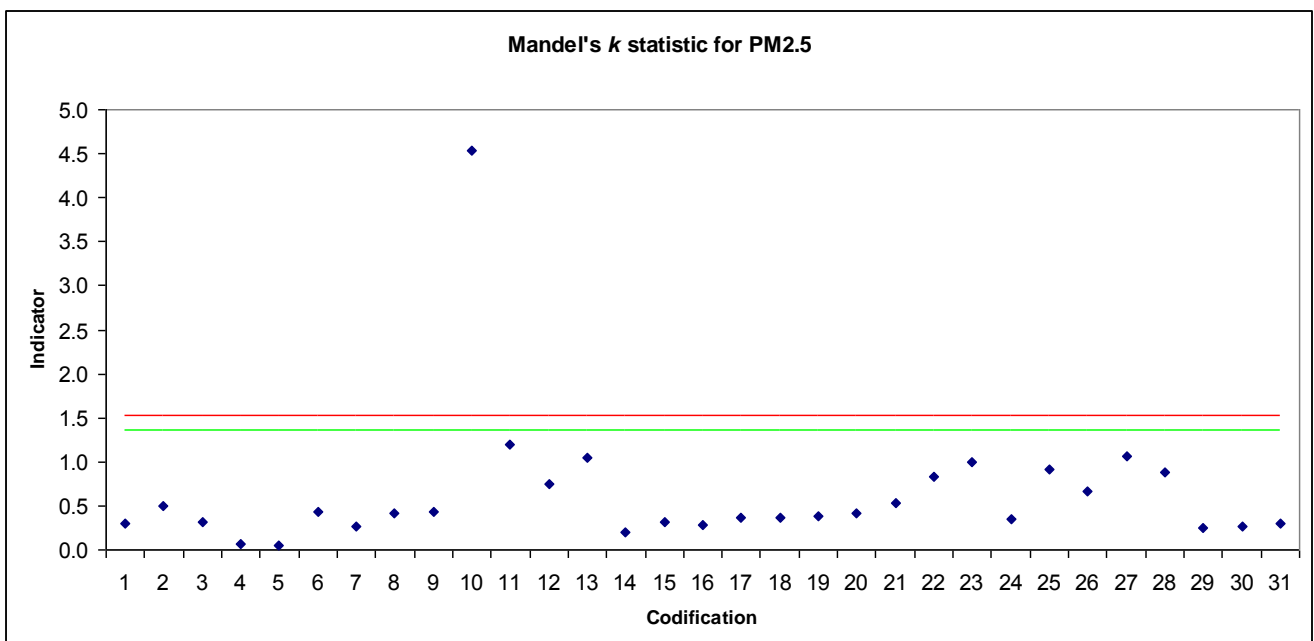
5.1.2.3 Grubbs outlier test

A Grubbs outlier test for one maximum or minimum observation was performed with all 31 data-sets. Starting G_{max} (3.5250) was higher than the 5% (2.924) and 1% (3.253) critical values [6] for Grubbs' test (p = 31). The test identified data-sets 10 and 11 as outliers for one maximum observation and data-set 12 as straggler for one minimum observation.

5.1.2.4 Cochran test

Within laboratory variances were assessed using Cochran test performed with all 31 data-sets (consisting of an average of 12 data each). Eliminating two doubtful data-sets (10,11) improved the result from a starting value of 0.6636 to a lowest value of 0.1241, but still higher than the Critical Value for the Cochran test interpolated from tables: 0.105 at the 1% and 0.093 at the 5% level of significance (p = 29 and n = 12) [12].

5.1.2.5 Summary of consistency and outlier tests

Mandel's *h* statistic pointed out the lack of between lab consistency for data-sets 10 and 11, also in agreement with the preliminary interpretation of figure 19. Mandel's *k* statistic signalled the lack of within lab consistency for data-set 10 which is coherent with the visual data spread resulting from figure 19. The Grubbs test identifies the data-sets 10 and 11 as outliers for maximum observations and 12 as a straggler for minimum observations. Differences in within laboratory variances appeared to be relevant as revealed by statistics above the critical level in the Cochran test too.

To summarize all PM2.5 measurements, the grand mean, median, repeatability and reproducibility (both expressed as standard deviation) were calculated for all data-sets (uncensored) and a reduced amount of data-sets (censored) with suspect data-sets code 10, 11 and 12 eliminated. Table 12 presents the consensus values in detail.

Table 12: PM2.5 consensus values for uncensored and censored data-sets

	uncensored	censored
number of data-sets	31	28
grand mean	0.926	0.903
median	0.90	0.90
repeatability	0.186	0.113
reproducibility	0.328	0.163

Based on the reproducibility standard deviation found after censoring, the relative uncertainty of PM2.5 measurement results from this study is estimated to be 16%. Using a coverage factor of 2, which for the number of datasets available represents a confidence interval of 95%, the relative expanded uncertainty is 33%. For an overall mean of reference values of 22.3 $\mu g/m^3$, this means an absolute expanded uncertainty of 7.2 $\mu g/m^3$.

5.1.3 Differentiation between samplers and automatic analyzers

In order to obtain information on possible effects of the method of measurement used, the ISO 5725 part 2 statistics have been applied to the three main groups of methods:

- Manual gravimetric methods using low-volume samplers
- Manual gravimetric methods using high-volume samplers
- Automatic analyzers.

The results obtained are presented in tables 13 and 14. As "censored" is understood, that data-sets were either identified as questionable by statistical analysis (see chapter 5.1.1 and 5.1.2) or consist of ≤10 daily averages.

Table 13: PM10 results differentiated by method

	LVS		**HVS**		**Autom. analyzer**	
	uncensored	*censored*	*uncensored*	*censored*	*uncensored*	*censored*
Number of datasets	29	18	13	11	37	33
Mean	0,986	0,966	0,957	0,932	0,947	0,931
Median	0,966	0,962	0,947	0,940	0,924	0,915
Repeatability	0,154	0,065	0,108	0,096	0,104	0,098
Reproducibility	0,185	0,102	0,144	0,119	0,170	0,154

Table 14: PM2.5 results differentiated by method

	LVS		**HVS**		**Autom. analyzer**	
	uncensored	*censored*	*uncensored*	*censored*	*uncensored*	*censored*
Number of datasets	16	10	3	2	12	10
Mean	1,009	0,932	0,912	0,910	0,832	0,876
Median	0,926	0,925	0,907	0,903	0,822	0,872
Repeatability	0,233	0,082	0,041	0,042	0,132	0,133
Reproducibility	0,405	0,147	0,041	0,042	0,227	0,192

When considering censored results only it is found that all methods slightly underestimate the reference values, with underestimations being less for PM10. Reproducibility standard deviations for methods with sufficient datasets (excluding HVS for PM2.5) are better for LVS and HVS for PM10, and LVS for PM2.5 when compared to automatic analyzers. When using reproducibility standard deviations as indicators for uncertainties, the relative uncertainties for results obtained by application of low-volume sampling are 10% for PM10 and 15% for PM2.5, and 12% for results for PM10 measured by applying high-volume sampling. Relative expanded uncertainties are thus in the range of 20 to 30%. When expressed at the level of the limit value, the relative expanded uncertainties are 13-15% for PM10 (LVS/HVS), and 26% for PM2.5 (LVS, taking the annual average target value for PM2.5).

5.2 Orthogonal regression and correlation analysis

In addition to the correlation coefficient between participants and reference in each data-set, orthogonal regression using the excel template for the Equivalence field-test of the Guide to the Demonstration of Equivalence of Ambient Air Monitoring Methods [5], was calculated. For both regression outputs and correlation coefficients, the minimum, maximum and median give generally better results for PM10 compared to PM2.5. Around 90% of the PM10 data-sets show $R^2 \geq 0.90$ while only 75% of PM2.5 data-sets have $R^2 \geq 0.90$. For PM10, data-sets code 4 and 66 present the lowest correlation factors (0.023 and 0.171 respectively), being linked to bad regression parameters too. For PM2.5, data-set code 11 presents the lowest correlation coefficient (0.086) linked to the worst regression parameters. This confirms the findings of the evaluations made in 5.1. In the following all delivered data are reported for the sake of completeness even though there are certain data-sets in which the number of daily averages is clearly too small for any statistical treatment. Detailed information on the regression output parameters, the correlation coefficient (R^2) and the associated amount of data (n) for each data-set is given in table 15 for PM10 and table 16 for PM2.5.

Table 15: Regression outputs and correlation coefficients for PM10 data-sets

Country	Codification	Laboratory	Instrument	Regression output				n	R²
				slope b	uncertainty of b	intercept a	uncertainty of a		
ES	1	ISCIII	Derenda A	0.87	0.02	0.52	0.71	13	0.996
	2	ISCIII	Derenda B	0.85	0.02	0.92	0.76	7	0.996
	3	AdM	Teom 1400	1.32	0.05	-2.77	2.21	13	0.984
PT	4	IdA	Tecora	7.04	0.49	-188.62	16.16	13	0.023
	5	IdA	Andersen	0.93	0.16	1.38	5.35	13	0.687
	6	IdA	Env. 101	0.92	0.10	-5.17	3.45	13	0.850
SI	7	EPA SI	Derenda	0.93	0.23	7.76	8.73	8	0.630
	8	EPA SI	Teom 1400	0.87	0.12	5.25	4.12	14	0.780
	9	EIMV	Tecora	1.23	0.06	-0.31	2.23	13	0.970
	10	Anhovo	Tecora	1.05	0.06	0.20	2.02	14	0.962
	11	EIMV	Andersen	1.35	0.13	-4.45	4.60	8	0.940
AT	12	UBA AT	Digitel	0.95	0.02	0.31	1.19	12	0.995
	13	LR OOe	Digitel	0.95	0.02	-0.25	0.82	12	0.997
	14	UBA AT	FDMS	0.96	0.03	-0.07	1.65	12	0.990
	15	LR OOe	FDMS	1.04	0.03	-6.64	1.55	12	0.992
	16	LR Stmk.	Digitel	0.82	0.04	1.55	2.07	12	0.978
	17	LR Stmk.	FH 62 IR	0.86	0.07	4.31	3.64	12	0.939
CZ	18	CHMI	FH95 Nitrocell.	0.91	0.03	0.73	0.74	14	0.987
	19	CHMI	FH95 glass	0.99	0.02	-2.94	0.41	14	0.996
	20	CHMI	Derenda LVS Seq	0.98	0.02	-1.84	0.50	14	0.995
	21	CHMI	Derenda Hvol B	0.94	0.06	1.91	1.36	14	0.957
	22	CHMI	Derenda Hvol A	0.91	0.04	1.34	0.88	14	0.981
	23	CHMI	MCZ/Andersen	0.80	0.04	4.14	1.09	14	0.963
	24	CHMI	FH 62 IR	0.92	0.03	-0.56	0.61	14	0.991
DE	25	LANUV	Digitel 4	1.04	0.02	-1.55	0.62	13	0.996
	26	LANUV	Digitel 37	1.02	0.03	-1.58	1.03	13	0.988
	27	HLUG	Leckel Seq	1.04	0.02	-0.62	0.45	13	0.998
	28	HLUG	Sharp	1.22	0.07	-6.04	2.25	13	0.958
	29	HLUG	FH62 IR	0.94	0.04	-2.89	1.28	13	0.977
DK	30	NERI	SM 200	1.00	0.08	-5.38	3.70	10	0.953
	31	NERI	Teom 1400	0.74	0.04	-0.84	2.06	11	0.966
SE	32	ITM	Leckel Seq	1.12	0.02	-4.65	1.79	12	0.997
	33	IVL	sampler A	1.52	0.52	-4.06	23.88	3	0.878
	34	IVL	sampler B	1.32	0.21	0.25	9.58	3	0.975
	35	EHAS	Teom 1400	1.22	0.04	-6.45	3.10	14	0.989
	36	EHAS	FDMS	1.32	0.03	-3.21	3.10	10	0.994
FI	37	FMI	FH62 IR_632	0.88	0.10	1.80	1.47	14	0.856
	38	FMI	FH62 IR_280	0.89	0.08	1.93	1.22	14	0.902
EE	39	EERC	Digitel container	0.83	0.07	0.09	0.80	12	0.938
	40	EERC	Digitel MobLab	0.85	0.06	-0.70	0.73	12	0.950
	41	EERC	FH62 IR container	0.75	0.07	2.32	0.80	12	0.925
	42	EERC	FH62 IR MobLab	1.07	0.09	1.88	1.14	12	0.923
NL	43	RIVM	Leckel Seq	1.03	0.01	-1.63	0.48	14	0.998
NL/BE	44	VMM	Leckel Seq	1.06	0.01	-0.30	0.47	13	0.999
NL	45	RIVM	FH62 IR	1.17	0.03	-1.62	1.10	14	0.994
	46	GGD	Derenda seq LV	1.02	0.03	-4.82	0.74	3	0.999
BE	47	VMM	Leckel Seq	1.05	0.04	1.19	1.20	14	0.987
	48	Issep	SW126 gravimetr.	0.98	0.02	-3.40	0.81	14	0.993
	49	Issep	SW129 gravimetr.	0.94	0.04	-1.87	1.45	13	0.978
BE/NL	50	RIVM	Leckel Seq	1.01	0.04	0.79	1.21	14	0.985
BE	51	VMM	ESM BOR801	1.08	0.13	-0.56	4.51	14	0.819
	52	VMM	Teom 1400	0.74	0.12	10.04	4.19	14	0.701
	53	VMM	FDMS	0.90	0.06	-2.54	2.18	11	0.954
	54	Issep	SW126 beta	0.93	0.03	-3.04	1.14	14	0.985
	55	Issep	SW129 beta	1.00	0.03	-5.31	1.20	13	0.987
	56	Issep	Env.101_33	0.78	0.05	1.86	1.83	14	0.943
	57	Issep	Env.101_78	0.76	0.06	0.15	2.00	13	0.937
	58	Issep	Grimm 180	0.95	0.06	-1.87	1.92	14	0.958
BE/NL	59	GGD	Derenda seq LV	1.01	0.05	-1.34	1.73	9	0.982
FR	60	Ineris	Partisol	0.98	0.05	-1.11	0.87	14	0.973
	61	EDM	Env.101	0.87	0.08	0.98	1.50	14	0.899
	62	Ineris	FDMS 9032	0.91	0.04	0.03	0.70	14	0.980
	63	Ineris	FDMS 15702	0.90	0.04	1.28	0.83	14	0.971
	64	Airparif	FDMS	0.87	0.04	0.86	0.76	14	0.974
IE	65	EPA	FDMS	0.80	0.02	2.82	0.43	17	0.988
	66	DCC	Partisol	0.46	0.32	4.46	8.41	6	0.171
GB	67	AEA	Partisol emfab	0.96	0.05	-0.70	1.28	9	0.979
	68	BV	Partisol quartz	1.20	0.08	-1.81	1.99	9	0.966
	69	BV	Partisol emfab	1.06	0.04	-2.43	1.06	9	0.988
	70	NPT	FDMS	1.00	0.05	3.06	1.95	7	0.898
IT	71	Ispra	Tecora	1.02	0.03	-3.62	1.41	15	0.985
	72	Arpa	Zambelli	1.16	0.13	-6.23	5.18	15	0.842
	73	Arpa	Tecora	0.89	0.04	1.48	1.71	15	0.972
	74	Arpa	SM200	0.91	0.05	2.04	2.20	15	0.954
	75	Arpa	FDMS	1.00	0.07	-7.31	2.72	14	0.949
HU	76	HMS	Digitel	0.92	0.02	0.01	1.05	14	0.994
	77	HMS	FH62 IR	0.92	0.04	-2.25	2.33	14	0.971
	78	MDV	FH62 IR	0.89	0.03	0.54	1.35	13	0.991
SK	79	SHMU	FDMS	0.93	0.04	-3.19	0.73	14	0.982
			Min	0.46	0.01	-188.62	0.41		0.023
			Max	7.04	0.52	10.04	23.88		0.999
			Median	0.95	0.04	-0.56	1.39		0.975

Table 16: Regression outputs and correlation coefficients for PM2.5 data-sets

Country	Codification	Laboratory	Instrument	Regression output				n	R²
				slope b	uncertainty of b	intercept a	uncertainty of a		
ES	1	ISCIII	Derenda	0.84	0.05	0.56	0.98	12	0.965
PT	2	IdA	Tecora	0.81	0.11	1.28	1.51	13	0.796
SI	3	EPA SI	Leckel Seq	0.93	0.07	2.05	1.76	14	0.931
AT	4	UBA AT	Digitel	1.01	0.03	-3.33	1.35	3	0.999
	5	LR OOe	Digitel	0.91	0.01	-0.14	0.51	12	0.998
CZ	6	CHMI	Leckel SEQ	0.79	0.03	-1.07	0.50	13	0.989
	7	CHMI	Derenda	0.99	0.02	-0.90	0.39	14	0.995
	8	CHMI	FH 62 IR	0.89	0.05	-1.27	0.92	14	0.967
DK	9	NERI	Teom 1400	0.74	0.06	-2.47	1.81	11	0.947
SE	10	IVL	sampler A	4.42	0.69	-27.60	9.80	9	0.789
	11	IVL	sampler B	25.10	7.14	-455.10	141.83	3	0.086
	12	EHAS	Teom 1400	0.22	0.03	3.49	1.04	14	0.826
EE	13	EERC	FH62 IR	0.53	0.09	1.41	0.70	13	0.719
NL	14	GGD	Derenda seq LV	0.95	0.03	-0.95	1.28	8	0.992
BE	15	VMM	Leckel SEQ Whatm.	1.18	0.03	-1.84	0.55	13	0.995
	16	VMM	Leckel SEQ Pall	1.08	0.02	-1.57	0.51	14	0.994
	17	Issep	SW126 gravimetr.	0.94	0.03	-2.20	0.60	14	0.989
	18	Issep	SW129 gravimetr.	0.99	0.03	-2.35	0.68	13	0.989
	19	Issep	SW126 beta	0.96	0.03	-2.45	0.65	14	0.988
	20	Issep	SW129 beta	1.02	0.02	-2.88	0.47	13	0.995
	21	Issep	Grimm 180	1.12	0.07	-0.64	1.54	14	0.950
	22	VMM	ESM	1.27	0.12	-5.25	2.57	14	0.891
BE/NL	23	GGD	Derenda seq LV	0.94	0.22	-2.62	4.77	10	0.576
FR	24	Airparif	FDMS	0.98	0.06	0.72	0.79	14	0.796
GB	25	BV	Partisol emfab	0.90	0.12	0.90	1.36	9	0.873
	26	NPT	Partisol	1.21	0.11	-0.96	1.32	14	0.898
	27	BV	FDMS	1.50	0.19	-5.73	2.25	14	0.794
IT	28	Arpa	Zambelli	0.70	0.21	3.21	5.18	7	0.627
	29	Arpa	SM200	0.92	0.08	-2.81	1.98	7	0.963
HU	30	MDV	Digitel	0.90	0.03	0.15	1.51	14	0.986
	31	MDV	FH62 IR	0.79	0.03	-3.11	1.45	14	0.846
		Min		0.22	0.01	-455.10	0.39		0.086
		Max		25.10	7.14	3.49	141.83		0.999
		Median		0.94	0.05	-1.27	1.32		0.950

5.3 Distinction of data measured by National Reference Laboratories and Local Networks

To verify if the quality of data measured by National Reference Laboratories distinguishes significantly from the quality of data measured by local networks, all data sets, independently from the used measurement technique, were split into a comparison of NRLs vs. JRC and a comparison of local networks vs. JRC.

To provide an overview of the spread of single measurements with respect to the Reference Values, the relative differences of the daily averages were plotted separately for NRLs and local networks. Some of the biggest spreads (> ±50 %) are linked to low data capture (SE, IE) indicating a technical/analytical problem, or to a measurement campaign with low PM concentration levels (EE). Figures 22 - 25 illustrate the spread split into PM10/PM2.5 and NRL/local network. To identify possible trends in relation to the used instrumentation, results are plotted in three different colours: Blue for LVS, pink for HVS and black for automatic analyzers.

Figure 22: Relative deviations from PM10 Reference Value for NRL (blue: LVS, pink: HVS, black: automatic analyzers)

Deviations of NRL to PM10 Reference Value
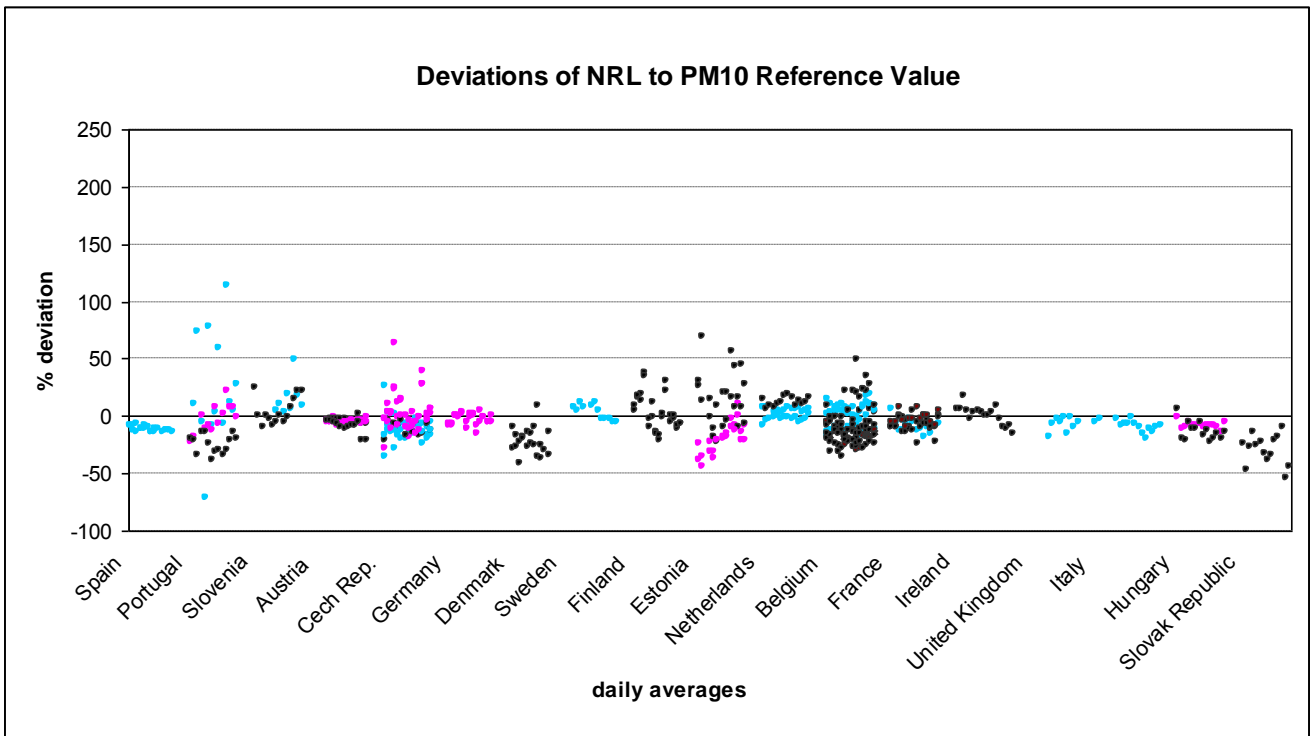
Figure 23: Relative deviations from PM10 Reference Value for local networks (blue: LVS, pink: HVS, black: automatic analyzers)

Deviations of local networks to PM10 Reference Value
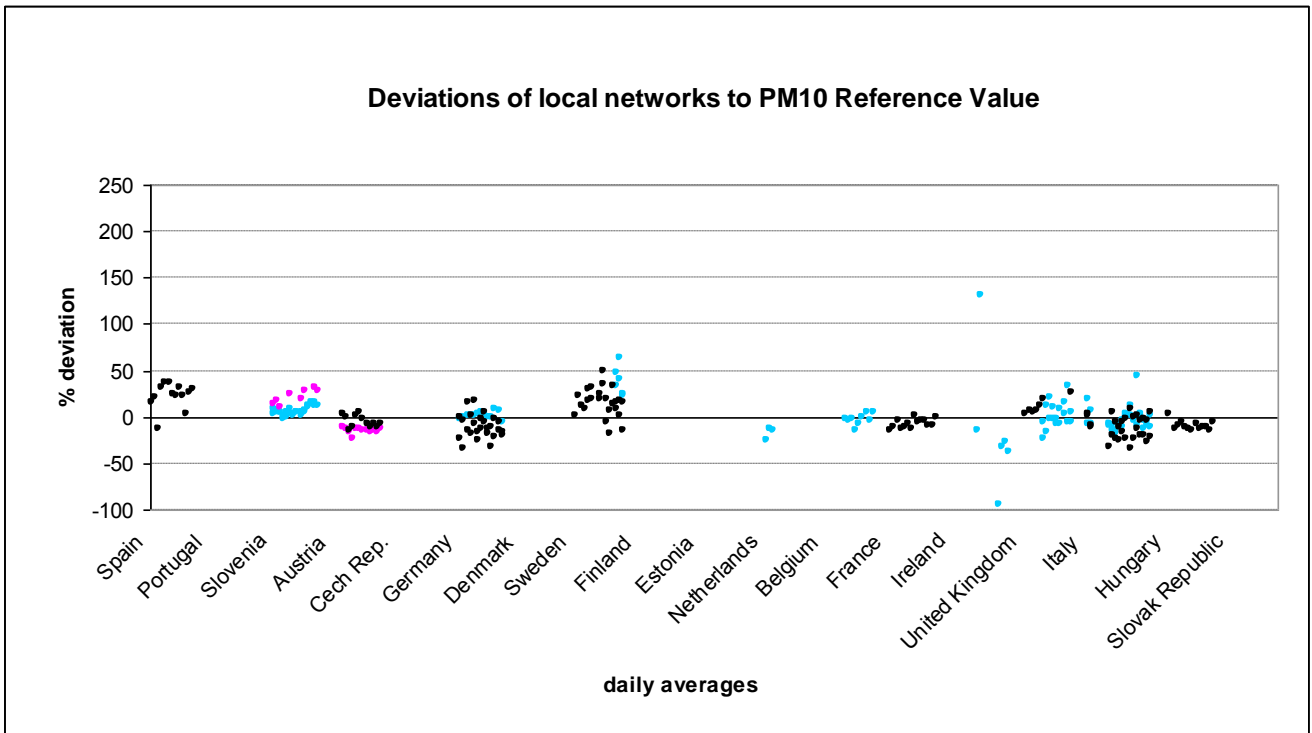
Figure 24: Relative deviations from PM2.5 Reference Value for NRL (blue: LVS, pink: HVS, black: automatic analyzers)

Deviations of NRL to PM2.5 Reference Value
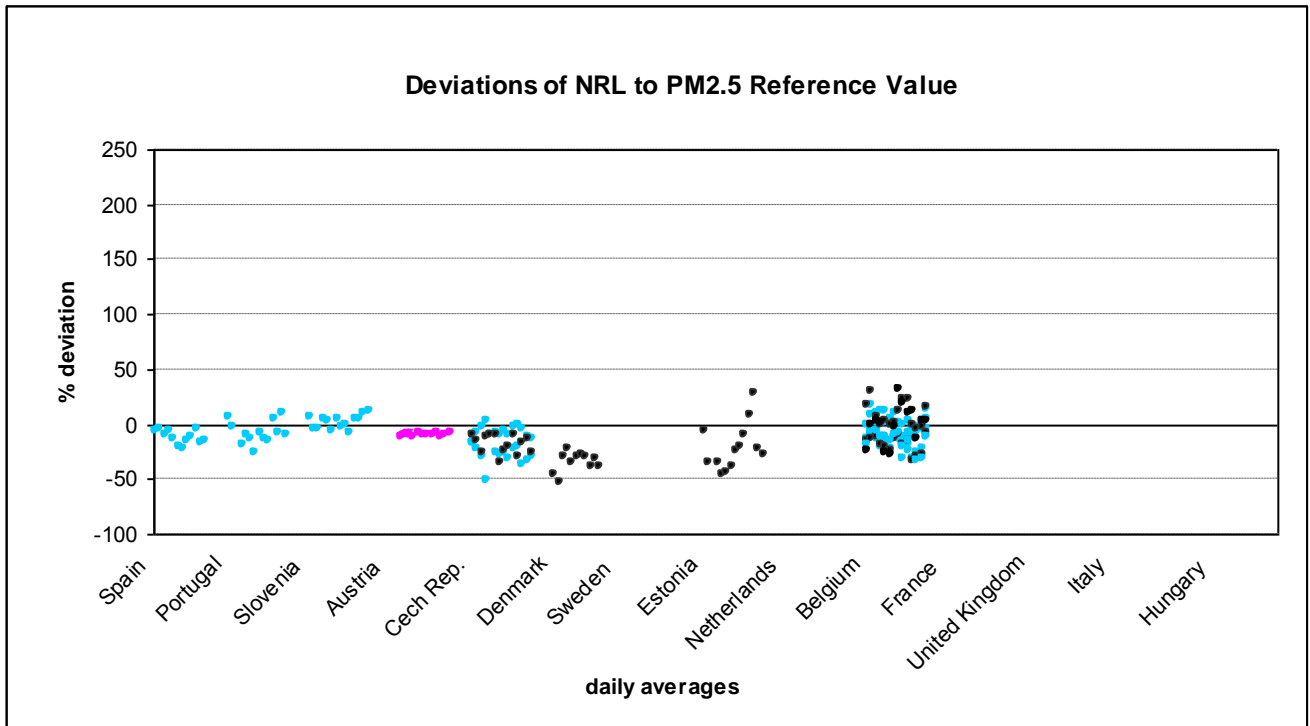
Figure 25: Relative deviations from PM2.5 Reference Value for local networks (blue: LVS, pink: HVS, black: automatic analyzers)

Deviations of local networks to PM2.5 Reference Value
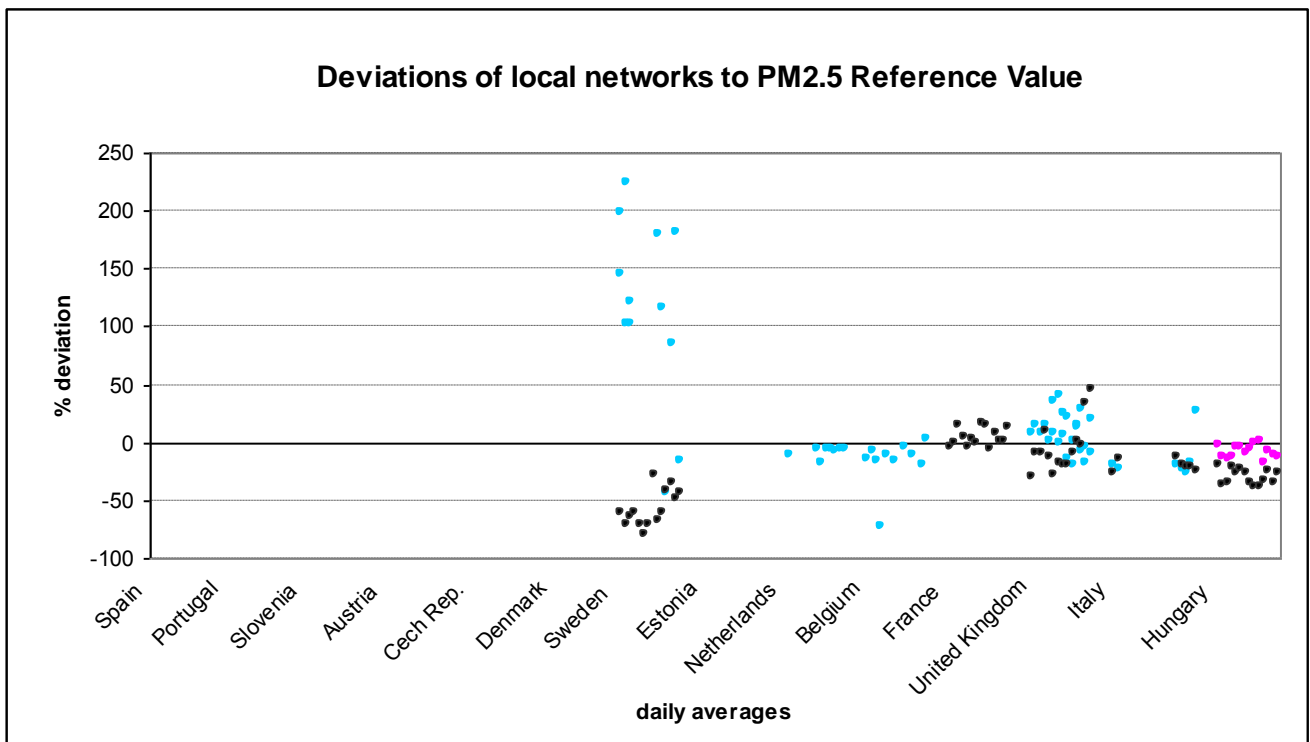
A summary of these relative deviations was done using "normalized" data (ratios) between values reported by

NRLs/local networks respectively and the Reference Values (as described in chapter 3.3.3). The averages and standard deviations of the ratios were calculated for the two types of laboratories. On average, for both PM10 and PM2.5, NRLs are measuring lower values than local networks. Regarding PM10, the reproducibility standard deviation is very similar for both types of laboratories, but differs considerably for PM2.5 with the NRLs performing better than local networks. Table 17 gives the ratios, reproducibility standard deviation and number of data-sets in detail.

Table 17: Ratios for PM10 and PM2.5 for all laboratories and separated into NRL and local networks; the number of data sets is given in parentheses

	all laboratories average (n)	all laboratories s(R)	NRL average (n)	NRL s(R)	Local Networks average (n)	Local Networks s(R)
PM10	0.962 (79)	0.17	0.947 (54)	0.16	1.000 (25)	0.19
PM2.5	0.926 (31)	0.33	0.891 (18)	0.15	0.984 (13)	0.50

Where:

        s(R)   is the standard deviation (reproducibility) of the ratios

        n   is the number of data sets

Further, for PM10 parametric and non-parametric tests were performed, all of them resulting in a p-value <0.025 thus indicating that data measured by NRLs are significantly different from data measured by local networks. Details of these tests can be found in Annex 8.

Further calculations in this report will not distinguish anymore between NRLs and local networks.

5.4 Compliance with Data Quality Objective (DQO) of European Directive

One of the goals of this project was to understand if routine PM measurements performed in the European Member States comply with the DQO for ambient air quality assessment given in Annex I of the European Directive 2008/50/EC. The DQO for PM10 and PM2.5 is given as 25% at the Limit Value (LV). The LV is 50 µg/m^3 for PM10 as a 24 h average, while for PM2.5 a target value of 25 µg/m^3 is given as annual average. Regarding PM2.5, the target value was considered as a daily average in the following calculations thus allowing also comparison to a "DQO" as for PM10. This has to be considered when PM2.5 data is interpreted.

5.4.1 Relative differences from reference values

To compare data to the DQO at the LV / target value the following procedure was applied:
Only data pairs where the Reference Value was higher than LV-25% (≥37.5 µg/m^3 for PM10 and ≥18.75 µg/m^3 for PM2.5) were compared to the DQO. The relative difference of each single daily average measured by a participant to the corresponding Reference Value was calculated. Their deviations from the DQO are shown in Figure 26 (PM10) and Figure 27 (PM2.5). To identify possible trends in relation to the used instrumentation, results are plotted in different colours. From a visual point of view it looks that automatic analyzers give worse results than gravimetric methods. The few PM2.5 LVS data (SE) with a deviation > 100% result from a particular instrument type with low data capture.

Figure 26: Deviations from the reference value for PM10 at the level of the DQO (blue: LVS, pink: HVS, black: automatic analyzers). The space between red lines represents the interval of compliance with DQO (+/- 25%)
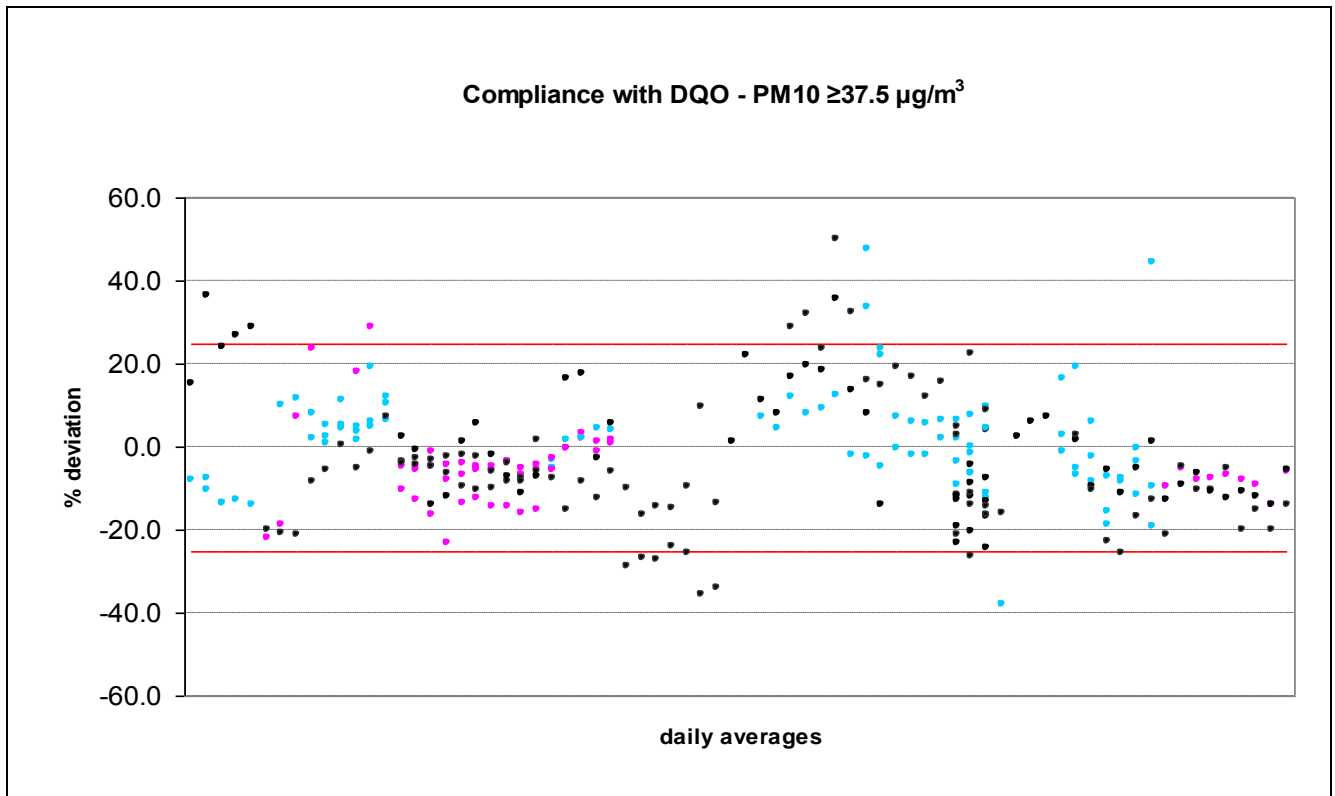
Figure 27: Deviations from the reference value for PM2.5 at the level of the "DQO" under the assumption that the target value is a 24h and not an annual average (blue: LVS, pink: HVS, black: automatic analyzers). The space between red lines represents the interval of compliance with DQO (+/- 25%)
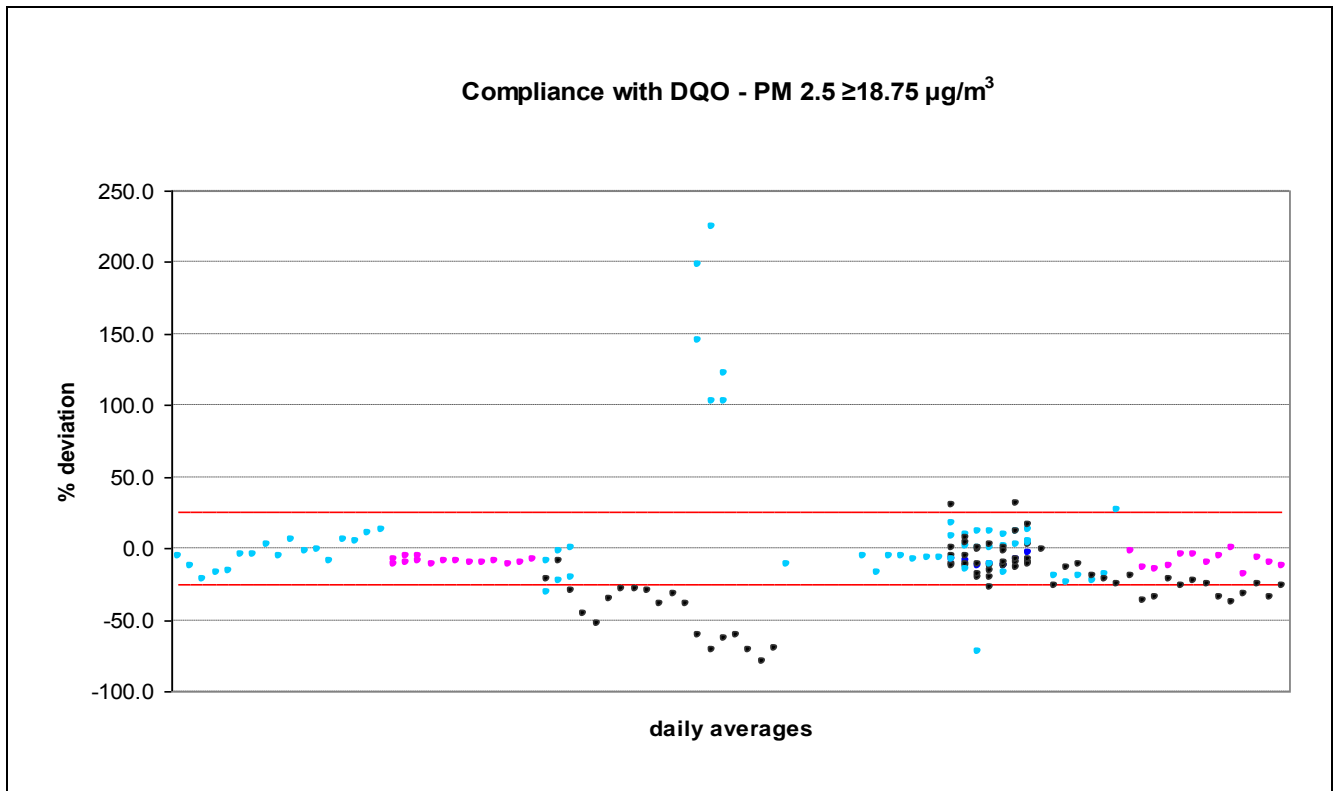
Summarizing the compliance with the DQO, 7.1 % of the considered PM10 measurements exceed the DQO. For PM2.5, 23.8 % of the considered measurements exceed the "DQO". Table 18 summarizes the exceedances of the DQO and allows comparing them to exceedances in case that all data, independent from their concentration level, had been taken into account.

Table 18: Exceedances of the DQO (PM2.5 under the assumption that the target value is a 24h and not an annual average)

	sum of daily averages	sum of daily avg.>DQO	% of daily avg. >DQO
PM10 all data	975	103	10.6
PM10>LV	294	21	7.1
PM2.5 all data	365	94	25.8
PM2.5>target value	172	41	23.8

Further, for PM10 parametric and non-parametric tests were performed to find out if LVS behave differently from HVS and automatic analyzers respectively. All tests between LVS and HVS showed a p-value >0.025 thus confirming that differences are not significant. However, all tests between LVS and automatic samplers indicated that differences are significant. Details of these tests can be found in Annex 8.

5.4.2 Calculation of uncertainty at the limit value

The uncertainties for PM10 at the LV and for PM2.5 at the "Target Value" (assumed to be a 24 h average) have been calculated using the Excel template for the Equivalence field test of the "Guide to the Demonstration of Equivalence of Ambient Air Monitoring Methods" [5]. For the demonstration of equivalence the cited guide requires at least 40 data pairs and at least 20% of data shall be greater than the upper assessment threshold specified for annual limit values (28 µg/m^3 for PM10 and 17 µg/m^3 for PM2.5) [2]. Demonstrating equivalence was not the objective of the present QA/QC program, therefore less data pairs are available for each campaign. This imposes caution in the interpretation of results. Notwithstanding the limitations accruing from the reduced number of data pairs for each single campaign, this exploratory estimation has been carried out to give a general picture of the situation in Europe taking advantage of the uniqueness of this database in which an overwhelming number of different instruments in different sites and conditions were compared against the same reference samplers.

To optimize the calculations, only data-sets with >10 data pairs and more then 20% of data greater than the upper assessment threshold have been taken into account. Consequently 53 (out of 79) data-sets for PM10 and 19 (out of 31) data-sets for PM2.5 were calculated. One third of the PM10 and half of the PM2.5 data-sets exceed the uncertainty at the LV ("target Value") according to this exploratory estimation. The result for PM2.5 is linked to the low PM2.5 "Target Value" (25 µg/m^3) compared to the PM10 LV (50 µg/m^3). Looking at the type of instrument, for both size fractions the automatic analyzers perform worse than the gravimetric methods thus confirming the findings in 5.4.1. However, at the time of the performance of the comparisons it is highly likely that only few networks have used experimental correction factors based on the approach given in [5].

Table 19 gives a summary for PM10, table 20 for PM2.5. Detailed information for each data-set can be found in Annex 6.

Table 19: Exceedances of expanded uncertainty at the LV for PM10

Type of instrument	Total data-sets	Data-sets exceeding U at LV	% of data-sets exceeding U at LV
Low Vol	18	3	
High Vol	10	2	
Automatic	25	12	
Sum	53	17	32.1%

Table 20: Exceedances of expanded uncertainty at the "target value" for PM2.5

Type of instrument	Total data-sets	Data-sets exceeding U at "Target Value"	% of data-sets exceeding U at "Target Value"
Low Vol	9	4	
High Vol	2	0	
Automatic	8	6	
Sum	19	10	52.6%

When comparing these results to those from 5.4.1 it is observed that the percentages "failure" are much higher. This is due to the fact that in the approach described in 5.4.1 single daily averages with a concentration in the range of the LV are compared to the DQO, however in 5.4.2 data-sets (containing usually 14 daily averages of all concentration ranges) are used to calculate exceedances of the DAQ. Hence in the latter case a few daily averages with high deviations can discriminate a whole data set.

5.5 Gravimetric methods: Influence of filter material and sampler type on PM measurement

To find out if the used filter material and the type of sampler (manufacturer) have an influence on the quality of the measured data, in a first step all PM10 and PM2.5 data were separated by these two criteria and plotted against the DQO. The used filter materials were quartz, glass, cellulose nitrate or Teflon (PTFE or Teflon-coated glass fibre also called Emfab).

Looking at the graphs it is difficult to identify clear trends regarding sampler type and the used filter material. However, it is obvious that some LVS data-sets suffer from poor repeatability: Tecora quartz (PT) and Partisol glass (IE) of the PM10 and IVL "unknown" (SE) of the PM2.5 results.

Figure 28 and 29 present, separated into PM10 and PM2.5, the relative deviations from the Reference Value for LVS; Figure 30 and 31 present the same results for HVS. In case information of a participant could not be retrieved it is labelled as "unknown".

Figure 28: PM10 LVS deviation from reference value split by filter material and sampler type (manufacturer). Colour indicates sampler type and symbol denotes filter material.

PM10 - Low Vol Samplers - split by filter material and sampler type (manufacturer)

—— upper limit	—— lower limit	— Zambelli PTFE	✳ Swam Quartz
✳ Swam Quartz	✳ Seq Leckel Quartz	✳ Seq Leckel Quartz	△ Seq Leckel Glass
— Seq Leckel PTFE	○ IVL unknown	○ IVL unknown	◆ FH95KF nitrocell
△ FH95KF glass	△ Seq Derenda LVS glass	✳ Seq Derenda LVS quartz	✳ Derenda MVS 6.1 quartz
✳ Derenda MVS 6.1 quartz	✳ Tecora quartz	○ Tecora unknown	— Tecora PTFE
✳ Derenda 3.1-15(LVS) quartz	— Partisol PTFE	— Partisol PTFE	△ Partisol glass
✳ Partisol quartz			
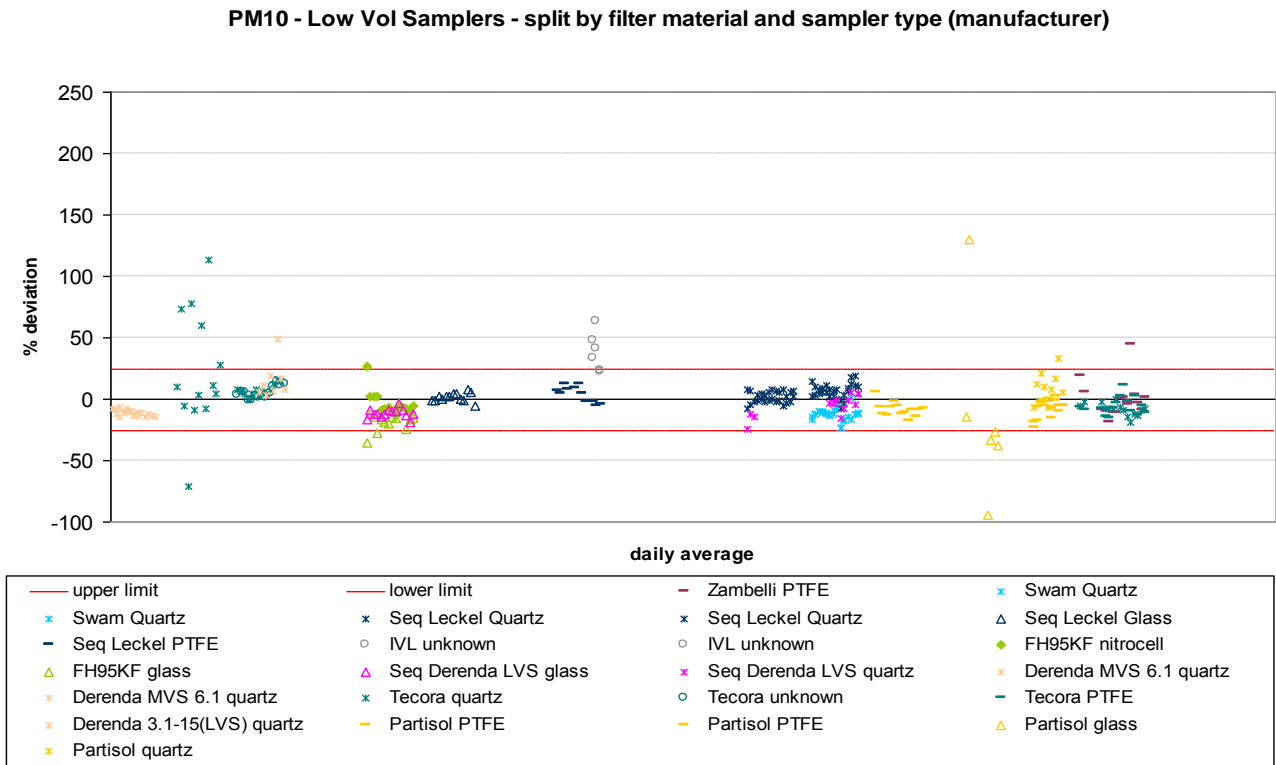
Figure 29: PM2.5 LVS deviation from reference value split by filter material and sampler type (manufacturer). Colour indicates sampler type and symbol denotes filter material.

PM2.5 - Low volume samplers - split by filter material and sampler type (manufacturer)

—— upper limit	—— lower limit	✳ Derenda MVS 6.1 quartz	✳ Tecora quartz
✳ SEQ Leckel quartz	◆ SEQ Leckel nitrocell	— SEQ Leckel PTFE	✳ Seq Derenda quartz
△ Seq Derenda glass	✳ Swam quartz	✳ Swam quartz	— Zambelli PTFE
— Partisol PTFE	✳ Partisol quarz	○ IVL unknown	○ IVL unknown
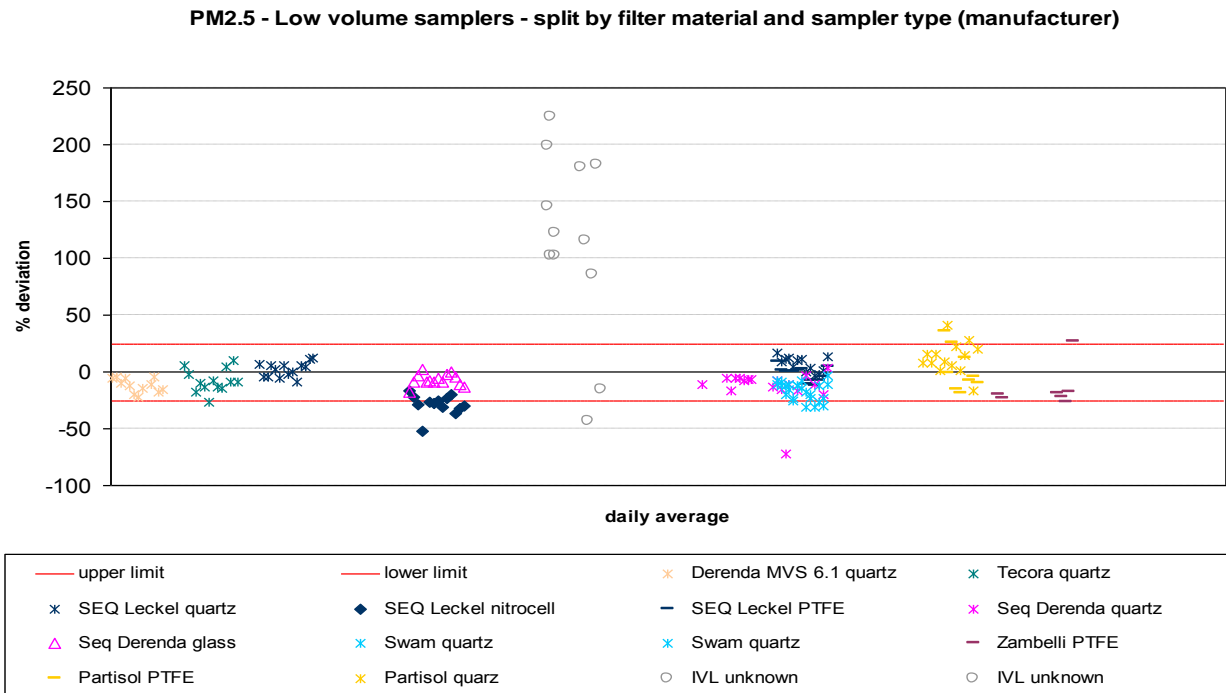
Figure 30: PM10 HVS deviation from reference value split by filter material and sampler type (manufacturer). Colour indicates sampler type and symbol denotes filter material.
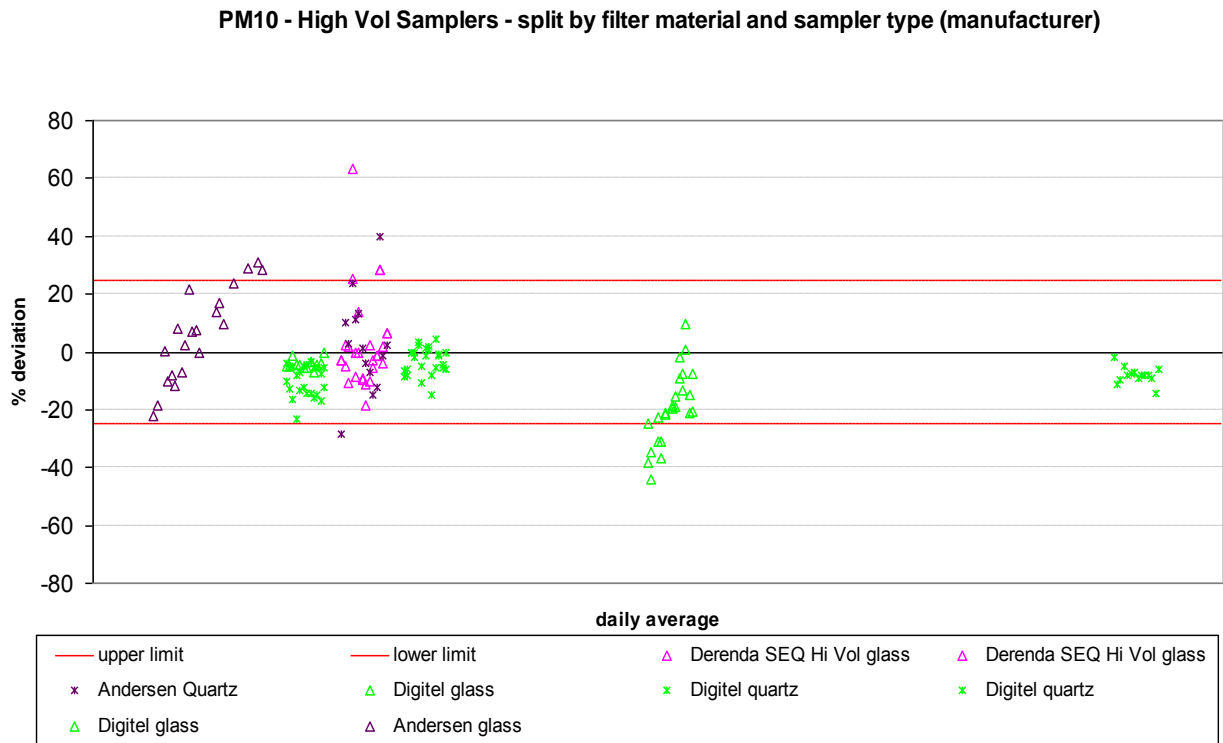
Figure 31: PM2.5 HVS deviation from reference value split by filter material and sampler type (manufacturer). Colour indicates sampler type and symbol denotes filter material.
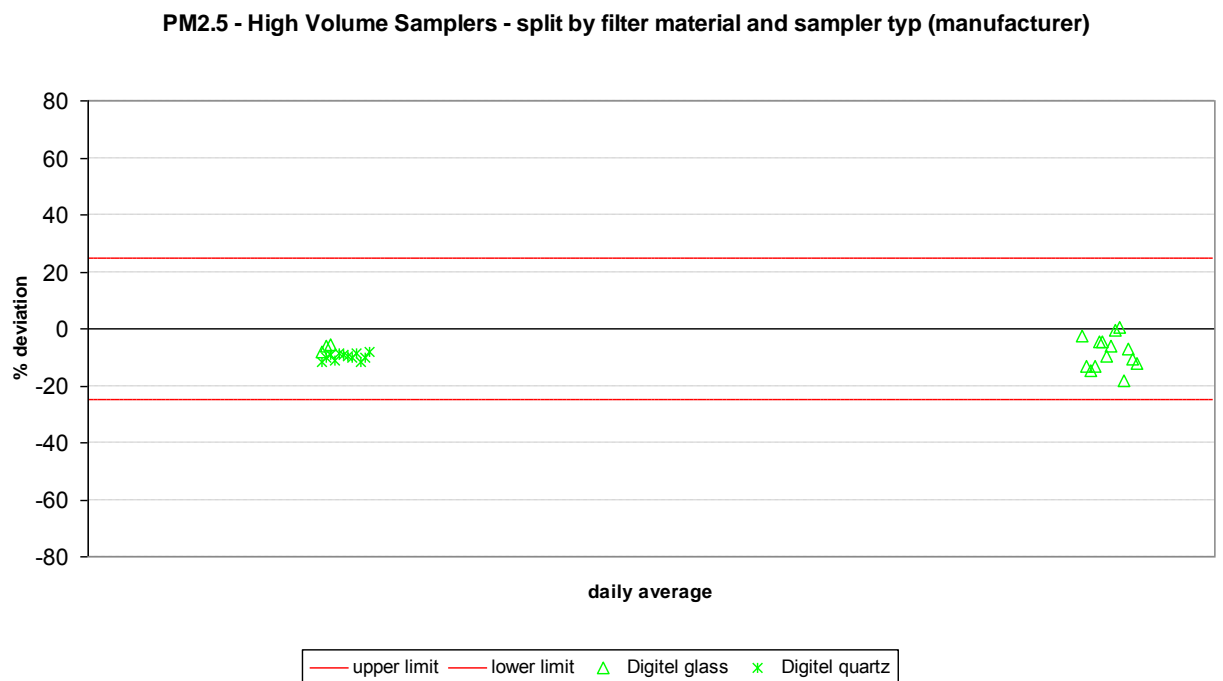
In a second step, limited to the PM10 results, Analysis of Variance (ANOVA) was used for the same purposes as above. Data sets, where the filter material was not specified by the participant, were omitted.

Regarding LVS, results obtained with instruments from Derenda, Thermo, Partisol and Zambelli are not significantly different. The value of information produced by Zambelli (1 instrument), Thermo and FAI (2 instruments each) is limited. Leckel and Tecora instruments produced on average the highest results and show a significant difference to most of the other sampler types. However, Leckel (together with FAI) has the smallest spreads of all types, even though it was used with three different filter materials. Zambelli and Thermo show already bigger spreads. The two above mentioned data sets with poor repeatability (PT and IE) are mainly responsible for the biggest spreads, observed for Tecora and Partisol samplers and quartz and glass filter material. The median of measurements with quartz filter material, also used for the Reference Value, shows a ratio of almost 1. Glass however, tends to produce the lowest results and shows significant differences to quartz and Teflon filter materials. Cellulose nitrate shows the lowest spread for filter material, but it was used by one sampler only thus limiting the value of information.

Regarding HVS, measurement results obtained from Digitel tend to be the lowest and show a significant difference to Andersen and Derenda. The filter materials used, glass and quartz, produced similar results and do not show a significant difference from each other.

Details of these tests can be found in Annex 8.

5.6 Discussion on applied correction factors for automatic analyzers

In 2005, when this project was launched, a common practise in EU - Member States was to correct the values of automatic analyzers using a coefficient as described in DIR1999/50/EC and EN 12341 (ETC Technical Paper 2005/6 [14]). Hence another goal of this program was to identify how such factors are influencing the measurement results.

During all measurement campaigns were produced a total of 37 datasets of PM10 measured with automatic analyzers, 15 of which included corrected data. In most of the cases this factor was constant all the year long, but also season-depending factors and the combination of a factor plus an offset were used. In 10 cases the application of a correction factor improved the results with respect to the DQO, in 3 cases the results remained unchanged and in 2 cases the results worsened; Table 21 shows a summary of the effect of correction factors on PM10 data quality. Details can be found in Annex 3.

Table 21: Influence of correction factors on PM10 data quality

Country	Institution	Analyzer	Correction factor	Change of result
ES	AdM	Teom 1400 AB	1.1	worsened
PT	IdA	Environnement MP 101	1.1	improved
SI	EPA	Teom 1400	1.03 (summer) 1.24 (winter)	equal
AT	LR Stmk.	Eberline FH 62 IR	1.3	improved
CZ	CHMI	FH 62 IR	1.3	improved
DE	HLUG	FH 62 IR	1.18	improved
EE	EERC	Thermo ESM FH 62 IR (container)	1.15	improved
		Thermo ESM FH 62 IR (mob lab)	1.15	worsened
NL	RIVM	Thermo FH 62 IR	1.17 + 2.7	equal
BE	VMM	ESM Andersen	1.37	improved
		Teom 1400	1.47	improved
BE	ISSeP	Environnement MP 101 sn 33	1.08	improved
		Environnement MP 101 sn 78	1.08	improved
HU	HMS	FH 62 IR	1.1	improved
	MDV	FH 62 IR	1.1	equal

During all measurement campaigns were produced a total of 12 PM2.5 - datasets measured with automatic analyzers, 3 of which included corrected data. In all cases this factor was constant all the year long and improved the results with respect to the DQO; Table 22 shows a summary of the effects of correction factors on PM2.5 data quality. Details for each participant applying a correction factor can be found in Annex 3.

Table 22: Influence of correction factors on PM2.5 data quality

Country	Institution	Analyzer	Correction factor	Change of result
CZ	CHMI	FH 62 IR	1.3	improved
EE	EERC	Thermo ESM FH 62 IR (container)	1.15	improved
HU	MDV	FH 62 IR	1.31	improved

5.7 Automatic methods: Influence of sampling temperature and instrument type on PM measurement

To evaluate whether the sampling temperature and the type of analyzer (manufacturer) have an influence on the quality of measurements, in a first step all PM10 and PM2.5 data from automatic monitors were split using these two criteria and plotted against the DQO. Sampling temperature differs considerably between the participants. Either the sampling line was not heated at all, surrounded by sheath air, equipped with a dynamic heating system (maintaining the temperature always a few degrees above ambient and/or regulating the heating as a function of the relative humidity), or heated with a constant temperature between 30 and 50 degrees Celsius.

In general terms analyzers with higher sampling temperatures are expected to measure lower values than analyzers without heating. But in fact the distribution, especially for PM10, shows no obvious dependency on sampling temperatures. This means that other parameters like calibration, applied correction factors or data expressed at standard conditions instead of ambient are overlapping with the influence of the sampling line temperature.

Figure 32 and 33 visualize the relative deviations from the Reference Value for PM10 and PM2.5 respectively.

Figure 32: PM10 automatic analyzers deviation from reference value split by sampling temperature and instrument type. Colour indicates type of analyzer and symbol denotes sampling temperature.

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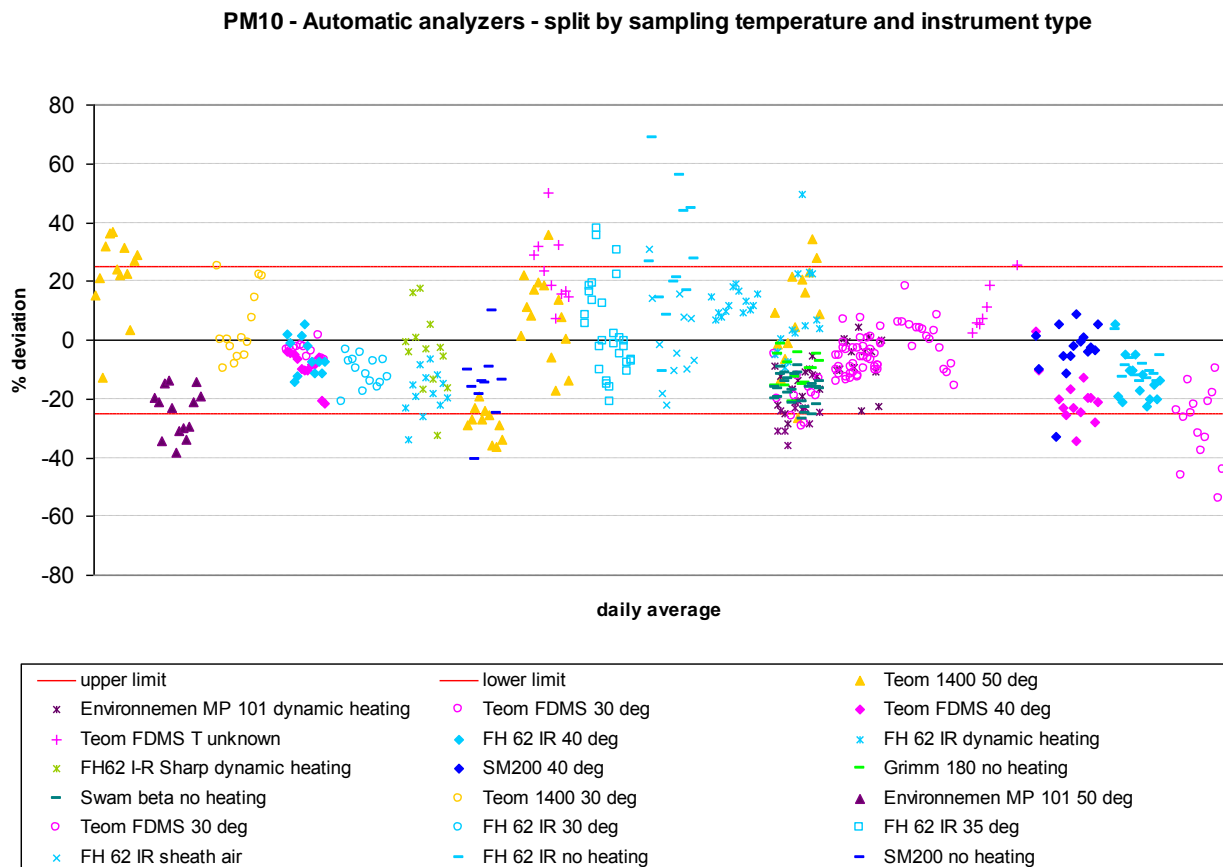
Figure 33: PM2.5 automatic analyzers deviation from reference value split by sampling temperature and instrument type. Colour indicates type of analyzer and symbol denotes sampling temperature.
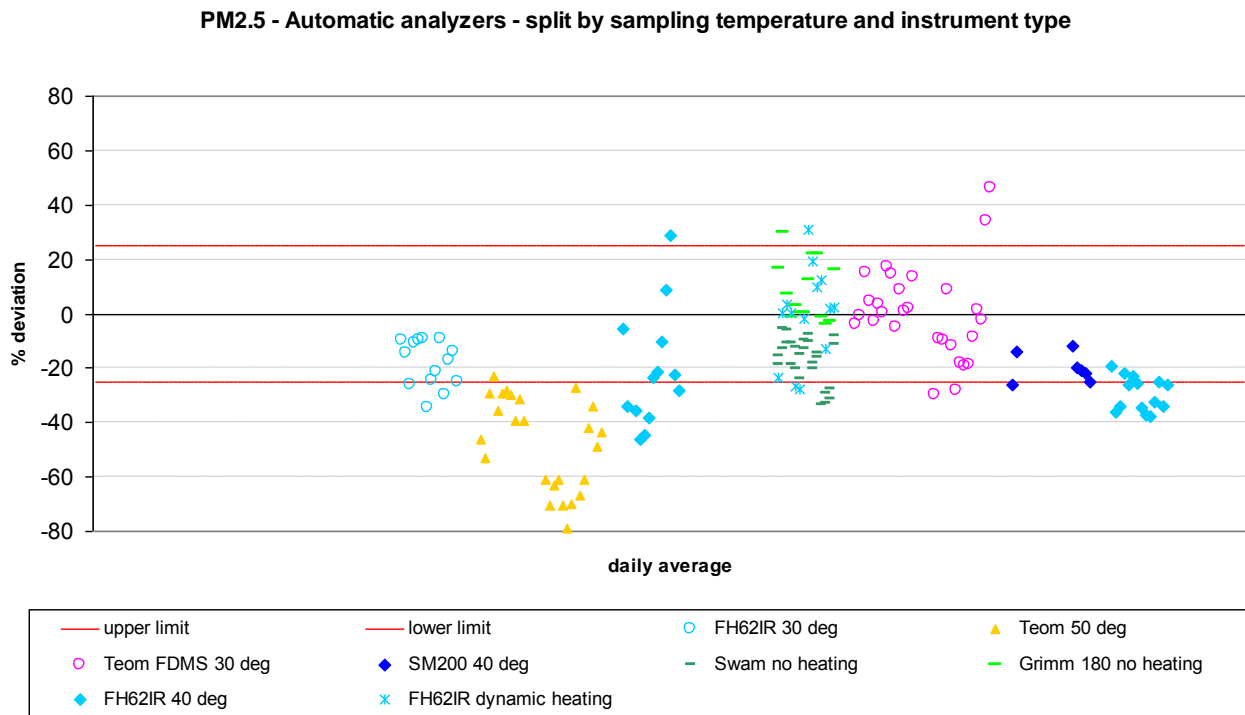
In a second step, limited to the PM10 results, Analysis of Variance (ANOVA) was used for the same purposes as above. Data sets, where the sampling temperature was not specified by the participant, were omitted.

Regarding the instrument type, FH62 shows the biggest spread of all instruments, what can be explained by the highest number of instruments (19). Teom instruments produced on average the highest results with a ratio of >1, even most of the Teom instruments were used with a sampling temperature of 50˚C. Environnement and Swam (two instruments used by the same laboratory only) produced the lowest averages. Only one instrument was used for the types Sharp and Grimm thus limiting the value of information. Regarding the sampling temperature, it is again evident that other factors are overlapping its influence on the measurement results. Otherwise it cannot be explained that data obtained with a sampling temperature of 50˚C are higher than most of the data obtained with lower sampling temperatures.

Details of these tests can be found in Annex 8.

5.8 Expression of data with consideration of applied pressure and temperature conditions

Directive 2008/50/EC [2] provides that PM sampling volume refers to ambient conditions in terms of temperature and atmospheric pressure at the date of measurement. The same directive defines the reference method for PM10 as EN 12341 [3] and for PM2.5 as EN 14907 [4]. Regarding the sampling volume conditions, EN 14907 is in line with the directive; however EN 12341 uses reference conditions of 273 K and 101.3 kPa to express the PM10 concentrations.

Most of the participants expressed their data at ambient conditions as foreseen in the directive, but, probably as

a consequence of the different conditions given in the two European standards, it occurred that some participants expressed data at reference conditions. In addition, applied reference conditions differ in the used reference temperature. In this report participants' data were used as delivered. This means that deviations between Reference and participant values might result from normalisation of conditions by the participant. Table 23 (PM10) and table 24 (PM2.5) present an overview of all participants using normalised instead of ambient conditions.

Table 23: Applied conditions different from ambient in terms of temperature and atmospheric pressure for PM10

country	institution	instrument	reference conditions
ES	AdM	Teom 1400 AB	101.3 kPa / 293 K
SI	EPA SI	Teom 1400	101.3 kPa / 293 K
	EIMV	Tecora	101.3 kPa / 273 K
		Andersen	101.3 kPa / 273 K
DK	NERI	Opsis	101.3 kPa/ 273 K
SE	EHAS	Teom 1400	101.3 kPa / 298 K
FR	AIRPARIF	Teom FDMS	101.3 kPa / 293 K
HU	MDV	FH 62 IR	101.3 kPa / 293 K
SK	SHMU	Teom FDMS	101.3 kPa / 293 K

Table 24: Applied conditions different from ambient in terms of temperature and atmospheric pressure for PM2.5

country	institution	instrument	reference conditions
SE	EHAS	Teom 1400	101.3 kPa / 298 K
FR	AIRPARIF	Teom FDMS	101.3 kPa / 293 K
HU	MDV	FH 62 IR	101.3 kPa / 293 K
		Digitel DHA 80	101.3 kPa / 293 K

5.9 Discussion on uncertainties

5.9.1 Individual participants

Each participant of a measurement campaign was asked to express the uncertainty of the reported results. 12 participants expressed an uncertainty for their PM10 measurements and 3 participants for their PM2.5 measurements. They are listed in table 25 for PM10 and table 26 for PM2.5.

Table 25: Combined uncertainties for PM10

Country	Institution	Sampler/Analyzer	Combined uncertainty u_c
ES	ISCIII	Derenda MVS 6.1	4% (will be adopted to EN14907)
SI	EIMV	Tecora Low Vol	5%
AT	LR OOe	Digitel High Vol	2.50%
DE	LANUV	Digitel High Vol	2.25 µg/m³ at 40 µg/m³
	HLUG	FH 62 IR	11 - 22%
		FH 62 IR sharp	9%
		Leckel SEQ 47/50	ca. 4%
NL	RIVM	Thermo FH 62 I-R	8.30%
		Leckel SEQ 47/50	3%
	GGD	Derenda SEQ Low Vol	2.15% (partly calculated)
BE	VMM	Leckel SEQ 47/50	only between sampler u
		ESM Andersen	11.06%
		Teom 1400	13.72%
		Teom FDMS	8.78%
	ISSeP	FAI Beta data	2.35%
		Environnement MP 101	6%
FR	EDM	Environnement MP101M-RST	6 - 7.5% at 50 µg/m³
	AIRPARIF	Teom FDMS	9% at 50 µg/m³
IT	Ispra	Tecora Low Vol	0.8 µg/m³ at 50 µg/m³

Table 26: Combined uncertainties for PM2.5

Country	Institution	Sampler/Analyzer	Combined uncertainty u_c
AT	LR OOe	Digitel High Vol	2.50%
NL	GGD	Derenda SEQ Low Vol	2.15% (partly calculated)
FR	AIRPARIF	Teom FDMS	9% at 50 µg/m³

For laboratories expressing an uncertainty, the E_n - numbers could be calculated (as described in chapter 3.3.2) according to ISO/IEC guide 43-1 [7]. In case an uncertainty was declared only for values above a certain PM concentration, the following procedure has been applied: 25% was subtracted from this stated PM concentration and only data above this "limit" were taken into consideration for the calculation of the E_n - numbers. For PM10, calculations were done for each data-set with JRC sequential sampler A and JRC sequential sampler B independently; a total amount of 500 E_n – numbers were calculated. For PM2.5 only one JRC sampler was available resulting in 30 E_n – numbers. Even if the amount of PM2.5 E_n - numbers is quite low, it seems more difficult to get satisfactory results (≤1) for this size fraction. A summary of E_n - numbers is given in table 27. All detailed En – numbers can be found in Annex 5.

Table 27: Summary of E_n – numbers for PM10 and PM2.5

	n of En – numbers	n of En – numbers >1	% non satisfactory results
PM10	500	191	38,2
PM2.5	30	15	50,0

5.9.2 Uncertainties based on grouped results

Reproducibility standard deviations found by applying ISO 5725 statistics (see 5.1) can be used as estimators of the uncertainties of grouped results for participants considered.

When considering all results after removal of outliers, the relative expanded uncertainties (95% confidence) for PM10 and PM2.5 grouped results are 28% and 33%, respectively. For PM10 uncertainties for NRL and local networks are comparable; for PM2.5 the uncertainty for local networks is considerably higher than that for NRL. When examining results differentiated by method it is found that LVS and HVS give comparable uncertainties for PM10; automatic analyzers always give higher results.

5.9.3 PM2.5 uncertainties at low concentration level

Directive 2008/50/EC [2] requires the EU member states to calculate for PM2.5 an Average Exposure Index, a three calendar year running annual mean concentration of several sampling points in urban background locations. This mean value, depending on its concentration, is linked to an exposure reduction target. Whilst for concentrations ≤8.5 µg/m^3 the reduction target is still 0%, for concentrations from >8.5 to <13 µg/m^3 it is already 10%, corresponding to 1.1 µg/m^3 on average. Even if the limited length of the monitoring campaigns does not allow the estimation of a PM2.5 annual mean uncertainty, it was considered informative to compare the PM2.5 uncertainty of 24 h means of the Reference Value with the reduction target in the concentration range <8.5 to <13 µg/m^3. For that purpose, due to the lack of a second PM2.5 reference sampler, the uncertainty was calculated with an u_{field} = 1 µg/m^3 as foreseen in EN 14907 [4] leading to an expanded uncertainty (k=2) of 2.12 µg/m^3 on average (field blank uncertainty excluded). In the latest revision of EN 14907, the expanded uncertainty, including a contribution for field blank effects, would be 2.5 µg/m^3 for a 1-year average (Hafkenscheid, Th., personal communication). This estimation is comparable with those obtained in a four years survey in an urban background site with PM2.5 mass average of 8.0 µg/m^3, where the long term propagated uncertainty (k=1) in mass measurements was 1.28 µg/m^3 (Dutton et al., 2009)[13]. Consequently it looks challenging to clearly distinguish a 10 % reduction of the PM2.5 Average Exposure Index from its associated uncertainty. Figure 34 illustrates all PM2.5 Reference Values and expanded uncertainties in the concentration range >8.5 to <13 µg/m^3 measured during the run of all 18 measurement campaigns.

Figure 34: PM2.5 Reference Values in the range >8.5 to <13 µg/m^3 with expanded uncertainties and associated reduction targets. The blue vertical bars indicate the expanded uncertainties whilst the gray field shows the reduction target.
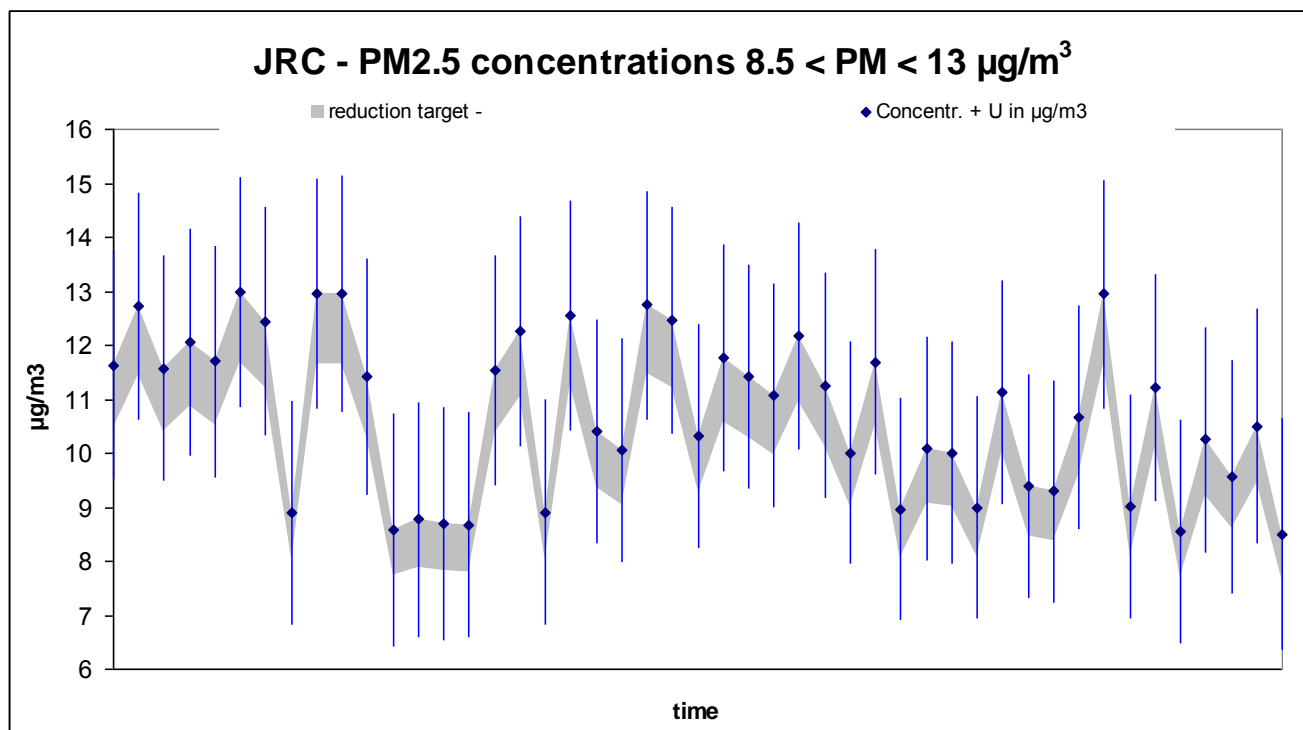
5.10 Investigation of field blanks

EN 14907 requires the use of field blanks which are weighed before and after a measurement campaign in the same way as filters used for sampling. In case the blank mass differs by more than 40 µg for LVS, the reason shall be investigated.

During all campaigns (apart from Madrid, where the available field blank had to be used instead of a damaged sampling-filter) field blanks are available for the reference values. During the run of the project, the amount of filed blanks varied from 2 to 8 filters per campaign such to get an idea about their repeatability. Further investigations were carried out to check whether filters exposed in a sampler inside the air conditioned mobile laboratory (PM10) behave differently from filters exposed in samplers placed outside (PM2.5, PM1) the mobile laboratory. Considering all field blanks together it was observed that 56% of the 110 field blanks exceeded the limit of 40 µg. In addition, a tendency of filters exposed in samplers outside the mobile laboratory to behave worse (62.5% exceedances) than filters exposed in samplers inside the mobile laboratory (46% of exceedances) was observed. In table 28 are listed the masses of all field blanks.

Table 28: JRC filed blanks in µg with data >40 µg marked in red

measurement site	PM1 (no.67)	PM2.5 (no.68/66)	PM10 A (no.64)	PM10 B (no.65)
Lisbon	14			15
Ljubljana	78	86	48	38
Graz	31	4	11	16
Prag	36	52	13	19
Wiesbaden	-25	-165	-118	
Copenhagen	41	11	35	48
	54	33	50	57
Stockholm	78	69	15	33
	73	68	9	21
Helsinki	26	20	17	
	21	0	7	-22
Tallinn	60	59	73	74
	62	62	55	61
Biest-Houtakker	32	45	18	27
	53	55	26	91
Borgerhout	22	4	12	12
		13	23	28
Paris	70	39		70
Dublin	28	54	11	18
	34	18	28	37
Port Talbot	73	49	28	44
	74	54	37	49
	117	134	96	89
Milan	68	52	55	41
	64	38	34	47
Budapest	340	331	274	292
	333	342	317	307
Bratislava	282	306	263	279
	310	285	288	299

None of the participants subtracted field blanks from their measurement results; the same is valid for the Reference Values with the exception of the campaigns in Budapest and Bratislava. During these two campaigns the field blank masses increased so much that their average contribution to the mass concentration reached

5.75 μg/m^3 in Budapest and 5.23 μg/m^3 in Bratislava. For Bratislava this led in the worst case to an influence of 50% on PM10 and 62% on PM2.5 results. A comparison of the gravimetric value to the JRC - Teom FDMS confirmed for both campaigns the influence of the filter matrix on the gravimetric results. Linear trend lines were calculated for both the gravimetric result and the gravimetric result minus the field blank against the FDMS. Whilst the slopes remained constant, the intercept changed in a magnitude comparable to field blank contribution to the mass concentration: 5.93 vs. 5.75 μg/m^3 in Budapest and 4.22 vs. 5.23 μg/m^3 in Bratislava. Such confirms the same increase in mass for filters used for sampling. Investigations after the measurement campaigns identified single boxes to contain unstable quartz filter material. However, the problem could not be linked to a whole batch – number. An experiment carried out at JRC revealed that quartz filters from suspect boxes increased their mass significantly (>200 μg within 14 days) when exposed outdoor in a Seq – sampler (identical to the ones used in the QA/QC programme). However, exposing quartz filters from the same boxes in the balance room or even in a Seq – sampler placed indoor did not change their mass significantly (1 μg and - 27 μg respectively within 14 days). Therefore the increase in mass of field blanks could not be foreseen during the weighing of the blank filters before these measurement campaigns. Flushing a field blank from Budapest with particle free air for 24 h did not reduce its mass; this implies that the mass increase due to storage of loaded filters may be approximated by the mass increase of the field blank. However, heating a field blank from Budapest to the same temperature to which sample is exposed in TEOM-FDMS (30° C) for 24 h removed almost all of the mass gained during its exposure (259 out of 342 μg removed). The good agreement between the gravimetric-TEOM regression intercept with the mass observed in the blanks plus the removal of such mass from the filters by heating, strongly suggest that adsorption of semi volatiles (or humidity) on filter matrix could have lead to the observed anomalous behaviour of the filters in Budapest and Bratislava all coming from the same boxes. Consequently, taking into account the exceptionality of these circumstances, the field blanks for Budapest and Bratislava were subtracted from the measurement results and an additional term, derived from the standard deviation of the field blanks, was added to calculate the uncertainty contribution for u$_{mass}$. For Budapest, figure 35 shows a scatter plot and the trend line - equation of the FDMS against the gravimetric result without subtracting the field blank, Figure 36 after subtraction of the field blank. Figure 37 and 38 show the same for Bratislava.

Figure 35: Budapest PM10: Gravimetric result without subtraction of field blank vs. FDMS

Budapest: Gravimetry / FDMS

$y = 0.9814x + 5.9302$

$R^2 = 0.9938$
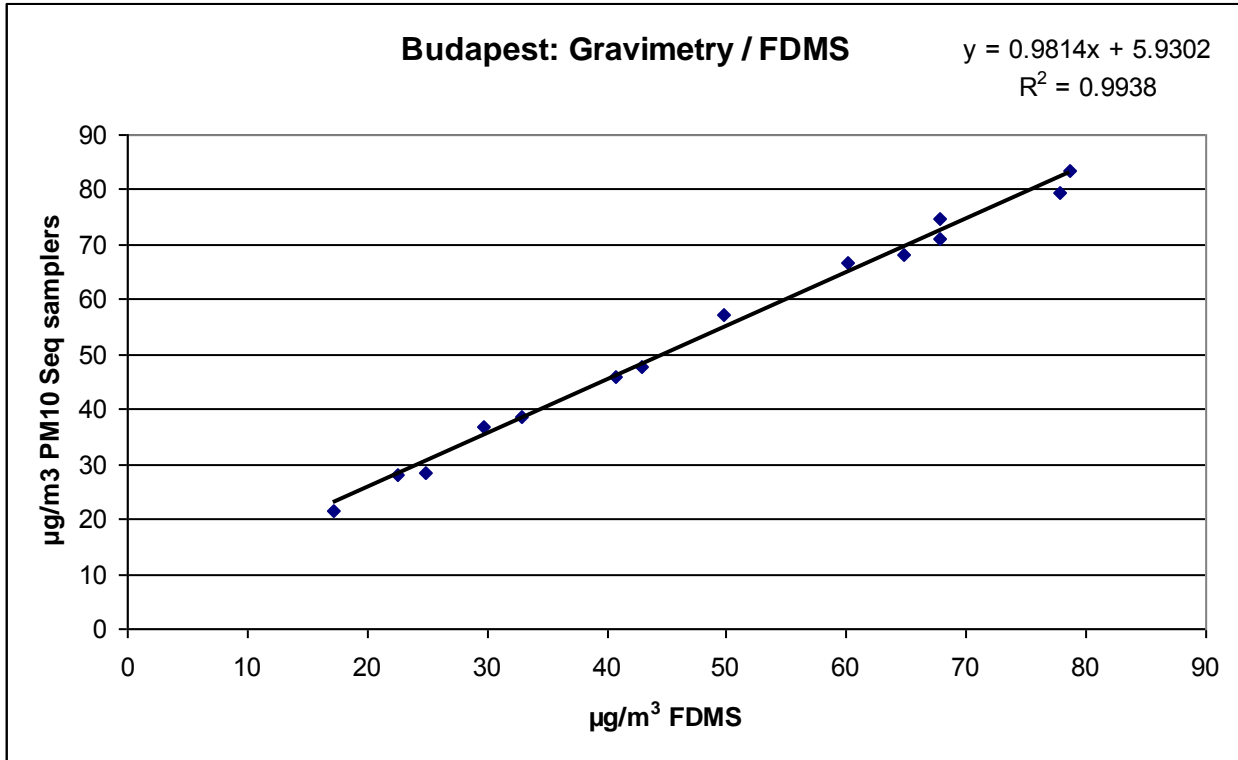
Figure 36: Budapest PM10: Gravimetric result after subtraction of field blank vs. FDMS

Budapest: Gravimetry - field blank / FDMS

$y = 0.9814x + 0.4302$

$R^2 = 0.9938$
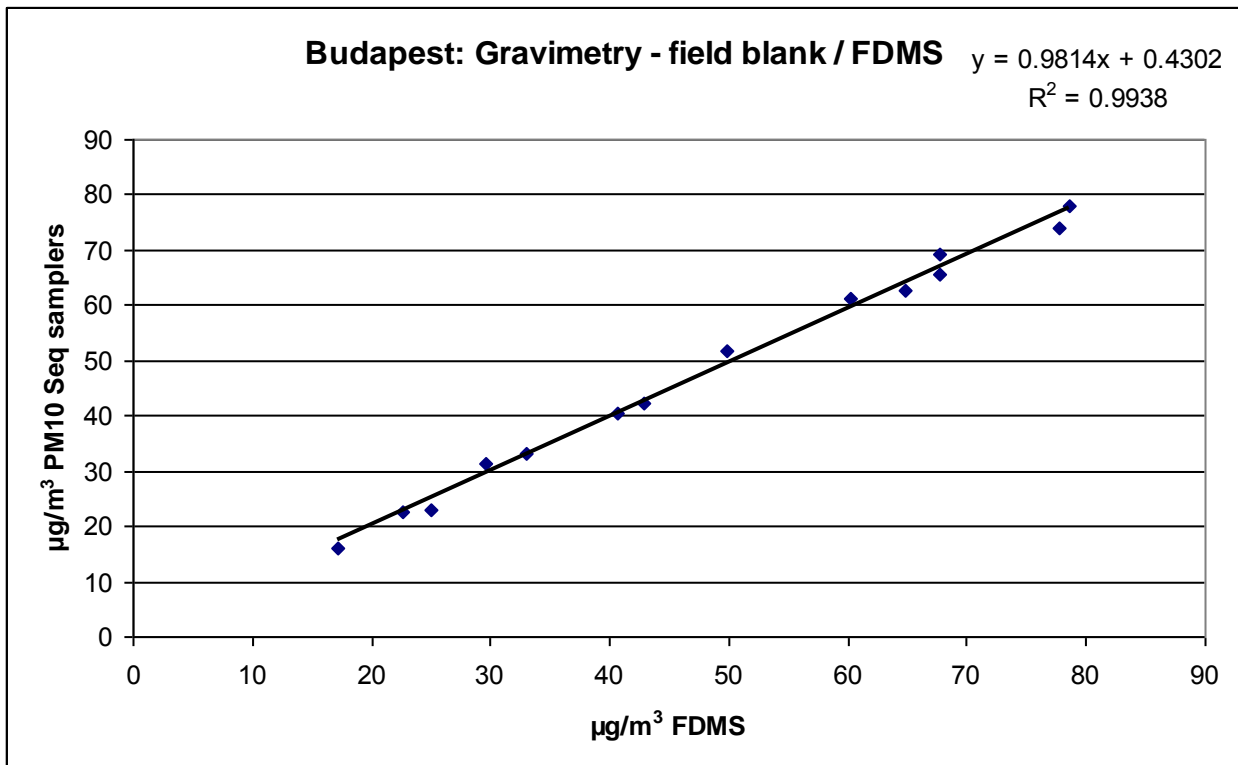
Figure 37: Bratislava PM10: Gravimetric result without subtraction of field blank vs. FDMS
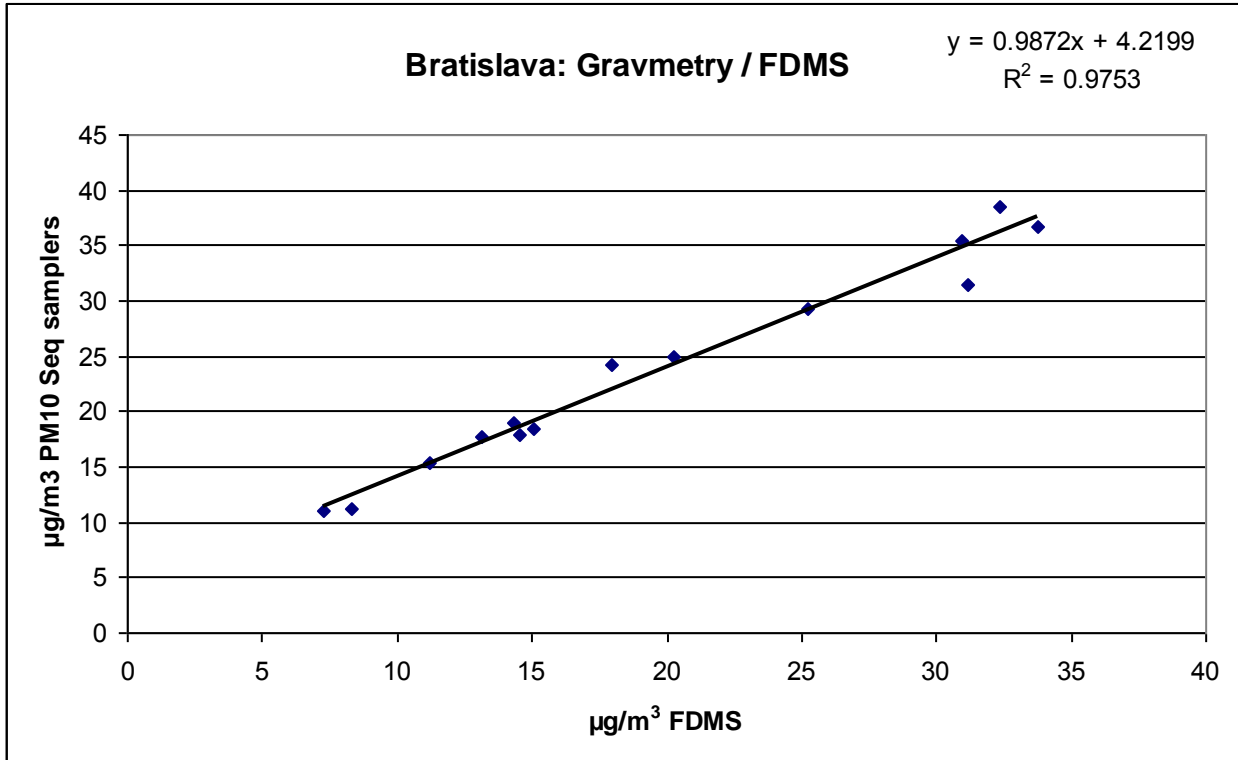
Figure 38: Bratislava PM10: Gravimetric result after subtraction of field blank vs. FDMS
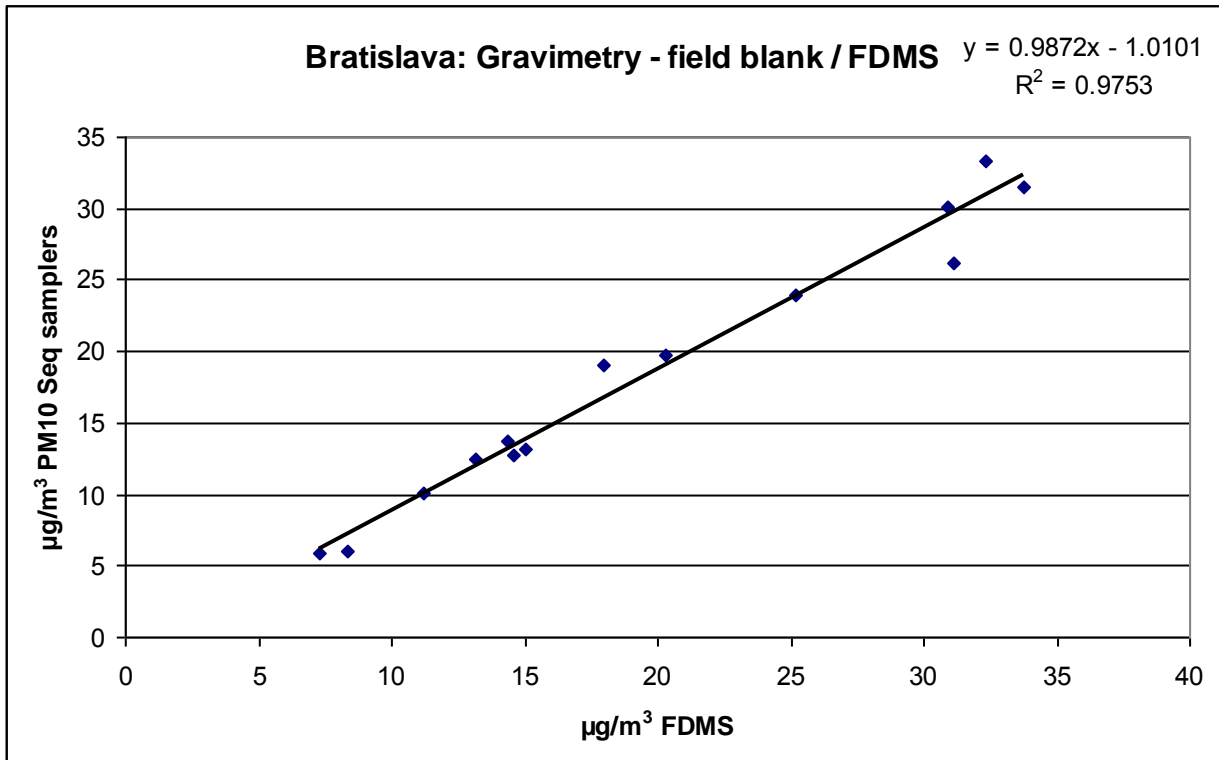
6.   Conclusions

With reference to the objectives of the study (see chapter "summary") the following conclusions can be drawn:

The methodology applied by the JRC has been shown to yield robust reference values. These have been further used for comparison with results obtained by National Reference Laboratories (NRL) and local networks.

A total of 79 datasets have been obtained for PM10, of which 54 are from NRL. For PM2.5 a total of 31 datasets have been obtained, of which 18 are from NRL. For PM10 6 datasets can be marked as suspect when applying ISO 5725 statistics; for PM2.5 3 datasets are suspect.

When using all data supplied, National Reference Laboratories are found to underestimate the Reference Values for PM10 by 5.3% with a reproducibility standard deviation of 16%. Local networks were found, on average, to almost exactly reproduce the Reference Values with a reproducibility standard deviation of 19%. For PM2.5 the underestimation of the Reference Values by National Reference Laboratories increased to about 11%, whereas the average of the local networks was 1.6% lower. However, the reproducibility of the local networks was considerably worse (50% vs. 15% for the National Reference Laboratories). On a whole, these findings indicate that – within the uncertainties associated with the measurements – the average results of National Reference Laboratories and local networks agree with the JRC Reference Values.

For assessment of compliance with the uncertainty data quality objectives of Directive 2008/50/EC both uncertainties of individual results and uncertainties of grouped results have been considered. Of individual PM10 measurements, 7.1% did not comply with the Data Quality Objective at the limit value given in Directive 2008/50/EC; of individual PM2.5 measurements 23.8% did not comply with the Data Quality Objective at the target value given in EU Directive 2008/50/EC. Deviations could not be directly attributed to specific parameters like filter material, sampling temperature or instrumentation type as too many variables are influencing the measurement results.

Around one third of the PM10 and half of the PM2.5 measurements exceed the required uncertainty at the limit respectively target value, with automatic analyzers performing worse than the gravimetric methods. The expectancy for these fractions would be 5%.

When considering relative uncertainties of grouped results based on reproducibility standard deviations after removal of outliers these are 28% (95% confidence) for PM10 and 33% (95% confidence) for PM2.5. For reference methodologies the uncertainties are lower than for automatic analyzers, which may partly be attributed to the use of default correction factors instead of factors derived from equivalence tests. The average findings are higher than the required uncertainty of 25% (95% confidence). For PM2.5 these findings will have consequences for the establishment of the reduction in the Average Exposure Indicator.

These findings indicate that at the time of the study problems have existed in meeting the uncertainty data quality objectives of 2008/50/EC. Meanwhile, it is expected that uncertainties of results for automatic analyzers will have decreased as a result of equivalence testing. However, also uncertainties for reference methodologies

are relatively high, showing a need for reduction of possible variations in methodologies existing at the time of this study.

Almost half of all users of automatic analyzers have used correction factors for the results obtained by the analyzers. The use of correction factors generally improves their results.

Furthermore, the following findings have been reported:

- When comparing low-volume sampling to high-volume sampling, results for low-volume sampling are generally found to be higher. For high-volume sampling, no difference can be found between results obtained using quartz-fibre or glass-fibre filters (the two mostly used filter types), however for low-volume sampling results obtained using quartz-fibre filters are higher.

- A considerable fraction of the field blanks examined during this study exceeds of the criterion given in EN 14907, with levels of up to 6 µg/m^3. The reason for this phenomenon requires further investigation.

7. References

1   1999/30/EC - Council Directive 1999/30/EC relating to limit values for sulphur dioxide, nitrogen dioxide and oxides of nitrogen, particulate matter and lead in ambient air (L 163, 29.06.1999)

2   Directive 2008/50/EC of the European Parliament and of the Council of 21 May 2008 on ambient air quality and cleaner air for Europe. OJ L152/1 of 11.6.2008

3   EN 12341:1998: Air Quality – Determination of the PM10 fraction of suspended particulate matter – Reference method and field test procedure to demonstrate reference equivalence of measurement methods, European Standard, CEN, Brussels

4   EN 14907:2005: Ambient air quality – Standard gravimetric measurement method for the determination of the PM2,5 mass fraction of suspended particulate matter, European Standard, CEN, Brussels

5   Guide to the Demonstration of Equivalence of Ambient Air Monitoring Methods http://ec.europa.eu/environment/air/quality/legislation/pdf/equivalence.pdf

6   ISO 5725-2:1994(E): Accuracy (trueness and precision) of measurement methods and results - Part 2: Basic method for the determination of repeatability and reproducibility of a standard measurement method, Geneva (CH)

7   ISO/IEC guide 43-1:1997(E): Proficiency testing by interlaboratory comparisons –Part 1: Development and operation of proficiency testing schemes, Geneva (CH)

8   ISO 5725-6:1994(E): Accuracy (trueness and precision) of measurement methods and results - Part 6: Use in practice of accuracy values, Geneva (CH)

9   http://ec.europa.eu/environment/air/quality/legislation/assessment.htm

10   Putaud et al, Atmospheric Environment 44 (2010) 1308-1320

11   http://www.statistics4u.info

12   http://www.watpon.com

13   Dutton S. J., Schauer J.J., Vedal S ,. Hannigan M. P, 2009. Atmospheric Environment 43 (2009) 1136–1146

14   ETC Technical paper 2005/6 PM10 measurement methods and correction factors in AirBase 2004 status report

ANNEX 1: Description of measurement sites

Spain (Madrid):

Location: On a crossing of major roads next to a huge park and residential area

Sampling: Free of local obstacles

Prevailing/local sources: Traffic
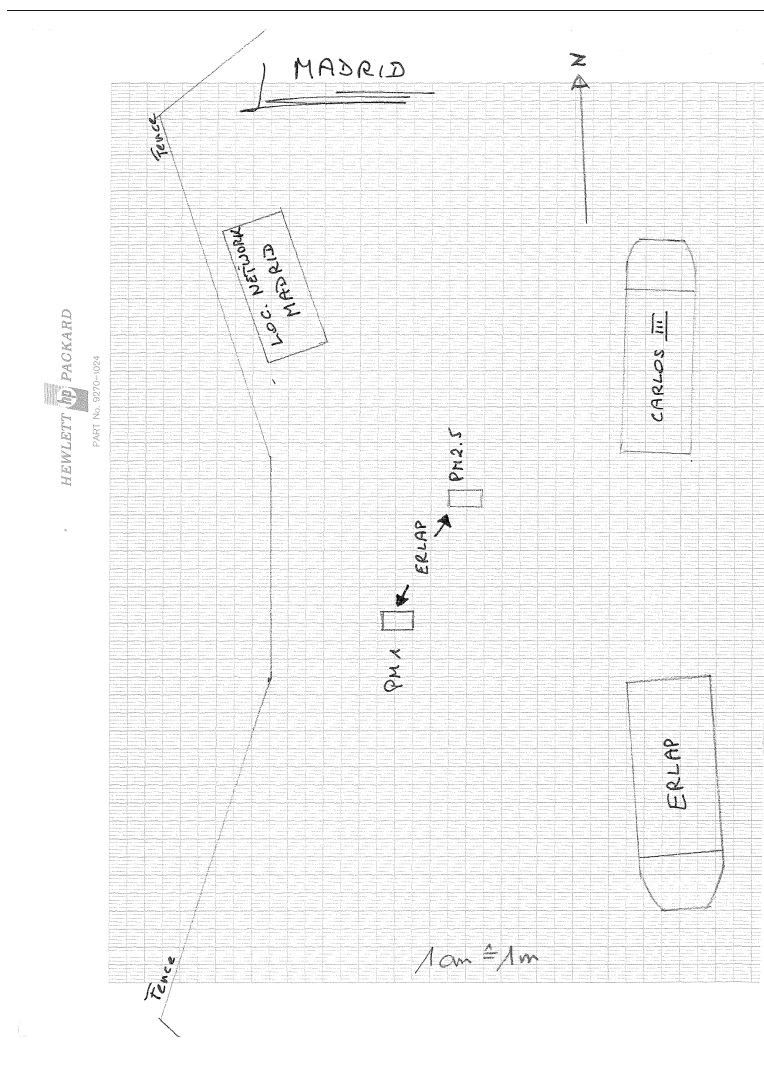
Portugal (Amadora):

Location: Next to "Istituto do Ambiente" in a residential area west of Lisbon

Sampling: Free of local obstacles

Prevailing/local sources: Residential combustion, traffic, sea salt
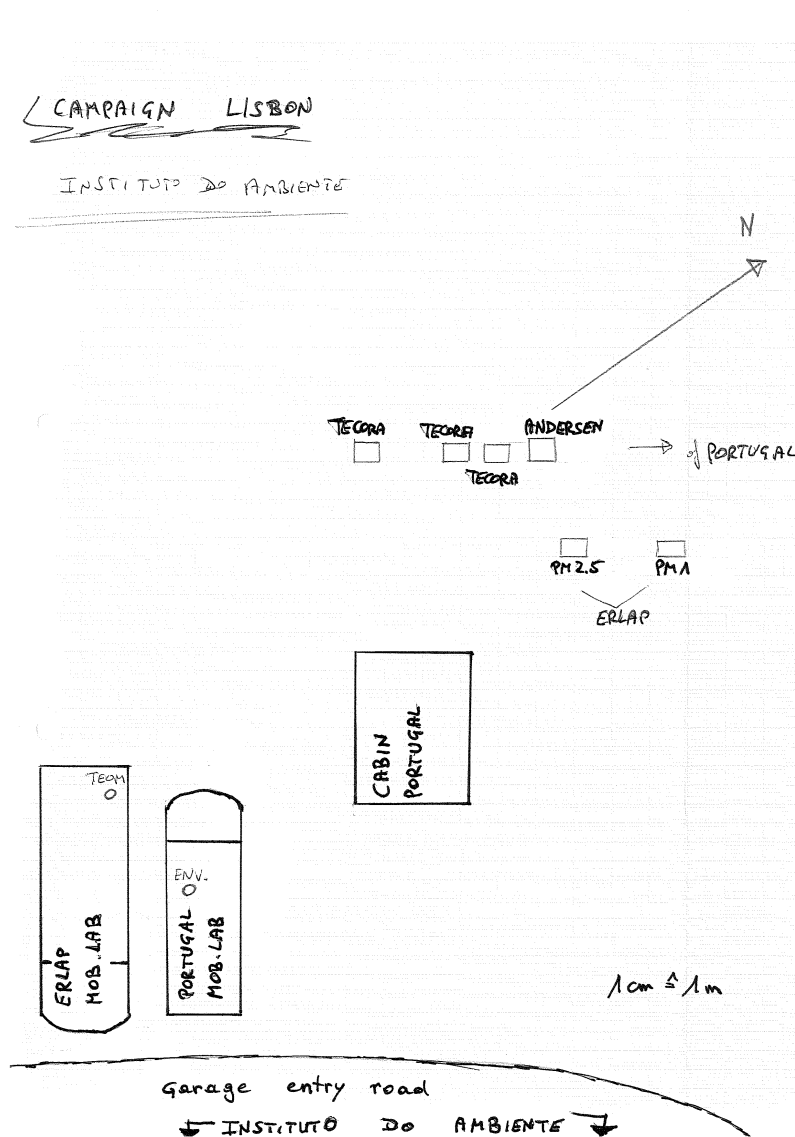
Slovenia (Ljubljana):

Location: Courtyard next to EPA in residential area

Sampling: Free of local obstacles

Prevailing/local sources: Residential combustion, traffic
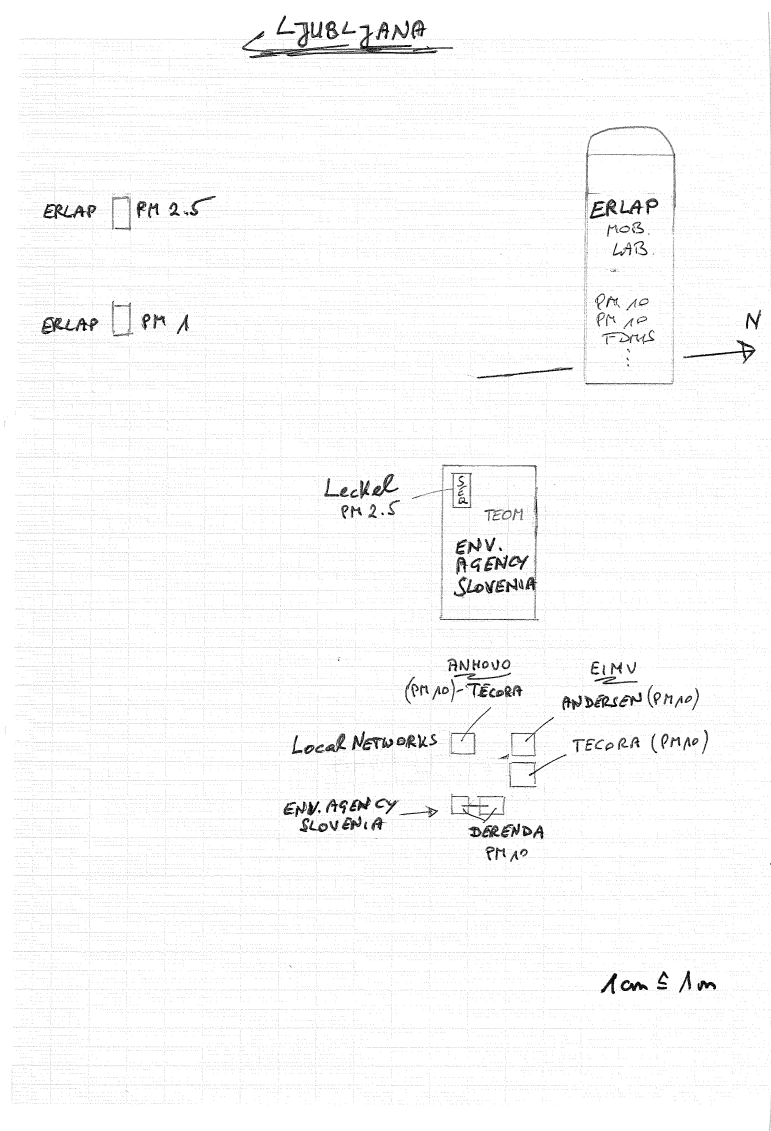
Austria (Graz):

Location: Residential area in the south of the city, single houses, fields

Sampling: Free of local obstacles

Prevailing/local sources: Residential combustion, traffic, carpentry (300 m distance), secondary aerosol and silicate are dominant
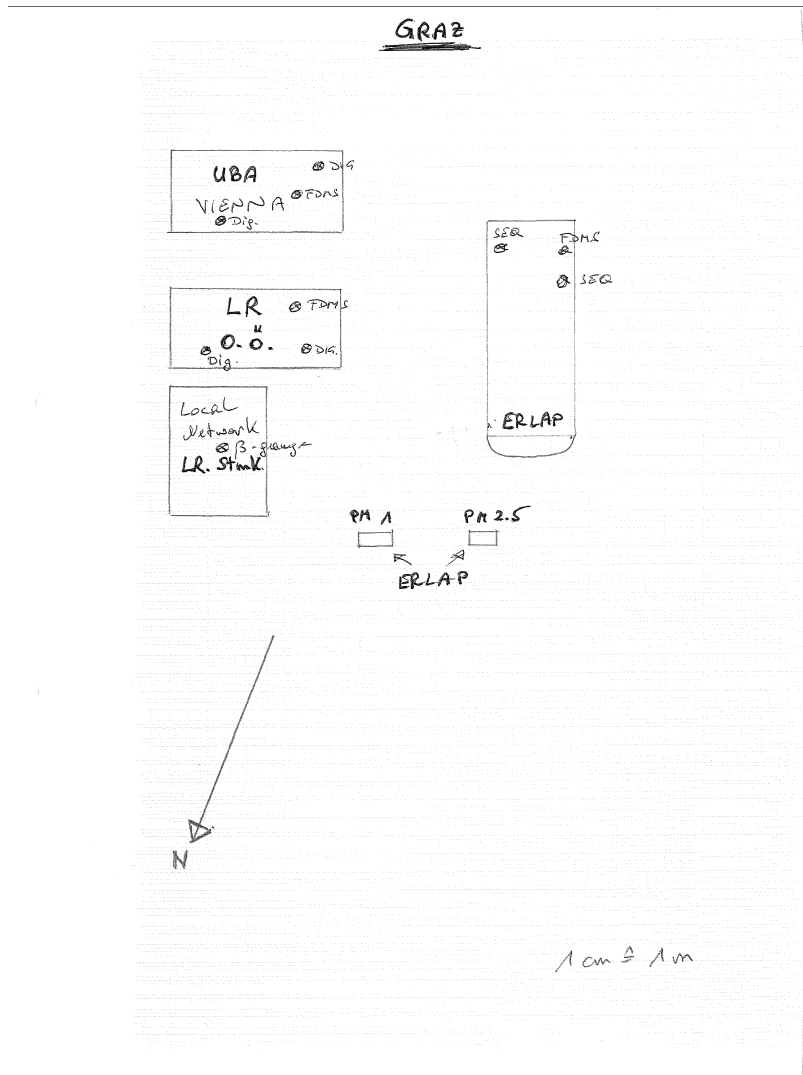
Czech Republic (Prague):

Location: Residential area in the south of the city next to the CHMI, fields

Sampling: Free of local obstacles

Prevailing/local sources: Residential combustion, traffic
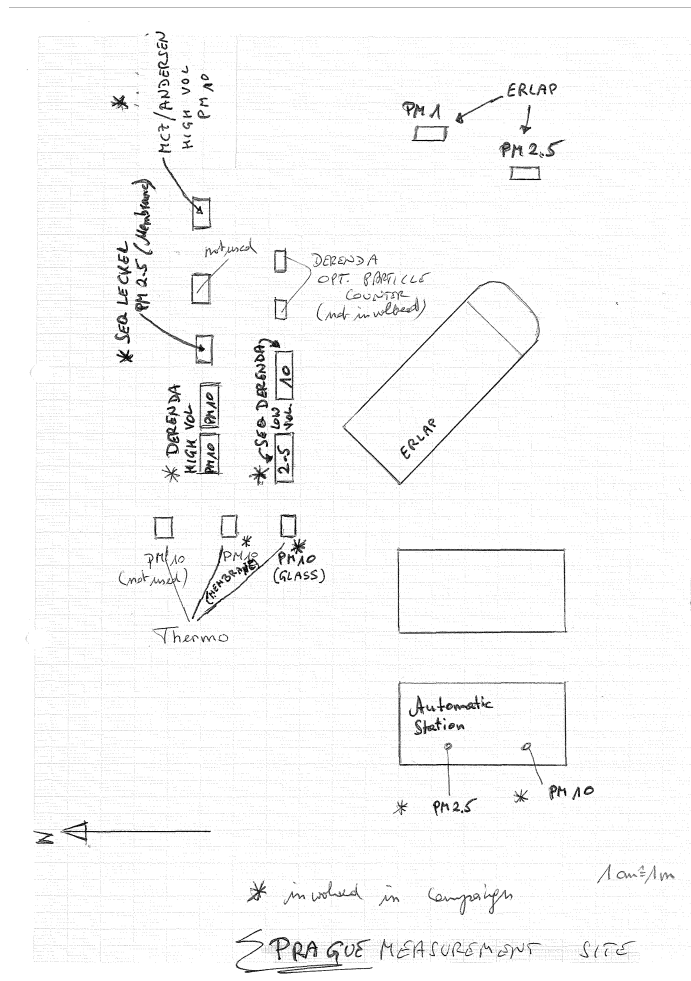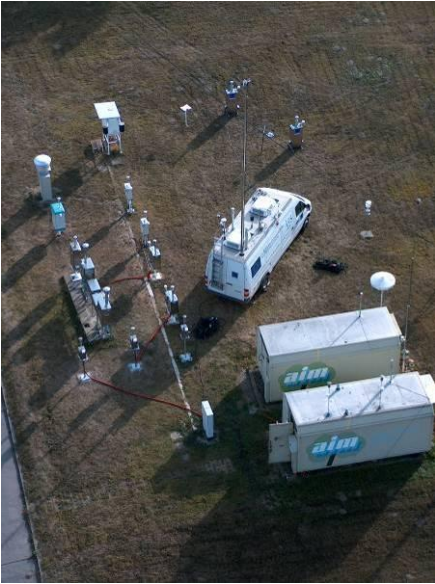
Germany (Wiesbaden):

Location: Courtyard next to the HLUG in Biebrich – south Wiesbaden, residential and industrial area (chemical industry, cement works) in the vicinity

Sampling: Free of local obstacles

Prevailing/local sources: Residential combustion, traffic, industry
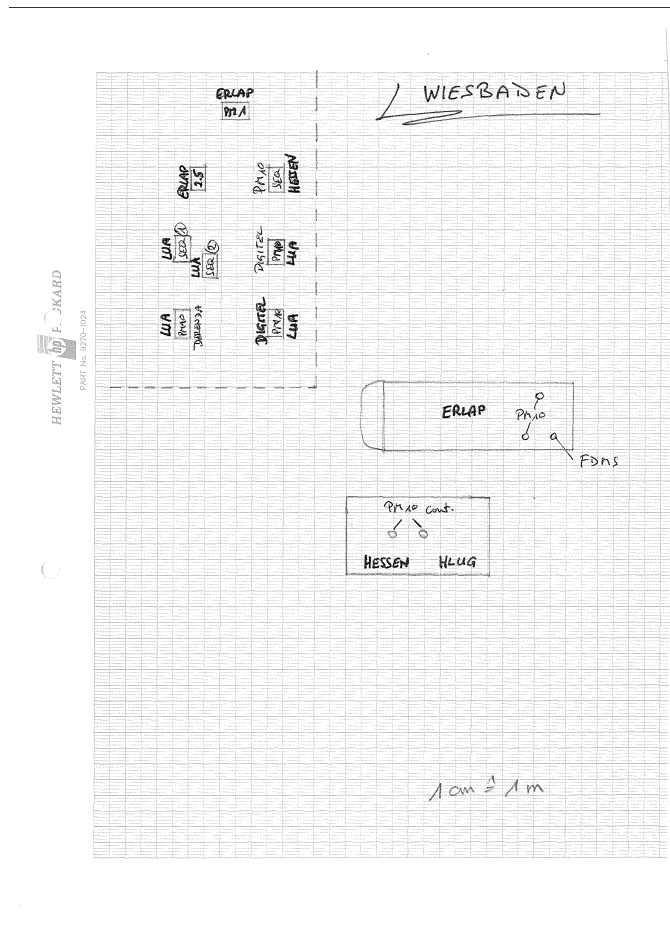
Denmark (Copenhagen):

Location: Along a major road in the city centre

Sampling: Free of local obstacles but buildings to the north-east of the measurement site

Prevailing/local sources: Traffic
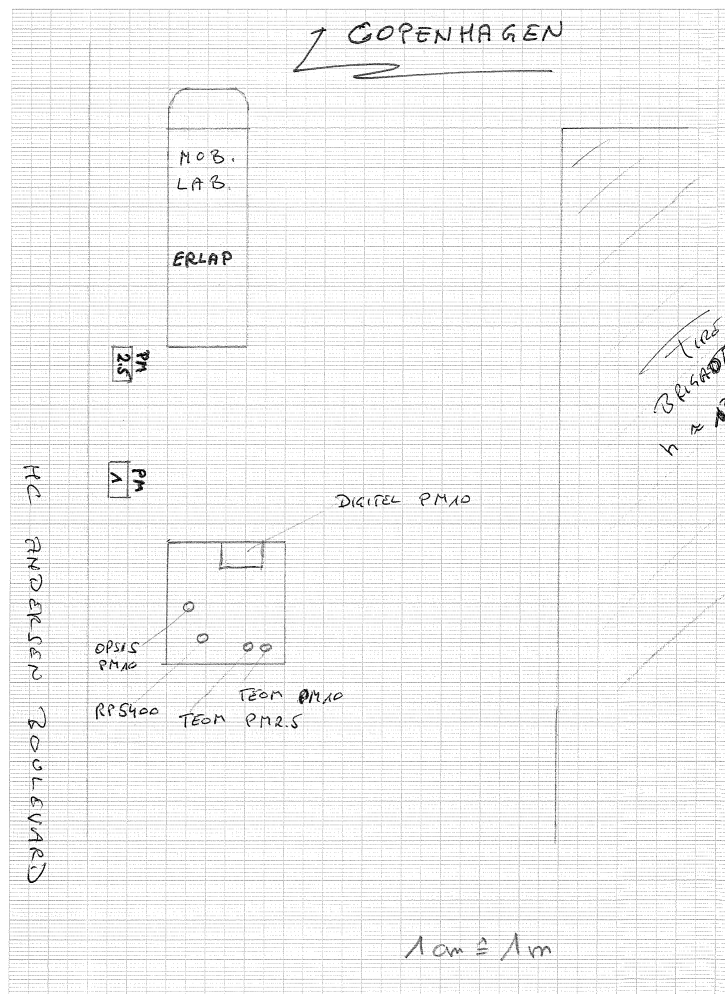
Sweden (Stockholm):

Location: Kerb-site in the city centre

Sampling: Buildings to both sides of the road

Prevailing/local sources: Traffic
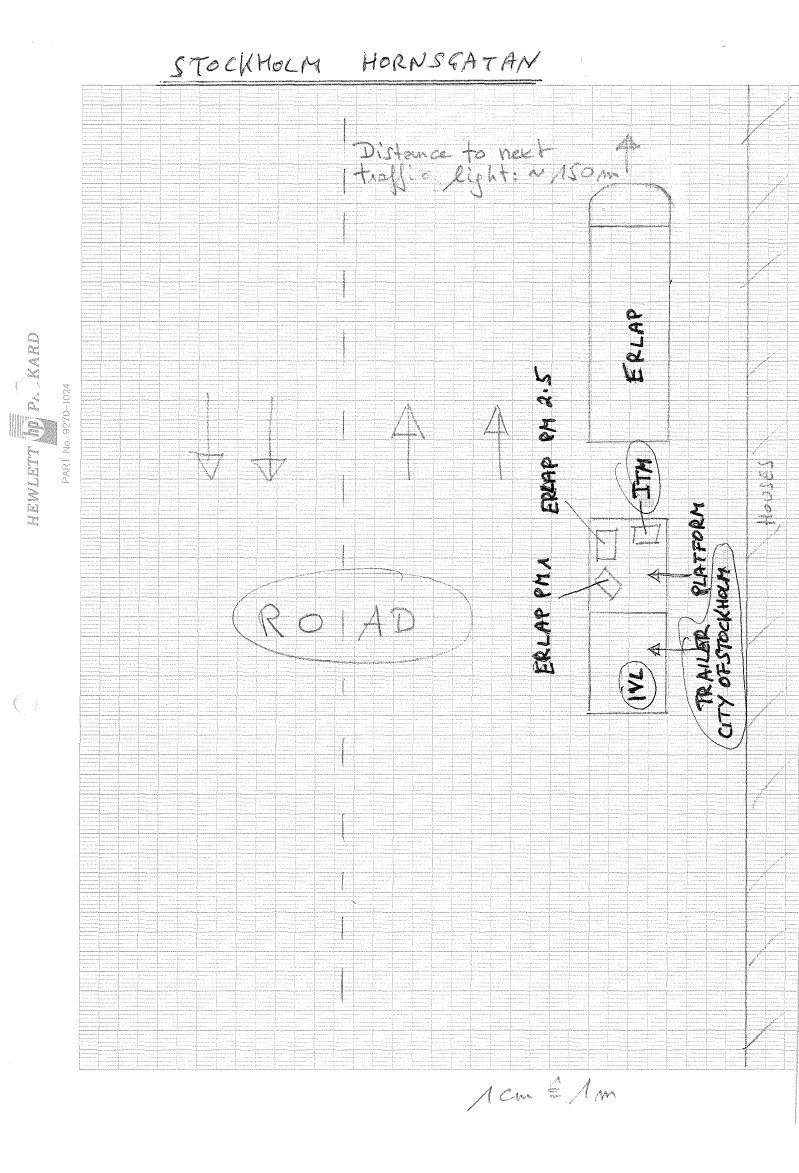
Finland (Helsinki):

Location: On a hill in the periphery, next to FMI and university campus, fields

Sampling: Free of obstacles

Prevailing/local sources: Domestic heating, traffic, long range transport, sea salt
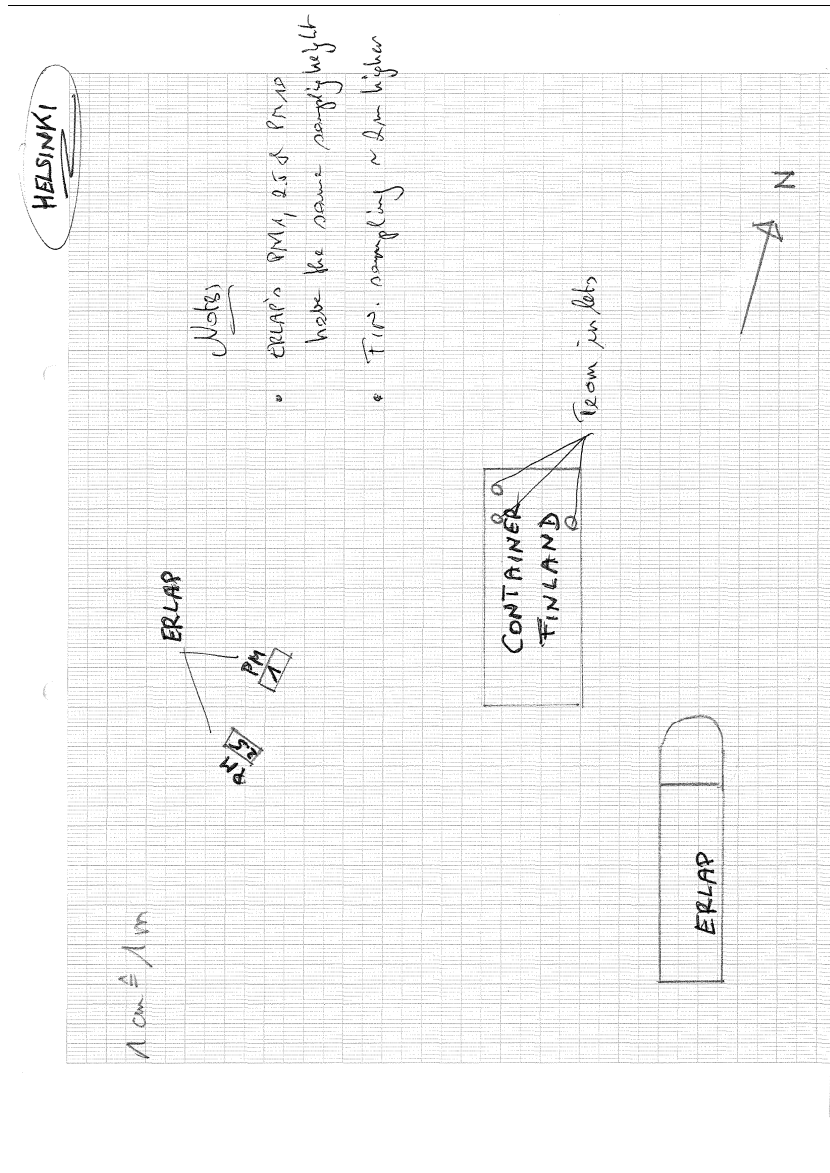
Estonia (Tallinn):

Location: In the west of the city in a court/park area surrounded by apartment buildings

Sampling: Free of obstacles

Prevailing/local sources: Domestic heating, traffic
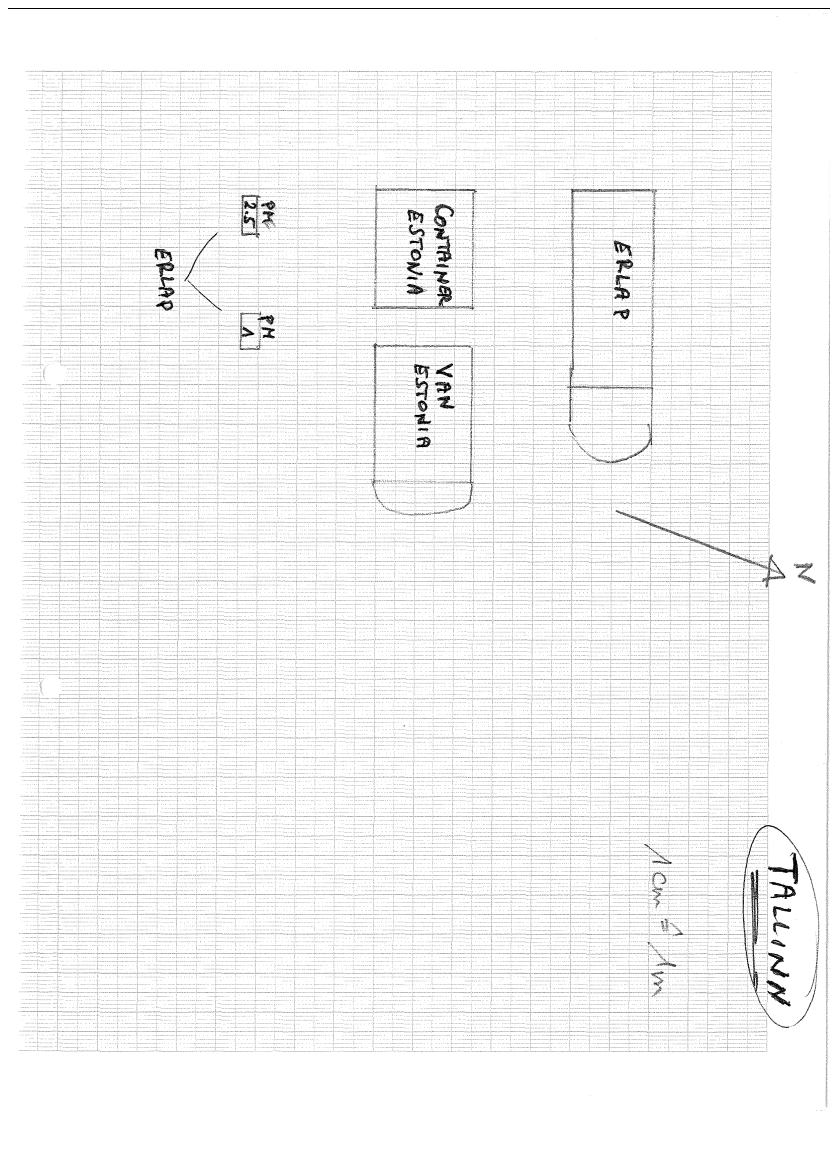
Netherlands (Biest - Houtakker):

Location: Around 10 km east of Tilburg, in the middle of fields and along a channel

Sampling: Free of obstacles

Prevailing/local sources: Agriculture
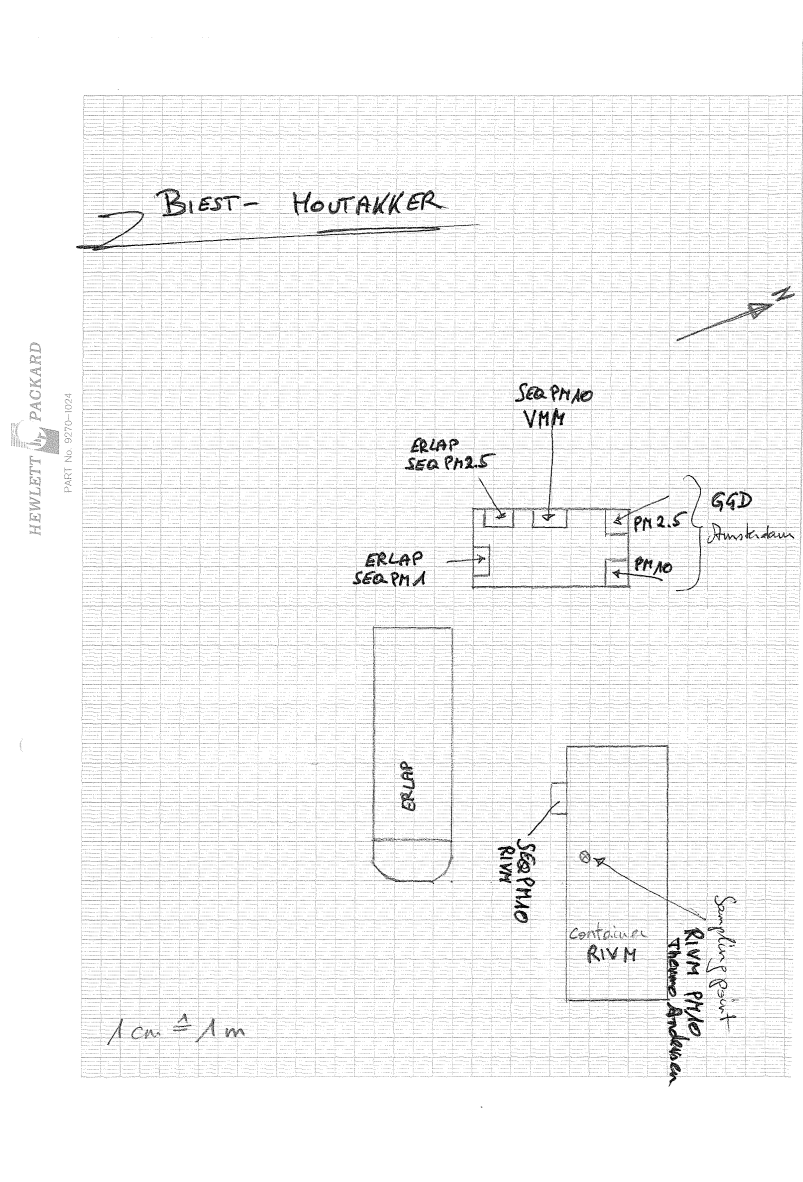
Belgium (Borgerhout):

Location: Suburb in the east of Antwerp, close to a school court and a major road

Sampling: Building in the east close to the measurement site

Prevailing/local sources: Traffic, loose terrain of schoolyard
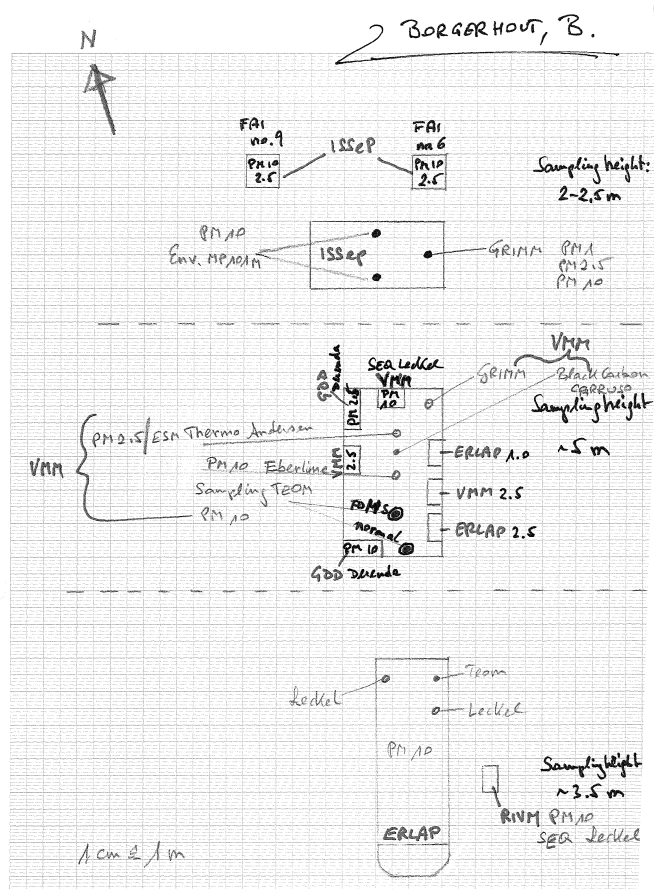
France (Bobigny):

Location: Suburb in the east of Paris, open park area

Sampling: Free of obstacles

Prevailing/local sources: Domestic heating
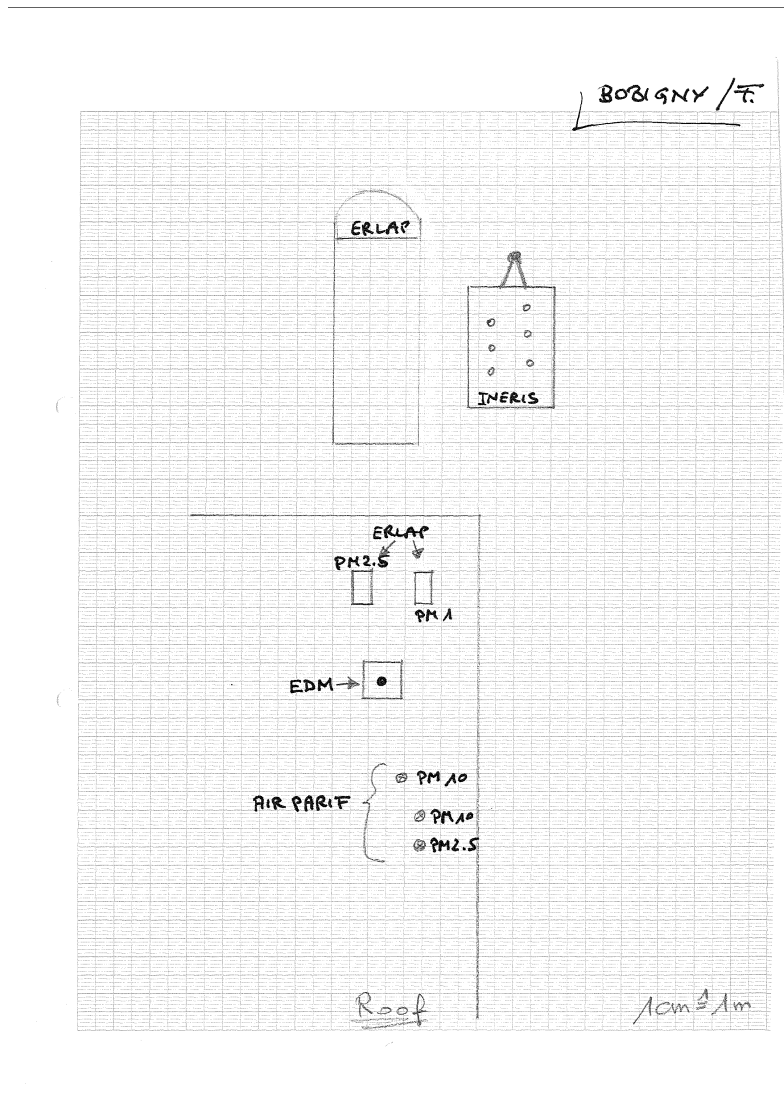
Ireland (Dublin):

Location: Suburb in the west of the city, open park area

Sampling: Free of obstacles

Prevailing/local sources: Domestic heating
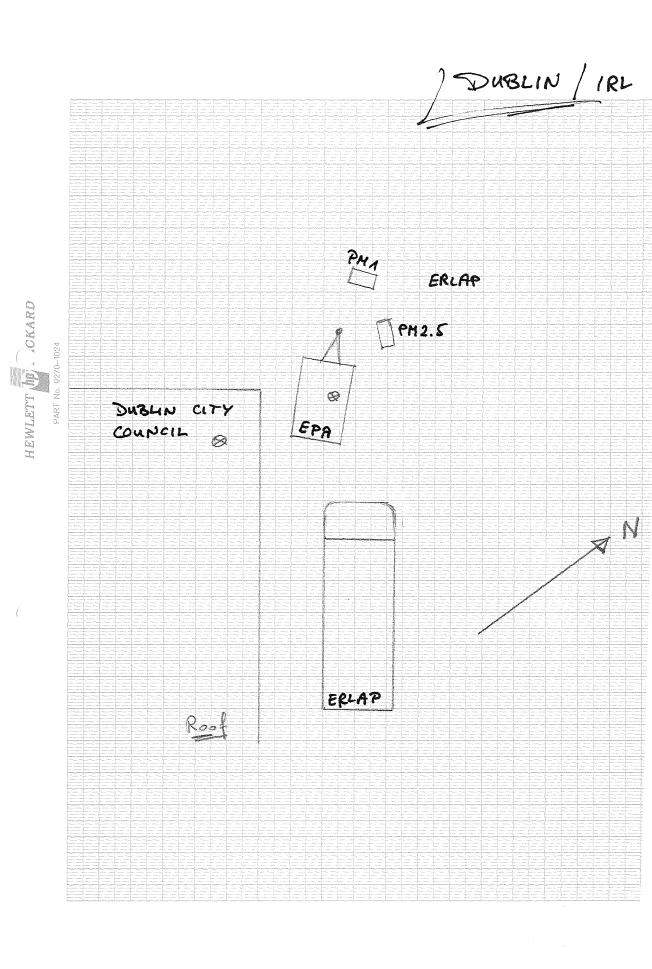
United Kingdom (Port Talbot/Wales):

Location: Suburb in the east of the city, next to single houses, railway and steel plant, close to the sea

Sampling: Free of obstacles

Prevailing/local sources: Steel plant, domestic heating, sea salt
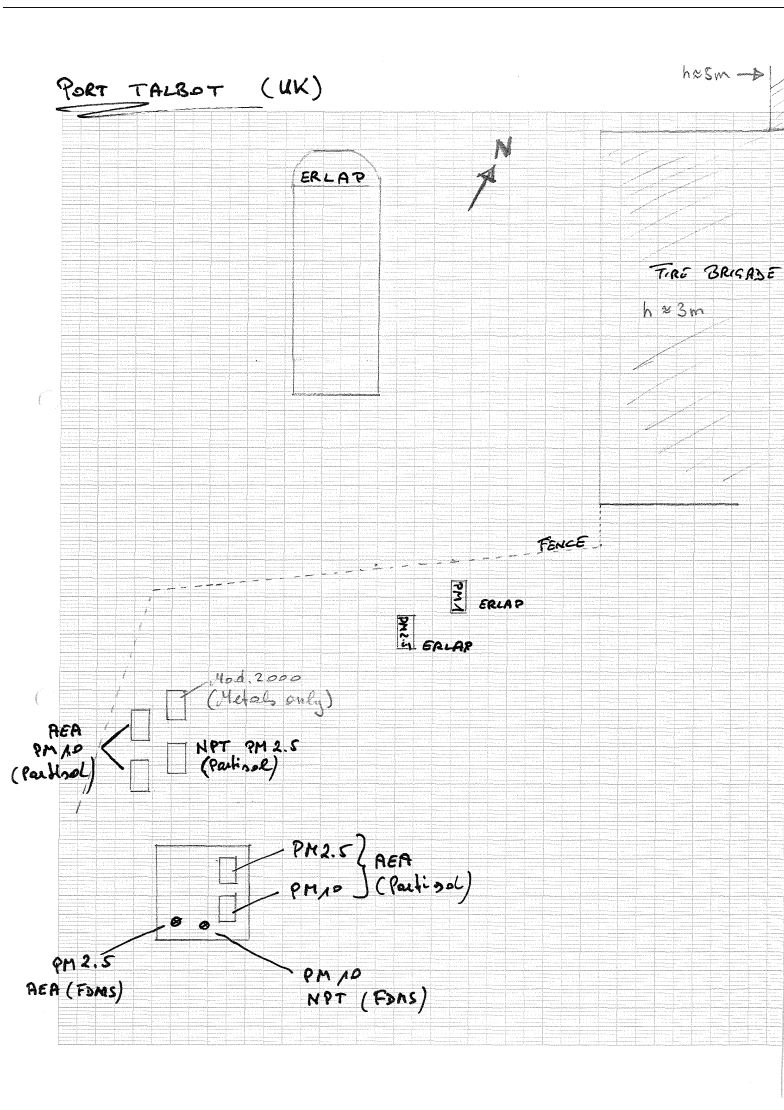
Italy (Milan)

Location: Parco Giuriati in the east of the city next to a sport yard and university campus

Sampling: Free of obstacles apart from some small but high trees

Prevailing sources: Domestic heating, traffic
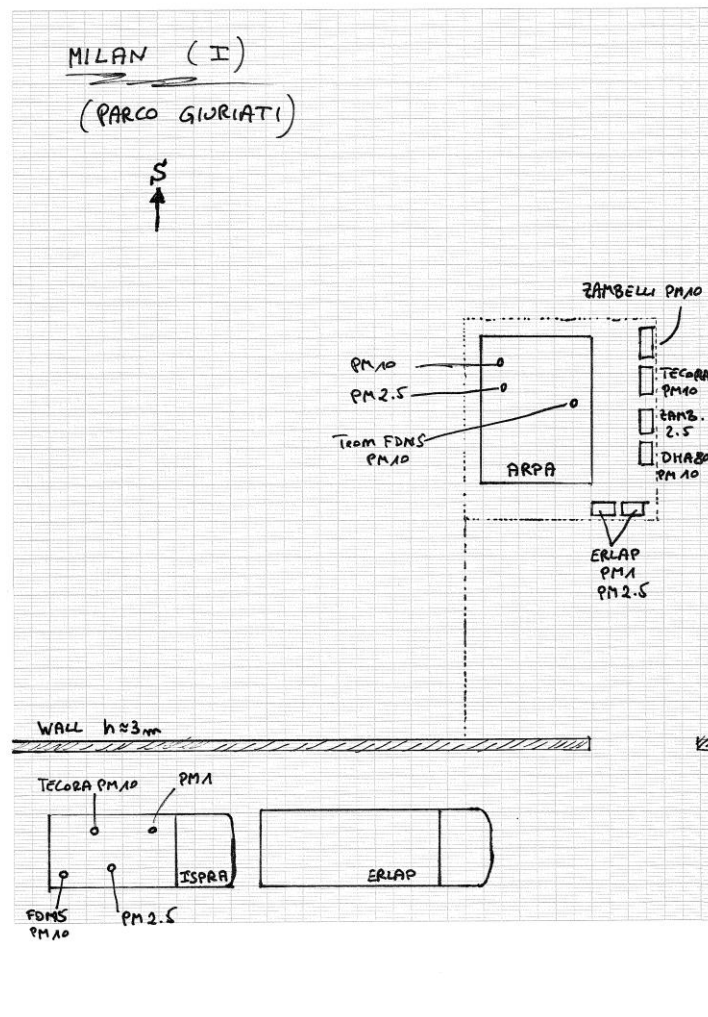
Hungary (Budapest)

Location: Meteorological observatory in the eastern suburb of the city

Sampling: Free of obstacles

Prevailing sources: Domestic heating, traffic
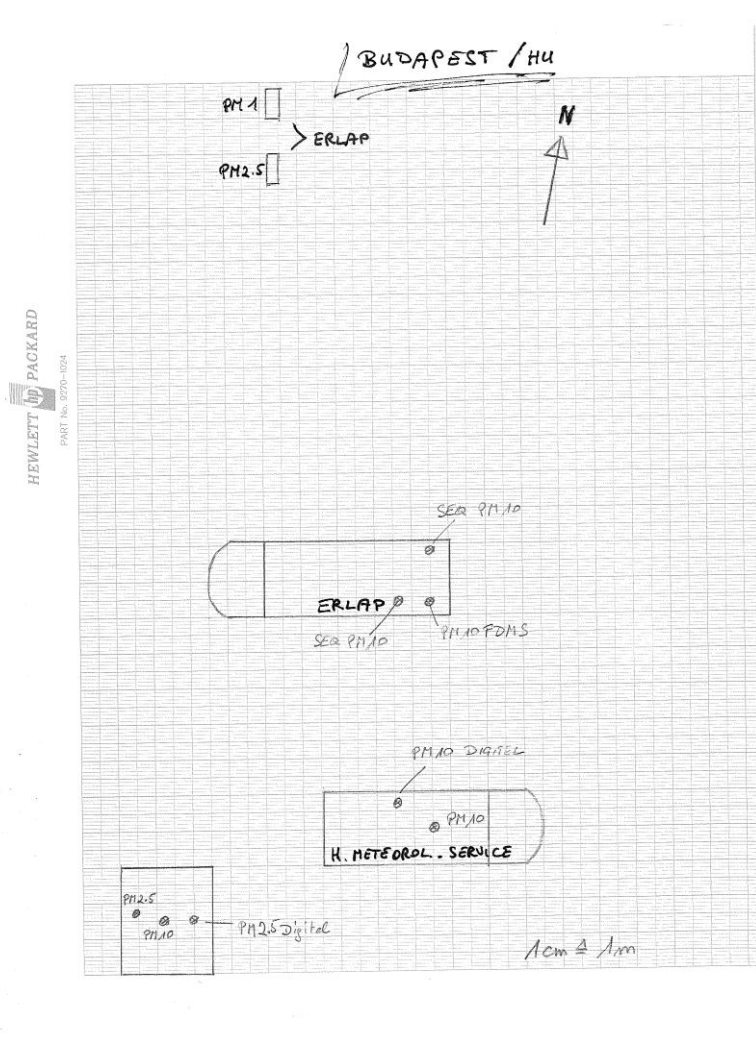
Slovakia (Bratislava)

Location: Next to a footpath on an open field surrounded by apartment buildings, suburb in the south of the city

Sampling: Free of obstacles

Prevailing sources: Domestic heating, traffic
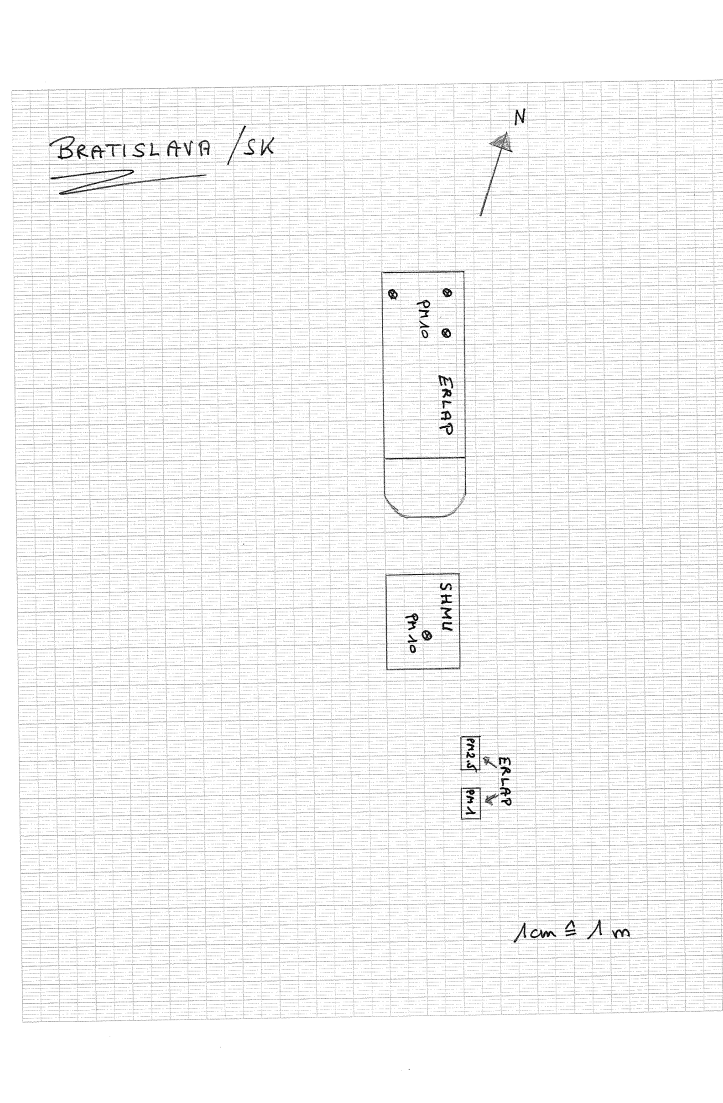
ANNEX 2: Inlets

Type 1: Derenda new (2.3m^3/h)

Type 2: Derenda old (2.3m^3/h)

Type 3: Leckel SEQ (2.3m^3/h)

Type 4: Tecora I (1m^3/h)

Type 5: Tecora II (2.3m^3/h)

Type 6: Andersen (68m^3/h)

Type 7: Digitel (1m³/h)

Type 8: Digitel High Vol (30m³/h)

Type 9: Teom I (1m³/h)

Type 10: Teom II (1m³/h)

Type 11: Leckel modified (2.3m³/h)

Type 12: FAI PM2.5 & PM10 (2.3m³/h)

Type 13: Derenda High Vol (30m³/h)

Type 14: Digitel (2.3m³/h)

Type 15: Grimm TSP (72 l/h)

Type 16: IVL (18 l/min)

No picture available

Type 17: Aquaria PM 2.5 (1m³/h)

Type 18: Aquaria PM 10 (1m³/h)

Type 19: Teom PM 1 (1m^3/h)

Type 20: Unitec (2.3m^3/h)

Type 21: Zambelli PM 2.5 (1m^3/h)

Type 22: Zambelli PM 10 (1m^3/h)

Type 23: Thermo PM10 / PM2.5 (1m^3/h)

ANNEX 3: Details of applied correction factors

PM10 data in μg/m³:

Ayuntamiento de Madrid

JRC Reference value	without correction factor	Difference in %	with correction factor	Difference in %
54.44	57.07	4.83	62.78	15.31
30.63	33.74	10.17	37.11	21.19
12.79	10.15	-20.66	11.17	-12.73
19.22	23.04	19.88	25.34	31.86
37.96	47.05	23.95	51.76	36.34
33.16	41.22	24.32	45.34	36.76
40.55	45.69	12.66	50.26	23.93
35.93	39.85	10.90	43.84	21.99
29.09	34.80	19.61	38.28	31.57
33.71	37.58	11.47	41.34	22.62
20.47	19.21	-6.17	21.13	3.22
61.95	71.50	15.41	78.65	26.95
70.99	83.13	17.10	91.44	28.82
69.15	77.11	11.51	84.82	22.67
Median:		12.09		23.30
Min:		-20.66		-12.73
Max:		24.32		36.76
Data within DQO:		**14**		**8**

Instituto do Ambiente

JRC Reference value	without correction factor	Difference in %	with correction factor	Difference in %
39.78	29.00	-27.10	31.90	-19.81
45.06	32.42	-28.06	35.66	-20.87
28.47	17.00	-40.28	18.70	-34.31
35.84	27.83	-22.34	30.62	-14.57
32.19	25.25	-21.55	27.78	-13.71
23.66	16.50	-30.25	18.15	-23.28
36.78	20.67	-43.81	22.73	-38.19
28.80	18.08	-37.21	19.89	-30.93
25.18	16.00	-36.45	17.60	-30.09
33.19	19.92	-39.99	21.91	-33.99
25.16	16.17	-35.75	17.78	-29.33
46.07	33.00	-28.37	36.30	-21.21
32.65	25.42	-22.16	27.96	-14.37
24.86	18.25	-26.58	20.08	-19.24
Median:		-29.31		-22.24
Min:		-43.81		-38.19
Max:		-21.55		-13.71
Data within DQO:		**3**		**8**

EPA of the Republic of Slovenia

JRC Reference value	without correction factor	Difference in %	with correction factor	Difference in %
24.9	30.15	21.23	31.05	24.87
29.7	28.85	-2.75	29.72	0.17
30.9	27.04	-12.43	27.85	-9.81
21.0	20.42	-2.80	21.04	0.11
28.0	26.47	-5.33	27.26	-2.49
40.4	35.91	-11.10	36.99	-8.43
40.9	37.40	-8.48	38.52	-5.74
38.7	37.78	-2.45	38.91	0.48
43.5	39.94	-8.09	41.13	-5.33
42.8	41.11	-3.93	42.35	-1.05
42.2	36.55	-13.45	45.32	7.32
28.9	26.63	-7.87	33.02	14.25
28.2	27.75	-1.48	34.41	22.16
29.5	28.96	-1.96	35.91	21.57
Median:		-4.63		0.14
Min:		-13.45		-9.81
Max:		21.23		24.87
Data within DQO:		**14**		**14**

LR Steiermark

JRC Reference value	without correction factor	Difference in %	with correction factor	Difference in %
	26.92		35.00	
	31.77		41.30	
54.4	42.77	-21.38	55.60	2.21
63.1	48.15	-23.71	62.60	-0.83
73.4	48.54	-33.91	63.10	-14.08
61.3	41.46	-32.35	53.90	-12.05
46.4	36.15	-22.10	47.00	1.27
39.3	31.85	-18.92	41.40	5.41
46.1	34.77	-24.57	45.20	-1.93
52.1	37.15	-28.66	48.30	-7.26
75.0	51.31	-31.58	66.70	-11.05
53.7	38.31	-28.73	49.80	-7.34
33.4	22.77	-31.85	29.60	-11.40
27.9	19.85	-28.78	25.80	-7.41
Median:		-28.69		-7.30
Min:		-33.91		-14.08
Max:		-18.92		5.41
Data within DQO:		**5**		**12**

CHMI

JRC Reference value	without correction factor	Difference in %	with correction factor	Difference in %
8.63	5.22	-39.47	6.79	-21.31
19.03	14.11	-25.86	18.34	-3.62
21.90	15.59	-28.80	20.27	-7.44
11.10	7.97	-28.18	10.37	-6.63
16.82	11.65	-30.76	15.14	-9.99
19.57	14.37	-26.57	18.68	-4.54
16.93	10.75	-36.53	13.97	-17.49
18.82	12.78	-32.12	16.61	-11.76
32.63	21.53	-34.00	27.99	-14.21
54.61	38.88	-28.80	50.55	-7.44
31.11	20.04	-35.59	26.05	-16.27
9.78	6.40	-34.57	8.32	-14.94
23.26	16.70	-28.21	21.71	-6.68
17.01	11.44	-32.72	14.88	-12.54
Median:		-31.44		-10.87
Min:		-39.47		-21.31
Max:		-25.86		-3.62
Data within DQO:		**0**		**14**

HLUG

JRC Reference value	without correction factor	Difference in %	with correction factor	Difference in %
23.0	15.00	-34.68	17.70	-22.93
16.1	9.00	-44.15	10.62	-34.10
44.4	32.00	-27.99	37.76	-15.03
30.6	21.00	-31.41	24.78	-19.07
42.5	33.00	-22.28	38.94	-8.29
31.9	20.00	-37.29	23.60	-26.01
41.8	31.00	-25.92	36.58	-12.59
44.0	35.00	-20.46	41.30	-6.14
26.0	18.00	-30.72	21.24	-18.25
13.4	10.00	-25.44	11.80	-12.02
10.6	7.00	-33.84	8.26	-21.93
16.6	12.00	-27.60	14.16	-14.57
16.2	11.00	-31.90	12.98	-19.64
Median:		-30.72		-18.25
Min:		-44.15		-34.10
Max:		-20.46		-6.14
Data within DQO:		**2**		**11**

Estonian Env. Research Centre (container)

JRC Reference value	without correction factor	Difference in %	with correction factor	Difference in %
7.0	7.98	14.01	9.17	31.11
6.5	6.42	-0.84	7.39	14.03
4.4	3.28	-25.56	3.78	-14.39
7.9	6.78	-14.34	7.80	-1.49
8.3	5.92	-28.64	6.81	-17.94
23.1	15.68	-32.09	18.03	-21.91
13.4	10.47	-22.02	12.04	-10.33
20.5	17.04	-16.91	19.60	-4.45
7.8	7.84	0.69	9.01	15.80
9.2	8.60	-6.41	9.88	7.63
9.8	7.64	-21.74	8.79	-10.00
7.3	6.77	-6.57	7.79	7.44
11.4	9.25	-19.18	10.64	-7.06
Median:		-16.91		-4.45
Min:		-32.09		-21.91
Max:		14.01		31.11
Data within DQO:		**10**		**12**

Estonian Env. Research Centre (mob lab)

JRC Reference value	without correction factor	Difference in %	with correction factor	Difference in %
7.0	7.69	9.86	8.84	26.34
6.5	9.51	46.83	10.94	68.86
4.4	4.37	-0.82	5.03	14.06
7.9	7.85	-0.78	9.03	14.10
8.3	6.43	-22.59	7.39	-10.98
23.1	21.76	-5.75	25.02	8.38
13.4	13.99	4.18	16.09	19.81
20.5	21.62	5.39	24.86	21.20
7.8	10.56	35.61	12.14	55.95
9.2	11.48	24.99	13.20	43.73
9.8	9.91	1.52	11.40	16.74
7.3	9.11	25.69	10.48	44.55
11.4	12.71	11.06	14.62	27.72
Median:		5.39		21.20
Min:		-22.59		-10.98
Max:		46.83		68.86
Data within DQO:		**10**		**7**

JRC	RIVM				
Reference value	without correction factor	Difference in %		with correction factor	Difference in %
18.17	15.52	-14.58		20.86	14.80
32.56	27.39	-15.86		34.75	6.74
31.56	27.21	-13.77		34.54	9.44
33.06	28.11	-14.97		35.59	7.65
32.21	27.92	-13.31		35.37	9.81
35.80	31.88	-10.94		40.00	11.74
36.32	34.36	-5.39		42.90	18.13
46.47	45.03	-3.09		55.39	19.19
40.11	37.70	-6.01		46.81	16.69
26.32	22.24	-15.51		28.72	9.11
26.41	23.30	-11.79		29.96	13.43
34.25	30.03	-12.32		37.84	10.47
67.86	62.56	-7.82		75.89	11.83
73.19	70.09	-4.23		84.71	15.74
Median:		-12.05			11.79
Min:		-15.86			6.74
Max:		-3.09			19.19
Data within DQO:		**14**			**14**

JRC	VMM - ESM Andersen				
Reference value	without correction factor	Difference in %		with correction factor	Difference in %
28.38	19.71	-30.55		27.00	-4.86
37.48	26.28	-29.90		36.00	-3.96
36.88	27.01	-26.76		37.00	0.33
37.40	24.82	-33.64		34.00	-9.09
30.26	20.44	-32.46		28.00	-7.47
33.79	25.55	-24.38		35.00	3.59
50.64	37.96	-25.05		52.00	2.68
48.95	43.80	-10.53		60.00	22.57
24.07	26.28	9.17		36.00	49.56
26.65	20.44	-23.30		28.00	5.08
22.72	20.44	-10.03		28.00	23.27
17.14	15.33	-10.58		21.00	22.51
23.43	18.25	-22.13		25.00	6.69
41.39	31.39	-24.17		43.00	3.88
Median:		-24.28			3.74
Min:		-33.64			-9.09
Max:		9.17			49.56
Data within DQO:		**8**			**13**

JRC	VMM - Teom 1400				
Reference value	without correction factor	Difference in %		with correction factor	Difference in %
28.38	21.09	-25.69		31.00	9.23
37.48	25.17	-32.85		37.00	-1.29
36.88	21.77	-40.97		32.00	-13.22
37.40	23.81	-36.34		35.00	-6.42
30.26	20.41	-32.55		30.00	-0.86
33.79	27.89	-17.45		41.00	21.35
50.64	36.05	-28.81		53.00	4.65
48.95	24.49	-49.97		36.00	-26.46
24.07	19.73	-18.04		29.00	20.48
26.65	21.09	-20.86		31.00	16.34
22.72	19.05	-16.15		28.00	23.27
17.14	15.65	-8.72		23.00	34.17
23.43	20.41	-12.91		30.00	28.02
41.39	30.61	-26.04		45.00	8.72
Median:		-25.87			8.98
Min:		-49.97			-26.46
Max:		-8.72			34.17
Data within DQO:		**6**			**11**

JRC	ISSeP - MP 101 sn 33				
Reference value	without correction factor	Difference in %		with correction factor	Difference in %
28.38	24.00	-15.43		25.92	-8.67
37.48	27.00	-27.97		29.16	-22.21
36.88	30.00	-18.65		32.40	-12.14
37.40	26.00	-30.48		28.08	-24.92
30.26	20.00	-33.90		21.60	-28.62
33.79	26.00	-23.04		28.08	-16.89
50.64	37.00	-26.94		39.96	-21.10
48.95	39.00	-20.33		42.12	-13.96
24.07	18.00	-25.22		19.44	-19.24
26.65	22.00	-17.43		23.76	-10.83
22.72	19.00	-16.36		20.52	-9.66
17.14	15.00	-12.49		16.20	-5.49
23.43	19.00	-18.92		20.52	-12.43
41.39	32.00	-22.69		34.56	-16.51
Median:		-21.51			-15.23
Min:		-33.90			-28.62
Max:		-12.49			-5.49
Data within DQO:		**9**			**13**

ISSeP - MP 101 sn 78

JRC Reference value	without correction factor	Difference in %	with correction factor	Difference in %
28.38				
37.48	24.00	-35.97	25.92	-30.85
36.88	26.00	-29.49	28.08	-23.85
37.40	24.00	-35.83	25.92	-30.70
30.26	18.00	-40.51	19.44	-35.75
33.79	26.00	-23.04	28.08	-16.89
50.64	36.00	-28.92	38.88	-23.23
48.95	36.00	-26.46	38.88	-20.58
24.07	17.00	-29.37	18.36	-23.72
26.65	19.00	-28.69	20.52	-22.99
22.72	15.00	-33.96	16.20	-28.68
17.14	14.00	-18.33	15.12	-11.79
23.43	19.00	-18.92	20.52	-12.43
41.39	29.00	-29.94	31.32	-24.33
Median:		-29.37		-23.72
Min:		-40.51		-35.75
Max:		-18.33		-11.79
Data within DQO:		**3**		**9**

Hungarian Meteoroloical Institute - FH62 IR

JRC Reference value	without correction factor	Difference in %	with correction factor	Difference in %
22.67	21.75	-4.03	23.93	5.57
31.14	22.87	-26.56	25.16	-19.21
51.48	36.95	-28.23	40.64	-21.06
62.31	53.83	-13.62	59.21	-4.98
60.91	49.55	-18.66	54.50	-10.53
77.86	63.43	-18.54	69.77	-10.39
73.63	63.55	-13.69	69.90	-5.06
32.94	24.86	-24.52	27.35	-16.97
15.90	12.73	-19.95	14.00	-11.94
22.22	15.60	-29.80	17.16	-22.78
42.01	30.53	-27.33	33.58	-20.06
40.04	30.94	-22.74	34.03	-15.02
68.96	50.19	-27.22	55.21	-19.94
65.44	51.25	-21.67	56.38	-13.84
Median:		-22.21		-14.43
Min:		-29.80		-22.78
Max:		-4.03		5.57
Data within DQO:		**9**		**14**

MDV Hungary - FH62 IR

JRC Reference value	without correction factor	Difference in %	with correction factor	Difference in %
22.67	21.36	-5.76	23.50	3.67
31.14				
51.48	40.73	-20.89	44.80	-12.98
62.31	51.55	-17.28	56.70	-9.01
60.91	51.73	-15.08	56.90	-6.59
77.86	63.00	-19.08	69.30	-10.99
73.63	58.73	-20.24	64.60	-12.26
32.94	25.73	-21.89	28.30	-14.08
15.90	13.27	-16.52	14.60	-8.17
22.22	17.55	-21.05	19.30	-13.15
42.01	34.09	-18.84	37.50	-10.73
40.04	32.09	-19.86	35.30	-11.85
68.96	53.82	-21.96	59.20	-14.16
65.44	56.18	-14.14	61.80	-5.56
Median:		-19.08		-10.99
Min:		-21.96		-14.16
Max:		-5.76		3.67
Data within DQO:		**13**		**13**

PM2.5 data in µg/m³:

JRC	CHMI				
Reference value	without correction factor	Difference in %		with correction factor	Difference in %
5.90	4.09	-30.73		5.31	-9.94
13.81	9.06	-34.39		11.78	-14.71
15.41	8.78	-43.02		11.42	-25.93
7.87	5.40	-31.33		7.02	-10.73
12.96	8.98	-30.71		11.68	-9.92
16.31	11.36	-30.35		14.77	-9.45
15.11	7.62	-49.57		9.91	-34.45
16.03	9.32	-41.84		12.12	-24.39
25.19	15.27	-39.39		19.85	-21.20
46.83	32.05	-31.56		41.66	-11.02
25.35	13.69	-46.01		17.80	-29.81
6.79	4.32	-36.46		5.61	-17.40
16.26	10.75	-33.84		13.98	-13.99
14.69	8.44	-42.55		10.98	-25.31
Median:		-35.42			-16.05
Min:		-49.57			-34.45
Max:		-30.35			-9.45
Data within DQO:		**0**			**10**

JRC	Estonian Env. Research Centre (container)				
Reference value	without correction factor	Difference in %		with correction factor	Difference in %
3.9	3.21	-17.65		3.69	-5.30
4.3	2.44	-42.84		2.81	-34.27
6.8	3.79	-44.09		4.36	-35.70
7.1	3.35	-53.06		3.85	-46.02
15.0	7.19	-51.95		8.27	-44.74
7.1	3.83	-46.18		4.41	-38.10
6.7	4.47	-33.62		5.14	-23.66
12.5	8.56	-31.71		9.85	-21.47
4.5	3.50	-21.98		4.03	-10.27
4.2	4.01	-5.51		4.61	8.67
4.5	5.05	11.95		5.80	28.74
5.1	3.42	-32.56		3.94	-22.44
6.7	4.15	-37.56		4.78	-28.20
Median:		-33.62			-23.66
Min:		-53.06			-46.02
Max:		11.95			28.74
Data within DQO:		**4**			**6**

JRC	MDV Hungary - FH62 IR				
Reference value	without correction factor	Difference in %		with correction factor	Difference in %
20.46	12.60	-38.44		16.50	-19.35
29.10	14.12	-51.47		18.50	-36.43
50.43	25.34	-49.75		33.20	-34.17
60.33	35.95	-40.41		47.10	-21.93
59.80	33.74	-43.58		44.20	-26.08
76.01	44.58	-41.35		58.40	-23.17
72.19	41.07	-43.11		53.80	-25.47
30.84	15.34	-50.25		20.10	-34.82
14.24	6.79	-52.28		8.90	-37.49
20.38	9.69	-52.44		12.70	-37.69
41.37	21.37	-48.34		28.00	-32.32
33.77	19.31	-42.82		25.30	-25.09
52.34	26.34	-49.68		34.50	-34.08
58.60	32.98	-43.72		43.20	-26.28
Median:		-46.03			-29.30
Min:		-52.44			-37.69
Max:		-38.44			-19.35
Data within DQO:		**0**			**3**

ANNEX 4: All "normalized" data-sets

PM10 codification and Mandel's *h* and *k* statistics

Codification	Laboratory	Instrument	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	mean	s	n	h	k
1	ISCIII	Derenda MVS 6.1 (LVS) A	0.918	0.914	0.860	0.885	0.922	0.905	0.863	0.891	0.894	0.860	0.879	0.872	0.859							0.886	0.023	13	-0.547	0.167
2	ISCIII	Derenda MVS 6.1 (LVS) B		0.882	0.938	0.885	0.896	0.905	0.863	0.863												0.890	0.026	7	-0.520	0.189
3	AdM	Teom 1400	1.153	1.212	0.873	1.319	1.363	1.368	1.239	1.220	1.316	1.226	1.032	1.270	1.288							1.221	0.138	13	1.869	0.994
4	IdA	Tecora Low Vol		1.099	1.730	0.943	0.286	1.778	0.911	1.035	1.597	0.928	2.138	1.115	1.043	1.273						1.221	0.481	13	1.868	3.462
5	IdA	Andersen High Vol	0.781	0.813		1.003	0.896	0.921	0.882	1.080	0.928	1.023	1.217	1.071	1.075	0.995						0.976	0.121	13	0.099	0.872
6	IdA	Environnemen MP 101	0.802	0.791	0.657	0.854	0.863	0.767	0.618	0.691	0.699	0.660	0.707	0.788	0.856	0.808						0.754	0.081	14	-1.498	0.586
7	EPA SI	Derenda 3.1-15(LVS)							1.052	1.110	1.036	1.192	1.066	1.488	1.172	1.083						1.150	0.147	8	1.353	1.061
8	EPA SI	Teom 1400, std..c/corr.fact	1.249	1.002	0.902	1.001	0.975	0.916	0.943	1.005	0.947	0.990	1.073	1.142	1.222	1.216						1.041	0.119	14	0.572	0.853
9	EIMV	Tecora	1.079	1.070	1.047	1.004	1.040	1.081	1.025	1.051	1.049	1.062	1.121	1.161	1.150							1.072	0.047	13	0.795	0.335
10	Anhovo	Tecora	1.037	1.055	1.055	0.984	0.988	1.022	1.007	1.044	1.015	1.048	1.105	1.139	1.111	1.121						1.052	0.050	14	0.649	0.357
11	EIMV	Andersen	1.138	1.167	1.097			1.236			1.182	1.288			1.308	1.283						1.212	0.078	8	1.804	0.559
12	UBA AT	Digitel			0.950	0.952	0.989	0.955	0.958	0.944	0.945	0.966	0.931	0.956	0.961	0.995						0.959	0.018	12	-0.026	0.131
13	LROOe	Digitel			0.960	0.945	0.952	0.920	0.931	0.951	0.953	0.966	0.947	0.944	0.927	0.947						0.945	0.013	12	-0.123	0.096
14	UBA AT	Teom FDMS			0.964	0.971	0.970	0.976	0.981	0.974	0.941	0.961	0.922	1.016	0.935	0.932						0.962	0.026	12	-0.001	0.186
15	LROOe	Teom FDMS			0.962	0.956	0.953	0.937	0.904	0.895	0.899	0.914	0.917	0.940	0.792	0.783						0.904	0.059	12	-0.417	0.424
16	LR Stmk.	Digitel			0.897	0.871	0.837	0.767	0.865	0.877	0.854	0.856	0.841	0.850	0.831	0.877						0.852	0.033	12	-0.794	0.235
17	LR Stmk.	FH 62 IR			1.022	0.992	0.859	0.879	1.013	1.054	0.981	0.927	0.890	0.927	0.886	0.926						0.946	0.064	12	-0.114	0.461
18	CHMI	FH95KF (nitrocell)	1.265	1.027	1.019	1.018	0.911	0.927	0.929	0.911	0.863	0.949	0.938	0.925	0.899	0.945						0.966	0.098	14	0.029	0.708
19	CHMI	FH95KF (glass)	0.642	0.874	0.860	0.720	0.838	0.810	0.797	0.852	0.847	0.950	0.911	0.756	0.828	0.839						0.823	0.078	14	-1.002	0.560
20	CHMI	Derenda SEQ Low Vol	0.831	0.911	0.880	0.878	0.852	0.875	0.911	0.904	0.904	0.969	0.909	0.861	0.808	0.879						0.884	0.040	14	-0.565	0.286
21	CHMI	Derenda SEQ Hi Vol B	0.970	1.026	1.019	1.633	0.995	1.141	0.906	0.815	1.026	0.971	0.986	1.284	1.019	1.066						1.061	0.196	14	0.715	1.411
22	CHMI	Derenda SEQ Hi Vol A	0.970	0.952	0.892	1.255	0.912	0.998	0.906	0.889	0.897	0.945	0.986	1.283	0.959	1.066						0.993	0.127	14	0.226	0.911
23	CHMI	MCZ/Andersen Hi Vol	0.716	1.103	1.028	1.238	1.114	1.133	1.011	0.963	0.932	0.852	0.878	1.396	0.987	1.021						1.027	0.169	14	0.464	1.215
24	CHMI	FH62IR	0.787	0.964	0.926	0.934	0.900	0.955	0.825	0.882	0.858	0.926	0.837	0.851	0.933	0.875						0.889	0.053	14	-0.524	0.381
25	LANUV	Digitel_4	0.936	0.939	0.997	0.999	1.033	0.950	1.013	1.017	0.920	0.947	0.988	0.946	0.999							0.976	0.037	13	0.099	0.266
26	LANUV	Digitel_37	0.913	0.918	0.997	0.984	1.021	0.893	0.987	1.009	0.851	1.046	0.992	0.953	0.940							0.962	0.056	13	-0.002	0.405
27	HLUG	SEQ Leckel	0.986	0.993	1.017	1.004	1.020	1.027	1.045	1.039	0.998	0.993	1.075	1.058	0.946							1.015	0.034	13	0.384	0.247
28	HLUG	FH62 I-R Sharp	0.993	0.962	1.163	1.009	1.178	0.834	0.970	1.054	0.870	0.678	0.973	0.947	0.836							0.959	0.135	13	-0.022	0.975
29	HLUG	FH62 I-R	0.771	0.659	0.850	0.809	0.917	0.740	0.874	0.939	0.817	0.880	0.781	0.854	0.804							0.823	0.076	13	-1.006	0.544
30	NERI	SM200	0.899	0.836	0.593	0.812	0.858	0.852	0.905	1.097	0.748		0.865									0.846	0.127	10	-0.834	0.912
31	NERI	Teom	0.711	0.732	0.768	0.807	0.728	0.759	0.744	0.642	0.635	0.708	0.661									0.718	0.054	11	-1.762	0.388
32	ITM	SEQ Leckel			1.072	1.045	1.122	1.081		1.093	1.123	1.044	0.982	0.980	0.978	0.948	0.950					1.035	0.065	12	0.524	0.467
33	IVL	IVL 10 A													1.474	1.634	1.221					1.443	0.208	3	3.467	1.498
34	IVL	IVL10 B													1.336	1.407	1.238					1.327	0.085	3	2.630	0.613
35	EHAS	Teom	1.013	1.220	1.114	1.081	1.170	1.195		1.186	1.357	0.940	0.826	1.138	1.079	1.006	0.860					1.085	0.146	14	0.883	1.047
36	EHAS	FDMS					1.290	1.320		1.237	1.499	1.188	1.074	1.326	1.159	1.169	1.150					1.241	0.122	10	2.012	0.876
37	FMI	FH-62 IR 632	1.054	1.163	1.193	1.379	0.899	0.995	0.857	0.790	0.983	1.305	0.952	0.976	0.892	0.926						1.026	0.173	14	0.460	1.244
38	FMI	FH-62 IR 280	1.084	1.180	1.134	1.353	0.974	1.124	0.850	0.838	1.018	1.221	1.006	0.997	0.921	0.930						1.045	0.146	14	0.597	1.054
39	EERC	Digitel Container	0.753	0.651		0.775	0.689	0.790		0.804	0.847	0.981	0.922	1.098	0.854	0.924						0.841	0.126	12	-0.875	0.906
40	EERC	Digitel Mob.Lab.	0.615	0.557		0.687	0.632	0.782		0.815	0.811	0.911	0.869	1.006	0.790	0.793						0.772	0.130	12	-1.368	0.933

#	Org	Instrument	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	Mean	SD	n		
41	EERC	Thermo FH 62 I-R Container	1.311	1.140		0.985	0.821	0.781		0.897	0.955	1.158	1.076	0.900	1.074	0.929						1.002	0.154	12	0.290	1.108
42	EERC	Thermo FH 62 I-R Mob.Lab.	1.263	1.689		1.141	0.890	1.084		1.198	1.212	1.560	1.437	1.167	1.445	1.277						1.280	0.220	12	2.294	1.581
43	RIVM	Seq Leckel	0.920	0.959	0.978	0.987	0.998	0.981	0.990	0.995	0.981	0.988	0.949	0.966	0.982	1.018						0.978	0.024	14	0.113	0.172
44	VMM	Seq Leckel	1.083	1.069		1.029	1.042	1.038	1.052	1.072	1.062	1.056	1.080	1.027	1.054	1.066						1.056	0.018	13	0.677	0.131
45	RIVM	FH 62	1.148	1.067	1.094	1.076	1.098	1.117	1.181	1.192	1.167	1.091	1.134	1.105	1.118	1.157						1.125	0.039	14	1.173	0.283
46	GGD	Seq Derenda Low Vol	0.754	0.876	0.859																	0.830	0.066	3	-0.955	0.475
47	VMM	Seq Leckel	1.146	1.102	1.081	1.086	1.107	1.081	1.064	1.075	0.991	1.028	1.094	1.178	1.189	1.097						1.094	0.052	14	0.953	0.376
48	Issep	Sw126 gravimetry	0.856	0.880	0.899	0.901	0.879	0.867	0.909	0.935	0.764	0.833	0.861	0.833	0.878	0.876						0.869	0.041	14	-0.669	0.296
49	Issep	Sw129 gravimetry	0.835	0.874	0.901	0.886	0.884	0.872	0.879	0.937	0.765	0.827		1.007	0.876	0.890						0.879	0.057	13	-0.596	0.407
50	RIVM	Seq Leckel	1.023	1.033	1.047	1.054	1.050	1.026	1.018	1.000	0.922	0.965	1.071	1.117	1.109	1.043						1.034	0.051	14	0.521	0.366
51	VMM	ESM BOR801	0.951	0.960	1.003	0.909	0.925	1.036	1.027	1.226	1.496	1.051	1.233	1.225	1.067	1.039						1.082	0.161	14	0.864	1.156
52	VMM	Teom	1.092	0.987	0.868	0.936	0.991	1.214	1.047	0.735	1.205	1.163	1.233	1.342	1.280	1.087						1.084	0.170	14	0.881	1.221
53	VMM	Teom FDMS	0.951	0.800				0.740	0.810	0.878	0.706	0.713	0.836	0.817	0.811	0.870						0.812	0.074	11	-1.082	0.529
54	Issep	Sw126 Beta	0.839	0.803	0.881	0.858	0.820	0.784	0.883	0.889	0.789	0.751	0.836	0.846	0.836	0.855						0.834	0.041	14	-0.927	0.292
55	Issep	Sw129 Beta	0.796	0.832	0.908	0.885	0.869	0.829	0.881	0.911	0.731	0.769		0.747	0.781	0.831						0.829	0.060	13	-0.963	0.434
56	Issep	MP101 33	0.913	0.778	0.879	0.751	0.714	0.831	0.789	0.860	0.808	0.892	0.903	0.945	0.876	0.835						0.841	0.067	14	-0.874	0.479
57	Issep	MP101 78		0.692	0.761	0.693	0.642	0.831	0.768	0.794	0.763	0.770	0.713	0.882	0.876	0.757						0.765	0.070	13	-1.423	0.507
58	Issep	Grimm 180	0.843	0.950	0.986	0.841	0.919	0.790	0.871	0.955	0.849	0.851	0.900	0.903	0.953	0.924						0.895	0.056	14	-0.481	0.405
59	GGD	Seq Derenda Low Vol						0.971	0.963	0.985	0.848	0.918	0.994	1.053	0.954	1.045						0.970	0.062	9	0.057	0.449
60	INERIS	Partisol +	1.055	0.928	0.877	0.872	0.937	0.982	0.945	0.875	0.894	0.819	0.910	0.853	0.916	0.926						0.914	0.058	14	-0.350	0.420
61	EMD	MP101-RST	0.899	0.903	1.002	0.995	0.960	0.909	1.045	0.761	0.961	1.010	0.959	0.890	0.776	1.002						0.934	0.084	14	-0.204	0.608
62	INERIS	Teom FDMS (9032)	0.899	0.908	0.992	0.862	0.866	0.889	0.873	0.942	0.903	0.934	0.929	0.899	0.899	0.984						0.913	0.040	14	-0.356	0.287
63	INERIS	Teom FDMS (15702)	0.948	0.948	1.069	0.966	0.908	0.970	0.970	1.073	0.974	1.006	1.010	0.953	0.913	1.047						0.982	0.052	14	0.146	0.376
64	AIRPARIF	Teom FDMS	0.860	0.880	0.968	0.874	0.882	0.918	0.877	1.006	0.943	0.957	0.964	0.907	0.910	0.991						0.924	0.047	14	-0.271	0.341
65	EPA	Teom FDMS	1.061	1.060	1.181	1.049	0.978	1.038	1.041	1.033	1.009	1.000	1.029	1.084	0.970	0.898	0.890	0.917	0.841			1.005	0.083	17	0.306	0.598
66	DCC	Partisol 2025								0.861	2.301					0.051	0.670	0.734	0.621			0.873	0.753	6	-0.643	5.420
67	AEA	Partisol Emfab						0.811	0.937	0.971	0.941	0.995	0.848	0.988	0.903	0.943						0.926	0.062	9	-0.258	0.448
68	BV	Partisol quartz						0.937	1.122	1.207	1.103	0.932	1.075	1.163	1.329	1.050						1.102	0.126	9	1.009	0.904
69	BV	Partisol Emfab						0.766	0.826	0.977	0.985	0.979	0.924	1.028	0.941	0.939						0.929	0.083	9	-0.236	0.597
70	NPT	Teom FDMS	1.023	1.060	1.054	1.073	1.113	1.188								1.256						1.110	0.084	7	1.064	0.602
71	ISPRA	Tecora	0.946	0.976					0.979	0.925	0.928	0.926	0.995	0.929	0.906	0.853	0.809	0.882	0.867	0.909	0.925	0.917	0.050	15	-0.326	0.357
72	ARPA	Zambelli	1.193	1.059					0.910	0.897	0.811	0.887	0.884	0.996	1.008	0.951	1.444	1.037	0.964	0.906	1.016	0.998	0.154	15	0.255	1.109
73	ARPA	Tecora	0.931	0.915					0.927	0.853	0.845	0.917	0.964	1.023	1.112	0.979	0.905	1.019	0.870	0.947	0.888	0.940	0.072	15	-0.162	0.515
74	ARPA	SM 200	1.016	0.902					0.671	1.052	0.945	0.889	0.947	0.979	1.086	0.995	1.011	0.962	0.975	0.965	1.055	0.963	0.098	15	0.009	0.702
75	ARPA	Teom FDMS	1.027	0.896						0.797	0.771	0.746	0.833	0.767	0.657	0.757	0.871	0.804	0.805	0.721	0.789	0.803	0.088	14	-1.148	0.632
76	HMS	Digitel DHA 80	0.984	0.889	0.906	0.949	0.918	0.923	0.931	0.908	0.922	0.919	0.919	0.907	0.858	0.942						0.920	0.029	14	-0.306	0.208
77	HMS	FH 62 IR	1.056	0.808	0.789	0.950	0.895	0.896	0.949	0.830	0.881	0.772	0.799	0.850	0.801	0.862						0.867	0.079	14	-0.686	0.565
78	MDV	FH 62 IR	1.037		0.870	0.910	0.934	0.890	0.877	0.859	0.918	0.868	0.893	0.882	0.858	0.944						0.903	0.049	13	-0.425	0.350
79	SMHU	Teom FDMS	0.759	0.538	0.736	0.861	0.748	0.780	0.679	0.622	0.665	0.787	0.818	0.901	0.458	0.558						0.708	0.128	14	-1.833	0.921

PM2.5 codification and Mandel's *h* and *k* statistics

			Measurement day																					Mandell	
Codification	Laboratory	Instrument	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	mean	s	n	h	k
1	ISCIII	Derenda MVS 6.1 (LVS)	0.942	0.954	0.902	0.946	0.873	0.796	0.782	0.851	0.884	0.950	0.825	0.844								0.879	0.061	12	-0.137	0.294
2	IdA	Tecora	1.058	0.980		0.819	0.897	0.871	0.733	0.924	0.866	0.855	1.049	0.916	1.097	0.909						0.921	0.103	13	-0.018	0.495
3	EPA SI	SEQ Leckel	1.071	0.954	0.956	1.051	1.023	0.942	1.055	0.975	0.995	0.913	1.054	1.048	1.108	1.124						1.019	0.064	14	0.261	0.311
4	UBA AT	Digitel			0.920	0.941	0.944															0.935	0.013	3	0.022	0.063
5	LROOe	Digitel			0.881	0.900	0.908	0.891	0.913	0.907	0.904	0.900	0.914	0.886	0.899	0.921						0.902	0.012	12	-0.072	0.057
6	CHMI	Seq Leckel LVS	0.834	0.783	0.709	0.480		0.736	0.724	0.741	0.690	0.768	0.795	0.628	0.674	0.695						0.712	0.089	13	-0.611	0.428
7	CHMI	Seq Derenda LVS	0.822	0.914	0.968	1.027	0.906	0.926	0.907	0.945	0.910	0.980	0.997	0.954	0.890	0.871						0.930	0.053	14	0.007	0.258
8	CHMI	FH62IR	0.901	0.853	0.741	0.893	0.901	0.906	0.656	0.756	0.788	0.907	0.702	0.826	0.860	0.747						0.817	0.085	14	-0.314	0.409
9	NERI	Teom	0.539	0.467	0.705	0.773	0.645	0.709	0.717	0.704	0.606	0.683	0.605									0.650	0.089	11	-0.786	0.431
10	IVL	IVL 2.5 A	2.985	3.249	2.220						2.801	2.159	0.565	1.857	2.817	0.848						2.167	0.940	9	3.518	4.537
11	IVL	IVL 2.5 B	2.452	2.022	2.021																	2.165	0.248	3	3.513	1.199
12	EHAS	Teom	0.389	0.293	0.367	0.389	0.293	0.213	0.299	0.727	0.333	0.391	0.582	0.657	0.513	0.562						0.429	0.154	14	-1.414	0.742
13	EERC	Thermo FH 62 I-R Container	0.947	0.657		0.643	0.540	0.553	0.619	0.763	0.785	0.897	1.087	1.287	0.776	0.718						0.790	0.217	13	-0.389	1.047
14	GGD	Seq Derenda Low Vol		0.887						0.940	0.828	0.948	0.948	0.923	0.936	0.935						0.918	0.041	8	-0.026	0.199
15	VMM	Seq Leckel (Whatman)		1.172	1.093	1.113	1.119	1.043	1.095	1.113	0.997	1.028	0.962	0.983	1.016	1.132						1.067	0.065	13	0.396	0.316
16	VMM	Seq Leckel (Pall)	0.998	1.088	1.009	1.002	1.005	0.999	1.015	1.019	0.891	0.927	0.881	0.919	0.959	1.050						0.983	0.060	14	0.158	0.289
17	Issep	Sw126 Grav.	0.829	0.889	0.875	0.800	0.844	0.770	0.877	0.861	0.689	0.763	0.684	0.874	0.698	0.893						0.810	0.077	14	-0.332	0.371
18	Issep	Sw.129 Grav.	0.857	0.923	0.915	0.878	0.892	0.741	0.877	0.926	0.823	0.803		0.732	0.767	0.962						0.854	0.074	13	-0.209	0.359
19	Issep	Sw126 Beta	0.846	0.872	0.890	0.812	0.799	0.759	0.871	0.898	0.815	0.855	0.666	0.707	0.722	0.920						0.817	0.078	14	-0.314	0.374
20	Issep	Sw.129 Beta	0.812	0.943	0.938	0.892	0.877	0.849	0.903	0.921	0.795	0.840		0.669	0.688	0.885						0.847	0.087	13	-0.228	0.421
21	Issep	Grimm 180	1.167	1.301	1.072	0.988	1.028	1.001	1.005	1.122	1.220	1.221	0.989	0.961	0.968	1.159						1.086	0.112	14	0.450	0.538
22	VMM	ESM BXR801	0.763	1.001	1.032	1.005	0.731	0.722	0.982	1.311	1.193	1.099	1.124	0.872	1.020	1.023						0.991	0.172	14	0.181	0.828
23	GGD	Seq Derenda Low Vol	0.862	0.925	0.848	0.273	0.885		0.833		0.963		0.892		0.801	1.035						0.832	0.207	10	-0.272	1.001
24	Airparif	Teom FDMS	0.960	0.993	1.151	1.046	0.969	1.035	1.002	1.174	1.146	0.951	1.086	1.006	1.020	1.134						1.048	0.077	14	0.346	0.369
25	BV	Partisol Emfab						1.356	0.987	1.259	0.850	0.811	1.127	0.924	0.959	0.902						1.019	0.188	9	0.261	0.906
26	NPT	Partisol	1.079	1.153	1.081	1.156	1.017	1.085	1.415	1.057	1.224	1.011	1.149	1.279	0.831	1.199						1.124	0.138	14	0.558	0.665
27	BV	Teom FDMS	0.702	0.907	0.904	1.090	0.882	0.717	0.818	0.806	0.812	0.911	1.011	0.974	1.339	1.464						0.952	0.219	14	0.071	1.057
28	ARPA	Zambelli	0.802	0.764													0.811	0.774	0.738	0.818	1.263	0.853	0.183	7	-0.211	0.884
29	ARPA	SM200	0.740	0.860													0.883	0.803	0.791	0.783	0.750	0.801	0.053	7	-0.357	0.256
30	MDV	DHA 80	0.975	0.868	0.853	0.870	0.956	0.953	0.902	0.938	0.997	1.004	0.817	0.927	0.893	0.879						0.916	0.057	14	-0.031	0.274
31	MDV	FH 62 IR	0.806	0.636	0.658	0.781	0.739	0.768	0.745	0.652	0.625	0.623	0.677	0.749	0.659	0.737						0.704	0.063	14	-0.634	0.304

ANNEX 5: En – numbers for participants with reported uncertainty

En – numbers for PM10

En - number between JRC sampler A / participant and JRC sampler B / participant

ES

Country	Measurement day	ISCIII Derenda A		ISCIII Derenda B	
		A	B	A	B
ES	1	0.99	0.81		
	2	1.12	0.62	1.47	0.97
	3	1.30	0.70	0.74	0.12
	4	1.10	0.94	1.10	0.94
	5	0.92	0.72	1.21	1.02
	6	1.21	0.76	1.21	0.76
	7	1.52	1.51	1.52	1.51
	8	1.44	0.87	1.76	1.19
	9	1.22	0.94		
	10	1.53	1.47		
	11	1.25	0.95		
	12	1.58	1.37		
	13	1.75	1.55		
	14	1.85	1.15		

SI

Country	Measurement day	EIMV Tecora	
		A	B
SI	1	1.67	1.75
	2	1.59	1.69
	3	1.49	1.53
	4	0.96	1.19
	5	1.43	1.43
	6	1.77	1.74
	7	1.41	1.37
	8	1.52	1.61
	9	1.56	1.51
	10	1.59	1.63
	11	2.03	2.04
	12	2.33	2.28
	13	2.33	2.17

AT

Country	Measurement day	LR OOe. Digitel	
		A	B
AT	1		
	2		
	3	0.76	0.30
	4	0.88	0.60
	5	0.86	0.48
	6	1.23	0.96
	7	0.95	0.79
	8	0.81	0.36
	9	0.87	0.30
	10	0.63	0.26
	11	0.82	0.67
	12	0.87	0.59
	13	0.96	0.68
	14	0.62	0.46

DE

Country	Measurement day	Lanuv Digitel 4		Lanuv Digitel 37		HLUG Leckel Seq		HLUG FH62IR		HLUG Sharp	
		A	B	A	B	A	B	A	B	A	B
DE	1					0.14	0.10	0.66	0.65	0.05	0.03
	2					0.02	0.08	1.09	1.11	0.17	0.20
	3	0.06	0.01	0.06	0.01	0.13	0.20	0.41	0.39	0.73	0.77
	4	0.02	0.01	0.11	0.08	0.01	0.06	0.53	0.52	0.03	0.06
	5	0.19	0.35	0.10	0.26	0.10	0.30	0.23	0.18	0.76	0.85
	6	0.36	0.29	0.72	0.65	0.20	0.30	0.80	0.77	1.04	0.97
	7	0.01	0.22	0.22	0.01	0.30	0.57	0.36	0.29	0.24	0.08
	8	0.14	0.14	0.07	0.07	0.38	0.38	0.15	0.15	0.27	0.27
	9					0.12	0.16	0.46	0.54	0.66	0.83
	10					0.04	0.13	0.26	0.33	1.78	1.87
	11					0.79	0.06	0.41	0.75	0.16	0.38
	12					0.41	0.45	0.38	0.36	0.28	0.24
	13					0.09	0.71	0.42	0.64	0.66	1.10

NL

	RIVM Leckel Seq		RIVM FH62IR		GGD Derenda Seq	
	A	B	A	B	A	B
1	1.01	0.58	0.60	0.82	2.96	2.49
2	0.52	0.46	0.35	0.37	1.76	1.69
3	0.30	0.23	0.48	0.51	2.01	1.92
4	0.14	0.18	0.41	0.40		
5	0.02	0.02	0.51	0.51		
6	0.29	0.16	0.58	0.63		
7	0.19	0.04	0.85	0.92		
8	0.22	0.10	0.87	1.00		
9	0.40	0.07	0.76	0.89		
10	0.39	0.12	0.35	0.59		
11	0.73	0.44	0.61	0.74		
12	0.38	0.45	0.56	0.53		
13	0.43	0.05	0.54	0.69		
14	0.17	0.29	0.77	0.82		

BE

	VMM ESM Andersen		VMM Teom		VMM FDMS		Issep Sw 126 beta		Issep Sw 129 beta		Issep Env.33		Issep Env.78		RIVM Leckel Seq		GGD Derenda Seq	
	A	B	A	B	A	B	A	B	A	B	A	B	A	B	A	B	A	B
1	0.19	0.24	0.32	0.28	0.24	0.29	1.81	1.86	2.32	2.36	0.61	0.68			0.28	0.17		
2	0.16	0.19	0.03	0.06	1.26	1.30	2.55	2.58	2.15	2.18	1.91	1.95	2.88	2.91	0.41	0.33		
3	0.12	0.09	0.44	0.63			1.23	1.76	0.87	1.42	0.79	1.15	1.91	2.29	0.78	0.26		
4	0.32	0.54	0.15	0.33			1.53	2.08	1.17	1.73	2.02	2.41	2.68	3.07	0.86	0.32		
5	0.29	0.40	0.01	0.07			2.02	2.23	1.41	1.64	2.42	2.59	3.24	3.39	0.65	0.38		
6	0.17	0.13	0.64	0.62	1.74	1.78	2.69	2.72	2.10	2.14	1.36	1.40	1.36	1.40	0.32	0.24	0.31	0.39
7	0.14	0.09	0.18	0.14	1.20	1.27	1.57	1.70	1.60	1.73	1.85	1.94	2.08	2.17	0.29	0.15	0.44	0.59
8	0.84	0.79	1.23	1.29	0.69	0.78	1.45	1.62	1.13	1.30	1.12	1.23	1.78	1.89	0.09	0.08	0.11	0.30
9	1.37	1.53	0.52	0.68	2.12	1.74	2.52	1.90	3.17	2.53	1.69	1.25	2.10	1.64	1.02	0.48	1.90	1.29
10	0.05	0.37	0.38	0.62	2.19	1.65	3.26	2.34	3.03	2.12	1.10	0.51	2.19	1.54	0.74	0.05	1.35	0.47
11	0.71	0.91	0.58	0.74	1.11	0.78	1.95	1.34			0.89	0.48	2.53	2.04	0.38	0.88	0.34	0.22
12	0.64	0.89	0.79	0.98	1.21	0.79	1.60	0.95	2.46	1.78	0.57	0.11	1.00	0.51	0.61	1.15	0.13	0.71
13	0.14	0.39	0.69	0.86	1.31	0.94	2.00	1.34	2.60	1.92	1.13	0.67	1.13	0.67	0.71	1.24	0.78	0.15
14	0.12	0.20	0.25	0.32	0.85	0.73	2.07	1.78	2.41	2.11	1.48	1.30	2.29	2.10	0.37	0.59	0.45	0.70

IT

	Ispra Tecora	
	A	B
1	1.01	1.08
2	0.61	0.36
3		
4		
5		
6		
7		
8		
9	1.56	1.25
10	1.56	1.34
11	0.11	0.08
12		
13		
14		
15	3.65	3.71

En – numbers for PM2.5

Country	Measurement day	En - number between JRC / participant
AT		LR OOe. Digitel
	1	
	2	
	3	1.44
	4	1.28
	5	1.24
	6	1.40
	7	1.03
	8	0.94
	9	1.04
	10	1.22
	11	1.15
	12	1.37
	13	0.93
	14	0.68
NL		GGD Derenda Seq
	1	
	2	1.05
	3	
	4	
	5	
	6	
	7	
	8	0.68
	9	2.00
	10	0.47
	11	0.45
	12	0.80
	13	0.90
	14	0.91
BE		GGD Derenda Seq
	1	0.90
	2	0.72
	3	1.72
	4	7.65
	5	0.99
	6	
	7	1.91
	8	
	9	0.18
	10	
	11	0.62
	12	
	13	1.09
	14	0.31

ANNEX 6: Uncertainty at the LV for PM10 and "target value" for PM2.5 for data-sets with n>10 and a minimum of 20% of data greater upper assessment threshold of annual limit value (exceedances in red).

PM10:

country	codification	laboratory	instrument	relative uncertainty at the LV %	n
ES	1	ISCIII	Derenda A	11.85	13
	3	AdM	Teom 1400	27.11	13
PT	4		Tecora	250.48	13
	5	IdA	Andersen	9.66	13
	6		Env. 101	19.44	14
SI	8	EPA SI	Teom 1400	6.88	14
	9	EIMV	Tecora	22.98	13
	10	Anhovo	Tecora	5.76	14
AT	12	UBA	Digitel	4.32	12
	14		FDMS	4.30	12
	13	LR OOe	Digitel	5.47	12
	15		FDMS	9.13	12
	16	LR Stmk.	Digitel	15.28	12
	17		FH 62 IR	8.40	12
CZ	18	CHMI	FH95 Nitrocell.	7.44	14
	19		FH95 glass	6.80	14
	20		Derenda LVS Seq	5.50	14
	21		Derenda Hvol B	5.10	14
	22		Derenda Hvol A	7.33	14
	23		MCZ/Andersen	12.61	14
	24		FH 62 IR	9.13	14
DE	25	Lanuv	Digitel 4	1.57	13
	26		Digitel 37	2.74	13
	27	HLUG	Leckel Seq	2.83	13
	28		Sharp	11.51	13
	29		FH62 IR	11.83	13
DK	31	Neri	Teom 1400	27.63	11
SE	32	ITM	Leckel Seq	6.66	12
	35	EHAS	Teom 1400	14.69	14
NL	43	RIVM	Leckel Seq	0.64	14
	45		FH62 IR	14.17	14
NL/BE	44	VMM	Leckel Seq	5.77	13
BE	47	VMM	Leckel Seq	7.96	14
	51		ESM BOR801	12.06	14
	52		Teom 1400	10.56	14
	53		FDMS	15.99	11
	48	Issep	SW126 gravimetr.	8.66	14
	49		SW129 gravimetr.	10.34	13
	54		SW126 beta	12.96	14
	55		SW129 beta	10.73	13
	56		Env.101_33	19.01	14
	57		Env.101_78	24.48	13
	58		Grimm 180	9.02	14
BE/NL	50	RIVM	Leckel Seq	2.96	14
IT	71	Ispra	Tecora	6.41	15
	72	Arpa	Zambelli	14.07	15
	73		Tecora	8.68	15
	74		SM200	7.62	15
	75		FDMS	15.61	14
HU	76	HMS	Digitel	8.52	14
	77		FH62 IR	14.32	14
	78	MDV	FH62 IR	10.66	13
SK	79	SHMU	FDMS	13.36	14

PM2.5:

country	codification	laboratory	instrument	relative uncertainty at the target value	n
				%	
ES	1	ISCIII	Derenda	13.88	12
PT	2	IdA	Tecora	14.05	14
SI	3	EPA	Leckel Seq	4.61	14
AT	5	LR OOe	Digitel	10.05	12
CZ	6	CHMI	Leckel SEQ	25.32	14
	7		Derenda	4.41	14
	8		FH 62 IR	16.95	14
DK	9	Neri	Teom 1400	37.32	11
SE	12	EHAS	Teom 1400	64.56	14
BE	22	VMM	ESM	15.72	14
	15		Leckel SEQ Whatman	10.37	13
	16		Leckel SEQ Pall	1.61	14
	17	Issep	SW126 gravimetr.	14.67	14
	18		SW129 gravimetr.	10.40	13
	19		SW126 beta	13.68	14
	20		SW129 beta	9.97	13
	21		Grimm 180	12.28	14
HU	30	MDV	Digitel	12.08	14
	31		FH62 IR	34.58	14

ANNEX 7: Speciation of PM10 filters

Analysis of the chemical composition was carried out on selected PM10 filters with the aim of investigating the coherence of the PM chemical composition compared with sites distinctive features and to explain differences between sites. Concentrations of major ions (Chloride, Nitrate, Sulphate, Sodium, Ammonium, Potassium, Magnesium and Calcium) were measured by ion chromatography while elements (Magnesium, Aluminium, Potassium, Calcium, Titanium, Vanadium, Chromium, Manganese, Iron, Zinc, Arsenic, Cadmium, Antimony, Lead, Nickel and Copper) were determined by ICP-MS. Where available, organic and elemental carbon, measured with on-line thermal-optical transmittance method with RT-quartz protocol (Sunset inc.), were also considered.

Among ions the content of nitrate and sulphate is the most relevant variable to explain the differences between sites. Samples from Budapest differ from all the others due to their high content in either ammonium nitrate or ammonium sulphate. In certain cases like Ljubljana sulphate is always more relevant than nitrate (maybe linked to a local source of SO_2), in other cases like Bratislava nitrate seems to be more relevant (figure A7.1).
Certain measurement sites like Borgerhout and Port Talbot show different patterns on different days, depending on the wind direction and wind speed (figure A7.2). Samples from Lisbon and partly Port Talbot (May 1st, 2008) present appreciable concentrations of sodium chloride which has been interpreted as contribution of sea salt. In the latter case this has a major influence on the ratio PM2.5/PM10: 0.32 with wind coming from the sea (prevailing wind-direction WSW on May 1st, 2008) or 0.70 with wind coming from inland (prevailing wind-direction E on May 3rd, 2008). On certain days (e.g. April 28th, 2008) the influence of the steel plant close to the measurement site in Port Talbot is evident due to the higher content of iron in the samples (figure A7.3).
Ion concentrations in samples from Stockholm (traffic site) are dominated by sodium chloride and have low concentrations of both nitrate and sulphate. This is considered to reflect the influence of re-suspension of road salting connected to the use of studded tires. In Copenhagen however, apart from sodium chloride also nitrate and sulphate are relevant. Madrid, a measurement site with an evident influence of traffic source, shows a significant amount of Calcium (a component of earth crustal material) and EC (figure A7.4).

Examples of these analyses are presented in the following figures:

Figure A7.1 Chemical composition in selected samples of PM10 from Budapest, Ljubljana and Bratislava

Bratislava, March 22nd, 2009

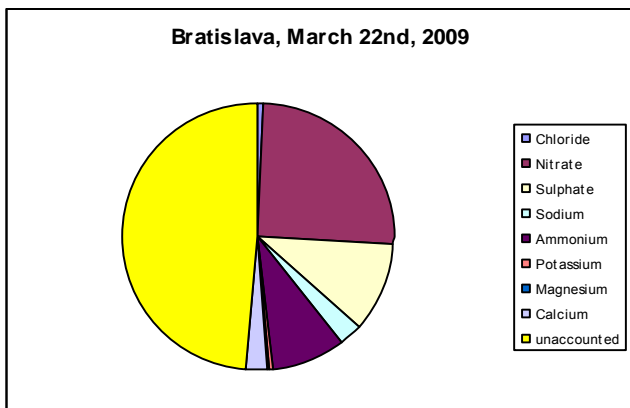**Legend:** Chloride, Nitrate, Sulphate, Sodium, Ammonium, Potassium, Magnesium, Calcium, unaccounted
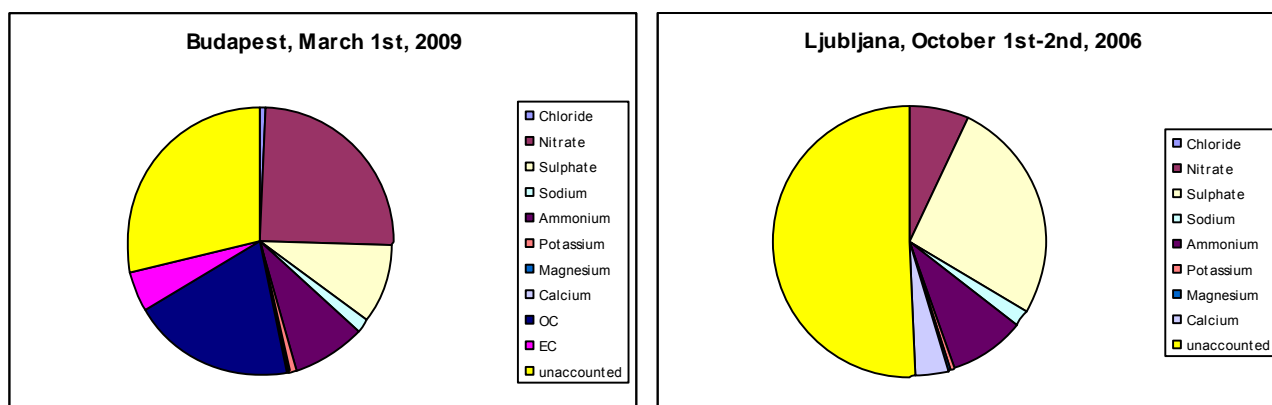
Figure A7.2 Chemical composition in selected samples of PM10 from Borgerhout, Port Talbot and Lisbon.

Borgerhout, February 29th, 2008

Legend: Chloride, Nitrate, Sulphate, Sodium, Ammonium, Potassium, Magnesium, Calcium, OC, EC, unaccounted

Borgerhout, March 1st, 2008

Legend: Chloride, Nitrate, Sulphate, Sodium, Ammonium, Potassium, Magnesium, Calcium, OC, EC, unaccounted

Ion chromatography
Port Talbot, May 1st, 2008

Legend: Chloride, Nitrate, Sulphate, Sodium, Ammonium, Potassium, Magnesium, Calcium, unaccounted

Ion chromatography
Port Talbot, May 3rd, 2008

Legend: Chloride, Nitrate, Sulphate, Sodium, Ammonium, Potassium, Magnesium, Calcium, unaccounted

Lisbon campaign average

Legend: Chloride, Nitrate, Sulphate, Sodium, Ammonium, Potassium, Magnesium, Calcium, OC, EC, unaccounted
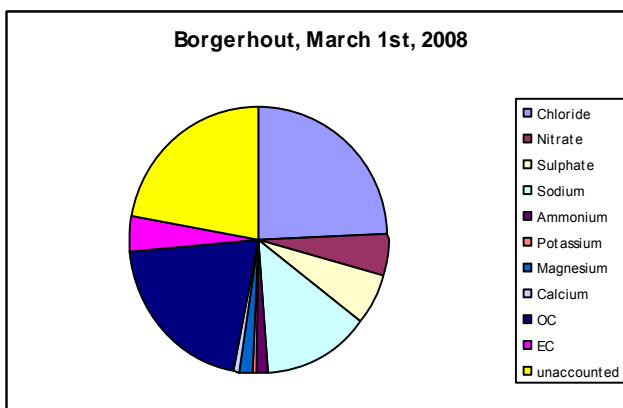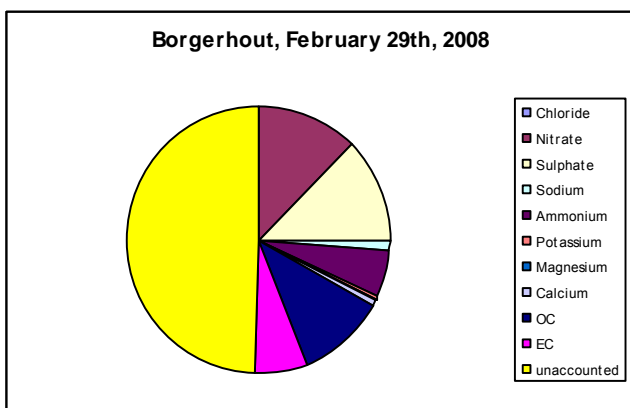
Figure A7.3 Day to day variability in the chemical composition in PM10 from Port Talbot
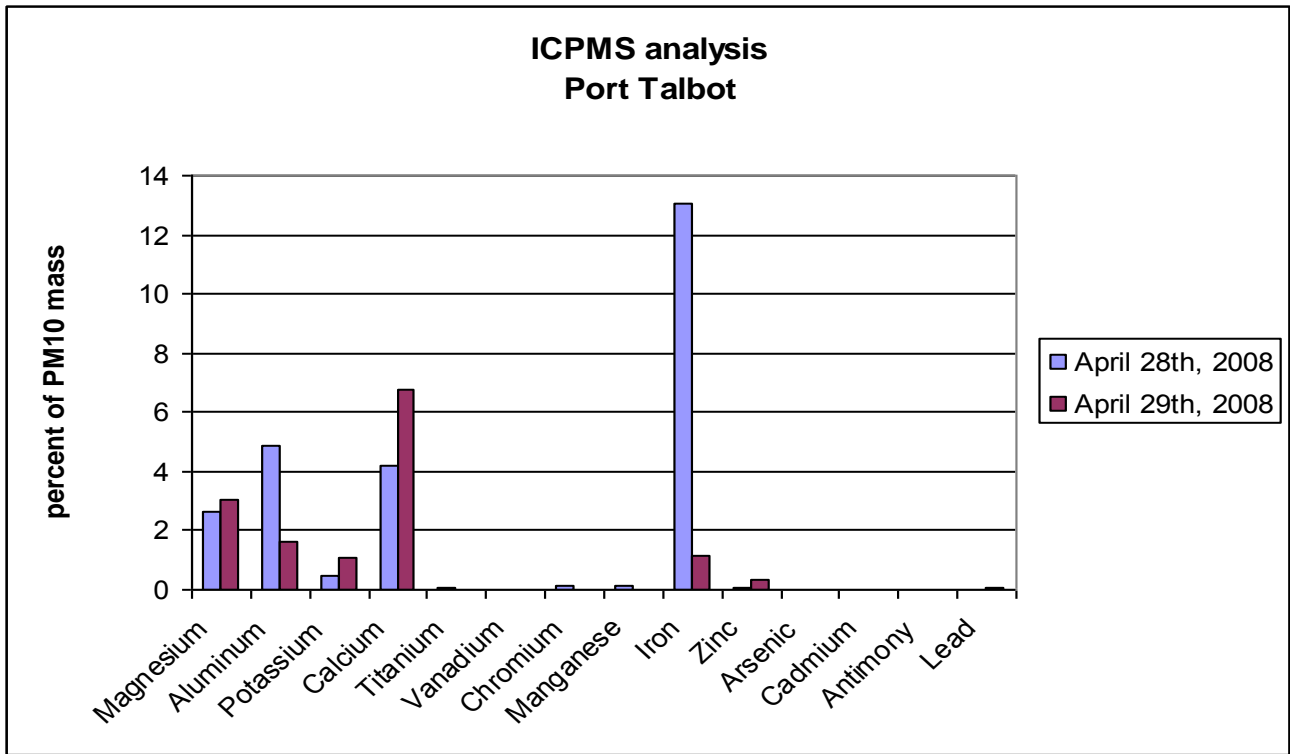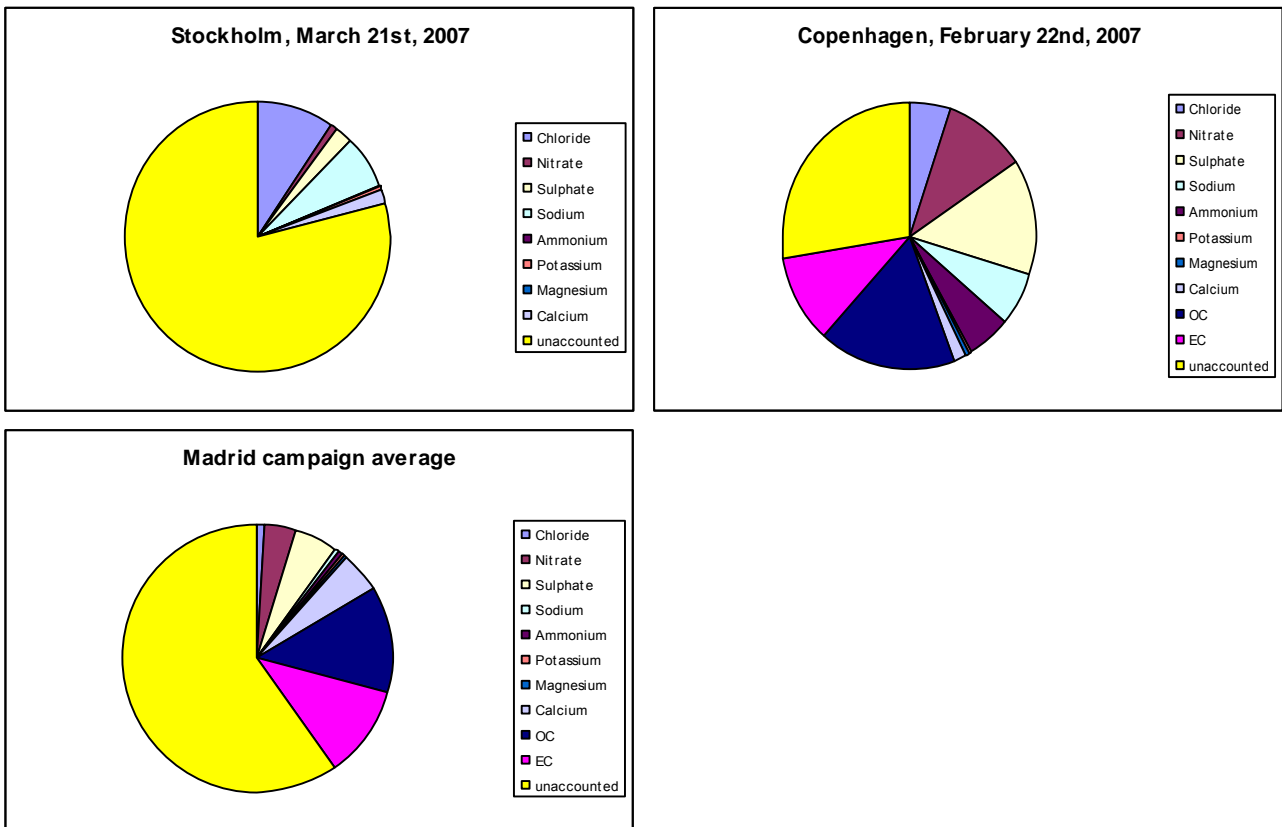

Figure A7.4 Chemical composition in selected samples of PM10 from Stockholm, Copenhagen and Madrid

ANNEX 8: Parametric, non-parametric tests and ANOVA for PM10 (significant p-values in red)

Differences between NRL and LOCAL NETWORKS (only for campaigns with both type of laboratories)
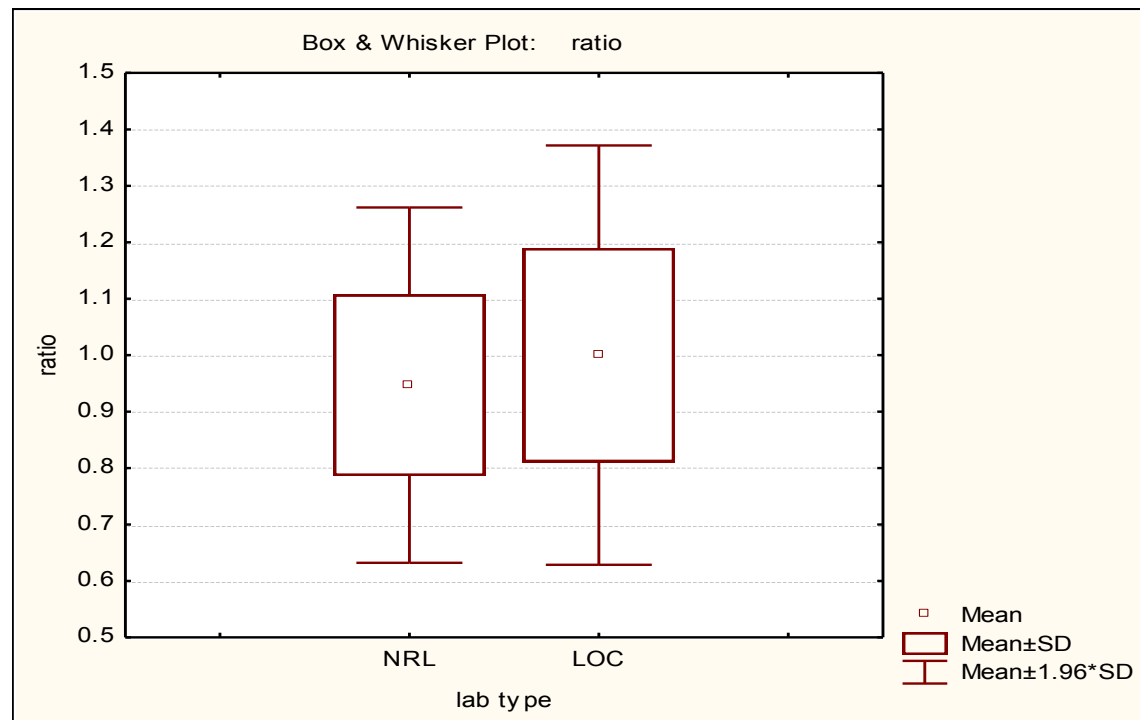
Parametric

		Mean NRL	Mean LOC	t-value	df	p	Valid N NRL	Valid N LOC	Std.Dev. NRL	Std.Dev. LOC	F-ratio Variances	p Variances
	ratio	0.944017	1.000131	-4.997811	702	0.000001	434	270	0.108201	0.189507	3.067549	0.000000

Non parametric

Wald-Wolfowitz		Valid N NRL	Valid N LOC	Mean NRL	Mean LOC	Z	p-level	Z adjstd	p-level	No. of Runs	No. of ties
	ratio	434	270	0.944017	1.000131	-2.62413	0.008687	2.584251	0.009760	301	0

Kolmogorov Smirnov		Max Neg Differnc	Max Pos Differnc	p-level	Mean NRL	Mean LOC	Std.Dev. NRL	Std.Dev. LOC	Valid N NRL	Valid N LOC
	ratio	-0.212221	0.023622	p < .001	0.944017	1.000131	0.108201	0.189507	434	270

U test (rank)		Rank Sum NRL	Rank Sum LOC	U	Z	p-level	Z adjusted	p-level	Valid N NRL	Valid N LOC
	ratio	141801.0	106359.0	47406.00	-4.26252	0.000020	-4.26252	0.000020	434	270

Box & Whisker Plot: ratio

Differences between LVS and HVS (only for campaigns with both type of instruments)

Parametric

	Mean LVS	Mean HVS	t-value	df	p	Valid N LVS	Valid N HVS	Std.Dev. LVS	Std.Dev. HVS	F-ratio Variances	p Variances
ratio	1.013300	1.019253	-0.221440	190	0.824988	103	89	0.216450	0.142111	2.319846	0.000070

Non parametric

Wald-Wolfowitz	Valid N LVS	Valid N HVS	Mean LVS	Mean HVS	Z	p-level	Z adjstd	p-level	No. of Runs	No. of ties
ratio	103	89	1.013300	1.019253	-1.08969	0.275849	1.016946	0.309180	89	0

Kolmogorov Smirnov	Max Neg Differnc	Max Pos Differnc	p-level	Mean LVS	Mean HVS	Std.Dev. LVS	Std.Dev. HVS	Valid N LVS	Valid N HVS
ratio	-0.142140	0.126868	p > .10	1.013300	1.019253	0.216450	0.142111	103	89

U test (rank)	Rank Sum LVS	Rank Sum HVS	U	Z	p-level	Z adjusted	p-level	Valid N LVS	Valid N HVS
ratio	9783.000	8745.000	4427.000	-0.407580	0.683582	-0.407580	0.683582	103	89

Box & Whisker Plot: Var3
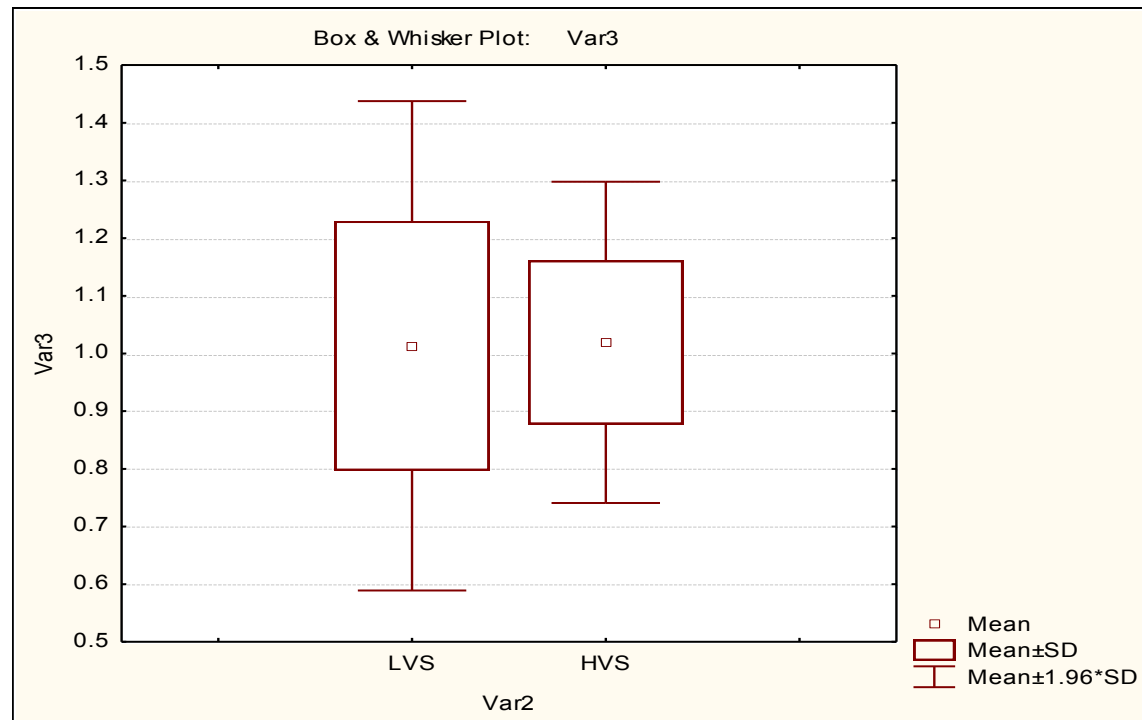
Differences between LVS and AUTOMATIC (only for campaigns with both type of instruments)

Parametric (t-test)

	Mean LVS	Mean AUT	t-value	df	p	Valid N LVS	Valid N AUT	Std.Dev. LVS	Std.Dev. AUT	F-ratio Variances	p Variances
ratio	0.985791	0.952285	2.503066	660	0.012553	327	335	0.184025	0.159804	1.326110	0.010491

Non parametric

Wald-Wolfowitz	Valid N LVS	Valid N AUT	Mean LVS	Mean AUT	Z	p-level	Z adjstd	p-level	No. of Runs	No. of ties
ratio	327	335	0.985791	0.952285	-4.27537	0.000019	4.236473	0.000023	277	0

Kolmogorov Smirnov	Max Neg Differn	Max Pos Differn	p-level	Mean LVS	Mean AUT	Std.Dev. LVS	Std.Dev. AUT	Valid N LVS	Valid N AUT
ratio	-0.069670	0.173782	p < .001	1	0.952285	0	0	327.000000	335.000000

| U test (rank)	Rank Sum LVS	Rank Sum AUT	U	Z	p-level	Z adjusted	p-level	Valid N LVS	Valid N AUT
ratio	116349.0	103104.0	46824.00	3.230894	0.001234	3.230895	0.001234	327	335

Box & Whisker Plot: RATIO
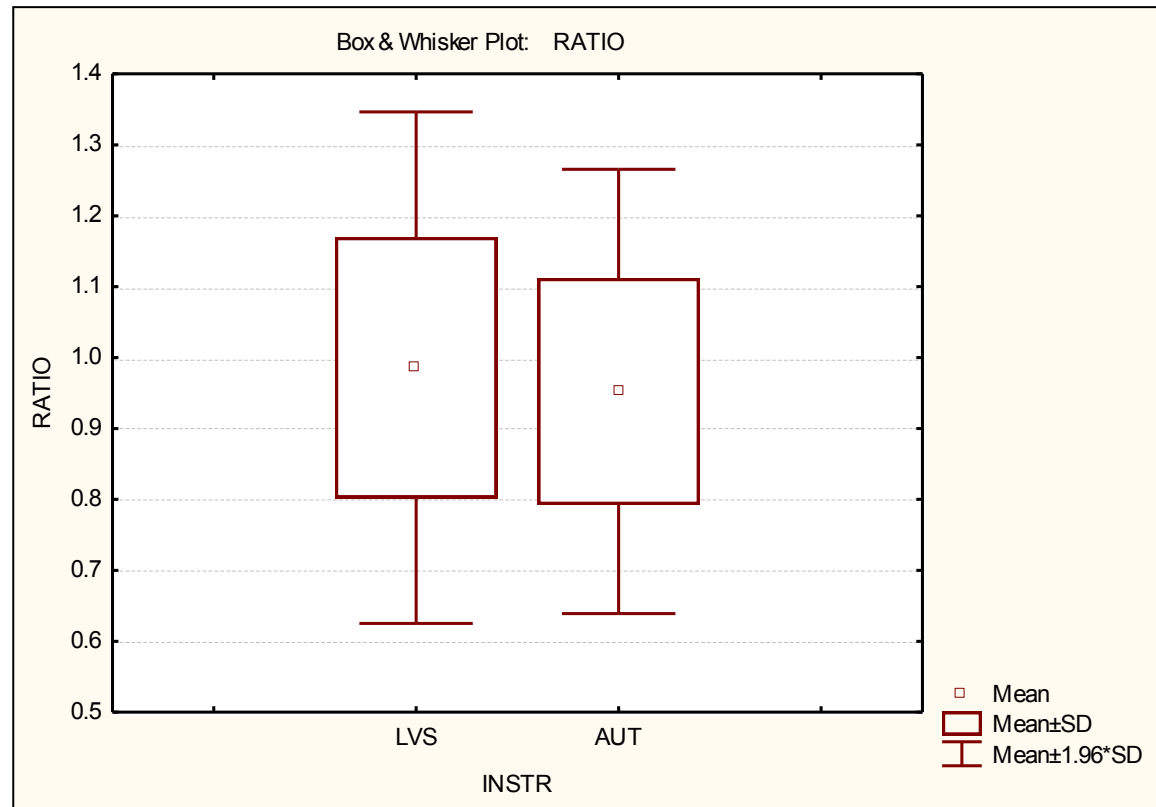
Differences between sampler type and filter material for LVS (median, 25 and 75 percentile and min-max)

Multiple Comparisons p values (2-tailed)

Independent (grouping) variable: INSTRUMENT TYPE
Kruskal-Wallis test: H (6, N= 307) =99.69777 p =0.000

|	Derenda R:117.65	Tecora R:175.23	Thermo R:94.679	Leckel R:222.39	FAI R:68.074	Partisol R:135.77	Zambelli R:163.40
Derenda		0.014085	1.000000	0.000000	0.374164	1.000000	1.000000
Tecora	0.014085		0.001854	0.048229	0.000005	0.516799	1.000000
Thermo	1.000000	0.001854		0.000000	1.000000	1.000000	0.326364
Leckel	0.000000	0.048229	0.000000		0.000000	0.000002	0.381962
FAI	0.374164	0.000005	1.000000	0.000000		0.033372	0.017931
Partisol	1.000000	0.516799	1.000000	0.000002	0.033372		1.000000
Zambelli	1.000000	1.000000	0.326364	0.381962	0.017931	1.000000	
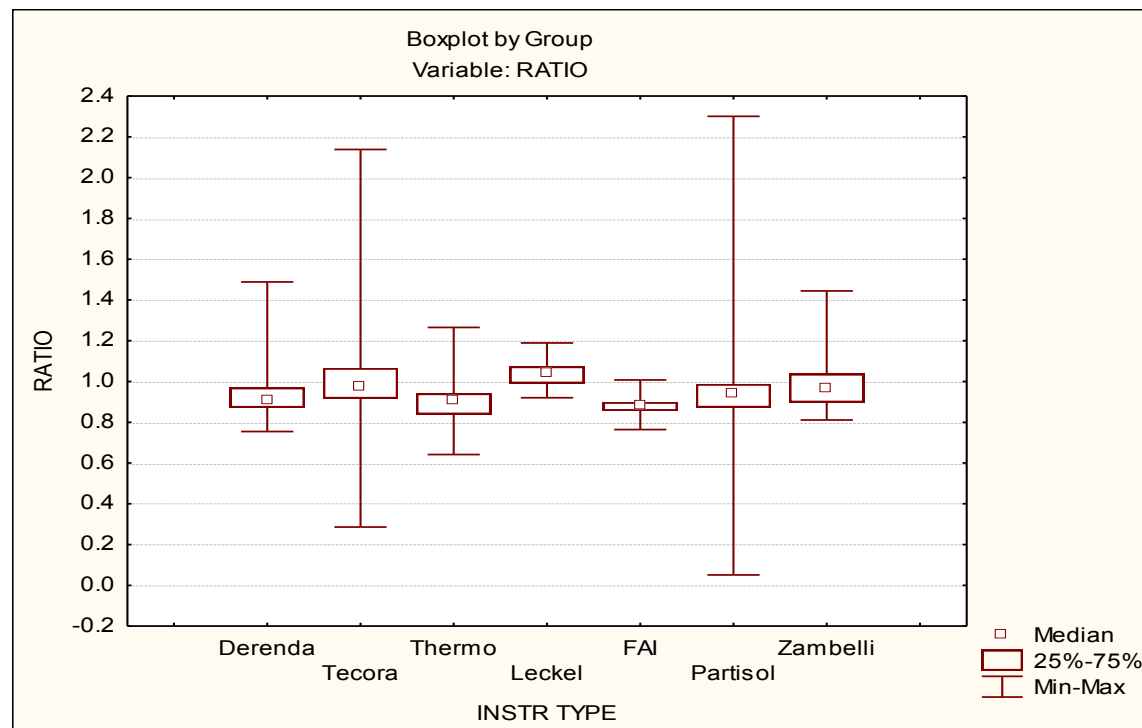
Multiple Comparisons p values (2-tailed)

Independent (grouping) variable: FILTER MATERIAL

Kruskal-Wallis test: H (3, N= 307) =25.46788 p =.0000

	Q R:172.26	NC R:149.79	G R:99.532	T R:146.96
Quartz (Q)		1.000000	0.000004	0.242290
Nitro cellulose (NC)	1.000000		0.377858	1.000000
Glass (G)	0.000004	0.377858		0.025060
Teflon (T)	0.242290	1.000000	0.025060	

Boxplot by Group
Variable: RATIO
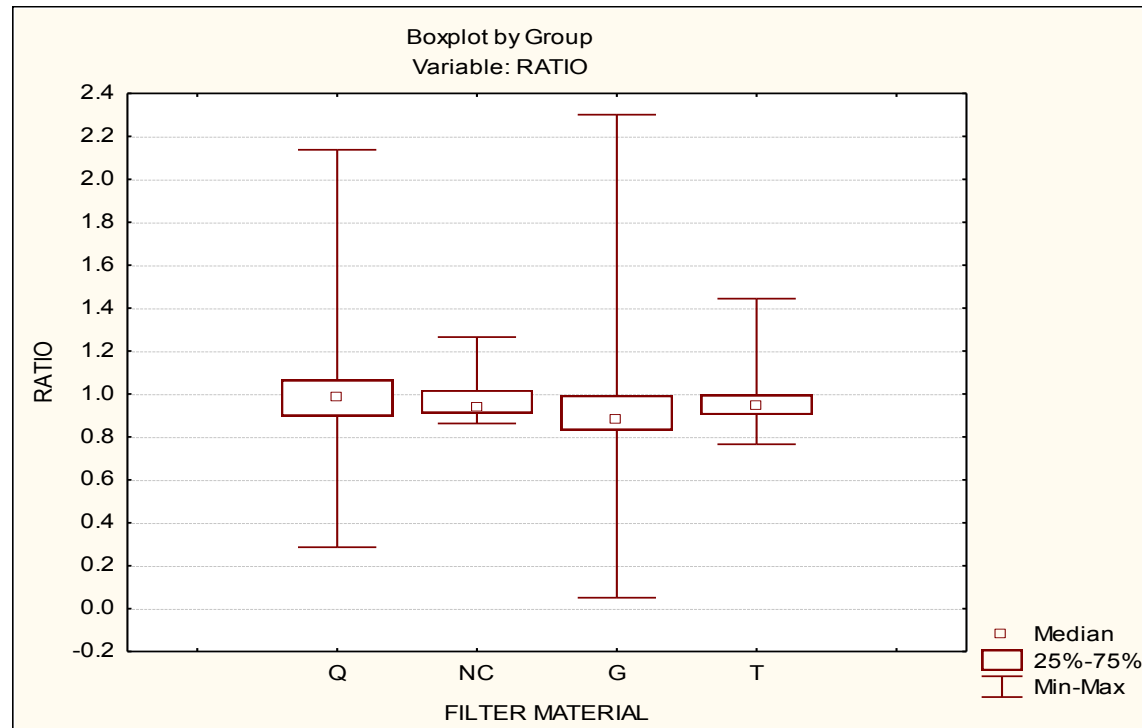
Differences between sampler type and filter material for HVS (median, 25 and 75 percentile and min-max)

Multiple Comparisons p values (2-tailed)
Independent (grouping) variable: INSTRUMENT TYPE
Kruskal-Wallis test: H (2, N= 163) =32.34319 p =.0000

	Andersen R:111.89	Digitel R:65.430	Derenda R:103.82
Andersen		0.000002	1.000000
Digitel	0.000002		0.000426
Derenda	1.000000	0.000426	

Boxplot by Group
Variable: RATIO

- 112 -
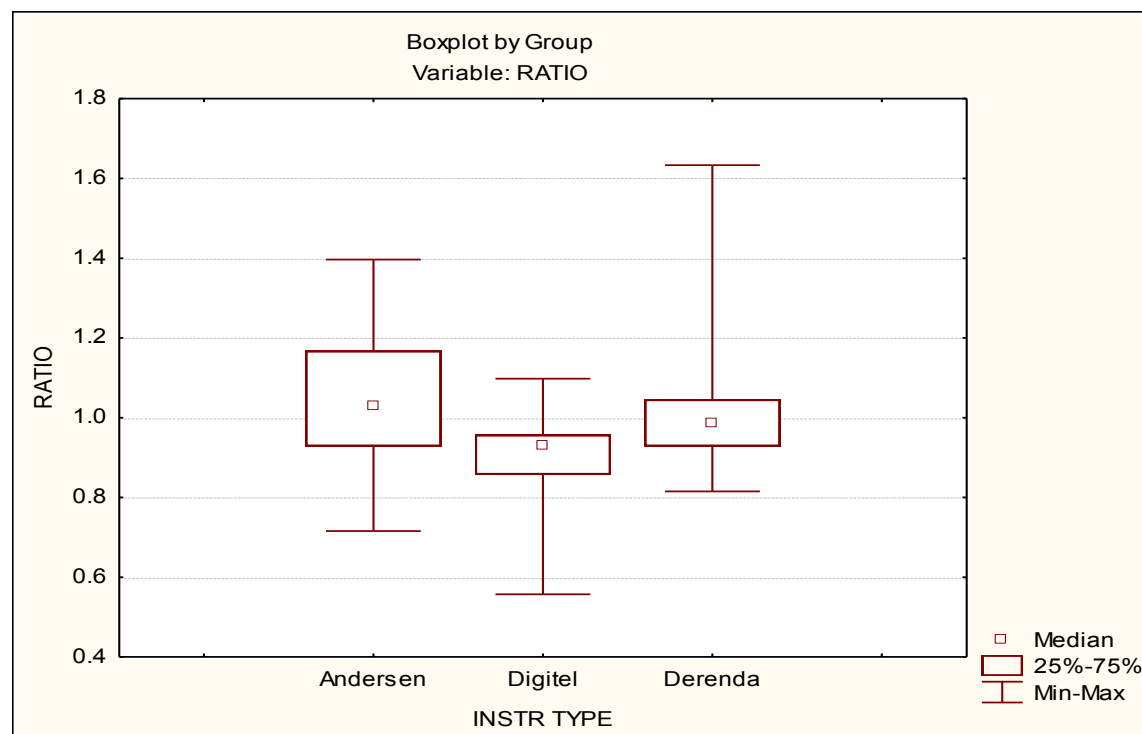
Multiple Comparisons p values (2-tailed)

Independent (grouping) variable: FILTER MAT

Kruskal-Wallis test: H (1, N= 163) =.6409999 p =.4233

|	G R:84.835	Q R:78.910
Glass (G)		0.423349
Quartz (Q)	0.423349	
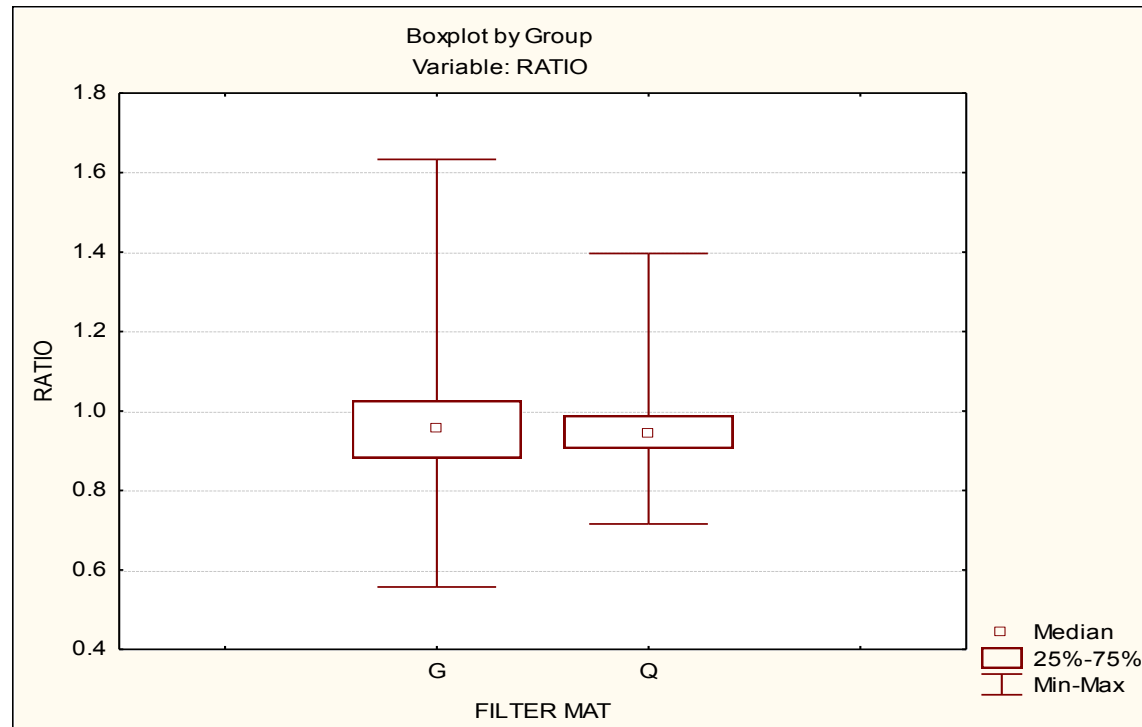
Differences between instrument type and sampling temperature for automatic analyzers (median, 25 and 75 percentile and min-max)

Multiple Comparisons p values (2-tailed)

Independent (grouping) variable: INSTRUMENT TYPE
Kruskal-Wallis test: H (7, N= 468) =91.93672 p =.0000

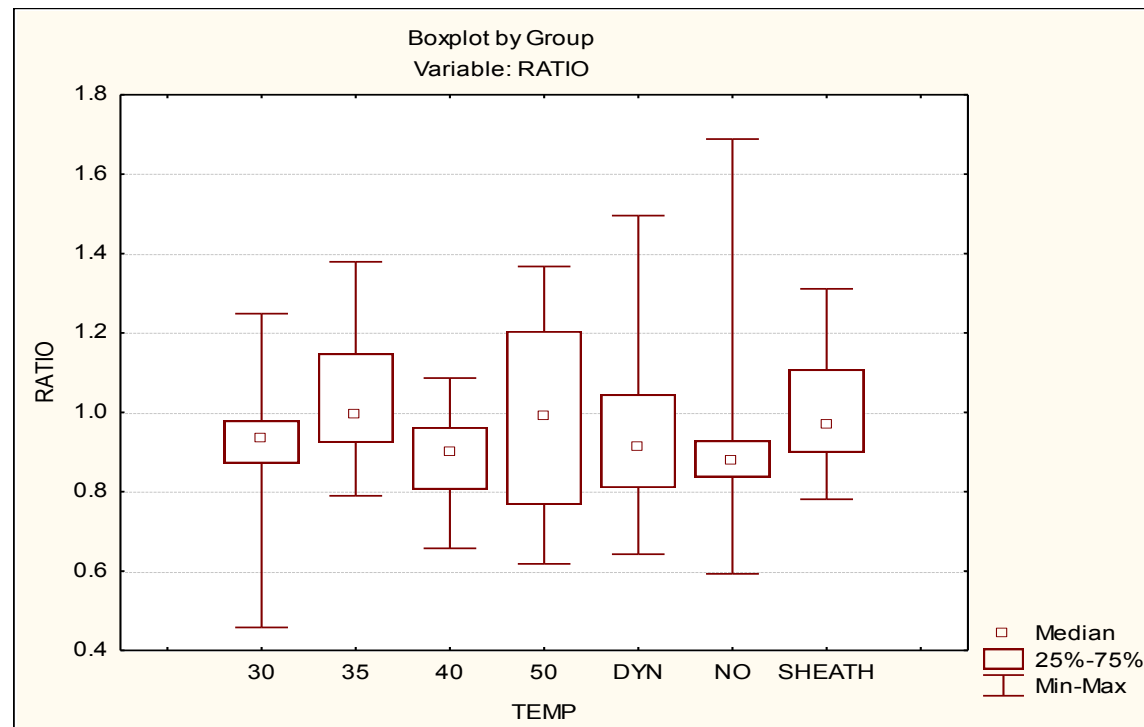|	TEOM R:310.70	ENV R:132.04	FDMS R:212.09	FH62 R:278.19	Sharp R:269.15	OPSIS R:236.08	SWAM R:120.54	GRIMM R:202.21
TEOM		0.000000	0.000051	1.000000	1.000000	0.526295	0.000000	0.179373
ENVIRONNEMENT	0.000000		0.007502	0.000000	0.028297	0.039925	1.000000	1.000000
FDMS	0.000051	0.007502		0.001893	1.000000	1.000000	0.040826	1.000000
FH62	1.000000	0.000000	0.001893		1.000000	1.000000	0.000001	1.000000
Sharp	1.000000	0.028297	1.000000	1.000000		1.000000	0.031732	1.000000
OPSIS	0.526295	0.039925	1.000000	1.000000	1.000000		0.058342	1.000000
SWAM	0.000000	1.000000	0.040826	0.000001	0.031732	0.058342		1.000000
GRIMM	0.179373	1.000000	1.000000	1.000000	1.000000	1.000000	1.000000	

Boxplot by Group
Variable: RATIO
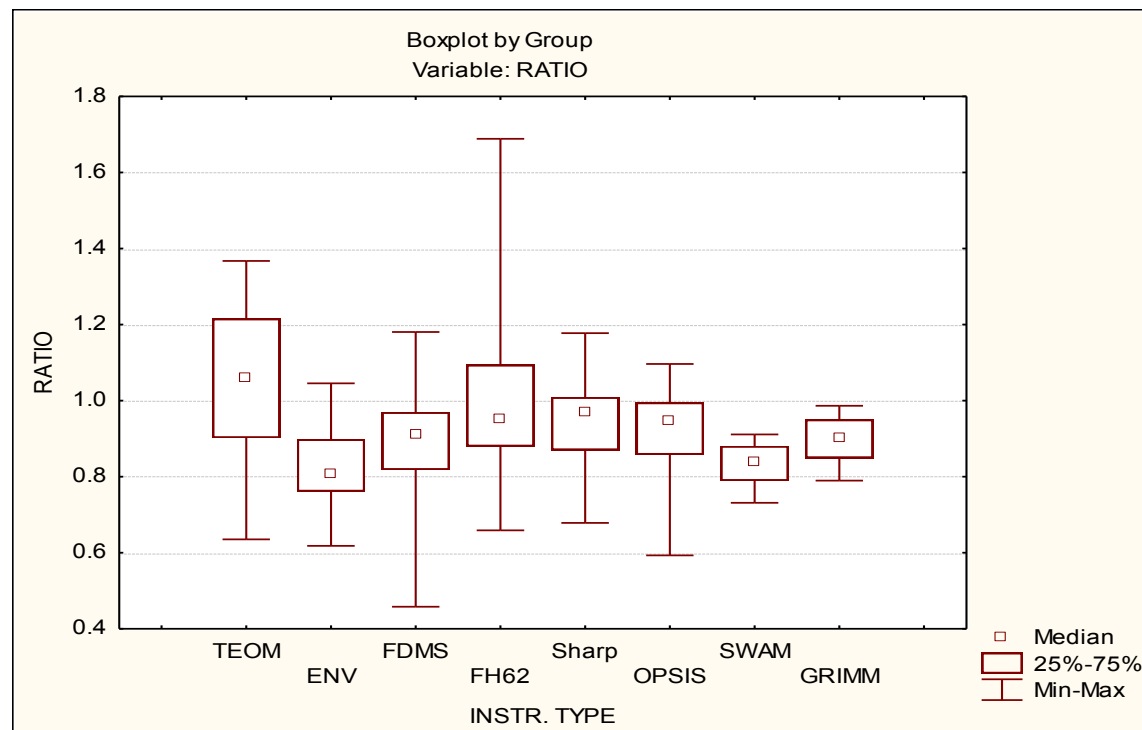
Multiple Comparisons p values (2-tailed)

Independent (grouping) variable: TEMPERATURE
Kruskal-Wallis test: H (6, N= 468) =21.01871 p =.0018

	30 R:236.56	35 R:317.68	40 R:207.36	50 R:251.86	DYN R:233.23	NO R:201.85	SHEATH R:292.08
30°C		0.087091	1.000000	1.000000	1.000000	1.000000	1.000000
35°C	0.087091		0.006071	0.649555	0.077441	0.002247	1.000000
40°C	1.000000	0.006071		1.000000	1.000000	1.000000	0.958872
50°C	1.000000	0.649555	1.000000		1.000000	0.587520	1.000000
DYN	1.000000	0.077441	1.000000	1.000000		1.000000	1.000000
NO	1.000000	0.002247	1.000000	0.587520	1.000000		0.666183
SHEATH	1.000000	1.000000	0.958872	1.000000	1.000000	0.666183	

Boxplot by Group
Variable: RATIO

Abstract
To harmonize PM measurements in the European Union, the JRC together with the AQUILA Network of National Air Quality Reference Laboratories organized a PM QA/QC program.
From 2006 – 2009, the JRC, equipped with a mobile laboratory, measured in 18 Member States, for a duration of two weeks each, PM10 and PM2.5 in parallel to measurement sites of local networks and to the National Reference Laboratories.
The main goals of the project were to find out to which degree PM measurements performed in the Member States agree with the requirements of the relevant EU directive and how correction factors for automatic analyzers were applied.

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