Report on

UK Equivalence Exercise on Particulate (PM_{10}) Monitoring in Accordance with CEN prEN 12341

August 2003

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Prepared by

CASELLA STANGER and
UNIVERSITY OF BIRMINGHAM – DIVISION OF ENVIRONMENTAL HEALTH AND RISK MANAGEMENT

Prepared for

DEPARTMENT FOR ENVIRONMENT, FOOD AND RURAL AFFAIRS
NATIONAL ASSEMBLY FOR WALES
SCOTTISH EXCEUTIVE
DEPARTMENT OF THE ENVIRONMENT, NORTHERN IRELAND

August 2003

Our Ref A30510109
Your Ref
Document Ref CS/AQ/A30510109/RM/1819

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EXECUTIVE SUMMARY

Introduction

The First Daughter Directive sets Limit values for particles (PM_{10}) based on measurements performed using the reference method or equivalent. For PM_{10}, the reference method is defined in prEN12341, and is based on filter-based gravimetric sampling (which relies upon weighing the mass of particles collected on a filter paper after a known volume of air has been drawn through it). Both low volume and high-volume samplers have been designated as transfer reference samplers.

The UK air quality monitoring networks are largely founded on the TEOM analyser. This method has the advantage over conventional filter-based gravimetric methods in the provision of data on continuous basis, which has contributed towards the understanding of pollution episodes, and allows data to be provided to the public in a timely manner. However, many previous studies comparing filter-based gravimetric samplers with the TEOM analyser, have shown that the TEOM tends to report lower concentrations of PM_{10}. This is attributed to the heated manifold of the TEOM, which will result in losses of semi-volatile components, such as ammonium nitrate, ammonium chloride and organic compounds.

The principal objective of this study has been to compare the performance of the reference sampler and the TEOM at a number of sites in the UK. The performance of another filter-based gravimetric sampler has also been evaluated. Whilst not a part of the main study, this report also considers the impact of secondary particulate episodes (notably ammonium nitrate) at Harwell and Marylebone Road, and the influence of environmental and meteorological parameters on the measurement methods.

Sites and monitoring methods

The monitoring sites included in this study have all been drawn from the UK Automatic Urban and Rural Network (AURN). All sites have TEOM analysers, and the data are ratified by the independent QA/QC Unit (netcen). The sites were chosen to provide a geographic spread and mix of pollution concentrations and sources across the UK, and included

London Marylebone Road (Kerbside)
Thurrock (Urban Background)
Harwell (Rural)
Port Talbot (Industrial)
Glasgow Centre (Urban Centre)

Belfast Centre (Urban Centre)
Birmingham Centre (Urban Centre)
London North Kensington (Urban Background)

A low-volume reference sampler (commonly referred to as the Kleinfiltergerat) was installed at each site for intercomparison with the TEOM analyser. A second filter-based gravimetric sampler (Partisol 2025) was also commissioned at some sites. The study is ongoing, but data considered in this report cover the period from Summer 1999 to Summer 2002.

SUMMARY OF RESULTS

TEOM vs Reference Sampler (KFG)

The TEOM analyser generally reports lower PM_{10} concentrations than the reference sampler. However, the ratio of TEOM to KFG concentrations varies from site to site, and from season to season. The lower seasonal ratios (close to unity) are consistently observed at Port Talbot, with the highest ratios observed at Thurrock (approximately 1.4 to 1.5). In general, higher ratios are recorded in the winter rather than the summer.

The application of the 'default' 1.3 correction factor that is currently applied to TEOM data, provides a variable level of agreement with the reference sampler. At some sites the default factor is quite conservative, whilst at other locations (e.g. Thurrock) this leads to a substantial underestimate of the number of exceedence days. The default factor provides a reasonable result for many sites when long term averages are considered, but is unsuitable for single concentrations and the accurate calculation of exceedence days.

Regression analysis (based on Reduced Major Axis) indicates R^2 values generally within the range of 0.6 to 0.9, although the relationship is again both site and seasonally dependant. The poorest relationship has been consistently observed at Harwell, with R^2 values in the range of 0.36 to 0.63.

An analysis of time series data indicates that, in general terms, the TEOM and the KFG compare relatively well on a day-to-day basis for much of the time, but may divert significantly, particularly when elevated levels are measured by the gravimetric sampler.

Partisol vs Reference Sampler (KFG)

In terms of the period means, the Partisol 2025 tends to report slightly higher concentrations than the reference sampler, with ratios generally in the range 0.91 to 1.01. However, the R^2 values (based on Reduced Major Axis regression) are generally quite poor (0.23 to 0.71). Further analysis of the data generally indicates that extreme outlying points drive the poor regressions, with the majority of the data clustered around the 1:1 line.

Examination of particulate ammonium nitrate

In order to improve the understanding of the TEOM underestimation of both PM_{10} and PM_{25} concentrations measured by the Partisol 2025 sampler, an examination of particulate ammonium nitrate has been carried out at two sites where routine measurements are carried out (Harwell and Belfast).

The addition of ammonium nitrate to the TEOM mass improves the relationship between the TEOM and the Partisol. The improvement is stronger at Harwell, where additionally it is noted the difference between the TEOM and Partisol is proportional to the nitrate concentration. At Harwell, and to a greater extent at Belfast, the contribution of ammonium nitrate does not explain the whole difference between the two methods, and it is concluded that an additional, important loss is associated with semi-volatile organic compounds or particle-bound water.

Examination of the influence of temperature and relative humidity

In order to better understand the spatial and temporal variations of the relationships between the TEOM and the Partisol samplers, and examination of the possible influential meteorological parameters (temperature and relative humidity) has been carried out.

For all sites, the difference between the TEOM and the Partisol decreases with temperature, and is likely to be related to a decrease in the amount of semi-volatile compounds in the particles. At Harwell, Glasgow and London North Kensington, the difference increases with relative humidity, and is likely to be related to the increase of the water content of particles, and possible also to the semi-volatile compounds.

The examination of TEOM versus Partisol relationship with temperature and relative humidity gives a better model than those established for different seasons, and there is the potential that such models could be used to ‘correct’ TEOM particle mass measurements at those sites where the required meteorological parameters are collected.

1 Introduction

1.1 Background to the study

The Air Quality Framework Directive (96/62/EC)[1] sets the strategic framework for ambient air quality assessment and management of twelve pollutants across Member States. The accompanying Daughter Directives set Limit Values and, where appropriate, Alert Thresholds for concentrations of individual pollutants in ambient air.

The First Air Quality Daughter Directive (DD1) sets limit values for particles (PM_{10}); the 24-hour mean limit value is 50 $\mu g/m^3$ with 35 permitted exceedences each year, and an annual mean limit value of 40 $\mu g/m^3$.

In setting the limit values, the European Union has tasked the European Committee for Standardisation (CEN) with developing reference methods to be used in the implementation of the Directives. For PM_{10}, the reference method[2] is promulgated in prEN12341 and is based on filter-based gravimetric sampling (which relies on weighing the mass of particles collected on a filter paper after a known volume of air has been drawn through it). Both low-volume samplers (LVS) and high-volume samplers (HVS) have been defined as transfer reference methods.

Member States are permitted to use other methods of assessment, but are required to demonstrate equivalence to the reference method. Monitoring of PM_{10} concentrations in the UK national networks is largely founded on the Tapered Element Oscillating Micro-balance (TEOM) analyser. Further details of the TEOM analyser, and the principals of operation are given in Chapter 3.

The TEOM analyser has the advantage over conventional filter-based gravimetric methods in the provision of data on an almost real-time basis. This has contributed significantly to understanding the temporal trends and source contributions to overall PM_{10} concentrations, including the production of the 1999 report of the Government's Airborne Particles Expert Group (APEG)[3]. However, many studies comparing various filter-based gravimetric PM_{10} samplers with TEOM analysers have shown that the TEOM tends to report lower concentrations (Allen et al., 1997; Ayers et al., 1999; Soutar et al., 1999; APEG, 1999; Salter and Parsons, 1999; Williams and Bruckmann, 2001; Cyrys et al., 2001). This is attributed to the heating of the inlet manifold of the TEOM

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[1] Council Directive 96/62/EC Ambient Air Quality Assessment and Management. Official Journal of the European Community No. L 296. Pp. 55 - 63

[2] PrEN12341: 1998 Air Quality – Determination of the PM_{10} fraction of suspended particulate matter – Reference method and field test procedure to demonstrate equivalence of measurement methods. European Committee for Standardization.

[3] APEG 1999. Source apportionment of airborne particulate matter in the United Kingdom. Prepared on behalf of the DETR, the Welsh Office, the Scottish Office and the Department of the Environment (Northern Ireland).

analyser to 50°C in order to minimise interference from condensation of water onto the filter, and to provide a stable and reproducible measurement. This results in the loss of semi-volatile components of particulate matter, including ammonium nitrate, ammonium chloride, and organic compounds[4].

The relative proportion of semi-volatile components in PM_{10} is expected to vary both temporally and geographically. As a consequence, both spatial and seasonal differences in the relationships between filter-based gravimetric samplers and TEOM analysers have been shown by many studies (Allen et al., 1997; APEG, 1999; Williams and Bruckmann, 2001). Whilst investigations of the relationship between the TEOM analyser and the reference method are in progress, a Commission working group has recommended that an interim default factor of 1.3 should be applied to all TEOM data in order to assess compliance with the limit values.

It should however be noted that filter-based gravimetric methods also have the potential to lose some semi-volatile species both during and after sampling. The loss will be dependent upon the environmental conditions that the filter is exposed to during sampling and after removal from the sampler, and before weighing.

1.2 Scope of assessment

The scope of this assessment has been principally to undertake a rigorous comparison between measurement methods of PM_{10} at sites which vary in particulate emissions source (and hence particle composition), and which encompass a wide geographic range in order to establish regional differences in PM_{10} across the UK.

The study is based on comparisons between TEOM analysers and the reference low volume sampler at a number of sites. Additionally, Partisol 2025 samplers (Rupprecht and Patashnick[5]) have been co-located at a number of sites and additional comparisons between the low volume sampler and Partisol 2025 have been made.

The low volume sampler used in the current assessment is the PNS-X8 system, which incorporates the Kleinfiltergerat (KFG) sampling head[2]. The PNS-X8 system enables up to 8 continuous days use without site attendance. Further details of the methods employed in the assessment are given in Chapter 3.

The following sites have been included in the study:

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[4] It should however be noted that filter-based gravimetric methods also have the potential to lose some semi-volatile species both during and after sampling. The loss will be dependent upon the environmental conditions that the filter is exposed to during sampling and after removal from the sampler, and before weighing.

[5] http://www.rpco.com

- Marylebone Road
- Harwell
- Thurrock
- Port Talbot
- Glasgow
- Belfast
- Birmingham Centre
- London North Kensington

Further details of site locations and characteristics are shown in Chapter 2.

The approach to the equivalence study is consistent with the guidance proposed by the EC Working Group on Particulate Matter issued in April 2001[6], a document that emerged from the various on-going programmes being undertaken by Member States in response to the First Daughter Directive.

Whilst outside the remit of the 'equivalence exercise', this report also considers the impact of secondary particulate episodes (notably ammonium nitrate) at Harwell and Marylebone Road, and the influence of environmental and meteorological parameters on the measurement methods.

1.3 Format of report

The format of this report is as follows:

- Chapter 2 considers the sites characteristics and historical particulate measurements in order to highlight the differences in occurrence of particulate pollution across the UK.
- Chapter 3 provides details with respect to the measurement methods for particulate pollution employed in the UK covering both 'reference' and 'candidate' samplers. Additional information with respect to the measurement of mass and data handling are given.
- Chapter 4 highlights the appropriate method of linear regression employed in determining the relationship between samplers, taking the most rigorous statistical approach to reporting
- Chapter 5 outlines the impact of the TEOM calibration factor on the relationships determined between the TEOM and other samplers
- Chapter 6 discusses the results of the multiple comparisons between 'reference' and 'candidate' samplers covering 'reference vs. TEOM'; 'reference vs. Partisol' and 'Partisol vs. TEOM'.

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[6] EC Working Group on Particulate Matter. A report on guidance to Member States on PM_{10} monitoring and inter-comparisons with the reference method. April 2001.

- Chapter 7 supplements the existing report with consideration to the $PM_{2.5}$ fraction and differences between the data gathered at Harwell and Marylebone Road between the Partisol and TEOM methods of sampling, whilst
- Chapter 8 provides additional information with respect to the influence of particulate ammonium nitrate on particulate monitoring methods.
- Chapter 9 highlights some of the influences with respect to environmental variables and seasonal differences on particulate pollution.
- Chapter 10 draws the main conclusions of the report in order to provide the necessary policy support for Government response to the First Daughter Directive.

Technical annexes are included where necessary at the end of the report in order to support the analysis of data and provide supplementary information where necessary.

2 Site Characteristics and Historical PM_{10} Measurements

This chapter provides details of the monitoring sites and the general PM_{10} concentrations based upon historical measurement data.

2.1 Site characteristics

The sites included in this study form a part of the UK Automatic Urban and Rural Network (AURN). The AURN is structured according to defined roles between the Central Management and Co-ordination Unit (CMCU) and the QA/QC units. For each site within the AURN, local site operators (LSOs) are appointed to undertake routine servicing and calibration checks of equipment. In most cases, LSOs are appointed environmental health professionals from local authorities, although consultants and scientific organisations also provide additional support at a number of sites. Data gathered through CMCU is verified and passed to the data dissemination unit for presentation to the public via the 'World Wide Web, CEEFAX, TELETEXT and other bulletin boards. QA/QC units provide an independent check to ensure integrity and quality, prior to the data being archived in fully ratified form every 3 months.

- *Marylebone Road: Kerbside (Grid ref'. TQ 281 820)*
  The site is located within 1 metre of the kerbside of a busy main arterial route in west London with approximate traffic flows in the region of 90,000 vehicles per day. The road is frequently congested. The surrounding area forms a street canyon.
- *Thurrock: Urban Background (Grid ref'. TQ 611 779)*
  The site is located within an existing building approximately 35 metres from the kerbside of the nearest busy road which experiences traffic flows in the region of 9,000 vehicles (12-hour average). The surrounding area is generally open with local light industry.
- *Harwell: Rural (Grid ref'. SU 474 863)*
  The site is located within the grounds of Harwell Science Centre surrounded by large open spaces encompassing agricultural land. The nearest road is for access to buildings on the site only and is approximately 300 metres away.
- *Port Talbot: Industrial Background (Grid ref'. SS780 882)*
  The site is located within the grounds of a small hospital where the nearest road (M4 motorway) passes some 75 metres distance from the site. Typical traffic flows in the range of 50,000 – 55,000 vehicles per day occur on a typical weekday. The site is approximately 700 metres from a large steelworks, which is known to contribute to local levels of pollution.

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[7] Ordnance Survey LandRanger 1:50000 map series

- *Glasgow Centre: Urban Centre (Grid ref. NS 589 650)*
  The site is located within a pedestrianised area of the city centre. The nearest road is approximately 20 metres distance from the site and used for commercial access with a traffic flow in the region of 20,000 vehicles per day. The surrounding area is open with city centre business and retail premises bordering on three sides.
- *Belfast Centre: Urban Centre (Grid ref. J 339 744)*
  The site is located within a pedestrianized area of the city centre. The nearest road is approximately 15 metres from the site and provides access to the precinct for goods deliveries only. The surrounding area is built-up with business and retail premises (typically 5 storeys high) creating street canyons.
- *Birmingham centre: Urban Centre (Grid ref. SP064868)*
  The monitoring station is within a self-contained, air-conditioned housing located within a pedestrianised area of the city centre. The nearest road is approximately 10 metres distance and is used for access to the adjacent car park. The nearest heavily trafficked urban road is approximately 60 metres from the station. The surrounding area is open and comprises urban retail and business outlets.
- *London North Kensington: Urban Background (Grid ref. TQ240817)*
  The site is located within the grounds of Sion Manning School. The samplers are on a cabin located in the school grounds next to St Charles square. The surrounding area is mainly residential.

Further details on site locations and characteristics can be found at the Site Information Archive http://www.stanger.co.uk/siteinfo/

2.2 Pollution profiles

Table 2.1 summarises the particulate pollution profiles for each of the sites as derived from historical ratified (TEOM) data from the UK National Air Quality Information Archive[8].

Results show that Marylebone Road consistently records the highest levels of particulate PM_{10} when compared to other sites across the period shown (1998 – 2001). Annual mean PM_{10} concentrations range from 32 – 37 $\mu g/m^3$. Port Talbot records the second highest annual mean PM_{10} concentrations of the six sites chosen; annual mean PM_{10} concentrations at this site fall within the range 23 – 27 $\mu g/m^3$.

Urban Centre background locations at Belfast, Thurrock and Glasgow show similar concentrations of PM_{10}. At these sites, annual mean PM_{10} concentrations fall within the range 18 – 21 $\mu g/m^3$. Of the six sites included in this study, the rural Harwell station shows the lowest annual mean PM_{10} concentrations across 1998 – 2001, with annual mean PM_{10} concentrations in the range 13 – 15 $\mu g/m^3$.

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[8] http://www.aeat.co.uk/netcen/airqual/index.html

Table 2.1. Annual mean and maximum hourly PM_{10} concentrations across assessment sites, 1998 – 2002[9].

Site	**1998**		**1999**		**2000**		**2001**		**2002[10]**	
	Mean	**Max 1hr**	**Mean**	**Max 1hr**	**Mean**	**Max 1hr**	**Mean**	**Max 1hr**	**Mean**	**Max 1hr**
Marylebone Road[11]	32	153	35	801	37	686	33	448	34	511
Thurrock	19	155	19	336	18	258	19	339	21	245
Harwell[12]	15	72	13	92	14	177	15	35	13	66
Port Talbot	27	264	26	352	25	290	23	296	21	155
Belfast	21	283	20	199	20	254	20	1233	17	212
Glasgow	20	245	18	183	22	724	17	193	15	161
Birmingham Centre	19	249	18	197	17	194	17	132	17	83
London North Kensington[11]	20	159	21	102	20	163	20	265	19	439

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[9] Unratified data for October – December 2002 for Thurrock, Port Talbot, Belfast, Glasgow and Birmingham

[10] Data for 2002 are provisional for period covering Oct – Dec.

[11] Unratified data for the whole of 2002 with the exception of July, August and September

[12] PM_{10} data for Harwell are subject to ratification by Casella Stanger and are not subject to independent QA/QC checks.

3 Methods of PM_{10} Monitoring

This Chapter provides details of each of the monitoring methods employed in the studies, and the principles of operation.

3.1 Reference Sampler

prEN12341 defines three reference samplers for use in the implementation of the First Daughter Directive and the measurement of PM_{10}. This study is based on the use of the low volume sampler (LVS). The LVS (PNS-X8 system)[13] provides up to 8 days unattended monitoring through a sequential switching solenoid system for automatic sampling on eight separate LVS heads. The LVS sampler is commonly referred to as the Kleinfiltergerat (KFG), and is notated as such in the remainder of this report.

The KFG sampler is operated with a constant regulated volume of 2.3 m^3/hr. The PM_{10} sampling head is equipped with a preliminary collector at which particles with an aerodynamic diameter of more than 10 µm are separated so that only the PM_{10} fraction is collected onto the filter. The PM_{10} sampling head and filter holder are separate units and are screwed together so as to be gas-tight during sampling. Each sampling head is connected to a solenoid switching system by tubing. This in turn is connected using a central single sampling point to the valve box, controlled by a micro-processor (X8-controller card), that enables sequential sampling in accordance with the monitoring schedule. The distance between inlets is approximately 600 mm in order to avoid interference in air-flow to each inlet.

The PM_{10} concentrations measured by the KFG is reported at ambient temperature and pressure, consistent with the requirements of the Daughter Directive.

3.2 Candidate Samplers

Tapered Element Oscillating Micro-balance (TEOM)

The 1400A series of Tapered Element Oscillating Micro-balance (TEOM) from Rupprecht & Patashnick[14] provides measurement of PM_{10} on a continuous basis.

The TEOM measures particulate concentrations by continuously weighing particles deposited onto a filter. The filter is attached to a hollow tapered element, which vibrates at its natural frequency of oscillation (*f*). As particles progressively collect on the filter, the frequency changes by an amount proportional to the mass deposited (m)

$$m = k/f^2$$

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[13] Ingenieurbüro Norbert Derenda, Iserstraße 8-10, 14513 Teltow, GERMANY

[14] Rupprecht & Patashnick Co., Inc., 25 Corporate Circle, Albany, NY 12203, USA

where, k is a constant determined during calibration of the TEOM. The flow rate through the analyser, which affects the size-selective cut-off for PM_{10}, is controlled using thermal mass flow controllers and is automatically measured to determine the mass concentration. The total flow of 16.67 litres per minute (1.002 m^3/h) is drawn through the sampling head until split between the filter cartridge (3 litres per minute) and an auxiliary flow (13.67 litres per minute). The inlet is heated to 50 ^oC prior to particles being deposited onto the filter.

The PM_{10} concentrations measured by the TEOM analyser are corrected to STP conditions (293K, 101.3 kPa).

Partisol Plus (Model 2025)

The Rupprecht & Patashnick Co. Inc[14]. Partisol Plus (Model 2025) is a microprocessor controlled sampler for the monitoring of particulates in ambient air. The instrument uses a filter-based gravimetric procedure, based on the same size-selective inlet design as that used on the TEOM. However, the inlet manifold is not heated.

The Partisol 2025 has a filter exchange mechanism that provides unattended monitoring for up to 16 consecutive days.

The PM_{10} concentrations measured by the Partisol 2025 is reported at ambient temperature and pressure, consistent with the requirements of the Daughter Directive.

3.3 Installation of equipment at sites

In accordance with the Directive requirement of reporting PM_{10} concentrations at ambient temperature, the KFG and Partisol 2025 units were installed at each sites on the external façade of the housing of the monitoring station.

3.4 Filter Mass measurements

Whatman[15] QMA 47mm diameter filters (0.6µm pore size) have been used in accordance with the criteria set down in prEN 12341. Pre-conditioning and post-conditioning of filters was undertaken in accordance with the requirements of the normative annex of prEN12341. The main features of this annex are:

- All filters (candidate and reference) shall be handled in a similar fashion;
- Quartz fibre filters shall be chosen;

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[15] The LabSales Company, Over Industrial Park, Norman Way, Over, Cambridgeshire CB4 5GR

- Unused filters shall be conditioned for 48 hours within an air-conditioned weighing room with a temperature of 20 ± 1°C and a relative humidity of 50 ± 3 % before weighing;
- Dust-loaded filters are to be equilibrated under the same conditions as those employed prior to use;
- The resolution of the balance shall be at least 10 μg and shall be installed and operated in the aforementioned air-conditioned room.

Filter weighing, conditioning and dispatch of filter for the KFG samplers was undertaken using UKAS-accredited procedures by AEA Technology Products and Systems from the commencement date of sampling (June 1999) until September 2000 when internal structural changes within AEA Technology passed these duties to AEA Technology – **netcen**.

In the case of the Partisol 2025 units, filter weighing, conditioning and dispatch to local site operators was undertaken by CRE Group Ltd using UKAS-accredited procedures.

3.5 Data handling and ratification

Local site operators (LSOs) were contracted to carry out local operations of the samplers and analysers. Such duties included undertaking receipt of the filters dispatched to sites from the laboratories, filter changes, and routine cleaning of the sampling heads. Additionally, local site operators were requested to provide comments where normal routine operations were either interrupted and/or damage to filters has occurred as a consequence of filter changes. For sites remote from the weighing laboratory, samples were despatched using the postal system.

Mass measurements for individual filters were provided by the relevant laboratory for the site in electronic or hard-copy format for determination of the mass concentrations in air when collated with the volume sampling data provided by local site operators. Additional commentary was provided where filters were apparently damaged in transit or during the weighing process. Ratification of data collected by the KFG and Partisol samplers was carried out by Casella Stanger.

In the case of the TEOM analysers, the data largely form part of the UK national networks, and are polled on a routine basis. Data within this part of the national networks are subject to independent QA/QC by **netcen**, who are responsible for the provision of final ratified datasets. It is noted however, that the TEOM data collected at the Harwell site are not subject to these same ratification procedures; in this case the data were ratified by Casella Stanger.

3.6 Monitoring periods

3.6.1 KFG Samplers

The initial phase of the study included the necessary consultation with local planning authorities with regards to the constraints that would be imposed in installing the KFG samplers at each of the sites.

The following constraints were identified thereby delaying the commencement of sampling:

- Belfast: as one of the earliest sites in the AURN the housing was deemed unacceptable for installation of the KFG sampler on the roof. In additional, other monitoring equipment earmarked for the site required the site to have a major upgrade. This necessitated the submission of a formal planning application in support of the new design. Planning permission was granted accordingly in August 2000 with the schedule of works completed in January 2001. Consequently, data included in this report only covers the period from February 2001 – September 2002.
- Port Talbot: an affiliate site in the AURN, delays of approximately 3 months were encountered as a result of consultation with relevant planning and environmental health departments. The data included in this report covers only the period September 1999 – September 2002.
- Glasgow: as a city-centre site the local planning authority raised concerns surrounding the visual intrusion of the KFG sampler alongside security of the equipment and possible vandalism. These concerns were ultimately addressed albeit with a delay of approximately 6 months over those sites already operational. Consequently, the data included in this report covers only the period from December 1999 – September 2002.

Commencement of sampling for the KFG samplers at Harwell, Marylebone Road and Thurrock commenced in May/June 1999. The results presented in this report cover the period May/June 1999 – September 2002.

3.6.2 Partisol 2025 Units

Partisol 2025 units were initially installed at a number of sites during the course of 2000 as a result of Defra-funded research into the biological toxicity of particles being undertaken by Napier University under contract EPG 1/3/147. Further details regarding this research are available at www.airquality.co.uk

Table 3.2 summarises the commencement of monitoring a periods covered in the reporting of data in the following sections. Table 3.3 provides further information with respect to exact dates for which sampling commenced and the date to which data were available for inclusion in this report.

For two sites, delays in commencement of sampling and equipment failure meant that only a small proportion of the relevant season was covered. At Belfast, delay in commissioning the equipment due to a major upgrade of the site meant that commencement of sampling did not occur until 07/02/01 in the 'Winter' period of 2000/2001 (September – March). Similarly, removal of the TEOM unit for repair (until 13/09/01) at the Thurrock site means that, for the 'Summer' season of 2001, data are available only up until 09/07/01 rather than 30/09/01.

Table 3.1 Summary of sampling periods using KFG, TEOM and Partisol 2025 systems.

Site	Season period data reported in this report[16]		
	Reference PM_{10} (KFG)	Candidate PM_{10} (TEOM)	Candidate PM_{10} (Partisol 2025)
Marylebone Road	Summer ’99	Summer ’99	N/A
	Winter ‘99/’00	Winter ‘99/’00	N/A
	Summer ’00	Summer ’00	N/A
	Winter ‘00/’01	Winter ‘00/’01	Winter ‘00/’01
	Summer ’01	Summer ’01	Summer ’01
	Winter ‘01/’02	Winter ‘01/’02	Winter ‘01/’02
	Summer ‘02	Summer ‘02	Summer ‘02
Harwell	Summer ’99	Summer ’99	N/A
	Winter ‘99/’00	Winter ‘99/’00	N/A
	Summer ’00	Summer ’00	N/A
	Winter ‘00/’01	Winter ‘00/’01	Winter ‘00/’01
	Summer ’01	Summer ’01	Summer ’01
	Winter ‘01/’02	Winter ‘01/’02	Winter ‘01/’02
	Summer ‘02	Summer ‘02	Summer ‘02
Thurrock	Summer ’99	Summer ’99	N/A
	Winter ‘99/’00	Winter ‘99/’00	N/A
	Summer ’00	Summer ’00	N/A
	Winter ‘00/’01	Winter ‘00/’01	N/A
	Summer ’01	Summer ’01	N/A
	Winter ‘01/’02	Winter ‘01/’02	N/A
Port Talbot	Summer ’99	Summer ’99	N/A
	Winter ‘99/’00	Winter ‘99/’00	N/A
	Summer ’00	Summer ’00	N/A
	Winter ‘00/’01	Winter ‘00/’01	Winter ‘00/’01
	Summer ’01	Summer ’01	Summer ’01
	Winter ‘01/’02	Winter ‘01/’02	Winter ‘01/’02
	Summer ‘02	Summer ‘02	Summer ‘02
Glasgow	Winter ‘99/’00	Winter ‘99/’00	N/A
	Summer ’00	Summer ’00	N/A
	Winter ‘00/’01	Winter ‘00/’01	Winter ‘00/’01
	Summer ’01	Summer ’01	Summer ’01
	Winter ‘01/’02	Winter ‘01/’02	Winter ‘01/’02
	Summer ‘02	Summer ‘02	N/A
Belfast	Winter ‘00/’01	Winter ‘00/’01	Winter ‘00/’01
	Summer ’01	Summer ’01	Summer ’01
	Winter ‘01/’02	Winter ‘01/’02	Winter ‘01/’02
	Summer ’02	Summer ’02	Summer ‘02

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[16] Summer period: 1 April – 30 September. Winter period: 1 October – 31 March

Table 3.2: KFG and TEOM PM$_{10}$ paired data included in the comparison. (N is the number of paired observations)

Site	Data included in the comparison		N
	From	To	
Belfast	01/10/00	09/12/02	450
Glasgow	01/10/99	30/09/02	660
Harwell	28/05/99	30/09/02	889
Marylebone Road	03/06/99	25/02/02	571
Thurrock	27/05/99	31/12/02	558
Port Talbot	01/09/99	25/05/02	630

Table 3.3: KFG and Partisol Plus 2025 PM$_{10}$ paired data included in the comparison. (N is the number of paired observations)

Site	Data included in the comparison		N
	From	To	
Belfast PM$_{10}$	07/02/01	02/07/02	304
Glasgow PM$_{10}$	20/10/00	12/03/02	168
Harwell PM$_{10}$	30/09/00	02/07/02	381
Marylebone Road PM$_{10}$	22/09/00	12/02/02	170
Port Talbot PM$_{10}$	12/10/00	03/06/02	273

4 Comparison between different linear regression models

The Least Square linear regression is the most commonly used method in atmospheric sciences. This method assumes that the dependent Y observations are linearly dependent of the independent X observations that are exactly known. The best fit linear slope is then computed assuming that all X observations are accurate (see Annex 2). This statistical tool is often used to compare pollution data from different instruments. The Least Square regression has been commonly used in comparison exercises between TEOM particle mass data and filter-based reference gravimetric particle mass data (e.g. Soutar et al., 1999; Salter and Parsons, 1999; Ayers et al., 1999). In this case, such an assumption on the set of X observations leads to biased evaluations of the relationship between two instruments. However, a recent paper from Ayers (2001) has suggested that the Least Square regression analysis is not appropriate for an instrument comparison exercise.

This study has compared two regression methods, which make no assumption regarding the X observations; the Orthogonal regression and the Reduced Major Axis (RMA) regression methods, with the traditional Least Square regression analysis. These methods are briefly described in Annex 1. More details on the RMA regression model can be found in Ayers et al. (2001).

The results are presented in Table 4.1. When the Pearson R^2 correlation coefficient is below 0.50, the linear correspondence between X and Y observations is weak (Belfast, Marylebone Road and Port Talbot).

The Least Square method gives a lower slope and a higher intercept than both Orthogonal and RMA regressions. These results are in agreement with Ayers et al. (2001). The Least Square regression has likely contributed to the intercepts significantly different than zero obtained by Ayers et al. (1999) and by Salter and Parson (1999).

The improvement is more obvious for the sites where weaker correlations are seen. As an example, the graph for Port Talbot is presented in Figure 4.1. This demonstrates that both RMA and Orthogonal regressions give a better fitting model than the Least Square regression, closer to the trend of the data.

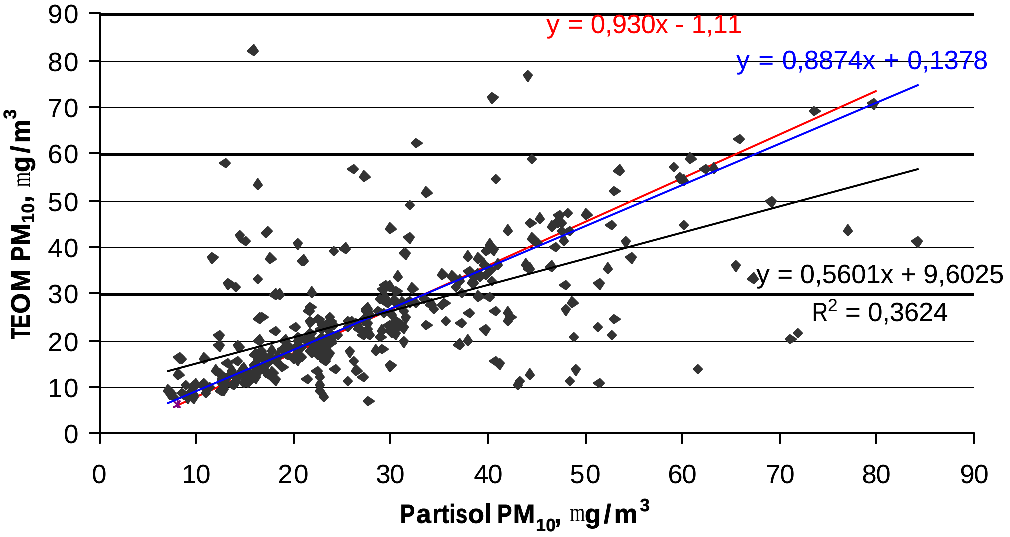
Unlike the Least Square regression, it is possible to exchange X and Y observations without changing the model for both orthogonal and RMA regressions. That constitutes another important advantage of these two methods (see Annex 2).

It is concluded that both Orthogonal and RMA regression analyses are suitable for the analysis of data in this study, but that Least Square regression is inappropriate. The RMA regression analysis has been used throughout the remainder of this report.

Table 4.1: Comparison between the Least Square regression (first line, in black), the Orthogonal regression (second line, in blue) and the RMA regression (third line, in red) for gravimetric PM_{10} from Partisol PM_{10} concentrations, from TEOM (AURN: 1.03 TEOM + 3µg). R^2 is the square of the Pearson correlation coefficient, N is the number of observations included in the comparison. Concentrations are in µg/m^3.

Site	Linear regressions	Pearson R^2	N
Belfast Centre	y = 0.260 x + 11.04 y = 0.316 x + 9.24 y = 0.508 x + 2.98	0.26	315
Birmingham centre	y = 0.485 x + 5.25 y = 0.506 x + 4.70 y = 0.537 x + 3.92	0.81	465
Glasgow centre	y = 0.562 x + 4.63 y = 0.624 x + 3.24 y = 0.670 x + 2.19	0.70	247
Harwell	y = 0.465 x + 5.14 y = 0.492 x + 4.65 y = 0.534 x + 3.91	0.76	436
London North Kens.	Y = 0.595 x + 5.00 y = 0.637 x + 3.97 y = 0.667 x + 3.24	0.80	353
Marylebone Road	y = 0.365 x + 17.00 y = 0.535 x + 9.20 y = 0.717 x + 0.896	0.26	150
Port Talbot	y = 0.560 x + 9.60 y = 0.887 x + 0.138 y = 0.930 x – 1.11	0.36	334

Figure 4.1: TEOM PM_{10} data versus gravimetric Partisol PM_{10} data for Port Talbot. In black, the Least Square regression and the Pearson correlation coefficient, in blue, the orthogonal regression, in red, the RMA regression.



5 Influence of the TEOM calibration factor

The TEOM concentrations reported as default by the instrument include a 'calibration factor' represented as [1.03 *'TEOM reading' + 3 µg]. This calibration factor has been determined through regression analyses of data from TEOMs and collocated filter-based reference methods located in a number of sites in the United States and Europe. This factor was determined in order to compensate for the loss of particle-bound water and semi-volatile compounds in the TEOM device and in order to achieve the US EPA certification (Patashnick and Rupprecht, 1991).

The influence of the TEOM calibration factor on the linear model has been investigated in the current work and results are shown in Table 5.1. The following terminology is used throughout this report:

- **TEOM (AURN)** – refers to data as directly read from the instrument (mass data calibrated with 1.03* TEOM + 3 µg)
- **TEOM (adjusted downward)** – refers to 'true' mass data, with the correction factor removed
- **1.3* TEOM (AURN)** – the adjusted data as reported to the Commission

It can be seen from Table 5.1 that the effect of the TEOM calibration factor is to change slightly the equation of the linear model, but not the quality of the linear relationship (represented by R^2). Moreover, it can be seen that the calibration factor applied to TEOM values explains a large part of the intercepts significantly higher than zero. For example, in the relationships between Partisol and TEOM mass (as shown in Table 5.1) the intercept is close to zero when the relationship between the two sets of data is considered good (i.e. $R^2 > 0.70$). Where linear relationships are observed of much poorer quality (i.e. Marylebone Road, Belfast and Port Talbot) results do not provide as consistent picture with respect to the impact of the TEOM calibration factor.

Table 5.1: Linear regressions with (in brackets), the confidence intervals for the slope and the intercept and the square of the Pearson correlation coefficients. First line: TEOM concentrations (AURN) vs. Partisol data; second line: TEOM (adjusted downward) concentrations vs. Partisol data. N is the number of observations included in the comparison. Concentrations in µg/m^3

Site	Linear regressions	Pearson R^2	N
Belfast Centre PM$_{10}$	$y = 0.508 (\pm0.025) x + 2.98 (\pm0.98)$ $y = 0.493 (\pm0.024) x - 0.02 (\pm0.95)$	0.26	315
Birmingham Centre PM$_{10}$	$y = 0.537 (\pm0.011) x + 3.92 (\pm0.31)$ $y = 0.522 (\pm0.010) x + 0.89 (\pm0.31)$	0.81	465
Glasgow Centre PM$_{10}$	$y = 0.670 (\pm0.023) x + 2.19 (\pm0.60)$ $y = 0.651 (\pm0.023) x - 0.79 (\pm0.58)$	0.70	247
Harwell PM$_{10}$	$y = 0.534 (\pm0.013) x + 3.91 (\pm0.26)$ $y = 0.518 (\pm0.012) x + 0.88 (\pm0.25)$	0.76	436
Harwell PM$_{2.5}$	$y = 0.437 (\pm0.012) x + 4.27 (\pm0.20)$ $y = 0.424 (\pm0.012) x + 1.24 (\pm0.19)$	0.63	461
London North Kens. PM$_{10}$	$y = 0.667 (\pm0.016) x + 3.24 (\pm0.44)$ $y = 0.648 (\pm0.016) x + 0.23 (\pm0.43)$	0.80	353
Marylebone Road PM$_{10}$	$y = 0.717 (\pm0.050) x + 0.90 (\pm2.52)$ $y = 0.696 (\pm0.049) x - 2.04 (\pm2.46)$	0.26	150
Marylebone Road PM$_{2.5}$	$y = 0.820 (\pm0.029) x + 2.51 (\pm0.87)$ $y = 0.796 (\pm0.028) x -0. 47 (\pm0.84)$	0.66	270
Port Talbot PM$_{10}$	$y = 0.930 (\pm0.041) x - 1.11 (\pm1.35)$ $y = 0.903 (\pm0.039) x - 3.99 (\pm1.31)$	0.36	334

In this report, both TEOM (adjusted downward) and TEOM (AURN) values are considered in the determination of certain relationships. The first to consider the 'true' TEOM values for the addition of particulate ammonium nitrate (Chapter 8), whilst the second is used to compare with other published data in considering the ratios of KFG to TEOM and Partisol to TEOM. For the comparison between KFG and TEOM and Partisol and TEOM, the consideration of whether raw or amended TEOM values are used does not change the conclusions.

For the relationship between the TEOM instrument and a filter-based gravimetric instrument, a zero intercept is expected. However, in reality a non-zero intercept is often found and interpreted as an artefact of the linear regression procedure, because it has no physical meaning. In this study, we have confirmed the influence of the linear regression procedure used. The TEOM calibration factor is also shown to contribute to the non-zero intercept.

6 Comparisons between Reference and Candidate Samplers

This Chapter details the results of the comparison studies between the reference (KFG) and candidate (TEOM and Partisol) samplers, and considers both period-mean statistics across summer and winter periods, and variations between years. Results are presented for contemporaneous daily measurements only.

6.1 Reference Sampler (KFG) vs. Candidate Sampler (TEOM)

6.1.1 Temporal Trends

Temporal trends in PM_{10} measurements across summer and winter seasons are shown in Appendix A (Figure A1 – Figure A6) for Marylebone Road, Harwell, Thurrock, Port Talbot, Glasgow and Belfast, respectively.

6.1.2 Period Mean Analysis

Table 6.1 summarises the seasonal period mean PM_{10} concentrations as measured by the KFG and the TEOM at the six sites. The number of paired observations varied from season-to-season and from site-to-site (depending upon data capture) and (in all but two cases) exceeded the recommended minimum number of forty observations, as specified in prEN12341.

In almost all cases, the TEOM has underestimated concentrations of PM_{10} when compared to filter-based gravimetric determinations using the KFG samplers. Exceptions to this were observed at Port Talbot (Summer '99) and Glasgow (Summer '01). In each of these cases, the TEOM analyser measured a slightly higher mean concentration of PM_{10} when compared to the KFG sampler, albeit by only about 1 $\mu g/m^3$.

The ratios of reference (KFG) to candidate (TEOM) concentrations vary from site to site, and from season to season. The lower ratios are consistently observed at Port Talbot (with ratios close to unity) with the highest ratios at Thurrock (with ratios in the general range of 1.4 to 1.5).

Table 6.1 Period mean PM_{10} measurements across sites and seasons alongside calculated ratios between reference and candidate samplers.

Site	Season (Dates)	Number of Obs. (n)	Period Mean		Ratio Ref.: Can.
			Ref. (KFG)	Cand. (TEOM)	
Marylebone Road	Summer ’99	81	42 (±17.4)	38 (±15.1)	1.11
	Winter ‘99/’00	141	45 (±17.3)	35 (±13.0)	1.29
	Summer ’00	84	50 (±21.7)	34 (±11.3)	**1.47**
	Winter ‘00/’01	76	46 (±15.8)	34 (±10.0)	**1.35**
	Summer ’01	118	37 (±16.1)	31 (±12.2)	1.19
	Winter ‘01/’02	71	42 (±17.3)	35 (±13.9)	1.20
Harwell	Summer ’99	68	17 (±9.4)	16 (±6.4)	1.06
	Winter ‘99/’00	144	17 (±10.2)	13 (±5.3)	**1.31**
	Summer ’00	135	18 (±14.5)	14 (±6.6)	1.29
	Winter ‘00/’01	117	18 (±13.8)	13 (±5.1)	**1.38**
	Summer ’01	127	15 (±9.2)	15 (±5.2)	1.00
	Winter ‘01/’02	151	18 (±11.4)	13 (±4.9)	**1.38**
	Summer ’02	147	18 (±12.2)	13 (±5.8)	**1.38**
Thurrock	Summer ’99	85	26 (±14.6)	19 (±9.0)	**1.37**
	Winter ‘99/’00	118	28 (±12.6)	20 (±8.1)	**1.40**
	Summer ’00	92	28 (±16.8)	18 (±8.3)	**1.56**
	Winter ‘00/’01	110	28 (±15.9)	17 (±7.8)	**1.65**
	Summer ’01	79	26 (±10.9)	18 (±5.3)	**1.44**
	Winter ‘01/’02	74	33 (±19.9)	22 (±13.2)	**1.50**
Port Talbot	Summer ’99[17]	18	22 (±10.1)	23 (±10.8)	0.96
	Winter ‘99/’00	90	26 (±14.9)	25 (±14.8)	1.04
	Summer ’00	108	27 (±19.1)	23 (±13.6)	1.17
	Winter ‘00/’01	130	25 (±14.9)	23 (±13.4)	1.09
	Summer ’01	131	25 (±14.3)	25 (±14.2)	1.00
	Winter ‘01/’02	132	31 (±21.2)	24 (±13.4)	1.29
	Summer ’02	29	26 (±11.5)	25 (±12.9)	1.04
Glasgow	Winter ‘99/’00	83	22 (±10.2)	21 (±7.6)	1.05
	Summer ’00	104	26 (±14.2)	25 (±12.8)	1.04
	Winter ‘00/’01	106	25 (±17.0)	17 (±7.3)	**1.47**
	Summer ’01	122	16 (±9.9)	17 (±8.7)	0.94
	Winter ‘01/’02	94	23 (±17.9)	17 (±10.8)	**1.35**
	Summer ’02	144	15 (±11.1)	14 (±6.4)	1.07
Belfast	Winter ‘99/’00[17]	19	32 (±21.4)	26 (±13.6)	1.23
	Summer ’00	144	21 (±13.6)	20 (±10.3)	1.05
	Winter ‘01/’02	153	23 (±14.1)	18 (±7.7)	1.28
	Summer ’02	134	18 (±12.6)	16 (±7.5)	1.13

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[17] The number of observations are less than 40 as specified in prEN12341.

6.1.3 RMA Regression Analysis

prEN12341 sets out the criteria in order to demonstrate equivalence between a candidate and the reference method. Notably, an R^2 of =0.95 is required. The RMA regression analyses for individual seasons across different sites are summarised in Table 6.2.

Table 6.2 Reduced Major Axis (RMA) regression analysis for the relationship between TEOM (AURN) and KFG concentrations across different sites and seasons.

Site	Season	Linear Regression Parameters	
		y = ax + b	R^2
Marylebone Road	Summer ’99	y = 0.8644x + 1.7027	0.8512
	Winter ‘99/’00	y = 0.7497x + 1.6576	0.8140
	Summer ’00	y = 0.5226x + 7.7738	0.3956
	Winter ‘00/’01	y = 0.6328x + 4.5749	0.7963
	Summer ’01	y = 0.7574x + 3.0330	0.7344
	Winter ‘01/’02	y = 0.8041x + 0.9366	0.7195
Harwell	Summer ’99	y = 0.6790x + 4.2770	0.3905
	Winter ‘99/’00	y = 0.5230x + 4.6880	0.4753
	Summer ’00	y = 0.4579x + 6.4020	0.3654
	Winter ‘00/’01	y = 0.3709x + 6.5660	0.4867
	Summer ’01	y = 0.5659x + 6.3617	0.4994
	Winter ‘01/’02	y = 0.4249x + 5.4193	0.6368
Thurrock	Summer ’99	y = 0.6183x + 2.8640	0.8687
	Winter ‘99/’00	y = 0.6443x + 1.4040	0.9160
	Summer ’00	y = 0.4948x + 4.5790	0.7778
	Winter ‘00/’01	y = 0.4939x + 2.6350	0.8308
	Summer ’01	y = 0.4838x + 5.1676	0.4775
	Winter ‘01/’02	y = 0.6628x + 0.0775	0.7494
Port Talbot	Summer ’99	y = 1.0739x – 0.8383	0.9357
	Winter ‘99/’00	y = 0.9943x – 04295	**0.9552**
	Summer ’00	y = 0.7098x + 3.7135	0.6057
	Winter ‘00/’01	y = 0.9113x – 0.5245	0.7433
	Summer ’01	y = 0.9930x + 0.5692	0.7681
	Winter ‘01/’02	y = 0.6315x + 4.3673	0.2724
Glasgow	Winter ‘99/’00	y = 0.6483x + 3.5080	0.7118
	Summer ’00	y = 0.8975x + 1.1019	0.6784
	Winter ‘00/’01	y = 0.4307x + 6.3457	0.4392
	Summer ’01	y = 0.8805x + 2.7990	0.7099
	Winter ‘01/’02	y = 0.6023x + 3.0080	0.3447
	Summer ‘02	y = 0.5751x + 5.3680	0.5589

Site	Season	Linear Regression Parameters	
Belfast	Winter '00/'01	y = 0.6387x + 5.7310	0.9258
	Summer '01	y = 0.7593x + 3.4627	0.7418
	Winter '01/'02	y = 0.5495x + 5.5257	0.6279
	Summer '02	y = 0.5933x + 4.5800	0.6887

Results of the RMA linear regression show that an R^2 of =0.95 was achieved on only one occasion at one site – Port Talbot in the winter of 1999/2000.

6.1.4 Exceedence Days

Table 6.3 summarises the number of days for each measurement method where the fixed 24-hour measurement exceeded 50 μg/m^3. The daily concentrations measured by the TEOM analyser have also been multiplied by a 1.3 factor, to investigate the application of the current default correction.

Table 6.3 Number of exceedence days (values > 50 μg/m^3) as measured by KFG, TEOM (AURN) and TEOM (AURN) x1.3 for different sites across different seasons. Figures in brackets highlight where occurrence of exceedence days is simultaneous between KFG and TEOM (AURN) and KFG and TEOM (AURN)x1.3

Site	Season	Number of Exceedence Days		
		KFG Daily conc > 50 mg/m³	TEOM (AURN) Daily conc > 50 mg/m³	TEOM (AURN) x 1.3 Daily conc > 50 mg/m³
Marylebone Road	Summer '99	15	9 (9)	29 (15)
	Winter '99/'00	53	18 (17)	58 (48)
	Summer '00	36	7 (7)	27 (22)
	Winter '00/'01	25	4 (4)	20 (15)
	Summer '01	23	5 (5)	36 (19)
	Winter '01/'02	23	9 (9)	23 (16)
	Total	**175**	**52 (51)**	**193 (135)**
Harwell	Summer '99	0	0 (0)	0 (0)
	Winter '99/'00	0	0 (0)	0 (0)
	Summer '00	8	0 (0)	0 (0)
	Winter '00/'01	5	0 (0)	0 (0)
	Summer '01	1	0 (0)	0 (0)
	Winter '01/'02	4	0 (0)	0 (0)
	Summer '02	2	0 (0)	1 (1)
	Total	**20**	**0 (0)**	**1 (1)**

Site	Season	Number of Exceedence Days		
		KFG Daily conc > 50 mg/m^3	TEOM (AURN) Daily conc > 50 mg/m^3	TEOM (AURN) x 1.3 Daily conc > 50 mg/m^3
Thurrock	Summer ’99	6	0 (0)	6 (4)
	Winter ‘99/’00	9	0 (0)	4 (3)
	Summer ’00	9	0 (0)	3 (3)
	Winter ‘00/’01	12	0 (0)	3 (3)
	Summer ’01	3	0 (0)	0 (0)
	Winter ‘01/’02	11	3 (3)	6 (5)
	Total	**50**	**3 (3)**	**22 (18)**
Port Talbot	Summer ’99	0	1 (0)	2 (0)
	Winter ‘99/’00	8	7 (7)	18 (8)
	Summer ’00	12	5 (5)	12 (8)
	Winter ‘00/’01	11	7 (7)	17 (8)
	Summer ’01	9	8 (6)	17 (8)
	Winter ‘01/’02	12	7 (6)	17 (6)
	Summer ‘02	2	2(1)	4 (1)
	Total	**53**	**36 (31)**	**86 (38)**
Glasgow	Winter ‘99/’00	2	0 (0)	2 (0)
	Summer ’00	9	5 (4)	13 (7)
	Winter ‘00/’01	13	0 (0)	2 (2)
	Summer ’01	0	0 (0)	4 (0)
	Winter ‘01/’02	11	2 (2)	2 (2)
	Summer ‘02	4	0 (0)	2 (1)
	Total	**40**	**7 (4)**	**27 (8)**
Belfast	Winter ‘00/’01	5	1 (1)	4 (4)
	Summer ’01	8	3 (3)	7 (6)
	Winter ‘01/’02	7	1 (1)	2 (2)
	Summer ‘02	3	0 (0)	2 (1)
	Total	**23**	**5 (5)**	**15 (13)**

The number of recorded exceedence days varies from site to site, and from season to season. The highest number of exceedences are recorded at those sites with the highest annual mean concentrations (i.e. Marylebone Road) as might be expected. Conversely, the site showing the lowest historical annual mean PM_{10} concentrations shows the lowest level of exceedences (i.e. Harwell).

Application of the current default 1.3 factor to the TEOM (AURN) data shows a variable agreement with the number of exceedences as measured by the KFG. At some sites, the 1.3 factor is generally conservative (e.g. Marylebone Road), whilst at other sites the default factor still leads to an under-estimation of the ‘true’ number of exceedence days.

6.2 Reference Sampler (KFG) vs. Candidate Sampler (Partisol 2025)

6.2.1 Temporal Trends

Temporal trends in PM_{10} measurements across summer and winter seasons are shown in Appendix A (Figure A1 – Figure A6) for Marylebone Road, Harwell, Thurrock, Port Talbot, Glasgow and Belfast, respectively.

Figure 6.1 describes the relationship for Partisol versus KFG data for the 5 sites (Marylebone Road, Harwell, Port Talbot, Glasgow and Belfast).

6.2.2 Period Mean Analysis

The following tables present: a) the mean PM_{10} particle mass collected with the KFG and the Partisol samplers (Table 6.4); b) the RMA linear regressions and Pearson correlation coefficients for Partisol versus KFG comparisons and the mean ratios KFG/Partisol (Table 6.5), and c) the number of exceedence days for the whole studied period from the Partisol and the KFG (Table 6.6).

Table 6.4: Daily arithmetic means (presented with standard deviations in brackets) for PM_{10} concentrations. Concentrations in $\mu g/m^3$

Site	Arithmetic mean (± Standard deviation)	
	LVS	Partisol
Belfast	22.0 (± 14.2)	32.2 (± 19.9)
Glasgow	21.1 (± 15.4)	22.8 (± 12.9)
Harwell	16.5 (± 11.3)	18.0 (± 9.7)
Marylebone Road	40.6 (± 15.7)	45.7 (± 16.6)
Port Talbot	27.0 (± 14.4)	29.4 (± 14.8)

6.2.3 RMA Regression Analysis

Table 6.5 shows the results of the RMA analysis across all seasons for the comparison of KFG v Partisol results.

Table 6.5: RMA linear regressions for Partisol PM_{10} vs. KFG PM_{10} data and mean ratios KFG/Partisol

Site	RMA linear regression	Pearson R^2	Ratios KFG/Partisol
Belfast Centre	-	0.23	0.78 (± 0.46)
Glasgow Centre	y = 0.837 (±0.047) x + 5.14 (±1.26)	0.48	0.93 (± 0.54)
Harwell	y = 0.855 (±0.024) x + 3.96 (±0.48)	0.71	0.91 (± 0.39)
Marylebone Road	y = 1.055 (±0.058) x + 2.87 (±2.57)	0.48	0.93 (± 0.30)
Port Talbot	-	0.35	1.01 (± 0.53)

Results of the analysis of the mean PM_{10} concentration data between KFG and Partisol samplers show that, in general, the Partisol unit measures marginally higher concentrations of PM_{10} when compared to the KFG, but the regression coefficients are poor (R^2 0.23-0.71). Whilst the best fit relationship is shown at Harwell, the computed linear model shows a slope significantly different than 1 and an intercept significantly different than 0 (albeit the later is approximately the TEOM 'calibration factor' value).

6.2.4 Exceedence Days

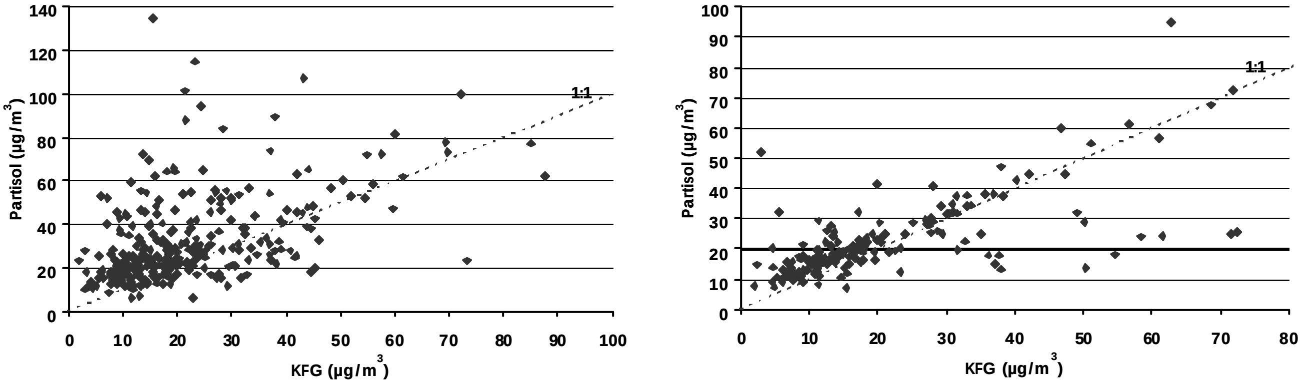
Table 6.6. summarises the number of exceedence days (daily mean values > 50 $\mu g/m^3$) measured by both the KFG and the Partisol samplers during the course of the work. Additional information with respect to the number of exceedence days when simultaneous measurements greater than 50 $\mu g/m^3$ are also included.

Table 6.6: Number of exceedence days from KFG and Partisol and number of exceedence days measured simultaneously by the two methods

Site	KFG Daily conc > 50 mg/m^3	Partisol Daily conc > 50 mg/m^3	No. Exceedence Days Measured Simultaneously
Belfast Centre	15	51	13
Glasgow Centre	13	8	6
Harwell	8	6	6
Marylebone Road	47	61	38
Port Talbot	23	26	11

The examination of the number of exceedence days for each sampler and each site is in agreement with the previous conclusions, although it appears that, in this instance the Partisol 2025 provides a generally more conservative estimate than the KFG.

Figure 6.1: Partisol versus KFG(LVS) for PM_{10} for (a) Belfast, (b) Glasgow, (c) Harwell, (d) Marylebone Road, (e) Port Talbot

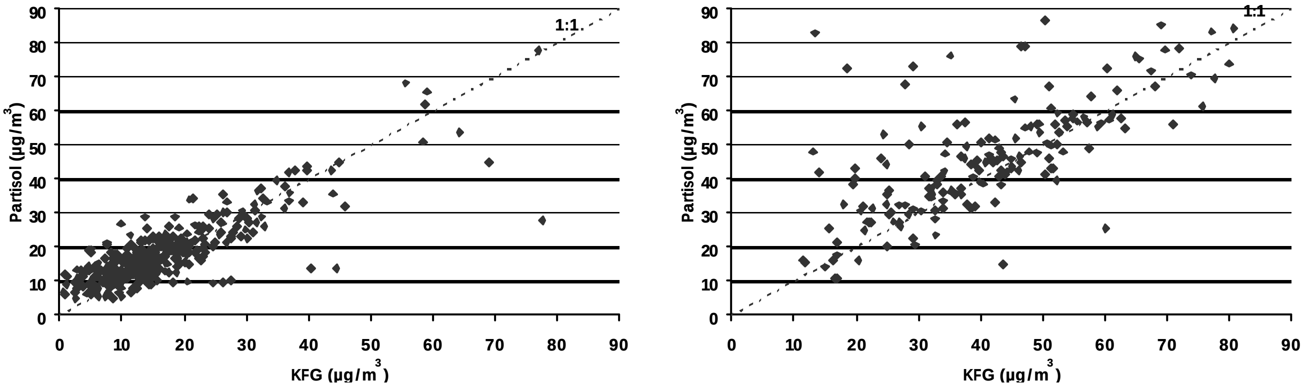


(a) Belfast

(b) Glasgow

(c) Harwell

(d) Marylebone Road



(e) Port Talbot

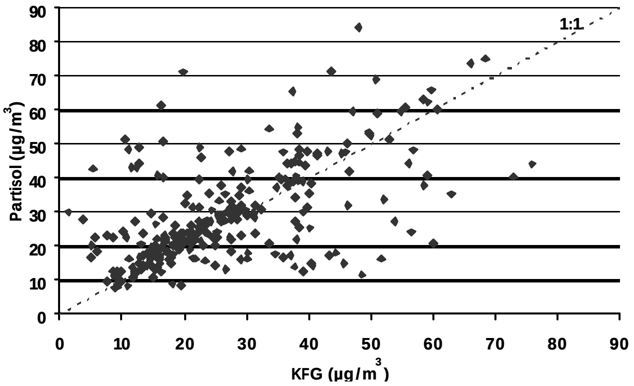
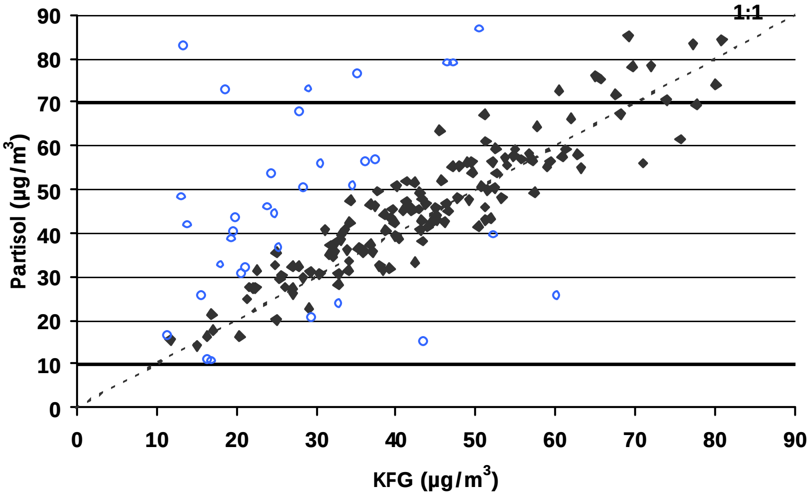


Figure 6.1 indicates that the poor relationships between the KFG and Partisol samplers found for Glasgow, Marylebone Road and Port Talbot, is the result of a large number of spread values. These sites have a significant number of paired data around the 1:1 line, indicating that for these paired data a relatively good agreement is found.

Th results indicate that some considerable 'uncertainty' exists with respect to the accuracy of some of the data points. Whether these values could be legitimately disregarded is open to debate, given that the quality assurance checks provide no reason to do so. However, if it were assumed that the data were suspect, and consequently removed, the relationship between the KFG and Partisol samplers is much improved. As an example, for Marylebone Road (see Figure 6.2), the regression on remaining values having discarded those that are 'suspect' gives the linear model y = 1.014 (±0.034) x + 1.33 (±1.55) and a square Pearson correlation coefficient of 0.85.

Figure 6.2 : Partisol versus KFG data for Marylebone Road. The blue circle dots are the discarded values.



6.2.5 Which PM$_{10}$ data are suspicious?

The study of how the three datasets (KFG, TEOM and Partisol) are related might suggest which data are not 'reliable'. Table 6.7 presents the results of a regression analysis between each paired dataset, and corresponding to simultaneous data with the three methods.

Table 6.7: Linear regressions for Partisol PM$_{10}$ vs. KFG; TEOM (AURN) vs KFG; TEOM (AURN) vs; Partisol for PM$_{10}$ data

Site	Paired data	RMA linear regressions	Pearson R^2	N
Belfast Centre	Partisol vs. KFG	-	0.23	260
	TEOM vs. KFG	y = 0.684 (±0.022) x + 3.76 (±0.62)	0.73	
	TEOM vs. Partisol	-	0.27	
Glasgow Centre	Partisol vs. KFG	-	0.38	157
	TEOM vs. KFG	-	0.47	
	TEOM vs. Partisol	y = 0.683 (±0.029) x + 2.12 (±0.79)	0.72	
Harwell	Partisol vs. KFG	y = 0.858 (±0.025) x + 3.88 (±0.51)	0.71	346
	TEOM vs. KFG	y = 0.452 (±0.017) x + 6.10 (±0.35)	0.53	
	TEOM vs. Partisol	y = 0.527 (±0.015) x + 4.06 (±0.31)	0.73	
Marylebone Road	Partisol vs. KFG	-	0.42	132
	TEOM vs. KFG	y = 0.812 (±0.035) x + 1.05 (±1.48)	0.76	
	TEOM vs. Partisol	-	0.35	
Port Talbot	Partisol vs. KFG	-	0.35	252
	TEOM vs. KFG	y = 0.962 (±0.030) x - 0.17 (±0.93)	0.75	
	TEOM vs. Partisol	-	0.40	

The poor relationships between paired data including the Partisol and the good relationship between TEOM and KFG for Belfast, Marylebone Road and Port Talbot may suggest that for these three sites the Partisol data are not 'reliable'.

The poor relationships between paired data including the KFG and the good relationship between TEOM and Partisol for Glasgow suggest that for this site the KFG data are not 'reliable'.

The poorer relationship between TEOM and KFG than between Partisol and KFG and TEOM and Partisol for Harwell shows that some KFG data in Harwell dataset are not 'reliable'.

6.2.6 Why should some gravimetric PM_{10} data be unreliable?

The data collected in this study have been subject to detailed verification procedures. All filter weighings have been undertaken by UKAS-accredited laboratories, and in instances where suspicious results have been reported, the data have been cross-checked.

There are however a number of issues that may give rise to uncontrolled loss of particles from the filters before they are weighed:

- The filters in the KFG sampler remain exposed beneath the metal sampling head for up to 7 days. It is possible that losses of some semi-volatile particles may occur, depending upon the ambient temperatures and nature of the particle mass.
- The flow rate of the Partisol sampler is about half of that in the KFG. Lower flow samplers are more likely to be affected by moisture and static effects during weighing, and a higher standard deviation would be expected.
- The filters in the Partisol 2025 sampler are retained in the filter magazine for up to 14 days. It is expected that particle loss from within the magazine would be lower than from the KFG, as the filters are not directly exposed to the ambient environment.
- The majority of filters are transported from the site to the laboratory via the postal system. There is the potential that loose particles on the filter surface may be lost during transport.

It is noted that some of these issues are being addressed in the CEN reference method for $PM_{2.5}$, and the most recent draft includes specifications for maintaining the filters in a controlled low-temperature environment within several hours of sampling completion.

6.3 Candidate Sampler (Partisol 2025) vs. Candidate Sampler (TEOM)

6.3.1 Temporal Trends

Temporal trends in PM_{10} measurements across summer and winter seasons are shown in Appendix A (Figure A1 – Figure A6) for Marylebone Road, Harwell, Thurrock, Port Talbot, Glasgow and Belfast, respectively.

6.3.2 Period Mean Analysis

Table 6.8 summarises the mean PM_{10} concentrations across Partisol samplers and TEOM analysers; the latter also includes a consideration to adjustment due to the TEOM calibration factor. Additionally, results are included for the 1.3* TEOM data. Standard deviations are included in order to provide a measure of the spread in daily mean values.

Table 6.8: Daily mean PM_{10} (presented with standard deviations in brackets) concentrations ($\mu g/m^3$)

Site	Arithmetic mean ± SD			
	Partisol	TEOM (AURN)	TEOM (adj.)	1.3 TEOM
Belfast Centre	32.6 (± 20.1)	19.5 (± 10.2)	16.0 (±9.9)	25.4 (± 13.3)
Birmingham Centre	25.3 (± 14.3)	17.5 (± 7.7)	14.1 (±7.4)	22.7 (± 10.0)
Glasgow Centre	22.5 (± 12.1)	17.3 (± 8.1)	13.9 (±7.9)	22.5 (± 10.6)
Harwell	18.0 (± 10.2)	13.5 (± 5.4)	10.2 (±5.3)	17.6 (± 7.0)
London North Kens.	24.6 (± 12.2)	19.6 (± 8.2)	16.1 (±7.9)	25.5 (± 10.6)
Marylebone Road	45.8 (± 17.9)	33.7 (± 12.8)	29.8 (±12.5)	43.8 (± 16.7)
Port Talbot	28.9 (± 14.7)	25.8 (± 13.7)	22.1 (±13.3)	33.5 (± 17.8)

Results indicate that the TEOM underestimates the particle mass at all sites, relative to the results of the Partisol measurements. The difference is larger at Belfast and Marylebone Road, and is smaller at Port Talbot. However, analysis in the previous section has shown that some suspicion may surrounds data in the Partisol data set, and therefore the conclusion should be treated with caution. With the exception of Belfast and Port Talbot, the 1.3 factor gives mean concentrations close to the Partisol values for all other sites.

Table 6.9 provides analysis of period mean ratios between the Partisol and the TEOM, alongside the corresponding standard deviation, covering the whole studied period.

Ratios close to 1.3 (± 10%) are found for almost all sites except Belfast and Marylebone Road. However, there are high standard deviations are found, especially for Glasgow and Port Talbot. This result is in agreement with other studies (King et al., 2000; Cyrys et al., 2001; Green et al., 2001) showing the variability from one day to another. Additionally, different ratios are found for the different sites, showing that a single correction factor cannot reasonably be applied to all sites.

Table 6.9: Mean and standard deviation for ratios Partisol/TEOM for PM_{10} particle mass

Site	Ratios Partisol/TEOM (AURN)	Ratios Partisol/ TEOM (adjusted)	N
Belfast Centre	1.80 (± 1.08)	2.36 (± 1.63)	315
Birmingham Centre	1.41 (± 0.37)	1.85 (± 0.54)	465
Glasgow Centre	1.34 (± 0.55)	1.80 (± 1.10)	247
Harwell	1.30 (± 0.35)	1.81 (± 0.51)	436
London North Kens.	1.24 (± 0.27)	1.55 (± 0.35)	353
Marylebone Road	1.51 (± 1.12)	1.80 (± 1.59)	150
Port Talbot	1.23 (± 0.61)	1.54 (± 0.89)	334

6.3.3 RMA Regression Analysis

The RMA linear regression between TEOM and Partisol data is presented in Table 6.10 across all sites.

Table 6.10: RMA linear regressions for Partisol PM_{10} vs. TEOM PM_{10} data

Site	Linear regressions	Pearson R^2	N
Belfast Centre	y = 0.508 x + 2.98	0.26	315
Birmingham centre	y = 0.537 x + 3.92	0.81	465
Glasgow centre	y = 0.670 x + 2.19	0.70	247
Harwell	y = 0.534 x + 3.91	0.76	436
London North Kens.	y = 0.667 x + 3.24	0.80	353
Marylebone Road	y = 0.717 x + 0.896	0.26	150
Port Talbot	y = 0.930 x - 1.11	0.36	334

The results of the RMA linear regression analysis show similar variability to that of previous relationships between gravimetric and TEOM samplers. For Birmingham, Glasgow, Harwell and London North Kensington an $R^2 > 0.70$ is found, whilst poorer relationships are observed for sites at Belfast, Marylebone Road and Port Talbot ($R^2 < 0.50$). With the exception of Marylebone Road and Port Talbot, the intercept of the relationship is approximately equal to that of the TEOM ‘calibration factor’.

6.3.4 Exceedence Days

Table 6.11 presents the number of exceedence days for the whole studied period from the Partisol, the TEOM (adjusted downward), the TEOM (AURN) values and the TEOM (AURN) values adjusted by the 1.3 calibration factor. Results show that the TEOM largely underestimates the number of exceedence days for all sites with the exception of Port Talbot. Any adjustment to the TEOM data taking into consideration the calibration factor (1.03* TEOM + 3 μg/m^3) does not improve significantly the number of exceedence days.

When we consider the total number of exceedence days, the 1.3 factor gives reasonably good results for Glasgow, London North Kensington and Marylebone Road, but it substantially underestimates the number of exceedences at Birmingham. Additionally, for most of the sites, the new exceedence days do not coincide with the filter-based method exceedence days, indicating the random character of occurrence.

Table 6.11: Number of exceedence days from Partisol, TEOM (AURN), TEOM (adjusted downward) and 1.3 TEOM data: second line shows the number of simultaneous TEOM and Partisol exceedence days out of the total number observed; N is the number of observations included in the comparison

Site	PARTISOL Daily conc > 50 mg/m^3	TEOM (AURN) Daily conc > 50 mg/m^3	TEOM (adjusted) Daily conc > 50 mg/m^3	1.3 TEOM Daily conc > 50 mg/m^3	N
Belfast Centre	53	6	5	16 [13/53]	315
Birmingham Centre	32	2	0	12 [11/32]	465
Glasgow Centre	10	1	1	7 [3/10]	247
Harwell	8	0	0	2 [2/8]	436
London N. K.	14	3	2	12 [8/14]	353
Marylebone Road	54	9	7	52 [33/54]	150
Port Talbot	30	22	18	58 [18/30]	334

7 Comparison between the Partisol and TEOM data for PM_{10} and for $PM_{2.5}$ (Harwell and Marylebone Road)

In addition to the gravimetric PM_{10} measurements made at Harwell and Marylebone Road sites (as reported in the previous Chapters of this report) gravimetric measurements of $PM_{2.5}$ are also undertaken. Table 7.1 shows the results of daily mean $PM_{2.5}$ measurements made at these two sites during the same period as those measured by a TEOM also measuring the $PM_{2.5}$ fraction as part of a UK-wide research project.

Table 7.1: Daily mean $PM_{2.5}$ (presented with standard deviations) concentrations (µg/m^3)

Site	Arithmetic mean ± SD		
	Partisol	TEOM (AURN)	TEOM (adj.)
Harwell	12.3 (±9.9)	9.6 (±4.3)	6.5 (±4.2)
Marylebone Road	27.3 (±11.2)	24.9 (±9.2)	21.2 (±8.9)

Results show that, when compared to the PM_{10} fraction reported in earlier Chapters the difference between Partisol data and TEOM (AURN) data is smaller. Because most of the semi-volatile material is contained in the $PM_{2.5}$ fraction, a good correspondence between the difference between Partisol and TEOM data for PM_{10} and for $PM_{2.5}$ is expected. Figures 7.1 and 7.2 show the absolute differences between Partisol and TEOM data for Harwell and Marylebone Road sites, respectively.

A good agreement is found for Harwell, whilst a much poorer one is found for Marylebone Road. At Marylebone Road, higher differences between Partisol and TEOM (adjusted downward) data are found for PM_{10} than for $PM_{2.5}$ and the data are more scattered (this may be the result of some 'unreliable' Partisol data (see comparison between Partisol and KFG data). At Harwell, most of the semi-volatile compounds are contained in the $PM_{2.5}$ fraction.

For both sites, a few large differences between Partisol and TEOM (adjusted downward) data for PM_{10} are found when compared to those for $PM_{2.5}$ which are low in comparison Moreover, some negative values of differences for $PM_{2.5}$ (i.e. TEOM data higher than Partisol data) are observed. The first type of difference between measurements may be the result of particle-bound water associated with PM_{coarse} particles, while the second type is more difficult to explain and may be due to artefacts in the monitoring procedures.

Figure 7.1 : Absolute difference between Partisol and TEOM (adjusted downward) PM_{10} data versus absolute difference between Partisol and TEOM (adjusted downward) $PM_{2.5}$ data for Harwell

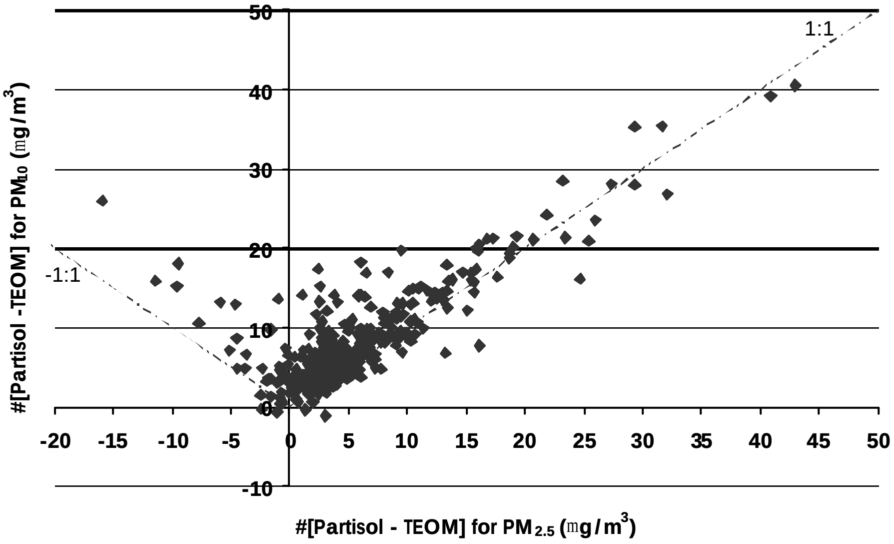
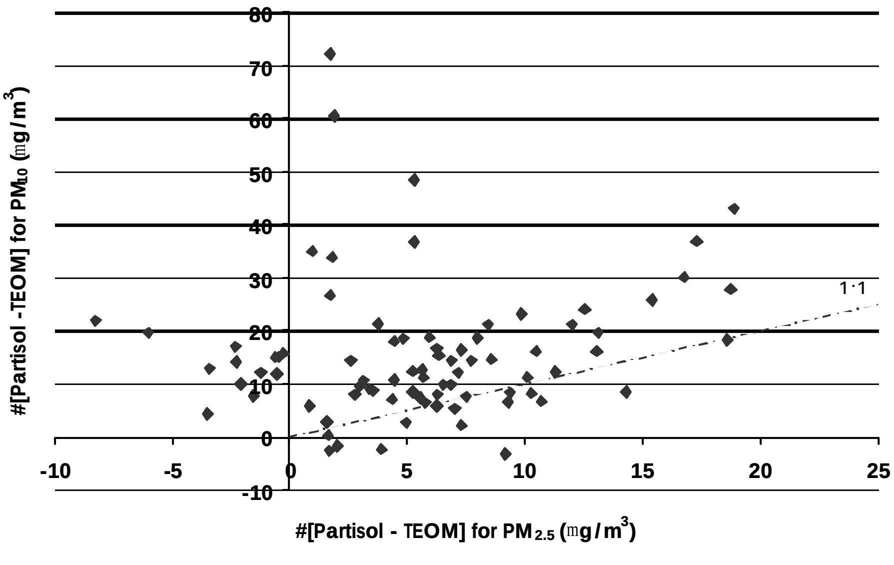


Figure 7.2 : Absolute difference between Partisol and TEOM (adjusted downward) PM_{10} data versus absolute difference between Partisol and TEOM (adjusted downward) $PM_{2.5}$ data for Marylebone Road



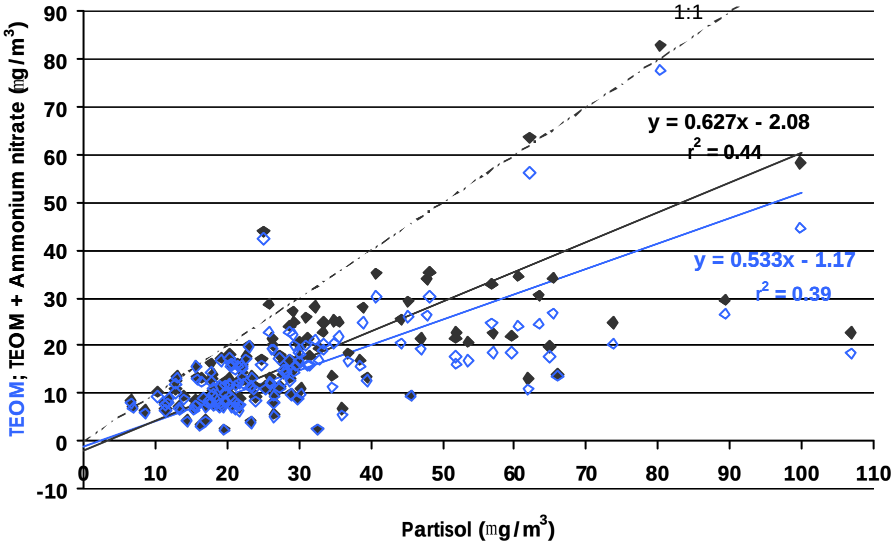
8 Examination of particulate ammonium nitrate

In order to improve understanding of the underestimation of the TEOM and the apparent lack of relationship between Partisol and TEOM mass concentrations, an examination of the particulate ammonium nitrate has been carried out. The particulate ammonium nitrate is well known to be very volatile depending on the atmospheric conditions (Stelson and Seinfeld, 1982a and 1982b) and is thought to be one of the major particulate volatile compounds lost in the TEOM inlet.

Particulate nitrate is measured at two sites, Belfast and Harwell. The particulate ammonium nitrate is computed from the particulate nitrate and assumes that all particulate nitrate is associated with ammonium ions. The particulate ammonium nitrate is added to the TEOM particle mass concentrations. The following figures represent the relationships between the sum of TEOM (adjusted downward) particle mass data and particulate ammonium nitrate with Partisol particle mass respectively for Belfast and Harwell.

The particulate ammonium nitrate corresponded on average to 8.9 ± 13.1 % of the particulate material lost by the TEOM at Belfast (assumed to be mainly semi-volatile inorganic compounds like ammonium nitrate, ammonium chloride, semi-volatile organic compounds and particle-bound water). The relationship between the two instruments is slightly improved adding the particulate ammonium nitrate. The contribution of the particulate ammonium nitrate is very small for the lowest concentrations of PM_{10}.

Figure 8.1 : TEOM (adjusted downward) PM_{10} data (in blue) and TEOM (adjusted downward) PM_{10} data + Particulate ammonium nitrate (in black) versus Partisol PM_{10} data for Belfast (N = 145)



There is no agreement between the differences in mass between the two instruments and the particulate ammonium nitrate for Belfast (see Figure 8.2). The influence of some not reliable Partisol values might explain this result. These results show that at Belfast, the particulate ammonium nitrate does not contribute significantly to the difference between the two instruments.

Figure 8.2: Absolute difference between Partisol PM_{10} data and TEOM (adjusted downward) PM_{10} data versus particulate ammonium nitrate for Belfast (N = 145)

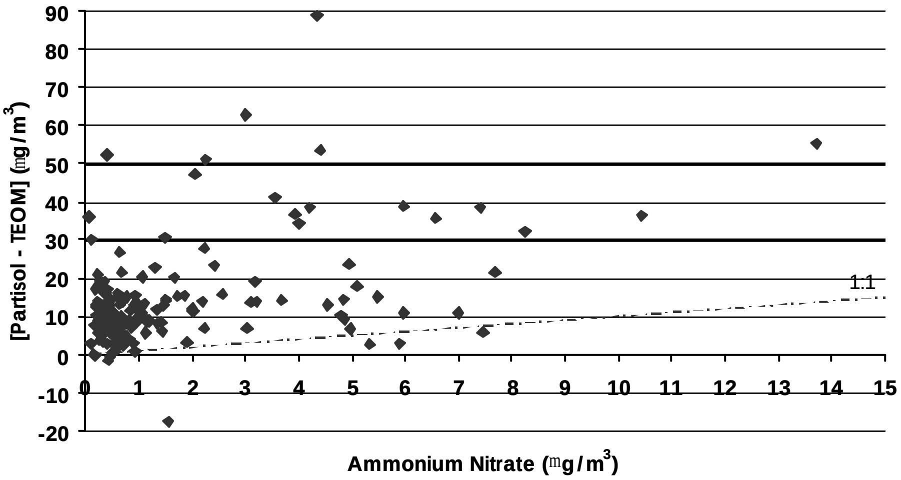


Figure 8.3: TEOM (adjusted downward) PM_{10} data (in blue) and TEOM (adjusted downward) PM_{10} data + Particulate ammonium nitrate (in black) versus Partisol PM_{10} data for Harwell data (N = 146)

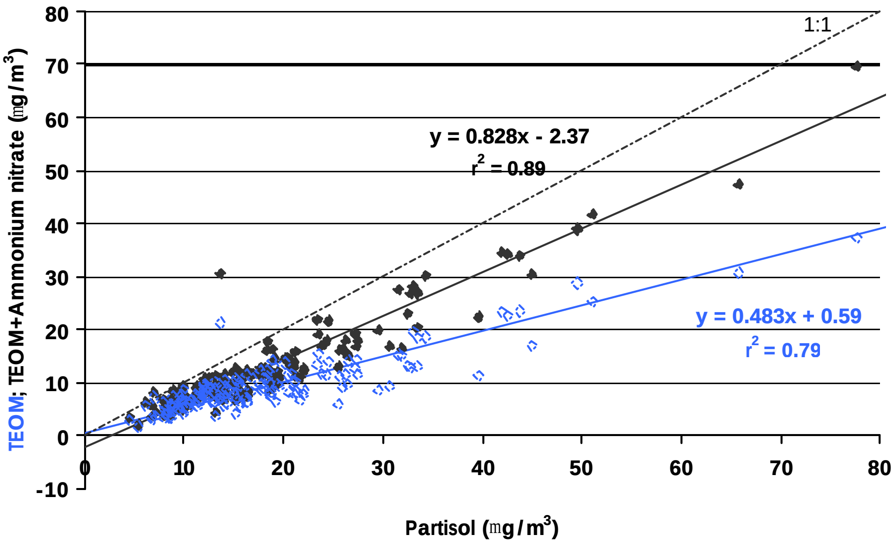
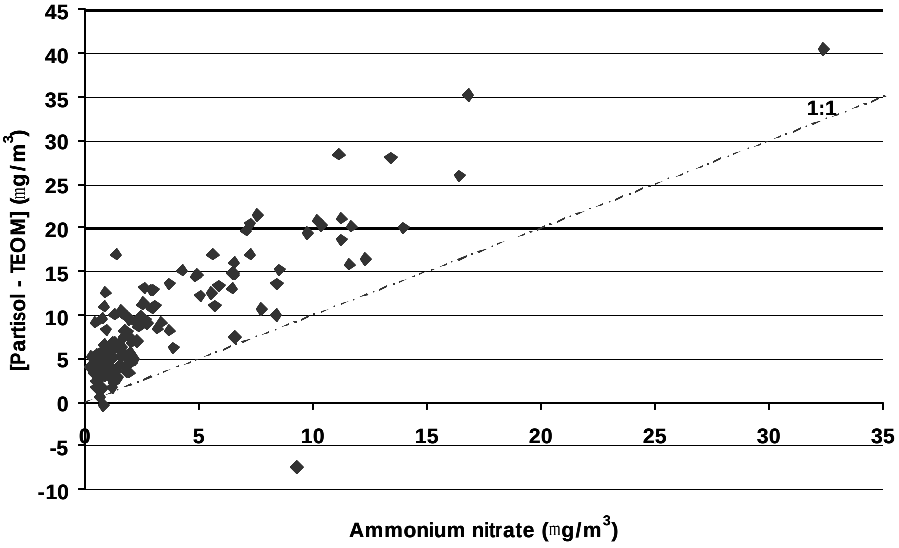


Figure 8.4 : Absolute difference between Partisol PM$_{10}$ data and TEOM (adjusted downward) PM$_{10}$ data versus particulate ammonium nitrate for Harwell (N = 146)



Both PM$_{10}$ and PM$_{2.5}$ Harwell TEOM data are significantly improved by adding the particulate ammonium nitrate (relationships with the Partisol data are significantly improved, see Figures 8.3 and 8.5). Good relationships are found between the differences between Partisol and TEOM (adjusted downward) data and the particulate ammonium nitrate for both PM$_{10}$ and PM$_{2.5}$. For concentrations of particulate ammonium nitrate higher than 2-3 µg/m^3, the relationship between the difference between Partisol and TEOM (adjusted downward) data and particulate ammonium nitrate is linear. For concentrations lower than 2-3 µg/m^3, the relationship is poor indicating the contribution of other species.

Figure 8.5: TEOM (adjusted downward) $PM_{2.5}$ (in blue) and TEOM (adjusted downward) $PM_{2.5}$ data + Particulate ammonium nitrate (in black) versus Partisol $PM_{2.5}$ for Harwell data (N = 161)

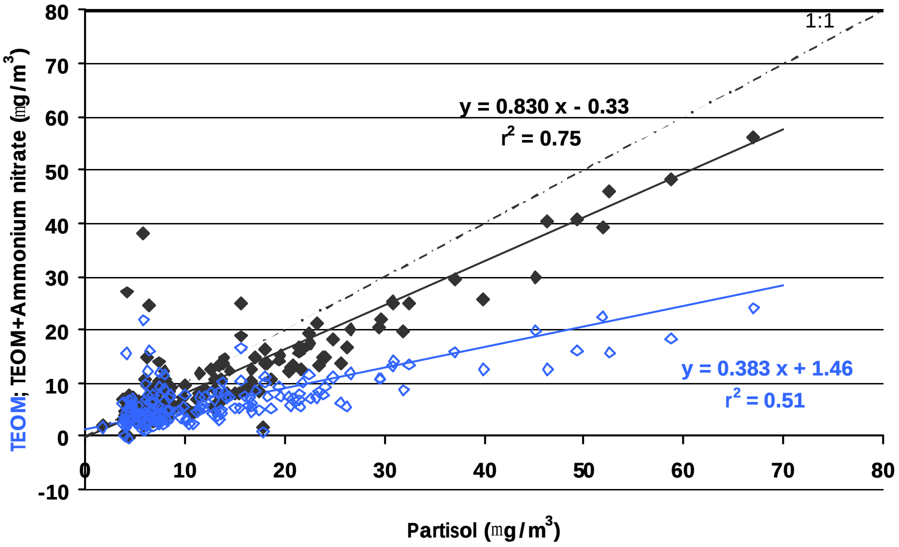
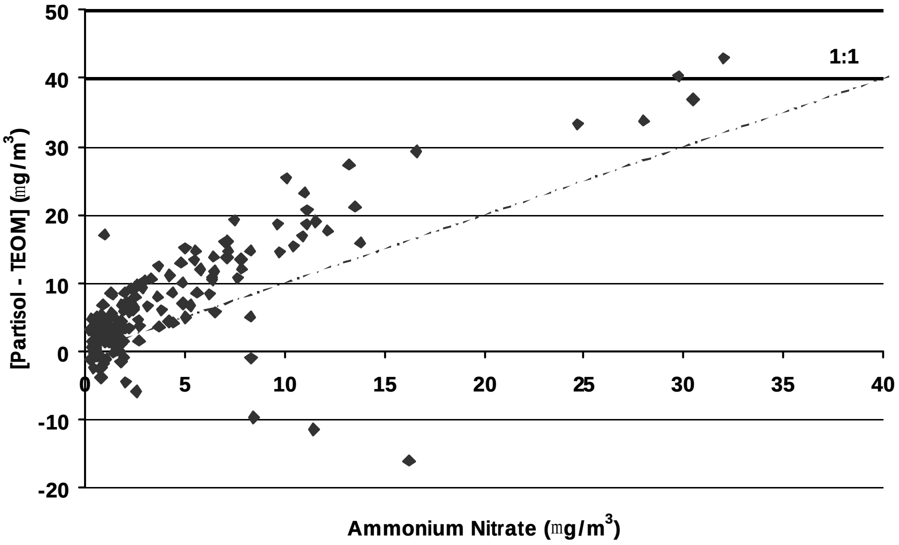


Figure 8.6: Absolute difference between Partisol $PM_{2.5}$ data and TEOM (adjusted downward) $PM_{2.5}$ data versus particulate ammonium nitrate for Harwell (N = 161)



The particulate ammonium nitrate corresponded on average to 26.4 ± 25.2 % of the material lost in PM_{10} and 40.5± 43.5 % of the material lost in the $PM_{2.5}$ in Harwell. It should be noted that Harwell has higher concentrations of particulate nitrate (median: 1.5 $\mu g/m^3$) than Belfast (median: 0.65 $\mu g/m^3$); while the underestimation of the TEOM at Belfast is much higher.

The addition of the ammonium nitrate to the TEOM (adjusted downward) mass improves the relationship between the Partisol and the TEOM data. The improvement is stronger for Harwell and additionally, for Harwell data, the nitrate concentrations and the difference between Partisol and TEOM are fairly proportional (that is not the case for Belfast). For Harwell and more especially Belfast, the contribution of the ammonium nitrate does not explain the whole difference between TEOM particle mass concentrations and filter-based Partisol particle mass concentrations, showing that an important part lost is likely semi-volatile organic compounds or particle-bound water.

Allen et al. (1997) found that the entire difference between a TEOM and a manual filter-based method for the Rubidoux site (California) can be attributed to the particulate ammonium nitrate. On the contrary, Cyrys et al (2001) found a small contribution of the ammonium nitrate at their site. These results are in agreement with those of this study; all are reflecting the different aerosol composition in different sites and explaining the wide range of relationships found.

9 Examination of the seasonal variations and influence of meteorological parameters

Comparisons between TEOMs and reference gravimetric methods in different countries have shown that for warmer and dryer regions the agreement is better than for colder and damper regions (Williams and Bruckmann, 2001; Noack et al., 2001). Similarly, other studies have shown that the agreement is better during the warmer months of the year than during the colder months (Allen et al., 1997; Williams and Bruckmann, 2001). Williams and Bruckmann (2001) recommend the examination of the seasonal variations of factors and equations to amend the data.

The amount of semi-volatile-compounds associated with the particles is expected to depend on the temperature, the relative humidity and its gas-phase concentrations. The above-cited results agree with this suggestion. In this part, we examine first the seasonal variations for the different studied sites and second, two meteorological factors, the temperature and the relative humidity, that influence the relationship between TEOMs and filter-based gravimetric methods.

9.1 Seasonal variations

The means, ratios Partisol/TEOM, and linear regression analyses (Tables 9.1, 9.2) are computed for two different seasons, the Summer season (from the 1st of April to 30th of September) and the Winter season (from the 1st of October to the 31st of March). The means and the ratios are not included when the number of paired observations is below 30 (the dataset is not considered sufficiently representative).

In Table 9.2, linear models are computed with TEOM (AURN) values. The linear models computed with TEOM (adjusted downward) values are in Annex 6. The linear model is not included when N is below 30 (dataset is not considered sufficiently representative) or when r^2 is below 0.50 (no meaning); the linear model is not considered reliable enough when $0.50 < r^2 < 0.80$.

It should be noted that PM_{10} and $PM_{2.5}$ mass data do not seem to vary seasonally at the different studied sites.

No obvious and strong seasonal variations come out from these results. Nevertheless, there are possible seasonal variations for Birmingham, Glasgow, Harwell and London North Kensington if Summer 2002 is excluded. Ratios for summer 2001 are lower than those for winter 2000/2001 and winter 2001/2002 for these sites; but summer 2002 shows higher ratios than summer 2001 and similar to both winter periods.

Stable seasonal linear regressions can be seen for the Birmingham (see Table 9.2) and possibly Glasgow sites (summer 2002 is missing in Glasgow data) and London North Kensington if summer 2002 is excluded. Similar linear models for PM_{10} have been found for summer 2001-summer 2002 and winter 2000/2001-winter 2001/2002 for Birmingham and for both winters for Glasgow and London North Kensington suggests that different models might be used according to the season (nevertheless, the correlation coefficient are sometimes not adequate).

No obvious seasonal variations come out from the ratios and the linear models for $PM_{2.5}$.

Table 9.1: Seasonal mean PM_{10} and $PM_{2.5}$ for Partisol, TEOM (AURN) and in brackets for TEOM (adjusted values) data; alongside mean ratios between Partisol and TEOM (AURN) with in brackets, ratios for TEOM (adjusted values) values.

PM_{10}	Seasons	Number of observations	Period Means		Ratio
			Partisol	TEOM	Partisol:TEOM
Belfast	Winter 01	18	-	-	-
	Summer 01	133	32.5	20.2 (16.7)	1.78 (2.33)
	Winter 01-02	86	32.3	18.6 (15.2)	1.83 (2.44)
	Summer 02	78	31.1	17.6 (14.2)	1.81 (2.40)
Birmingham	Summer 00	4	-	-	-
	Winter 00-01	127	28.6	17.7 (14.3)	1.59 (2.06)
	Summer 01	157	21.7	16.7 (13.3)	1.28 (1.71)
	Winter 01-02	124	25.8	17.6 (14.2)	1.44 (1.86)
	Summer 02	57	27.6	19.1 (15.7)	1.42 (1.79)
Glasgow	Winter 00-01	90	25.3	17.9 (14.5)	1.47 (2.00)
	Summer 01	114	19.8	16.8 (13.4)	1.21 (1.62)
	Winter 01-02	43	24.1	17.1 (13.7)	1.40 (1.87)
Harwell	Summer 00	1	-	-	-
	Winter 00-01	130	18.3	13.0 (9.7)	1.36 (1.91)
	Summer 01	138	18.1	15.1 (11.8)	1.17 (1.55)
	Winter 01-02	91	17.8	13.0 (9.7)	1.34 (1.84)
	Summer 02	76	17.9	12.4 (9.1)	1.40 (2.06)
London N.K.	Summer 00	3	-	-	-
	Winter 00-01	51	24.1	17.9 (14.4)	1.33 (1.70)
	Summer 01	121	22.3	19.7 (16.3)	1.13 (1.40)
	Winter 01-02	140	25.5	19.7 (16.2)	1.28 (1.60)
	Summer 02	38	28.9	21.7 (18.2)	1.29 (1.60)
Marylebone Road	Summer 00	5	-	-	-
	Winter 00-01	43	52.4	35.1 (31.2)	1.83 (2.25)
	Summer 01	54	39.0	29.8 (26.0)	1.39 (1.65)
	Winter 01-02	48	48.0	36.3 (32.3)	1.41 (1.62)
Port Talbot	Winter 00-01	87	27.7	26.0 (22.3)	1.25 (1.58)
	Summer 01	93	29.2	26.7 (23.0)	1.27 (1.59)
	Winter 01-02	95	28.9	25.4 (21.7)	1.18 (1.46)
	Summer 02	59	30.3	24.9 (21.3)	1.24 (1.52)

Table 9.1 (cont'd.): Seasonal mean PM$_{10}$ and PM$_{2.5}$ for Partisol, TEOM (AURN) and in brackets for TEOM (adjusted values) data; alongside mean ratios between Partisol and TEOM (AURN) with in brackets, ratios for TEOM (adjusted values) values.

PM$_{2.5}$	Seasons	Number of observations	Period Means		Ratio Partisol:TEOM
			Partisol	TEOM	
Harwell	Summer 00	14	-	-	-
	Winter 00-01	134	12.3	9.0 (5.8)	1.25 (2.21)
	Summer 01	120	11.7	10.1 (6.9)	1.11 (1.73)
	Winter 01-02	131	11.7	10.3 (7.1)	1.12 (2.22)
	Summer 02	62	15.3	9.1 (6.0)	1.50 (2.40)
Marylebone Road	Summer 00	1	-	-	-
	Winter 00-01	56	31.3	25.9 (22.3)	1.21 (1.45)
	Summer 01	106	25.0	23.4 (19.8)	1.06 (1.29)
	Winter 01-02	48	29.2	29.2 (25.4)	1.05 (1.24)
	Summer 02	59	25.8	23.0 (19.4)	1.10 (1.32)

Table 9.2: Seasonal linear regressions for TEOM (AURN)vs.Partisol for PM$_{10}$ with in brackets the confidence intervals for the slope and for the intercept; alongside the Pearson correlation coefficients.

PM$_{10}$	Seasons	Number of observations	RMA linear regression	Square Pearson correlation coefficient
Belfast	Winter 01	18	-	-
	Summer 01	133	-	0.17
	Winter 01-02	86	-	0.24
	Summer 02	78	$y = 0.463\ (\pm 0.037)\ x + 3.22\ (\pm 1.35)$	0.50
Birmingham	Summer 00	4	-	-
	Winter 00-01	127	$y = 0.491\ (\pm 0.019)\ x + 3.68\ (\pm 0.63)$	0.82
	Summer 01	157	$y = 0.622\ (\pm 0.022)\ x + 3.25\ (\pm 0.54)$	0.80
	Winter 01-02	124	$y = 0.534\ (\pm 0.020)\ x + 3.87\ (\pm 0.58)$	0.82
	Summer 02	57	$y = 0.572\ (\pm 0.021)\ x + 3.37\ (\pm 0.69)$	0.92
Glasgow	Winter 00-01	90	$y = 0.582\ (\pm 0.036)\ x + 3.22\ (\pm 1.05)$	0.65
	Summer 01	114	$y = 0.910\ (\pm 0.041)\ x - 1.16\ (\pm 0.89)$	0.77
	Winter 01-02	43	$y = 0.609\ (\pm 0.033)\ x + 2.46\ (\pm 0.97)$	0.87
Harwell	Summer 00	1	-	-
	Winter 00-01	130	$y = 0.506\ (\pm 0.017)\ x + 3.70\ (\pm 0.37)$	0.85
	Summer 01	138	$y = 0.588\ (\pm 0.024)\ x + 4.49\ (\pm 0.49)$	0.77
	Winter 01-02	91	$y = 0.456\ (\pm 0.025)\ x + 4.82\ (\pm 0.49)$	0.74
	Summer 02	76	$y = 0.512\ (\pm 0.026)\ x + 3.22\ (\pm 0.59)$	0.80
London N.K.	Summer 00	3	-	-
	Winter 00-01	51	$y = 0.609\ (\pm 0.030)\ x + 3.17\ (\pm 0.81)$	0.88
	Summer 01	121	$y = 0.813\ (\pm 0.030)\ x + 1.62\ (\pm 0.74)$	0.83
	Winter 01-02	140	$y = 0.641\ (\pm 0.026)\ x + 3.32\ (\pm 0.74)$	0.78
	Summer 02	38	$y = 0.603\ (\pm 0.028)\ x + 4.25\ (\pm 0.94)$	0.92
Marylebone Road	Summer 00	5	-	-
	Winter 00-01	43	-	0.05
	Summer 01	54	-	0.42
	Winter 01-02	48	-	0.34
Port Talbot	Winter 00-01	87	-	0.17
	Summer 01	93	-	0.21
	Winter 01-02	95	$y = 0.888\ (\pm 0.054)\ x - 0.34\ (\pm 1.80)$	0.64
	Summer 02	59	$y = 0.842\ (\pm 0.048)\ x - 0.61\ (\pm 1.60)$	0.81

Table 9.2 (cont'd): Seasonal linear regressions for TEOM (AURN)vs.Partisol for PM_{10} with in brackets the confidence intervals for the slope and for the intercept; alongside the Pearson correlation coefficients.

$PM_{2.5}$	Seasons	Number of observations	RMA linear regression	Square Pearson correlation coefficient
Harwell	Summer 00	14	-	-
	Winter 00-01	134	y = 0.440 (±0.011) x + 3.58 (±0.18)	0.91
	Summer 01	120	y = 0.531 (±0.027) x + 3.89 (±0.38)	0.69
	Winter 01-02	131	-	0.29
	Summer 02	62	y = 0.383 (±0.016) x + 3.27 (±0.33)	0.89
Marylebone Road	Summer 00	1	-	-
	Winter 00-01	56	y = 0.723 (±0.044) x + 3.29 (±1.47)	0.79
	Summer 01	106	y = 0.823 (±0.029) x + 2.77 (±0.77)	0.87
	Winter 01-02	48	-	0.47
	Summer 02	59	y = 0.607 (±0.045) x + 7.40 (±1.27)	0.68

9.2 Examination of the influence of the temperature and the relative humidity

Figures 9.1and 9.2 show that the differences between the TEOM and the Partisol for PM_{10} mass concentrations measured at Harwell depend on both the temperature and the relative humidity. Similar results are found for Birmingham, Glasgow, London North Kensington and Marylebone Road (see Annex 4, no meteorological data available for the other sites). Nevertheless, the results for Birmingham and Marylebone Road show that the relationship with the relative humidity is not as obvious as the one with temperature (however, at Marylebone Road, a dependence is seen for the $PM_{2.5}$ and all PM_{10} Partisol data are not reliable).

For all sites, the difference between the two instruments decreases with temperature. This is likely to be related to a decrease in the amount of semi-volatile compounds in the particles. For Harwell, Glasgow and London North Kensington the difference increases with the relative humidity, which is likely to be related to the increase of the water-content of particles and possibly also to the semi-volatile compounds. Contrary to the present study, Cyrys et al. (2001) have not found any relationship between the underestimation of the TEOM and the temperature or the relative humidity.

Unfortunately, due to both the limited data available and the variability in the composition of the particles, it is difficult to quantify the influence of these parameters and further work is required in order to understand these impacts.

Figure 9.2 clearly shows that the differences between Partisol and TEOM (AURN) data are higher than 30 % for lower temperatures (below 2°C) and lower than 10 % and close to zero for higher temperatures (above 18°C).

Figure 9.1: Boxplots of relative differences[18] between Partisol and TEOM (AURN) PM_{10} data for different Temperature ranges for Harwell

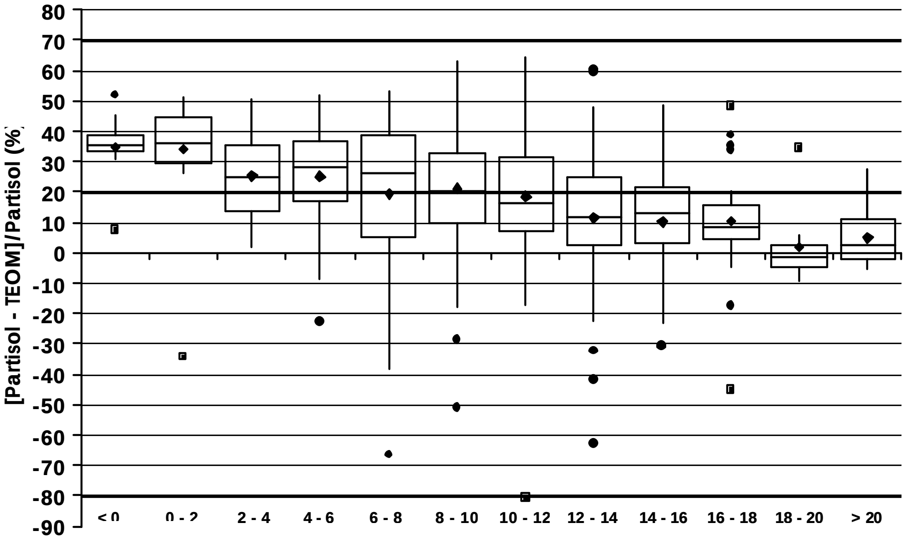


Figure 9.2 shows that half of the differences between Partisol and TEOM (AURN) data are below 10% where the relative humidity is lower than 70% and higher than 30% where the relative humidity is higher than 90%.

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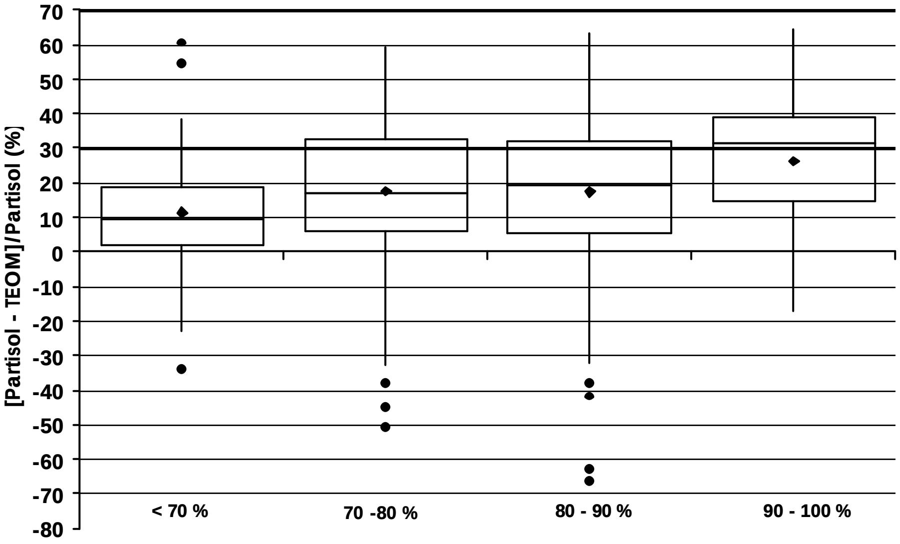
[18] the relative difference is computed as follow:
Relative difference = (Partisol mass – TEOM mass)/Partisol mass *100 (in %)

Figure 9.2: Boxplots of relative differences[1] between Partisol and TEOM (AURN) PM_{10} data for different relative humidity ranges for Harwell



Because of this dependence on meteorological parameters, the linear models and the ratios Partisol/TEOM are now examined according to the temperature and the relative humidity. Tables 9.1 and 9.2 present the results of this examination.

Three bins are considered in order to take in consideration the simultaneous anti-correlation of the temperature and the relative humidity:

- T < 10°C ; RH > 80 % (colder and damper weather)
- T < 10°C ; RH < 80 % or T > 10°C ; RH > 80 % ("intermediate weather")
- T > 10°C ; RH < 80 % (warmer and dryer weather)

Results in Tables 9.1 and 9.2 are with TEOM (AURN) values, the ones with TEOM (adjusted downward) values are in Annex 5.

The different linear models and ratios computed for different temperature and relative humidity bins confirm the influence of the 2 meteorological parameters. The linear relationships found are better (better correlation coefficients) than those computed for the different seasons; showing that this allocation is more appropriate. These relationships might be used to amend TEOM PM_{10} data measured in Birmingham, London North Kensington and possibly also Glasgow and Harwell (even if R^2 is slightly lower than 0.8).

The ratios found are higher than 1.40 (and often higher than 1.50) for lower temperatures and higher relative humidities. They are below 1.24 for higher temperatures and lower relative humidities. For the "intermediate weathers", the ratios are in general close to 1.30.

Despite fairly similar ratios for most of the sites, the computed linear relationships are different confirming the site specificity. These differences (for both the ratio and the linear relationships) cannot be attributed to the different mean temperatures and mean relative humidities associated with each dataset (see Annex 6) suggesting the significance of the contribution of the particulate matter composition for each site

Table 9.1: Linear regressions TEOM (AURN) vs. Partisol for PM_{10} (in brackets, the confidence intervals for the slope and the intercept,) the square of the Pearson correlation coefficients and the mean and the standard deviation for ratios Partisol/TEOM for different temperature and relative humidity bins.

PM_{10}	Temperature & relative humidity	N	RMA linear regression	Square Pearson correlation coefficient	Ratio Partisol/ TEOM
Birmingham	T < 10°C ; RH > 80 %	67	$y = 0.567\ (\pm 0.022)\ x + 2.19\ (\pm 0.66)$	0.90	1.52 ± 0.30
	T < 10°C ; RH < 80 % ou T > 10°C ; RH > 80 %	107	$y = 0.551\ (\pm 0.019)\ x + 3.77\ (\pm 0.58)$	0.87	1.39 ± 0.29
	T > 10°C ; RH < 80 %	51	$y = 0.601\ (\pm 0.031)\ x + 4.06\ (\pm 0.76)$	0.86	1.24 ± 0.23
Glasgow	T < 10°C ; RH > 80 %	98	$y = 0.623\ (\pm 0.033)\ x + 1.93\ (\pm 0.97)$	0.73	1.49 ± 0.77
	T < 10°C ; RH < 80 % ou T > 10°C ; RH > 80 %	105	$y = 0.720\ (\pm 0.038)\ x + 1.84\ (\pm 0.88)$	0.71	1.26 ± 0.31
	T > 10°C ; RH < 80 %	43	$y = 0.963\ (\pm 0.070)\ x - 1.86\ (\pm 1.48)$	0.77	1.18 ± 0.26
Harwell	T < 10°C ; RH > 80 %	134	$y = 0.508\ (\pm 0.018)\ x + 3.42\ (\pm 0.41)$	0.83	1.41 ± 0.35
	T < 10°C ; RH < 80 % ou T > 10°C ; RH > 80 %	178	$y = 0.505\ (\pm 0.017)\ x + 4.33\ (\pm 0.35)$	0.80	1.29 ± 0.36

	T > 10°C ; RH < 80 %	124	**y =** 0.646 (±0.031) **x +** 3.19 (±0.60)	0.71	1.19 ± 0.29
London N.K.	T < 10°C ; RH > 80 %	25	**y =** 0.578 (±0.048) **x +** 1.23 (±1.63)	0.83	1.63 ± 0.33
	T < 10°C ; RH < 80 % ou T > 10°C ; RH > 80 %	148	**y =** 0.603 (±0.018) **x +** 3.88 (±0.48)	0.87	1.28 ± 0.24
	T > 10°C ; RH < 80 %	180	**y =** 0.731 (±0.023) **x +** 3.16 (±0.61)	0.83	1.17 ± 0.23
Marylebone Road	T < 10°C ; RH > 80 %	16	-	0.42	1.73 ± 0.86
	T < 10°C ; RH < 80 % ou T > 10°C ; RH > 80 %	79	-	0.12	1.67 ± 1.44
	T > 10°C ; RH < 80 %	55	**y =** 0.849 (±0.071) **x –** 0.51 (±3.22)	0.61	1.24 ± 0.34

Table 9.2: Linear regressions TEOM (AURN) vs. Partisol for $PM_{2.5}$ (in brackets, the confidence intervals for the slope and the intercept), the square of the Pearson correlation coefficients and the mean and the standard deviation for ratios Partisol/TEOM for different temperature and relative humidity bins.

$PM_{2.5}$	Temperature & relative humidity	N	RMA linear regression	Square Pearson correlation coefficient	Ratio Partisol/ TEOM
Harwell	T < 10°C ; RH > 80 %	169	$y = 0.473\ (\pm 0.024)\ x + 3.89\ (\pm 0.39)$	0.58	1.25 ± 0.48
	T < 10°C ; RH < 80 % ou T > 10°C ; RH > 80 %	182	$y = 0.384\ (\pm 0.015)\ x + 4.51\ (\pm 0.24)$	0.73	1.23 ± 0.59
	T > 10°C ; RH < 80 %	110	$y = 0.486\ (\pm 0.030)\ x + 4.24\ (\pm 0.43)$	0.59	1.11 ± 0.46
Marylebone Road	T < 10°C ; RH > 80 %	18	$y = 0.767\ (\pm 0.103)\ x + 0.45\ (\pm 3.53)$	0.68	1.30 ± 0.26
	T < 10°C ; RH < 80 % ou T > 10°C ; RH > 80 %	99	$y = 0.834\ (\pm 0.049)\ x + 1.73\ (\pm 1.41)$	0.66	1.11 ± 0.25
	T > 10°C ; RH < 80 %	153	$y = 0.817\ (\pm 0.038)\ x + 3.27\ (\pm 1.14)$	0.67	1.07 ± 0.21

Higher distinctions might be found considering bins with higher or lower temperature/relative humidity, but the number of data available in these cases is small and not sufficient to permit the establishment of linear models. For example, at Harwell the mean ratio is only 1.04 (standard deviation, SD = 0.11) for temperatures higher than 18°C and RH < 80% and is 1.65 (SD = 0.25) for temperatures below 2°C and RH > 80 %.

10 Summary and Conclusions

- PM_{10} data from manual filter-based Partisol and TEOM instruments are compared for 7 sites in the UK with different characteristics. Additionally, $PM_{2.5}$ data from Partisol and TEOM instruments are compared for 2 sites.

- Both the use of an unsuitable linear regression method and the US EPA calibration factor are shown to influence the linear models for the relationship between TEOM and gravimetric data. The use of a linear model making no assumption on the X observations is recommended for this study.

- The TEOM instrument largely underestimates PM_{10} (and $PM_{2.5}$) data for most of the sites. The underestimation is thought to be mainly particulate semi-volatile compounds both inorganic (ammonium nitrate, ammonium chloride) and organic lost in the inlet of the TEOM. Results for Harwell have shown that a significant part of the particulate material lost is ammonium nitrate and belongs to the $PM_{2.5}$ fraction; while those for Belfast have shown that mainly other volatile compounds, likely semi-volatile organic compounds, are lost.

- The results have shown the spatial and temporal variability of the relationships between TEOM and LVS and TEOM and Partisol data. Linear models for the relationships between TEOM and LVS and TEOM and Partisol mass concentrations vary seasonally and from one site to another and ratios between the results vary from one day to another.

- The 1.3 factor amending TEOM (AURN) data gives reasonably good results for many sites when we consider averages but was shown unsuitable for single concentrations and for the calculation of the exceedence days.

- In order to better understand the spatial and temporal variations of the relationships between TEOM and Partisol instruments, an examination of the possible influential meteorological parameters (temperature, relative humidity) has been carried out. This examination would also lead to a better understanding of the lack of strong relationship (or presence of variability) between the mass values measured with the two kinds of instruments. The underestimation of the TEOM depends on both the relative humidity and the temperature; it increases with decreasing temperatures and increasing relative humidities.

- The examination of the TEOM versus Partisol relationships for different temperature and relative humidity bins has given better models than the relationships established for different seasons. These models may be used to amend TEOM particle mass concentrations for Birmingham, Glasgow, Harwell and London North Kensington for PM_{10}.

- The relationships between the KFG and Partsiol samplers at co-located sites has indicated that some of the data might be suspect. Potential reasons for loss of particles from the filters include ‘storage’ in the ambient environment, and despatch to the weighing laboratory via the postal system. It may prove necessary to investigate these factors in greater detail, or to revise the filter storage procedures that are currently used.

11 References

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12 Report Statement

Casella Stanger completed this report on the basis of a defined programme of works and within the terms and conditions agreed with the Client. This report was compiled with all reasonable skill and care, bearing in mind the project objectives, the agreed scope of works, prevailing site conditions and degree of manpower and resources allocated to the project as agreed.

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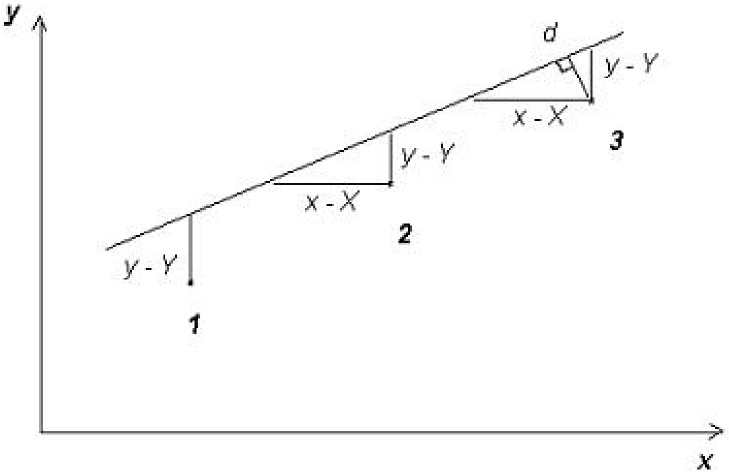
Annex 1: Least Square regression, Orthogonal regression, Reduced Major Axis regression.

The following figure represents 3 dots and the "best fitted line". For the calculation of the "best line", the minimised distances between the points and the fitted line depend on the model, they are:

For the Least Squares Regression : $\sum (y - Y)^2$
That is to say, a projection according to the y-axis. X-values are not changed and are considered as accurate.

For the RMA Regression : $\sum (x - X)(y - Y)$
That is to say, proportional to the surface area and is done according both x- and y-axes.

For the Orthogonal regression : $\sum d^2$
d is the orthogonal projection (i.e. according both x and y axes) onto the line



Important differences:

1. Both RMA and Orthogonal regressions consider that deviations between fitted and observed values may occur for both x and y observations

2. With RMA and Orthogonal regressions we have :

   $y = a\,x + b$ <u>and</u> $x = 1/a\,y - b/a$

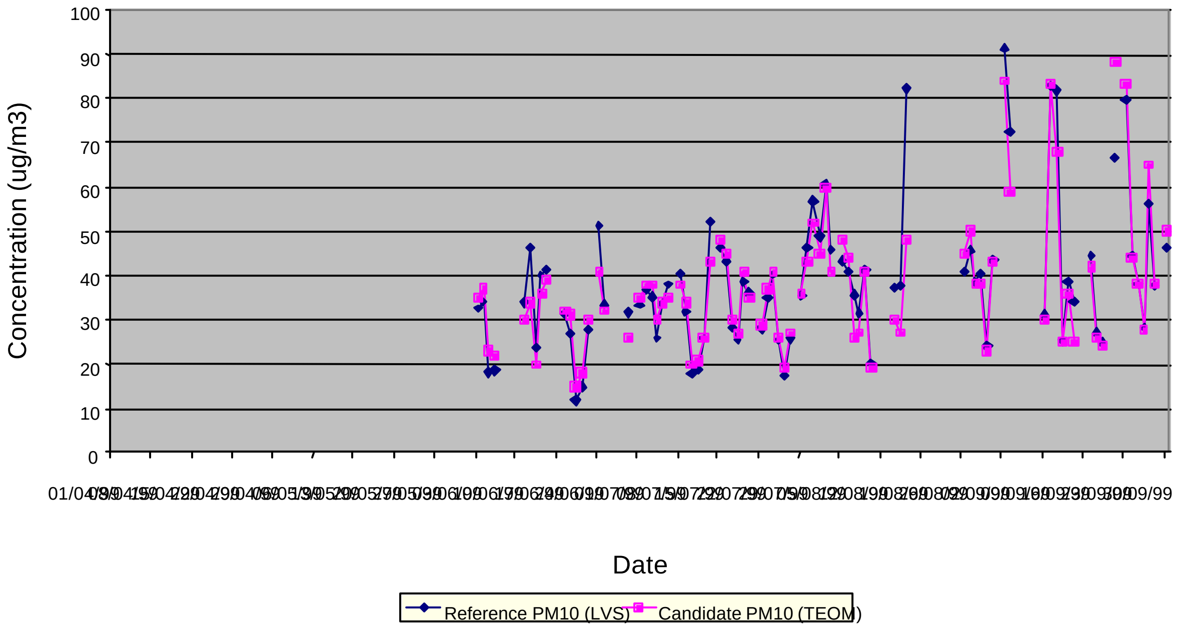
   i.e. the model is unchanged if we exchange x and y observations

   With the Least Square regression, the fitted model is changed whether we exchange x or y observations

Appendix 2: Temporal Season Trends

Figure A1: Temporal PM_{10} trends (fixed daily means) at Marylebone Road

(a) Summer 1999



(b) Winter 1999 - 2000

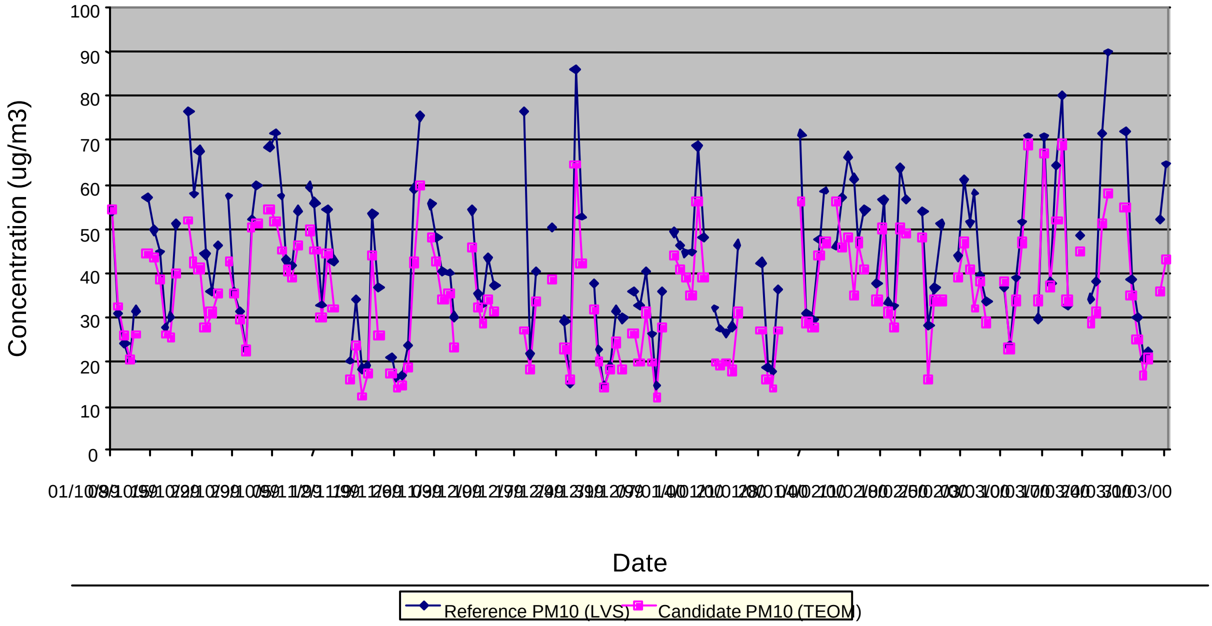
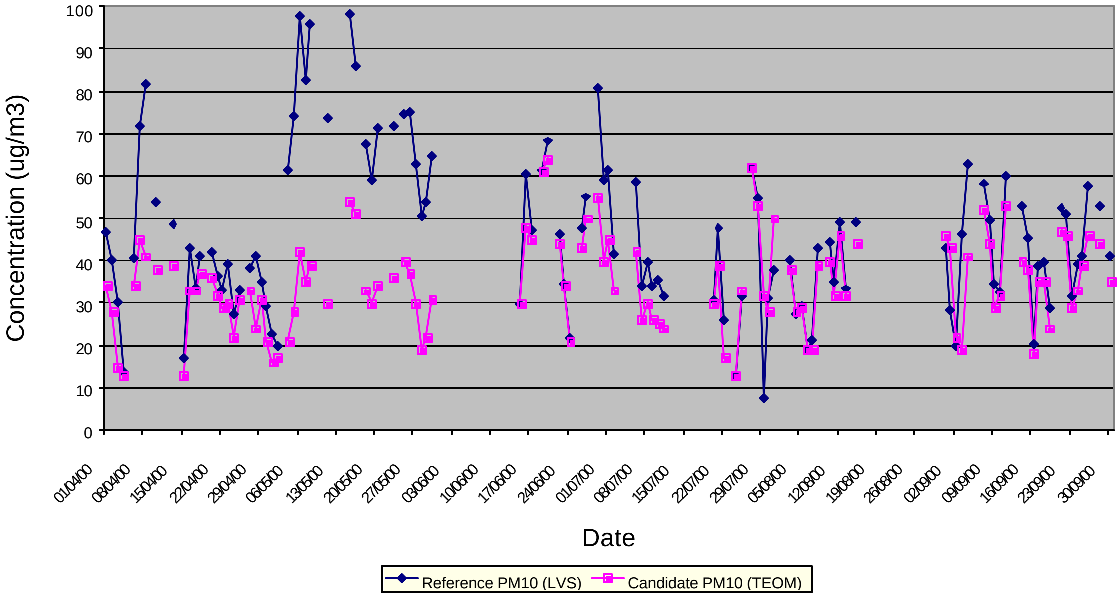


Figure A1: (contd.).

(c) Summer 2000



(d) Winter 00-01

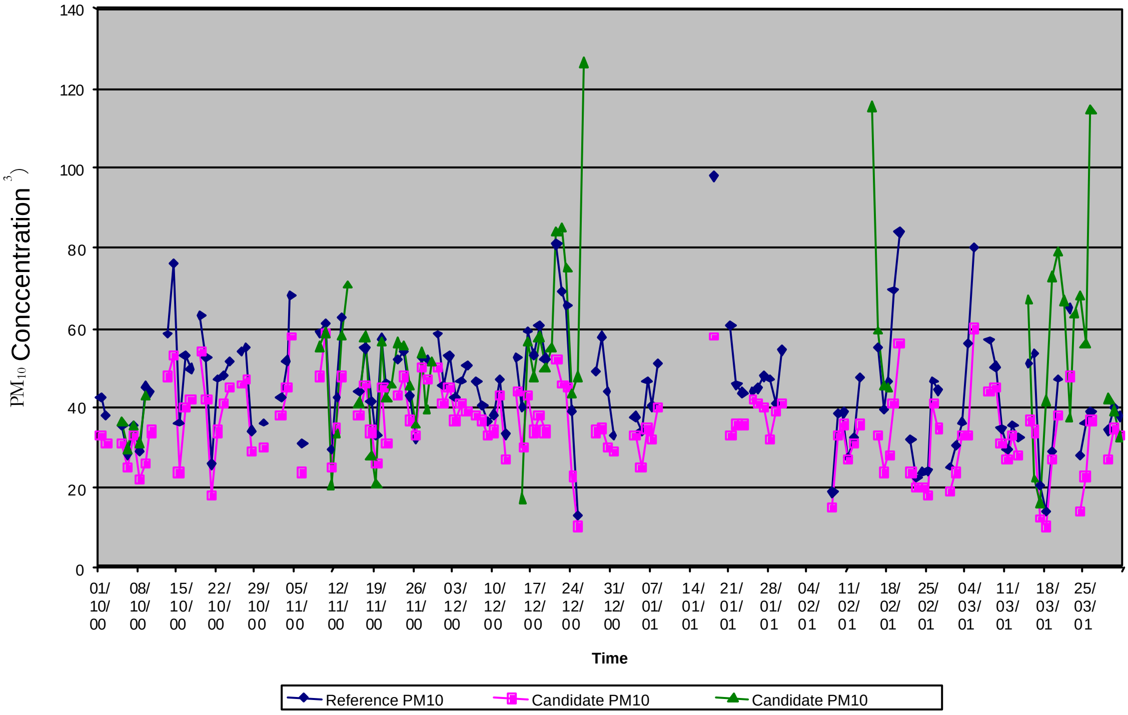
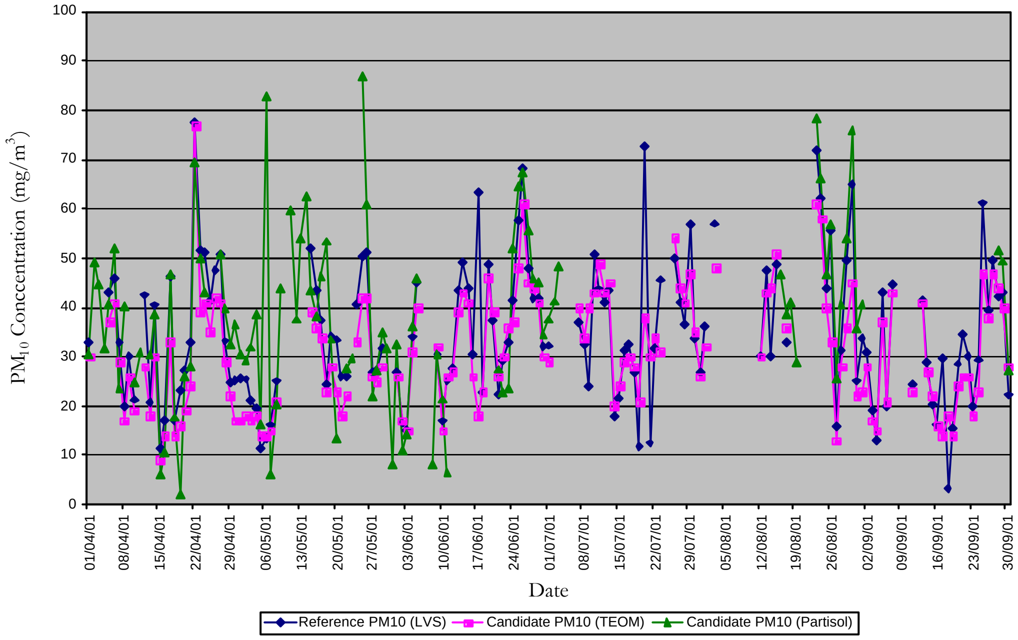


Figure A1: (contd.).

(e) Summer 2001



(f) Summer 2002

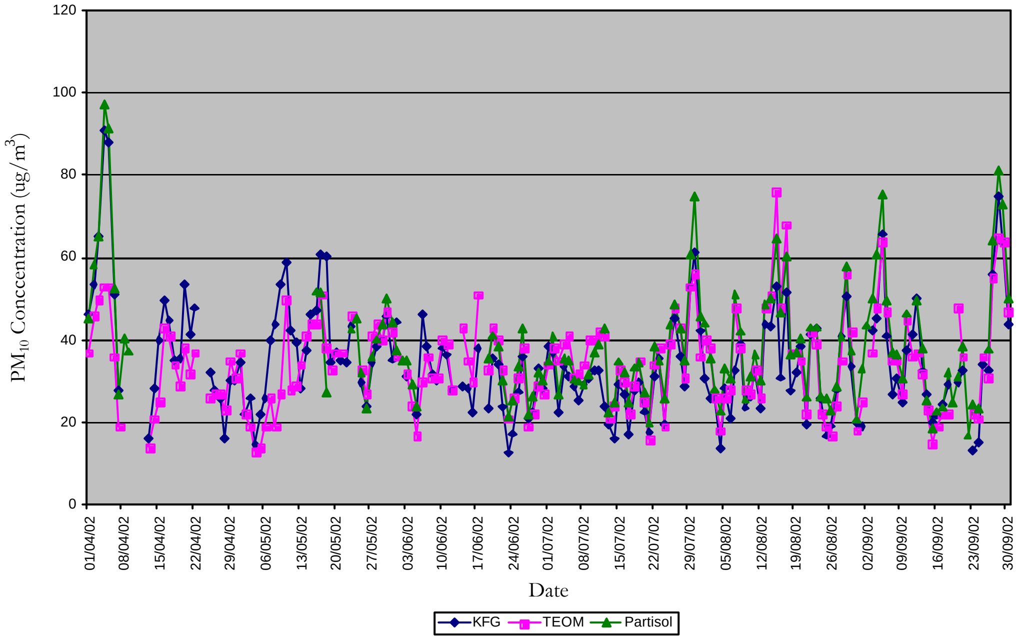
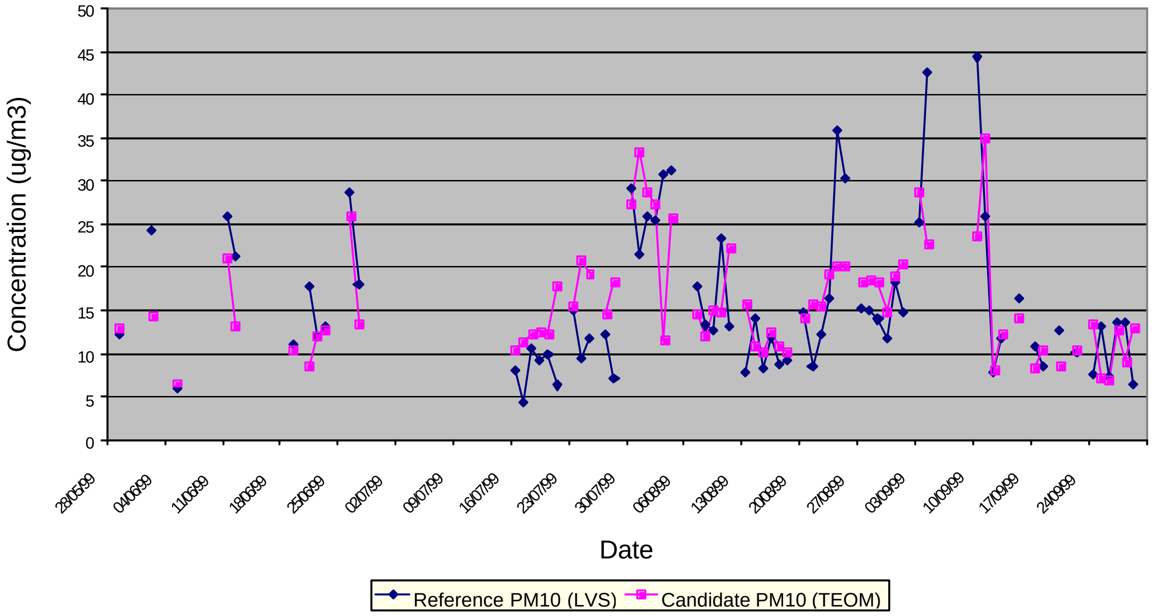


Figure A2: Temporal PM_{10} trends (fixed daily means) at Harwell

(a) Summer 1999



(b) Winter 1999 - 2000

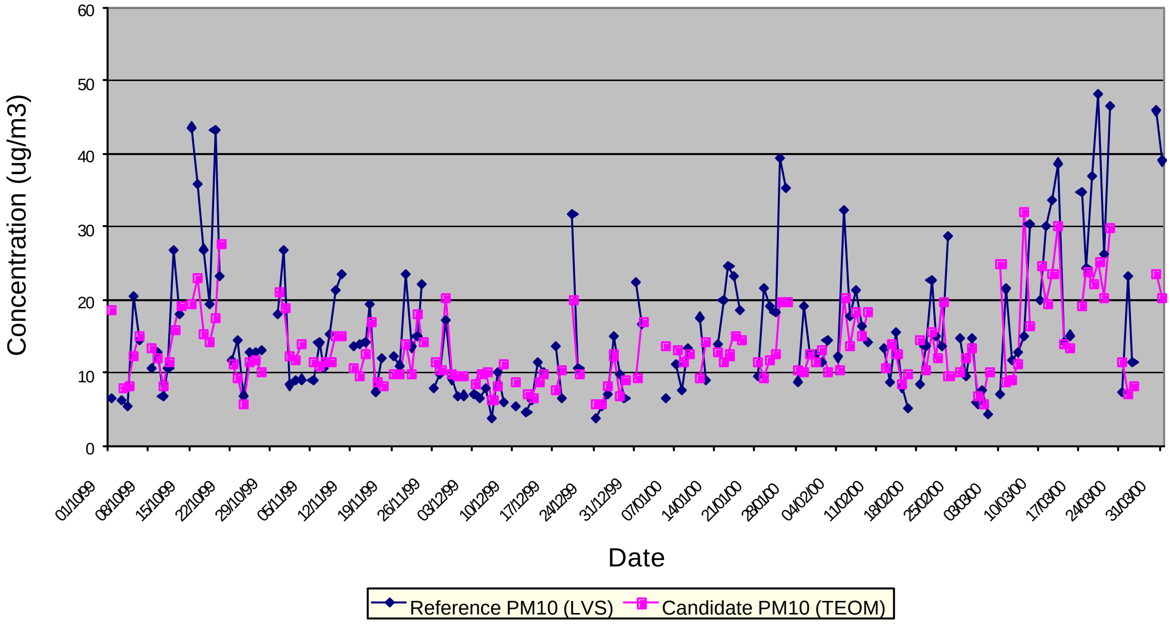
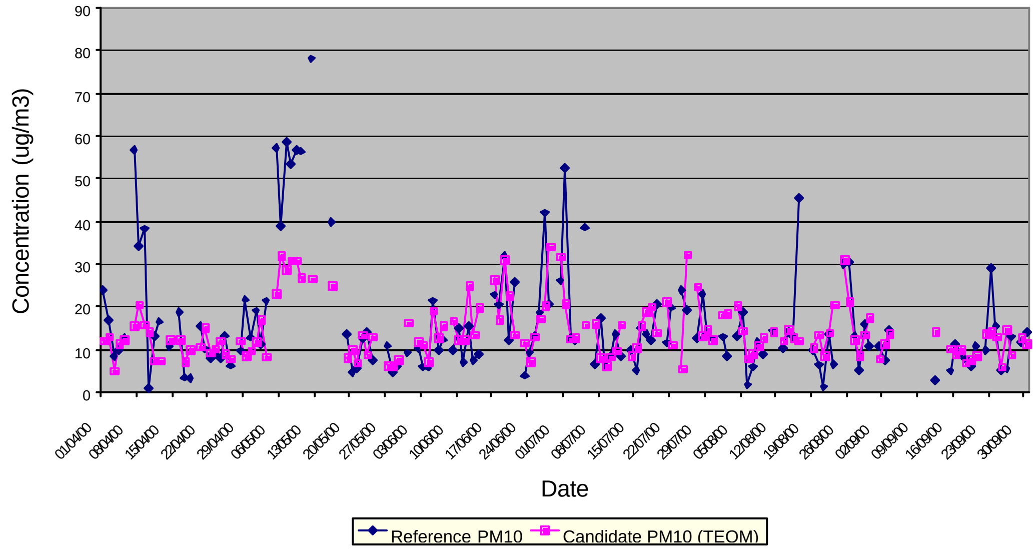


Figure A2: (contd.).

(c) Summer 2000



(d) Winter 00-01

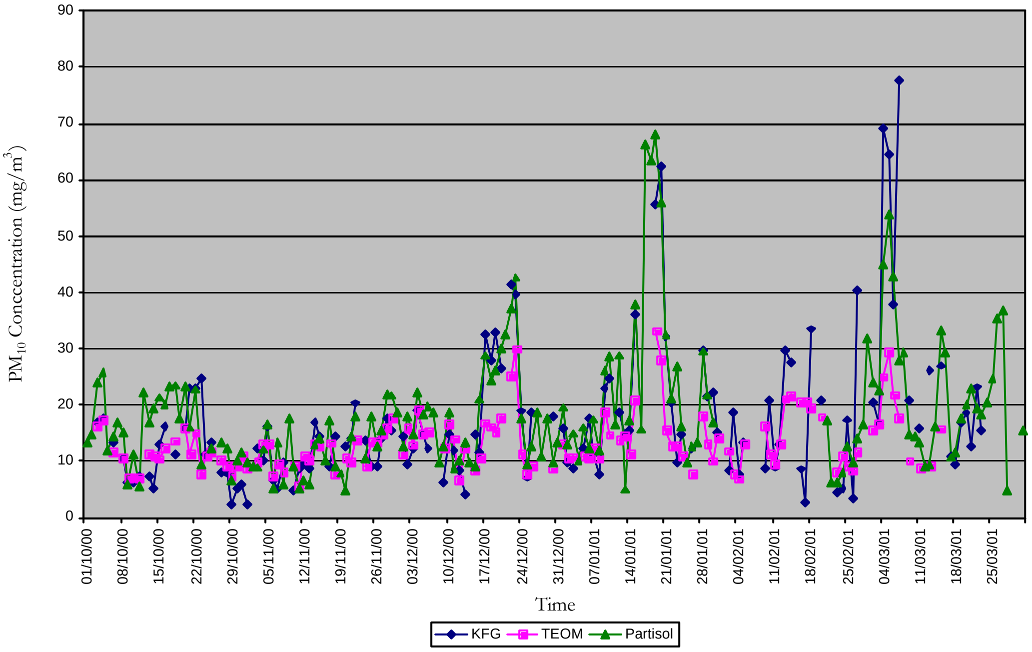
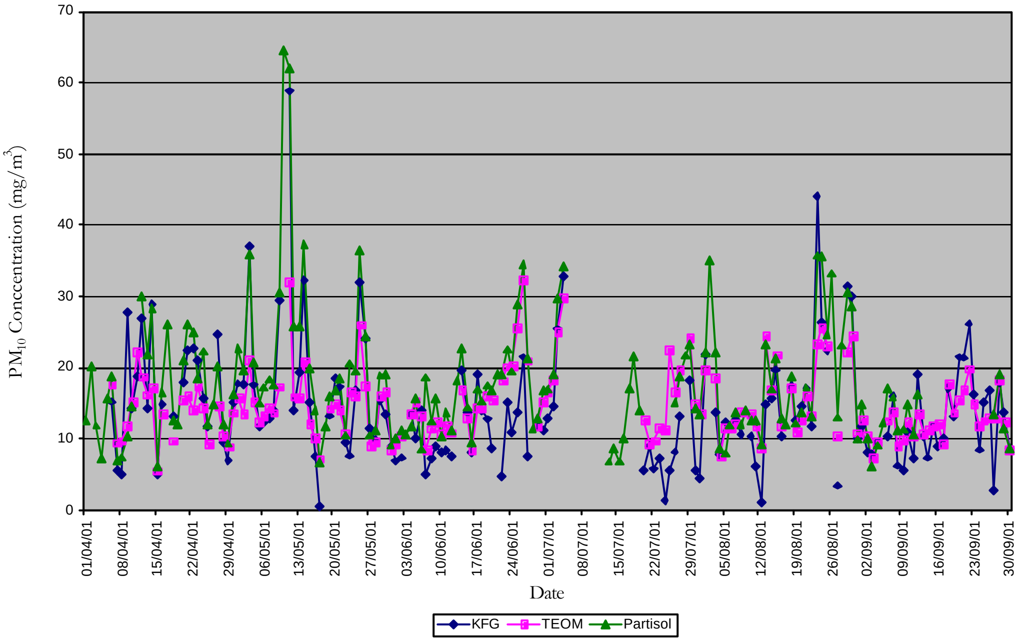


Figure A2 (contd.)

(e) Summer 01



(f) Winter 2001/2002

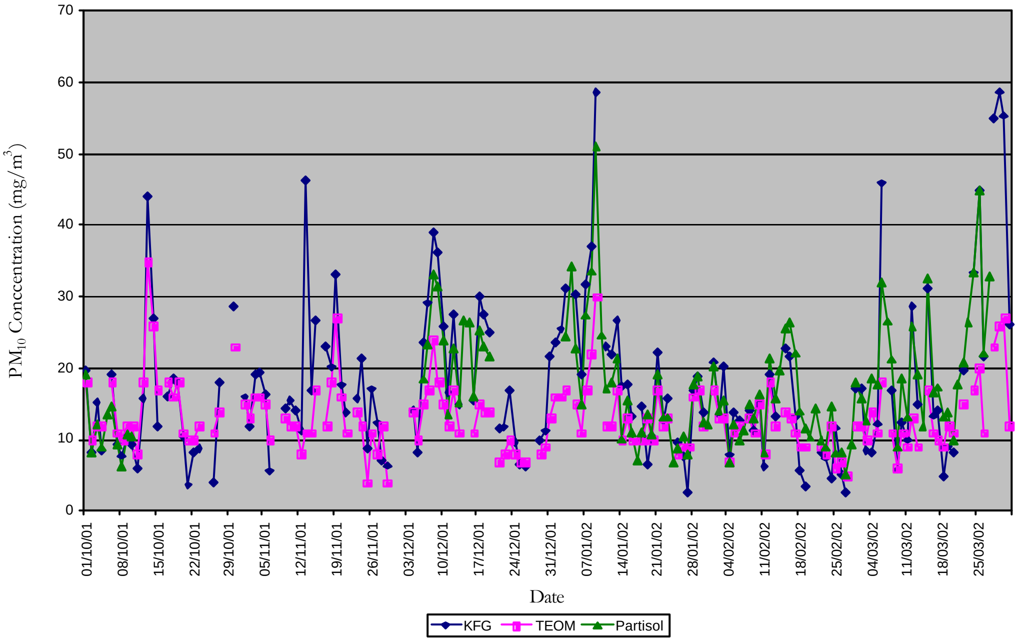


Figure A2 (contd.)

(g) Summer 2002

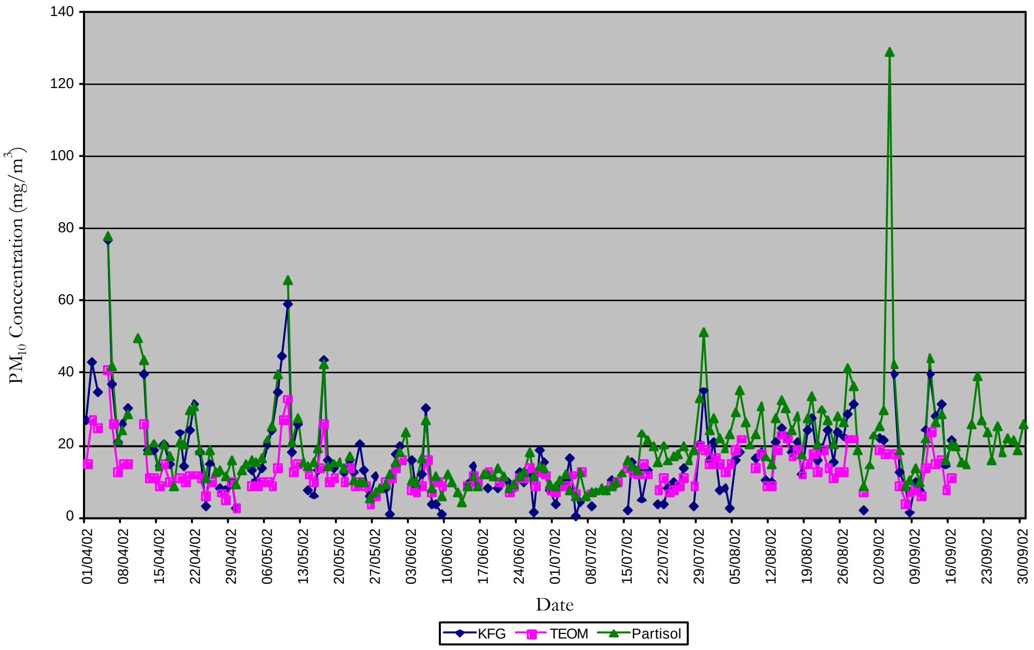
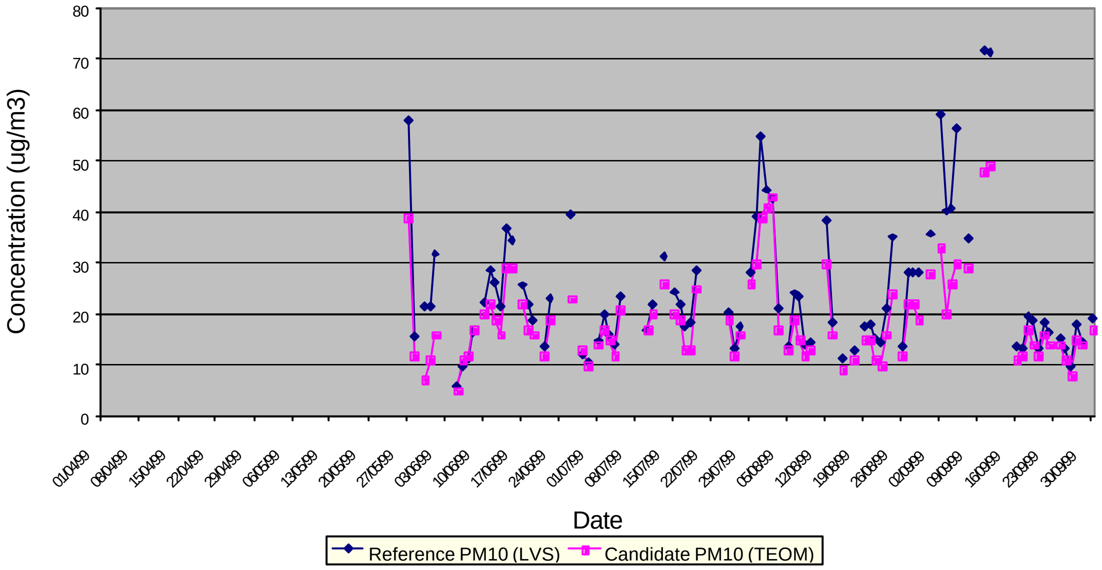


Figure A3: Temporal PM$_{10}$ trends (fixed daily means) at Thurrock

(a) Summer 1999



(b) Winter 1999 - 2000

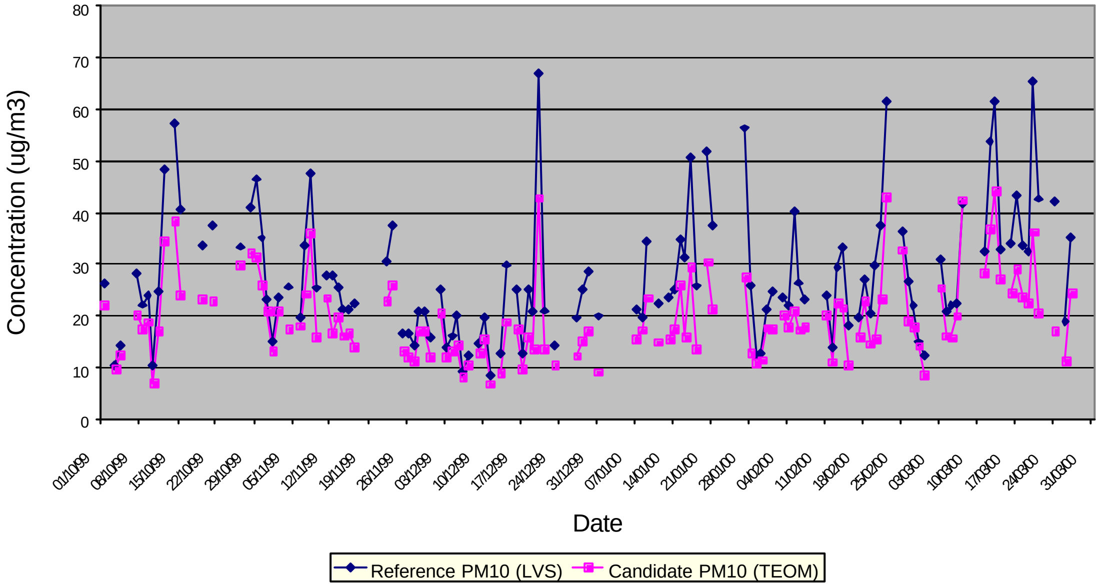
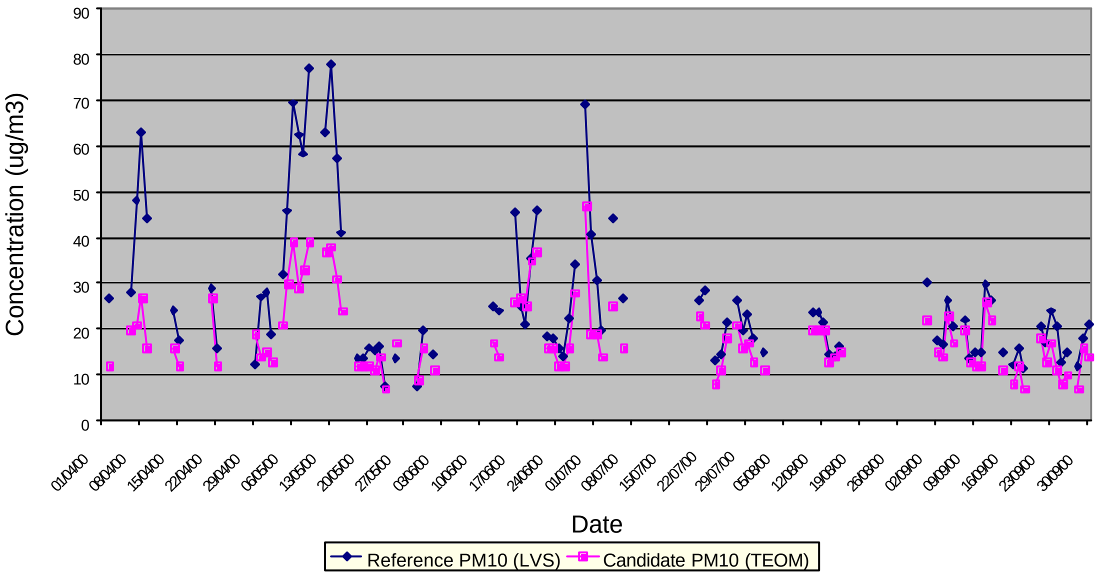


Figure A3: (contd.)

(c) Summer 2000



(d) Winter 2000 - 2001

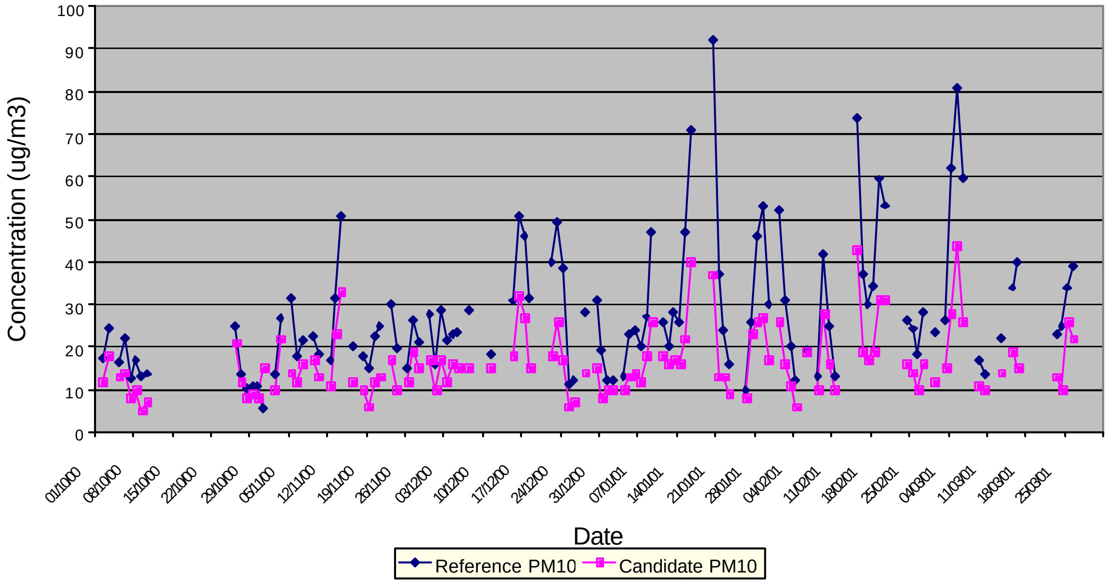


Figure A3: (contd.)

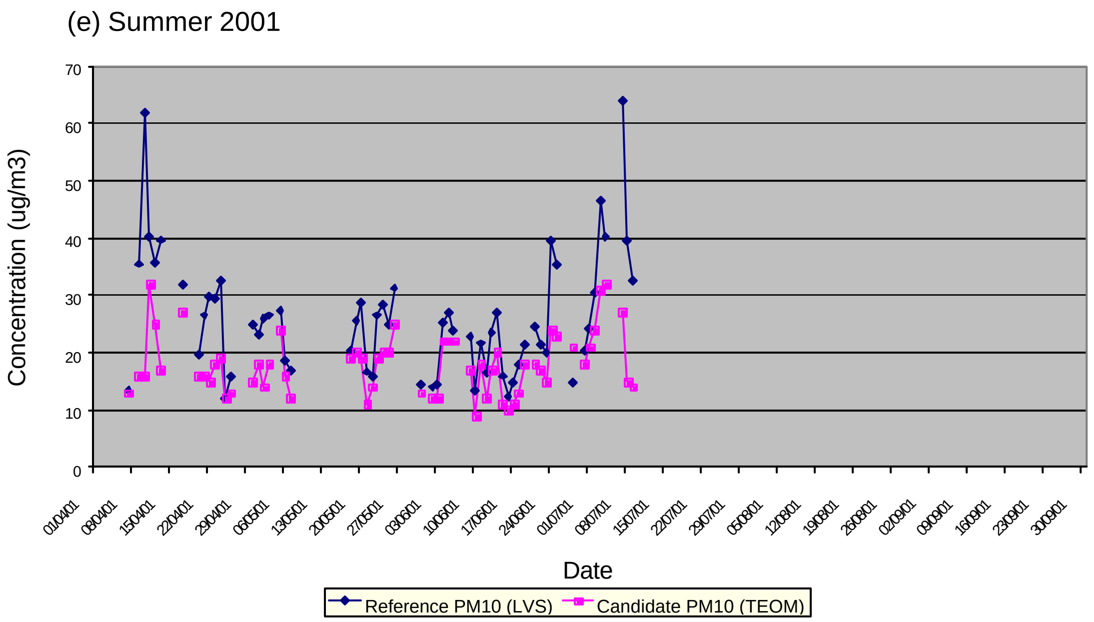
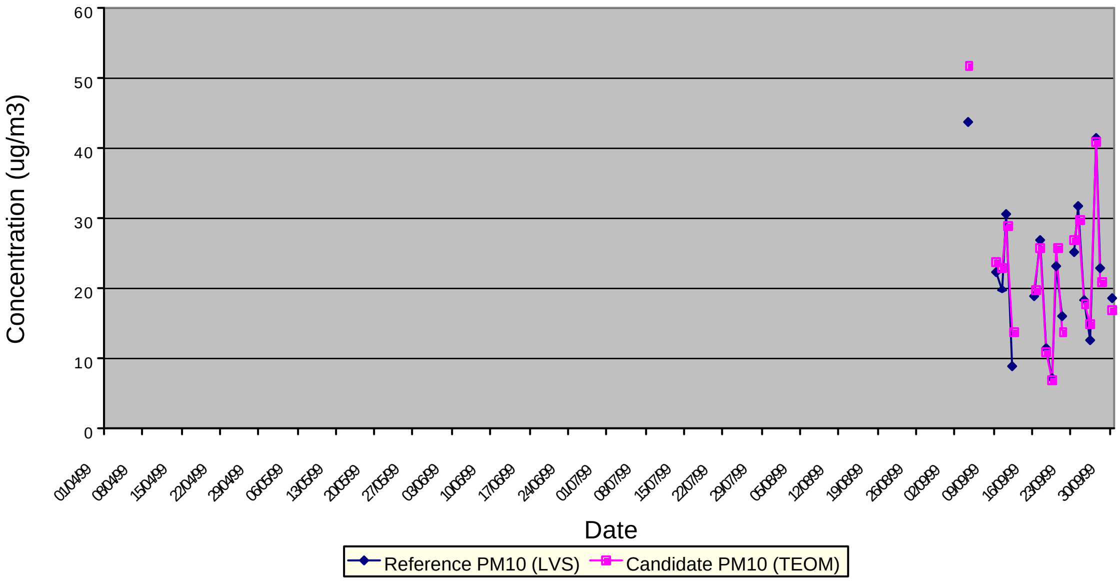


Figure A4: Temporal PM_{10} trends (fixed daily means) at Port Talbot

(a) Summer 1999



(b) Winter 1999 - 2000

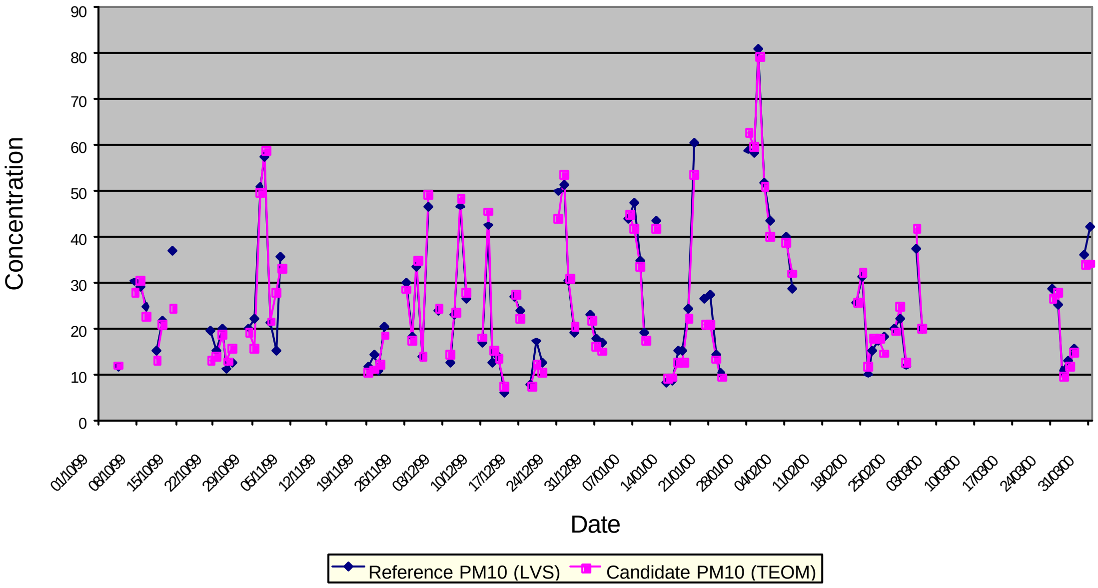
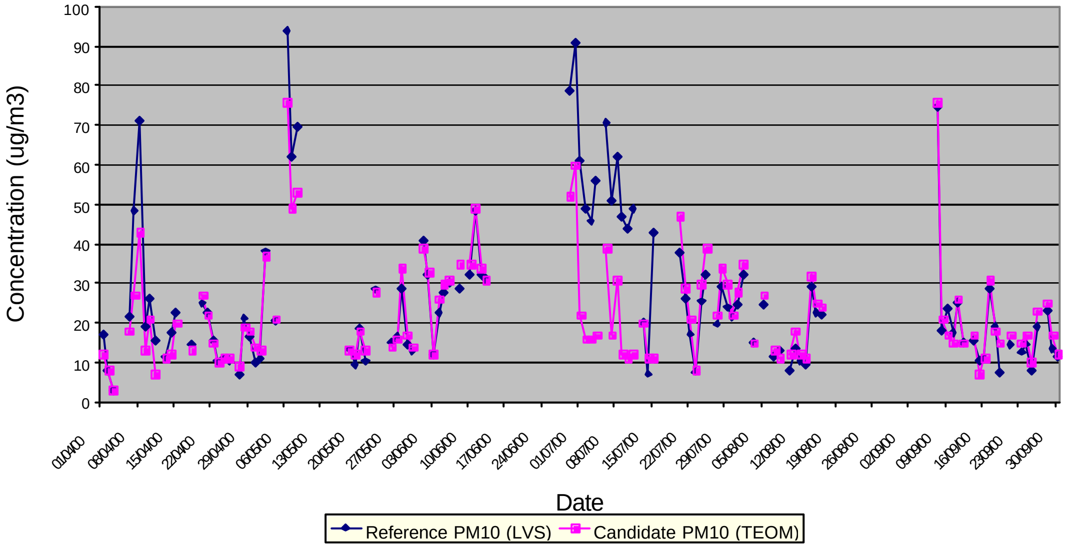


Figure A4: (contd.)

(c) Summer 2000



(d) Winter 00-01

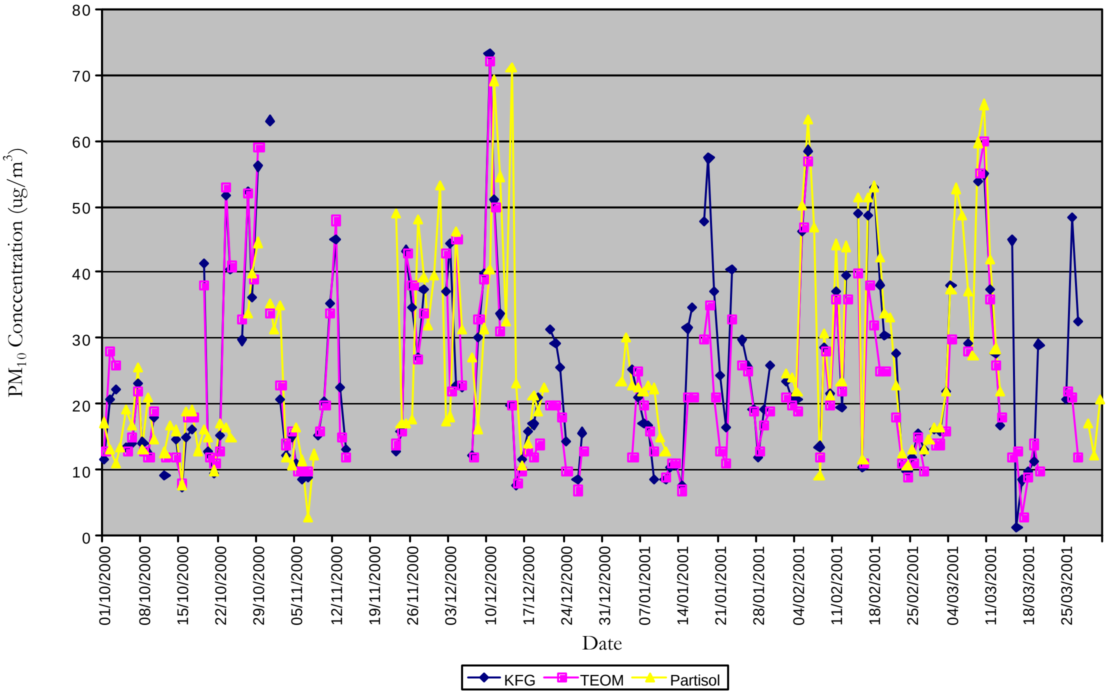
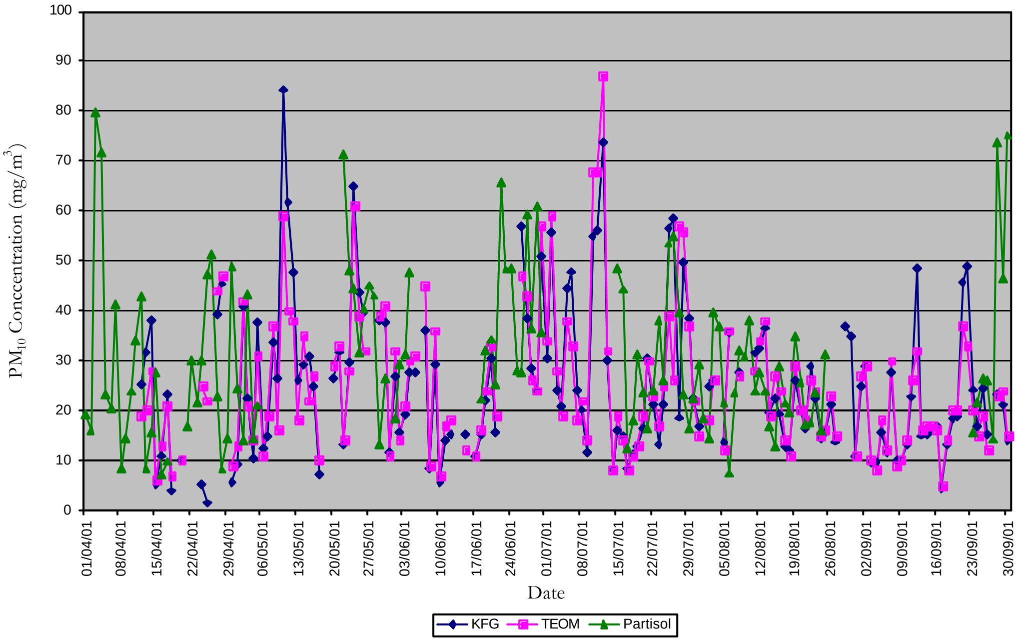


Figure A4: (contd).

(e) Summer 2001



(f) Winter 01-02

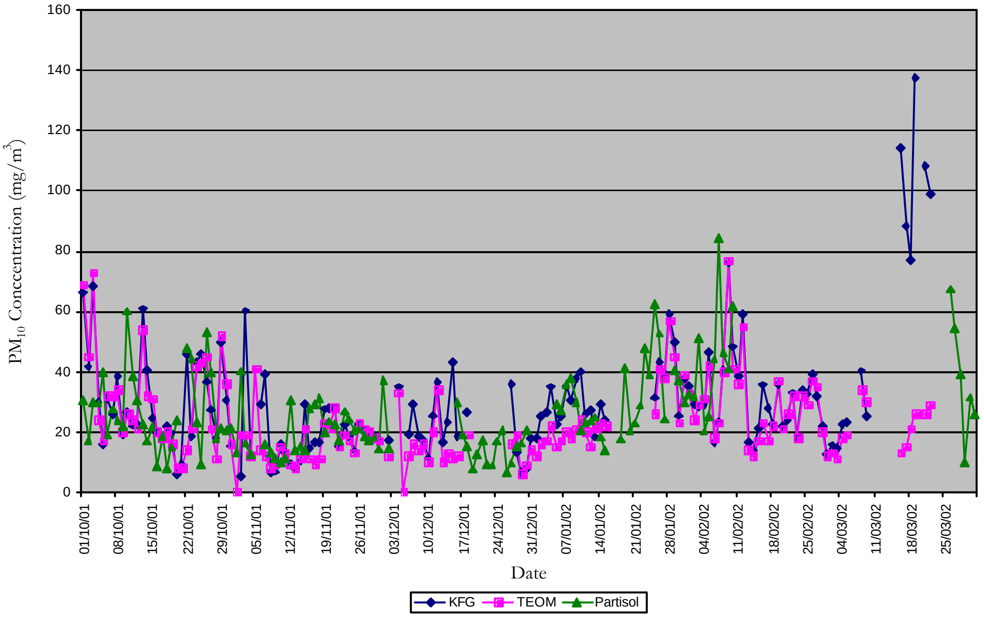


Figure A4: (contd).

(g) Summer 2002

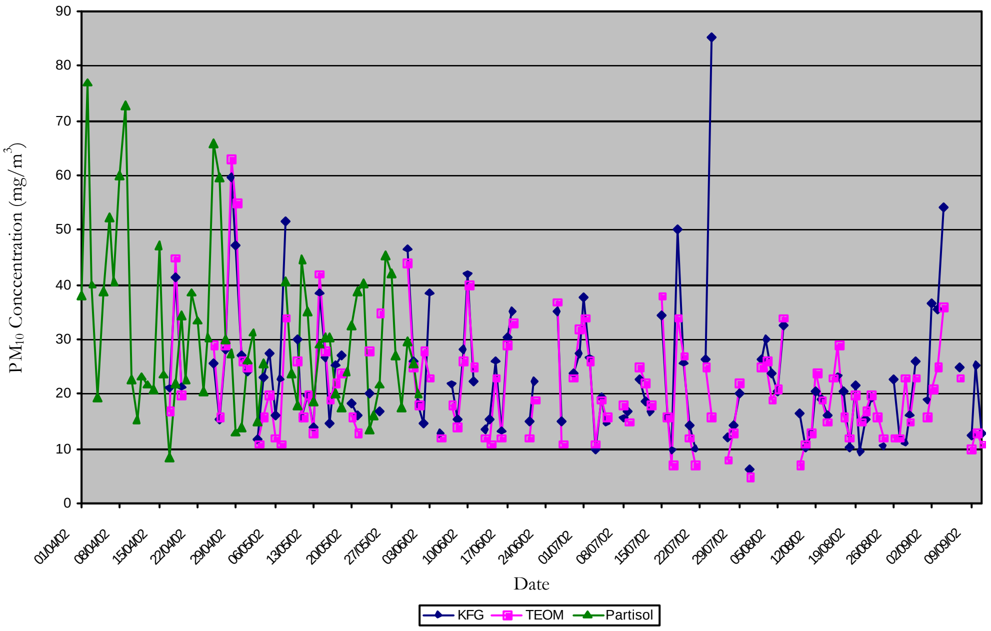
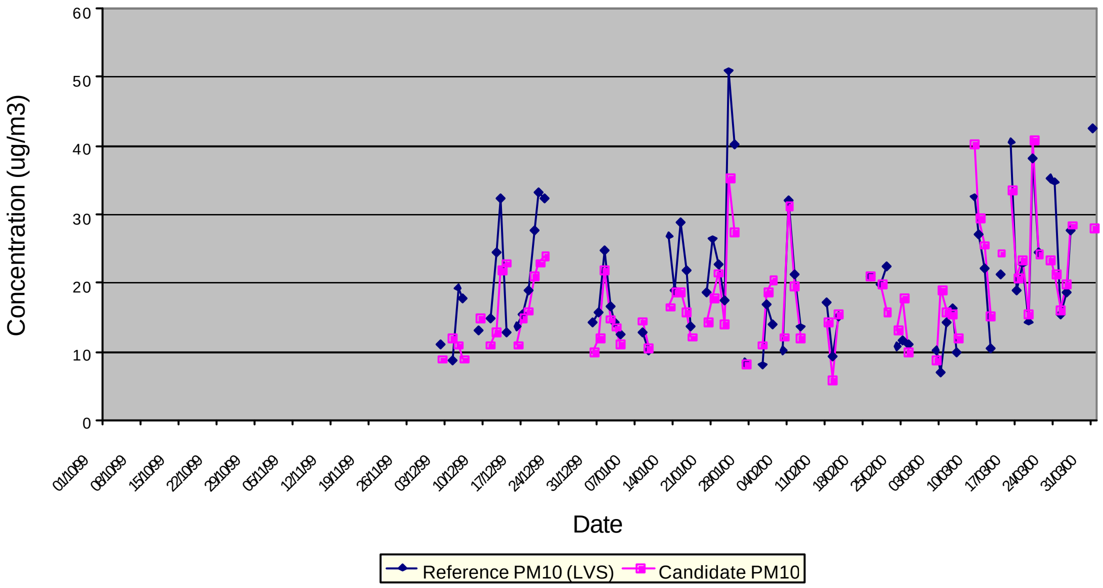


Figure A5: Temporal PM_{10} trends (fixed daily means) at Glasgow

(a) Winter 1999 - 2000



(b) Summer 2000

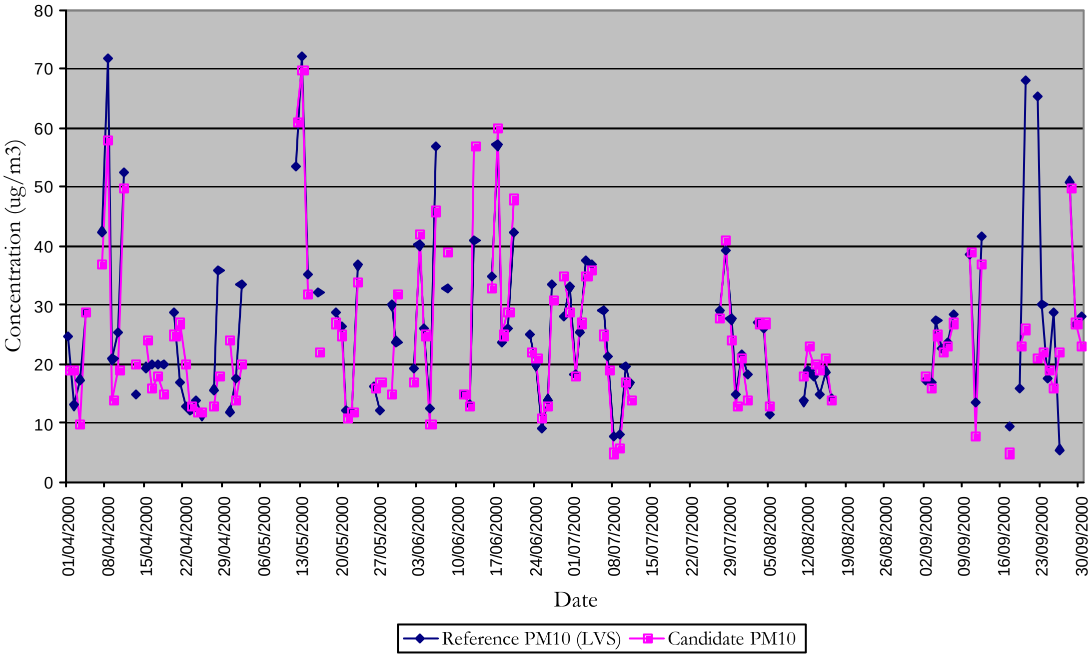
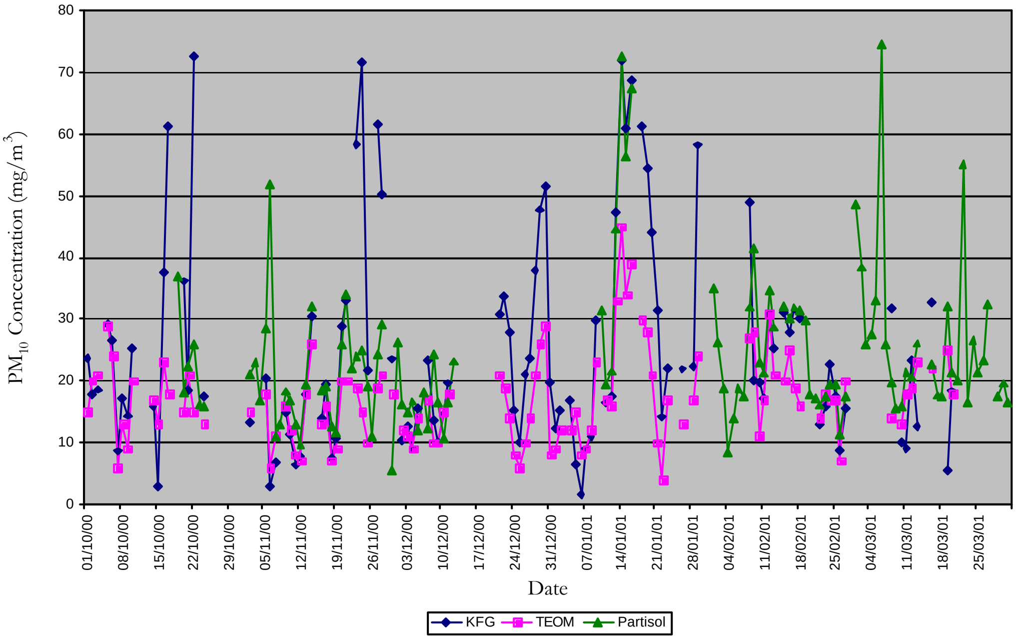


Figure A5: (contd.)

(c) Winter 2000/2001



(d) Summer 2001

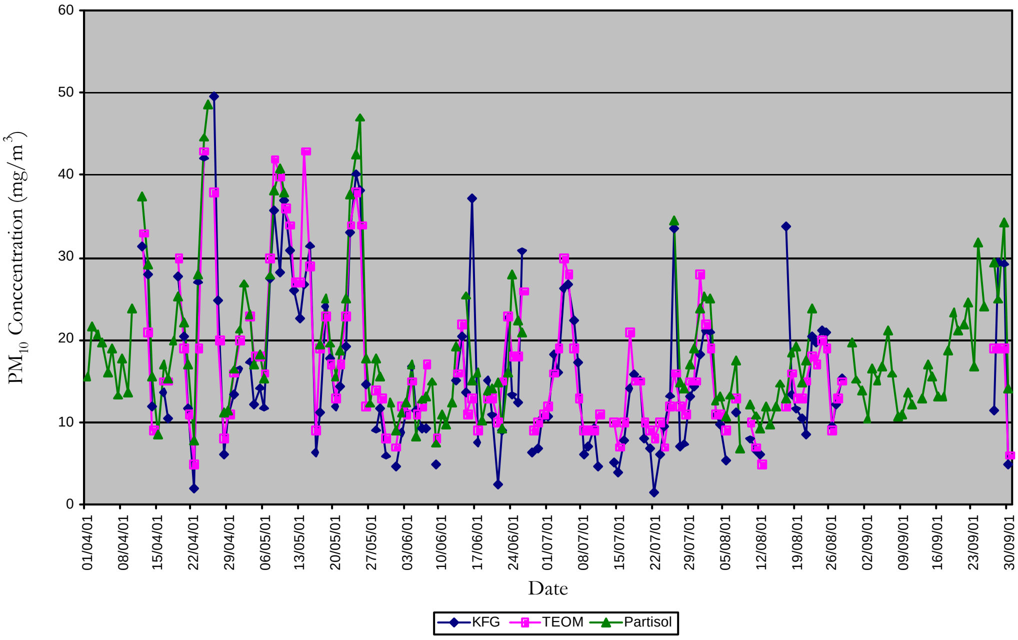
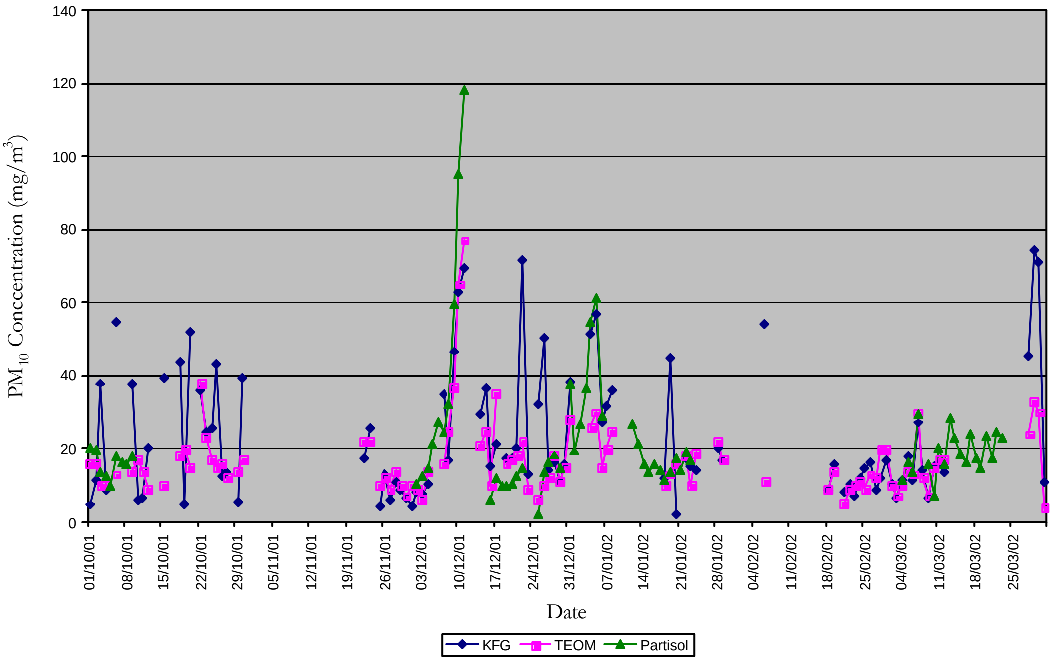


Figure A5: (contd.)

(e) Winter 2001/2002



(f) Summer 2002

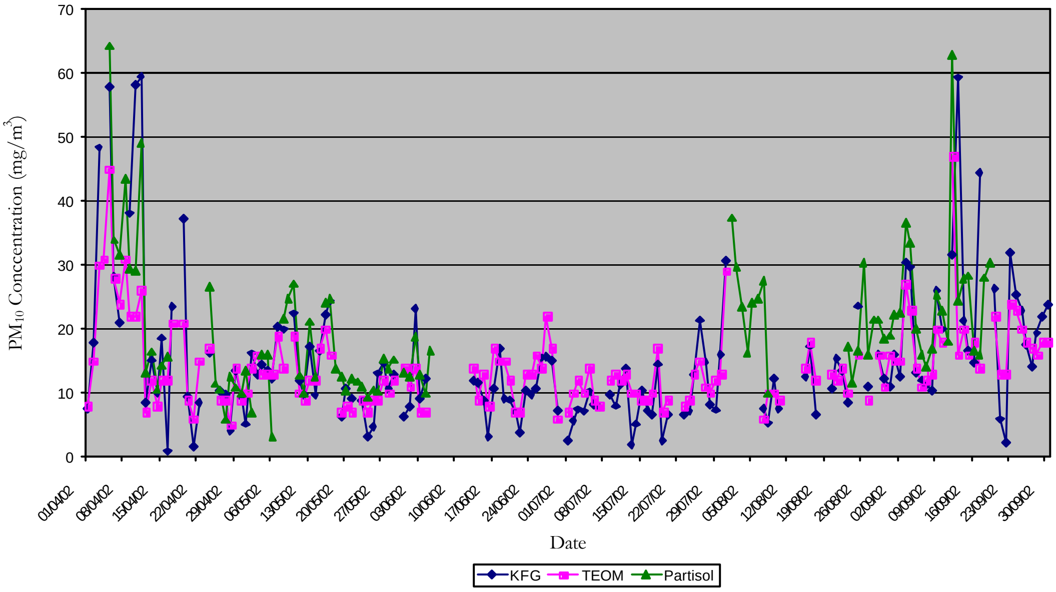
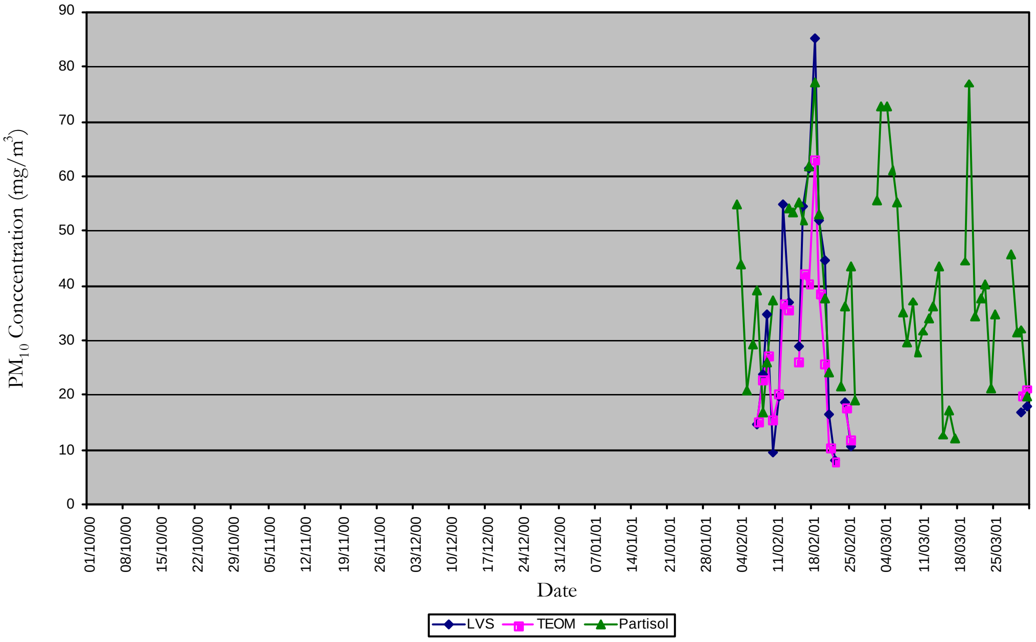


Figure A6: Temporal PM$_{10}$ trends (fixed daily means) at Belfast

(a) Winter 2000/2001



(b) Summer 2001

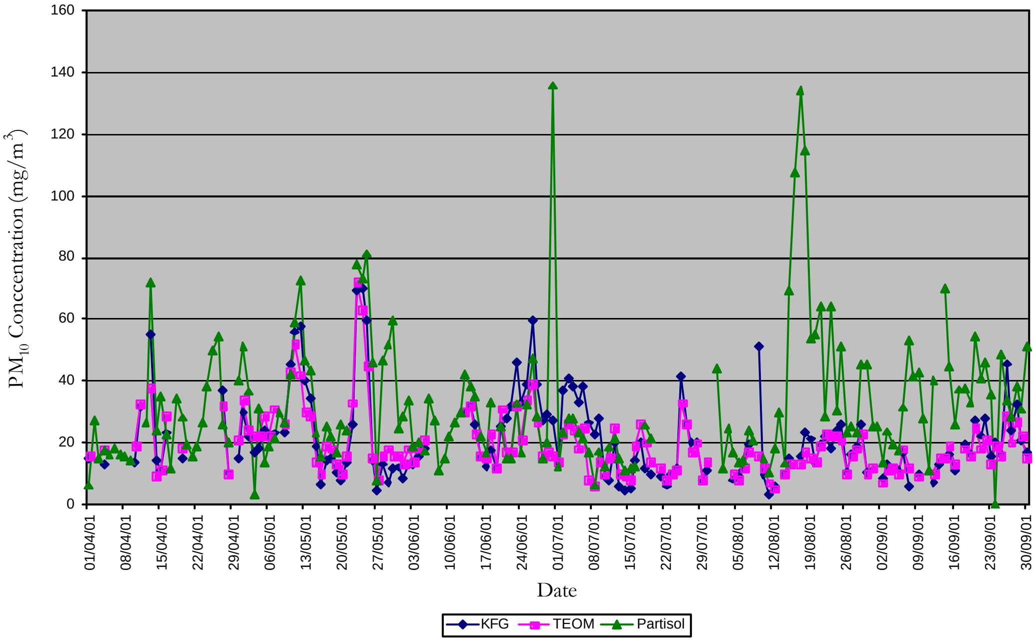
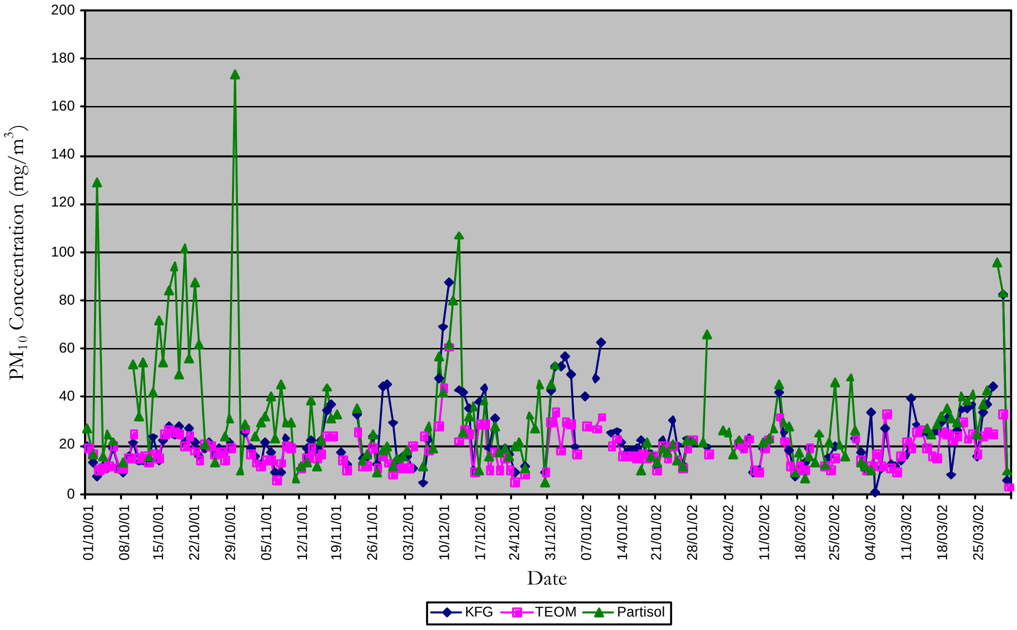
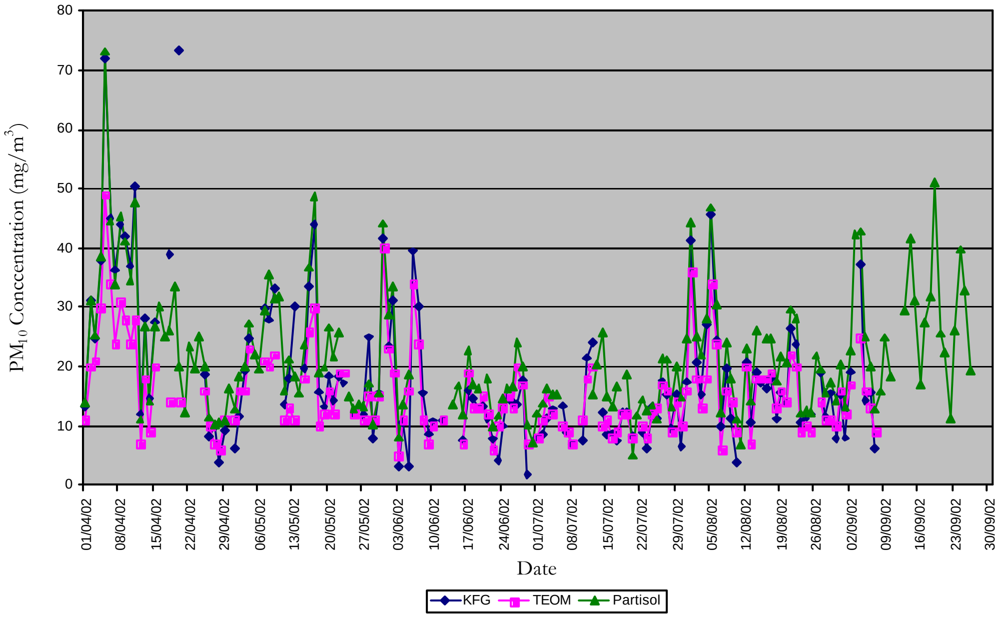


Figure A6: (contd.)

(c) Winter2001/2002



(d) Summer 2002



Annex 3: Data Capture Statistics

Percentage of PM_{10} and $PM_{2.5}$ data available per year for each site. Percentages below 50% are underlined in the tables.

Numbers and percentages of data available in 1999 (from the commencement of sampling)

	B'ham centre	London N. Kensington	Marylebone Road	Harwell	Glasgow	Port Talbot	Thurrock	Belfast
PM_{10} LVS	-	-	153	142	17	67	146	-
	-	-	72.2%	65.1%	54.8%	54.9%	66.7%	-
PM_{10} Partisol	72	17	46	92	45	53	-	-
	59.0%	13.9%	37.7%	75.4%	36.9%	43.4%	-	-

Numbers and percentages of data available in 2000 (from the commencement of sampling)

	B'ham centre	London N. Kensington	Marylebone Road	Harwell	Glasgow	Port Talbot	Thurrock	Belfast
PM_{10} LVS	-	-	174	270	236	212	203	-
	-	-	47.5%	73.9%	64.6%	58.1%	55.6%	-
PM_{10} Partisol	72	17	46	92	45	53	-	-
	59.0%	13.9%	37.7%	75.4%	36.9%	43.4%	-	-
$PM_{2.5}$	77	71	79	106	48	92	-	-
	63.1%	58.2%	64.7%	86.9%	39.3%	75.4%	-	-

Numbers and percentages of data available in 2001

	B'ham centre	London N. Kensington	Marylebone Road	Harwell	Glasgow	Port Talbot	Thurrock	Belfast
PM_{10} LVS	-	-	223	280	223	263	209	243
	-	-	61.1%	76.7%	61.1%	72.0%	57.3%	74.1%
PM_{10} Partisol	361	276	183	247	218	235	-	296
	98.9%	75.6%	50.1%	67.7%	59.7%	64.4%	-	81.1%
$PM_{2.5}$	335	325	300	271	198	229	-	291
	91.8%	89.0%	82.2%	74.2%	54.2%	62.7%	-	79.7%

Numbers and percentages of data available in 2002 (until July 2002)

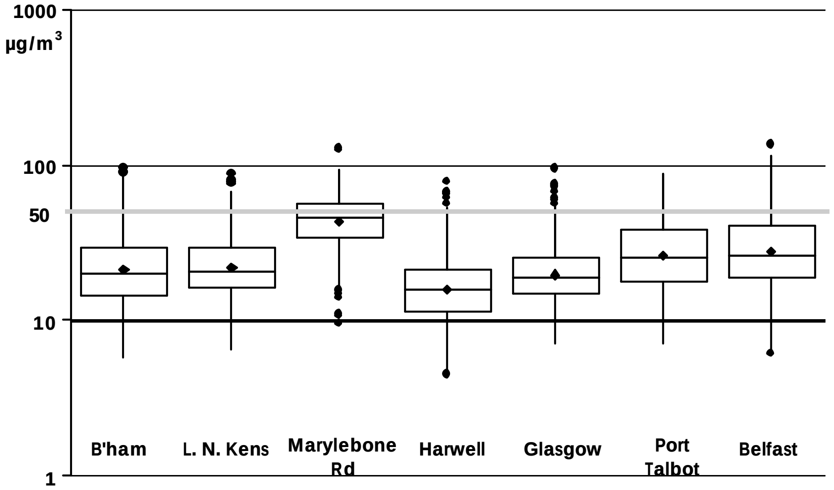
	B'ham centre	London N. Kensington	Marylebone Road	Harwell	Glasgow	Port Talbot	Thurrock	Belfast
PM_{10} LVS	-	-	21	225	184	168	-	207
	-	-	23.3%	82.4%	67.4%	61.3%	-	75.8%
PM_{10} Partisol	116	142	32	173	26	101	-	133
	63.4%	77.6%	17.5%	94.5%	14.2%	55.2%	-	72.7%
$PM_{2.5}$	113	128	141	169	45	119	-	137
	61.7%	69.9%	77%	92.3%	24.6%	65.0%	-	74.9%

Annex 4: Boxplots for concentrations measured in the different sites (Gravimetric Partisol data).

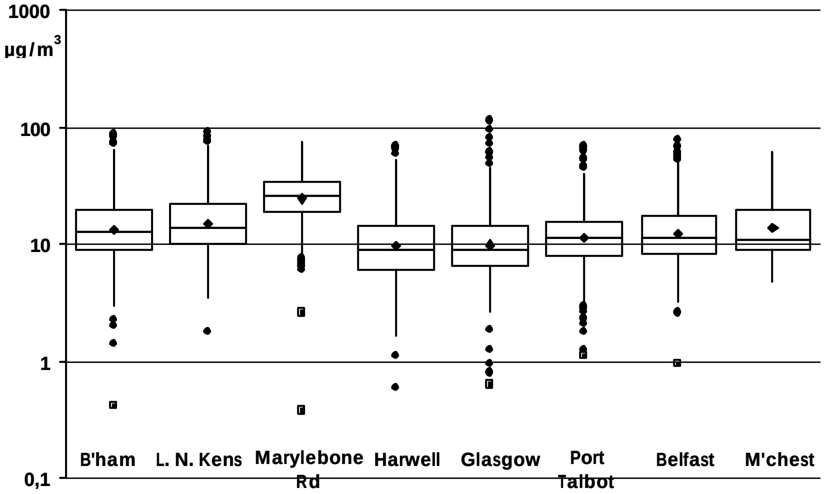
Description of the boxplots:

The upper part of the box represents the 75th percentile ; the lower part the 25th percentile; the line inside the box, the median; the distance between the 25th percentile and the 75th percentile is the interquartile distance (50% of the data are included in the interquartile distance) ; the length of the upper part of the whisker is the shorter of these two distances : the distance between the 75th percentile and the maximal value or 1.5 time the interquartile distance (in this case, 'outlier values' are drawn outside the boxplots) and similarly, the length of the lower part of the whisker is the shorter of these two distances : the distance between the minimal value and the 25th percentile or 1.5 time the interquartile distance (and 'outlier values' are drawn outside the boxplots).

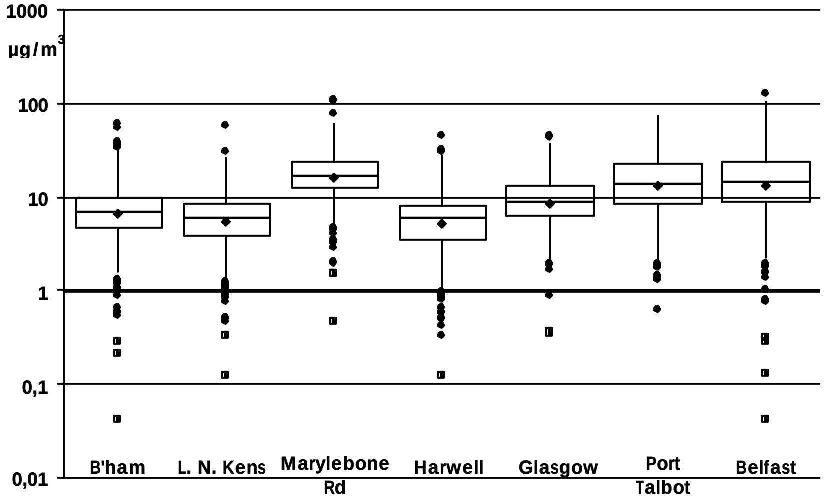
PM_{10} concentrations (the line corresponds to the daily standard of 50 µg/m^3)



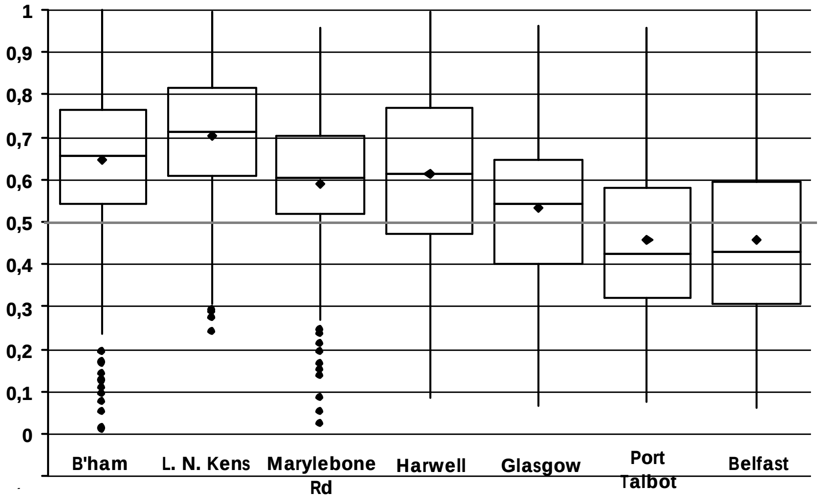
$PM_{2.5}$ concentrations



PM_{coarse} concentrations

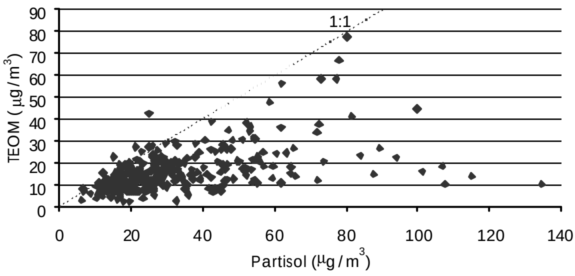


Ratio $PM_{2.5}/PM_{10}$

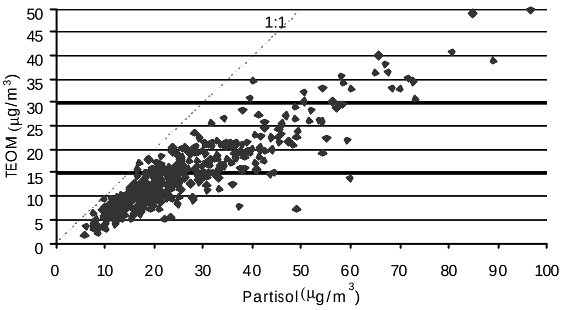


Annex 5: Charts TEOM (adjusted downward) versus Partisol for all sites

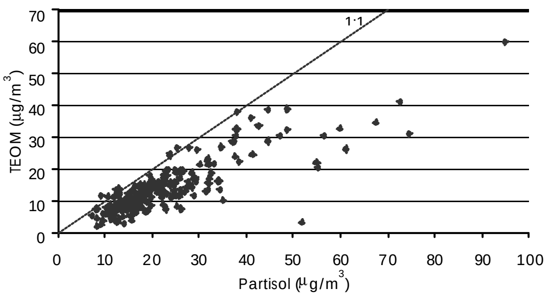
Belfast PM_{10}



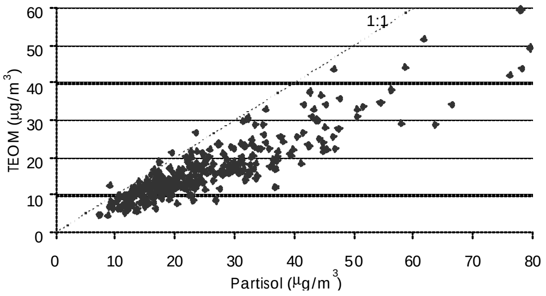
Birmingham centre PM_{10}



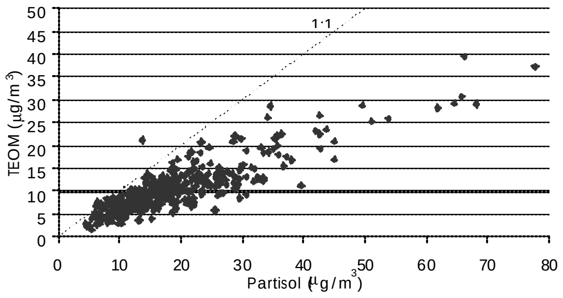
Glasgow centre PM_{10}



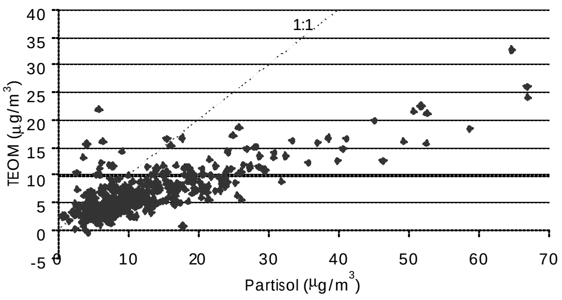
London North Kensington PM_{10}



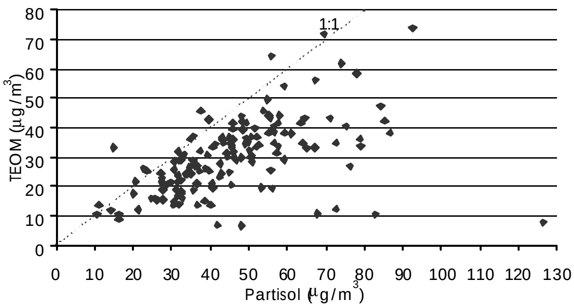
Harwell PM_{10}



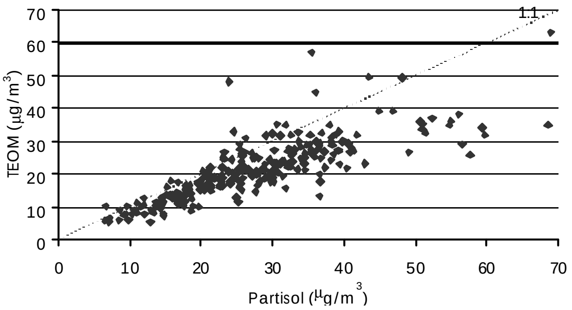
Harwell PM_{25}



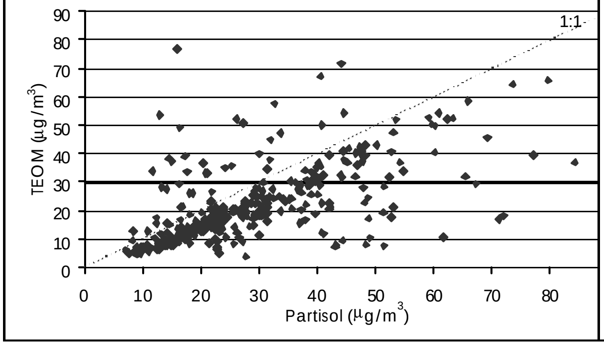
Marylebone Road PM_{10}



Marylebone Road $PM_{2.5}$



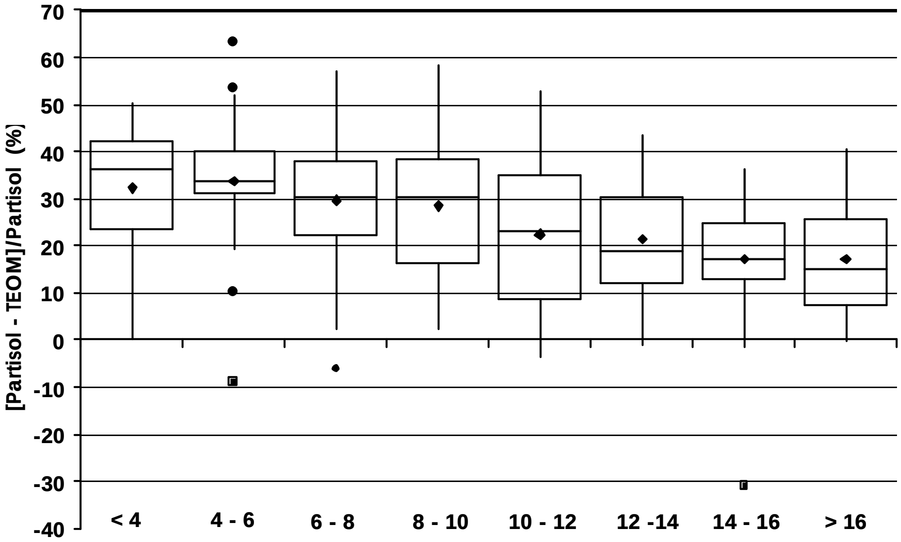
Port Talbot PM_{10}



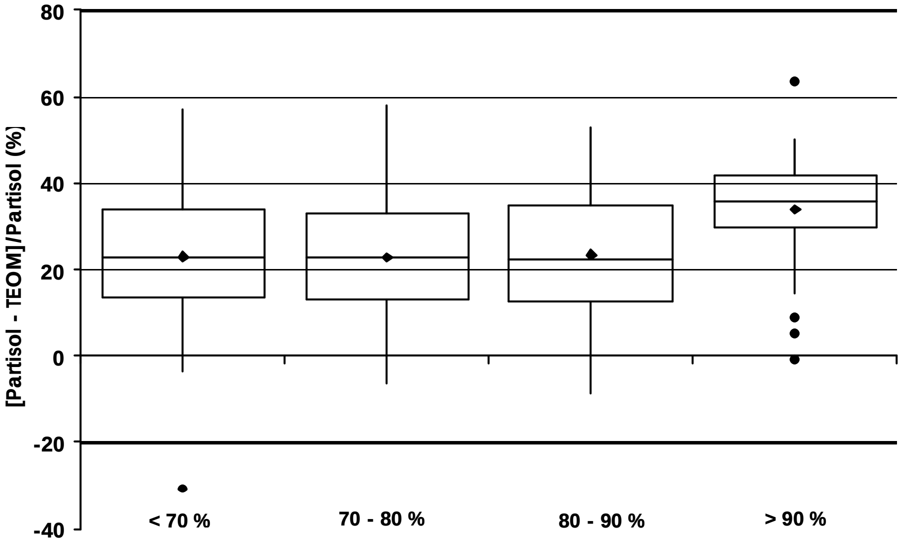
Annex 6: Boxplots for relative differences versus temperature relative and relative humidity

Birmingham centre PM_{10}

Temperature (°C)

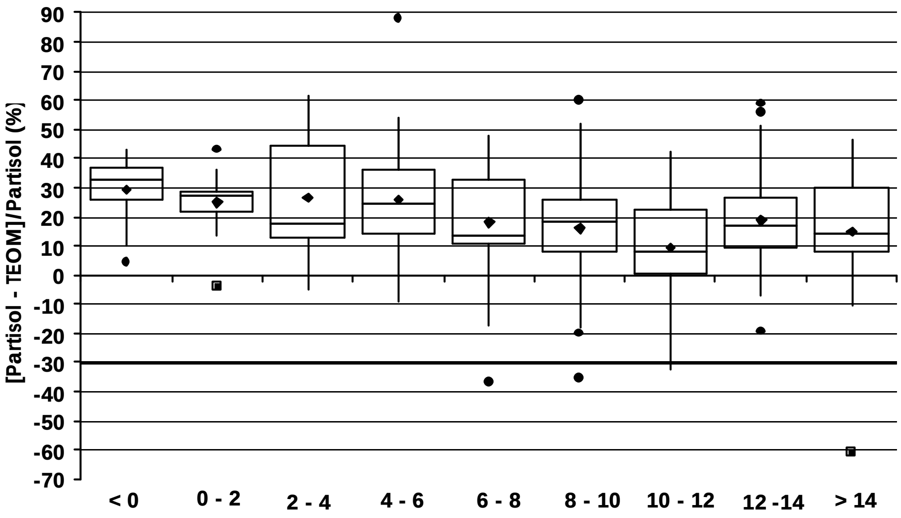


Relative humidity (%)

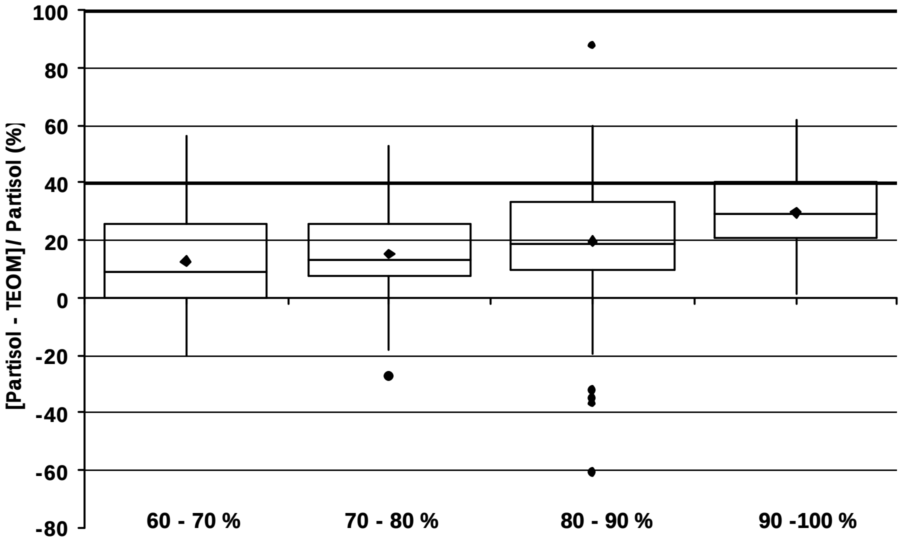


Glasgow centre PM_{10}

Temperature (°C)

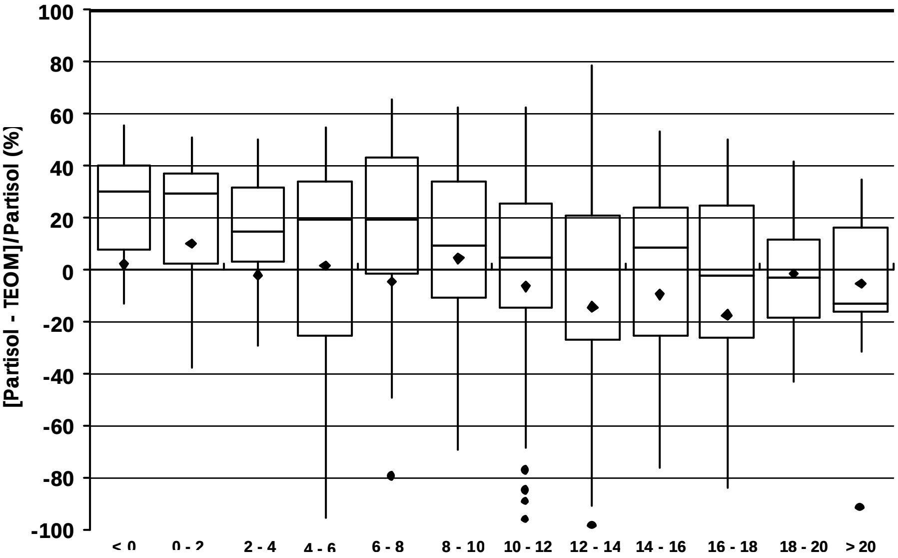


Relative humidity (%)

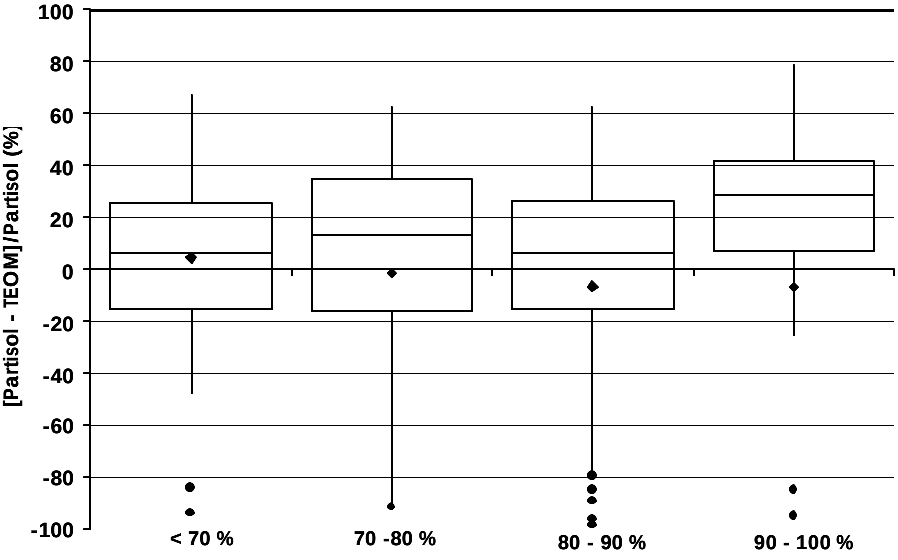


Harwell $PM_{2.5}$

Temperature (°C)



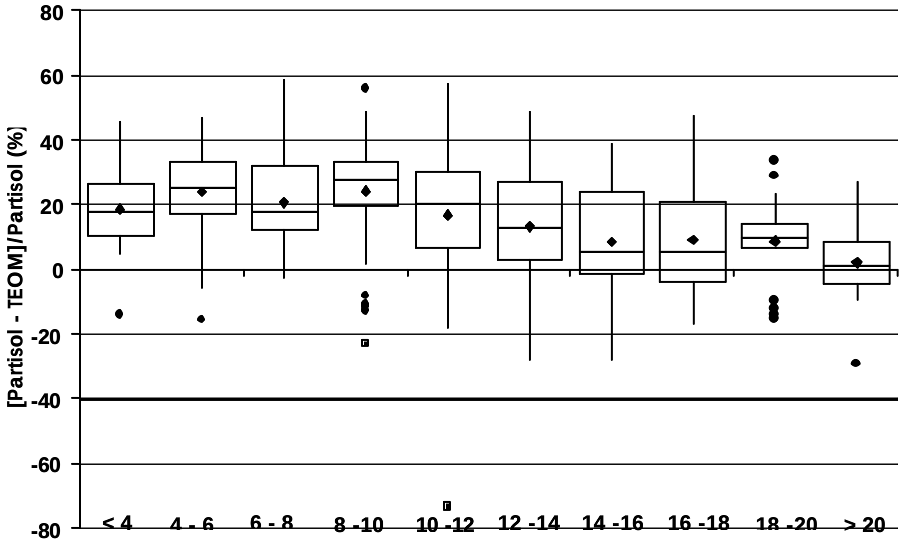
Relative humidity (%)



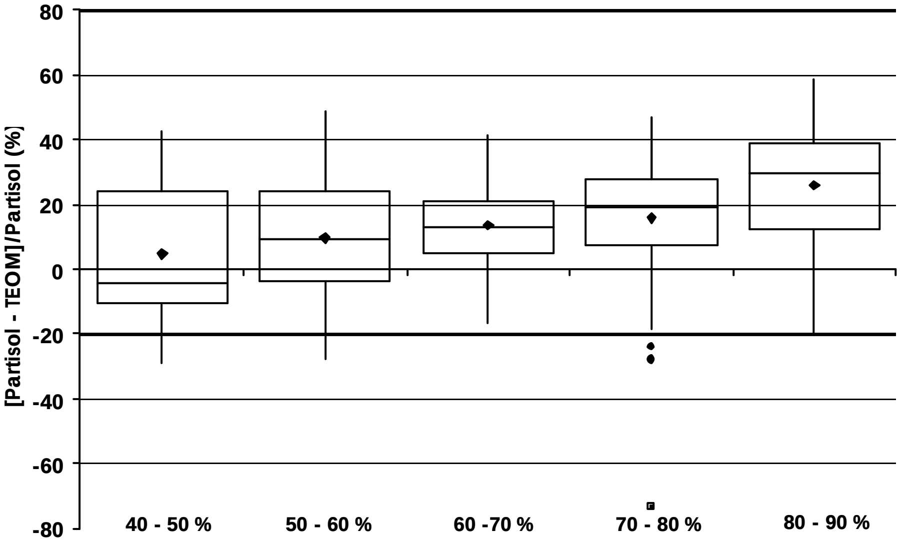
The means are strongly influenced by few very low values, not represented on the charts.

London North Kensington PM_{10}

Temperature (°C)

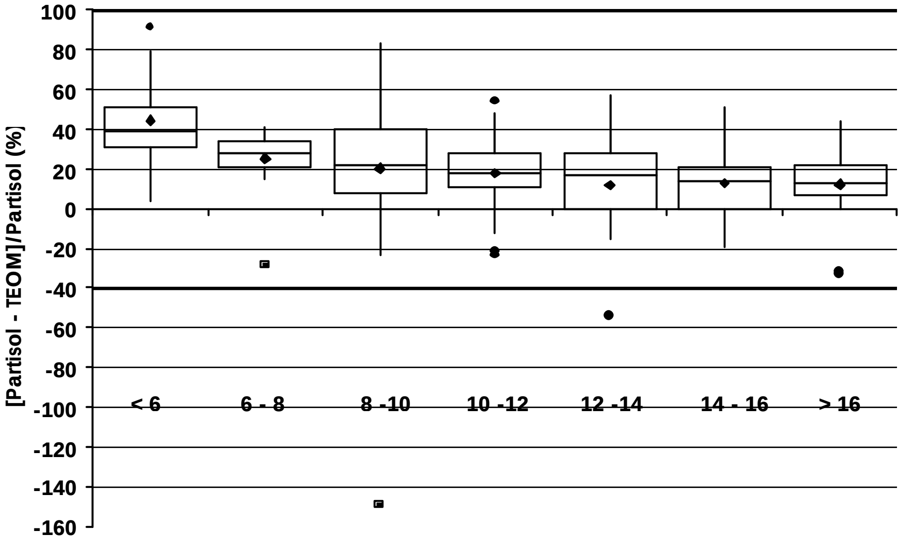


Relative humidity (%)

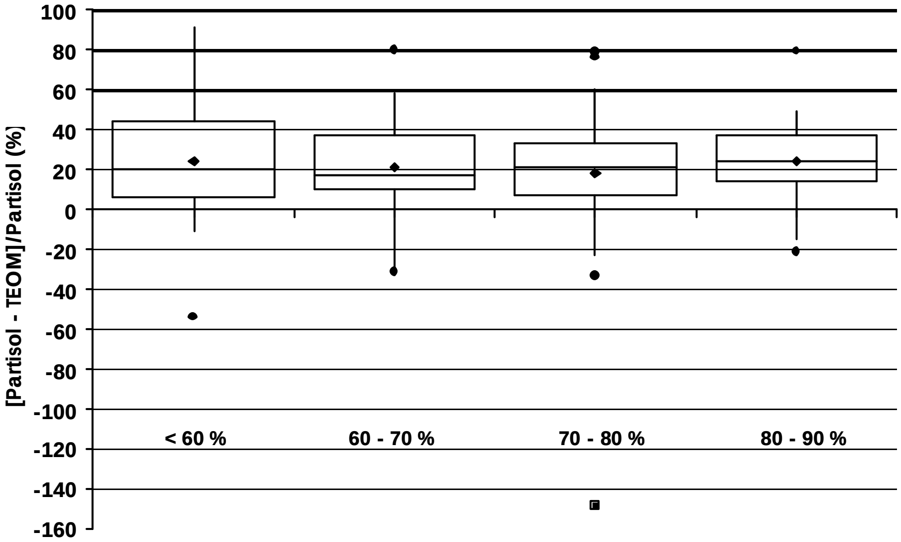


Marylebone Road PM_{10}

Temperature (°C)

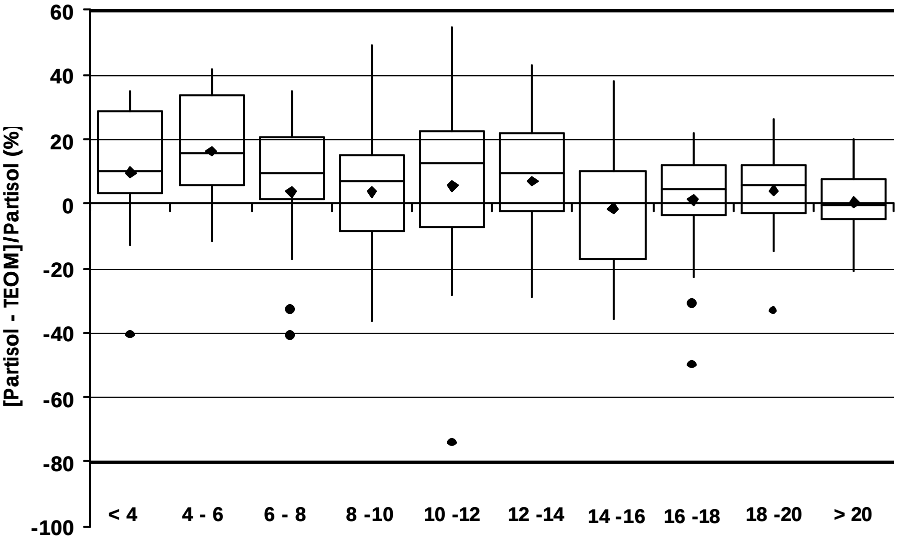


Relative humidity (%)

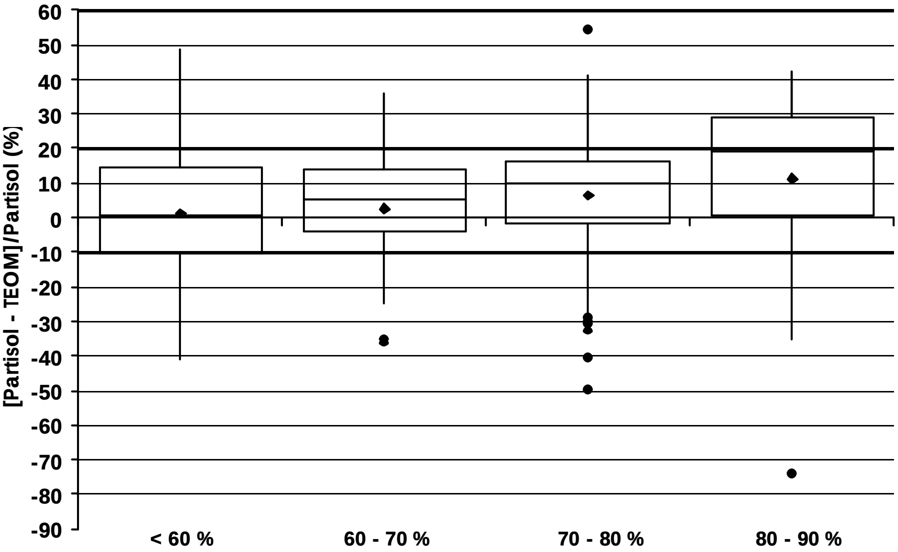


Marylebone Road $PM_{2.5}$

Temperature (°C)



Relative humidity (%)



Annex 7: Linear regression models for TEOM (adjusted downward) mass concentrations versus Partisol mass concentrations for different season and different temperature and relative humidity bins

Seasonal variations

Seasonal linear regressions for PM$_{10}$ with in brackets the confidence intervals for the slope and for the intercept and Pearson correlation coefficients.

PM$_{10}$	**Seasons**	**Number of observations**	**RMA linear regression**	**Square Pearson correlation coefficient**
Belfast	Winter 01	18	-	-
	Summer 01	133	-	0.17
	Winter 01-02	86	-	0.24
	Summer 02	78	$\mathbf{y} = 0.449\ (\pm 0.036)\ \mathbf{x} + 0.21\ (\pm 1.31)$	0.50
Birmingham	Summer 00	4	-	-
	Winter 00-01	127	$\mathbf{y} = 0.476\ (\pm 0.018)\ \mathbf{x} + 0.66\ (\pm 0.62)$	0.82
	Summer 01	157	$\mathbf{y} = 0.604\ (\pm 0.021)\ \mathbf{x} + 0.24\ (\pm 0.52)$	0.80
	Winter 01-02	124	$\mathbf{y} = 0.518\ (\pm 0.020)\ \mathbf{x} + 0.84\ (\pm 0.57)$	0.82
	Summer 02	57	$\mathbf{y} = 0.556\ (\pm 0.020)\ \mathbf{x} + 0.35\ (\pm 0.67)$	0.92
Glasgow	Winter 00-01	90	$\mathbf{y} = 0.565\ (\pm 0.035)\ \mathbf{x} + 0.21\ (\pm 1.02)$	0.65
	Summer 01	114	$\mathbf{y} = 0.884\ (\pm 0.040)\ \mathbf{x} - 4.04\ (\pm 0.87)$	0.77
	Winter 01-02	43	$\mathbf{y} = 0.591\ (\pm 0.032)\ \mathbf{x} - 0.52\ (\pm 0.94)$	0.87
Harwell	Summer 00	1	-	-
	Winter 00-01	130	$\mathbf{y} = 0.491\ (\pm 0.017)\ \mathbf{x} + 0.68\ (\pm 0.36)$	0.85

PM$_{10}$	**Seasons**	**Number of observations**	**RMA linear regression**	**Square Pearson correlation coefficient**
	Summer 01	138	$y = 0.571\ (\pm 0.023)\ x + 1.44\ (\pm 0.48)$	0.77
	Winter 01-02	91	$y = 0.443\ (\pm 0.024)\ x + 1.78\ (\pm 0.48)$	0.74
	Summer 02	76	$y = 0.497\ (\pm 0.026)\ x + 0.22\ (\pm 0.57)$	0.80
London N.K.	Summer 00	3	-	-
	Winter 00-01	51	$y = 0.591\ (\pm 0.029)\ x + 0.16\ (\pm 0.78)$	0.88
	Summer 01	121	$y = 0.789\ (\pm 0.030)\ x - 1.34\ (\pm 0.72)$	0.83
	Winter 01-02	140	$y = 0.623\ (\pm 0.025)\ x + 0.31\ (\pm 0.72)$	0.78
	Summer 02	38	$y = 0.585\ (\pm 0.027)\ x + 1.22\ (\pm 0.91)$	0.92
Marylebone Road	Summer 00	5	-	-
	Winter 00-01	43	-	0.05
	Summer 01	54	-	0.42
	Winter 01-02	48	-	0.34
Port Talbot	Winter 00-01	87	-	0.17
	Summer 01	93	-	0.21
	Winter 01-02	95	$y = 0.862\ (\pm 0.053)\ x - 3.24\ (\pm 1.75)$	0.64
	Summer 02	59	$y = 0.817\ (\pm 0.046)\ x - 3.51\ (\pm 1.56)$	0.81

Seasonal linear regressions for $PM_{2.5}$ *with (in brackets) the confidence intervals for the slope and for the intercept and Pearson correlation coefficients.*

$PM_{2.5}$	Seasons	Number of observations	RMA linear regression	Square Pearson correlation coefficient
Harwell	Summer 00	14	-	-
	Winter 00-01	134	$y = 0.427\ (\pm0.011)\ x + 0.57(\pm0.18)$	0.91
	Summer 01	120	$y = 0.515\ (\pm0.026)\ x + 0.86\ (\pm0.37)$	0.69
	Winter 01-02	131	-	0.29
	Summer 02	62	$y = 0.372\ (\pm0.016)\ x + 0.26\ (\pm0.33)$	0.89
Marylebone Road	Summer 00	1	-	-
	Winter 00-01	56	$y = 0.702\ (\pm0.043)\ x + 0.28\ (\pm1.43)$	0.79
	Summer 01	106	$y = 0.799\ (\pm0.028)\ x - 0.22\ (\pm0.75)$	0.87
	Winter 01-02	48	-	0.47
	Summer 02	59	$y = 0.589\ (\pm0.043)\ x + 4.27\ (\pm1.23)$	0.68

Meteorological parameters

Linear regressions TEOM vs.Partisol for PM_{10} *(with in brackets, the confidence intervals for the slope and the intercept), the square of the Pearson correlation coefficients and the mean and the standard deviation for ratios Partisol/TEOM for different temperature and relative humidity bins.*

PM_{10}	**Temperature & relative humidity**	**N**	**RMA linear regression**	**Square Pearson correlation coefficient**	**Ratio Partisol/ TEOM**
Birmingham	T < 10°C ; RH > 80 %	67	**y =** 0.551 (±0.021) **x –** 0.79 (±0.64)	0.90	1.98 ± 0.45
	T < 10°C ; RH < 80 % Ou T > 10°C ; RH > 80 %	107	**y =** 0.535 (±0.019) **x +** 0.74 (±0.56)	0.87	1.84 ± 0.49
	T > 10°C ; RH < 80 %	51	**y =** 0.583 (±0.030) **x +** 1.03 (±0.74)	0.86	1.63 ± 0.35
Glasgow	T < 10°C ; RH > 80 %	98	**y =** 0.605 (±0.032) **x +** 1.04 (±0.94)	0.73	2.05 ± 1.57
	T < 10°C ; RH < 80 % Ou T > 10°C ; RH > 80 %	105	**y =** 0.699 (±0.037) **x -** 1.13 (±0.86)	0.71	1.69 ± 0.61
	T > 10°C ; RH < 80 %	43	**y =** 0.935 (±0.068) **x –** 4.72 (±1.43)	0.77	1.55 ± 0.39
Harwell	T < 10°C ; RH > 80 %	134	**y =** 0.493 (±0.018) **x +** 0.40 (±0.39)	0.83	1.98 ± 0.48
	T < 10°C ; RH < 80 % Ou T > 10°C ; RH > 80 %	178	**y =** 0.490 (±0.016) **x +** 1.30 (±0.34)	0.80	1.80 ± 0.53

PM_{10}	Temperature & relative humidity	N	RMA linear regression	Square Pearson correlation coefficient	Ratio Partisol/ TEOM
	T > 10°C ; RH < 80 %	124	**y =** 0.627 (±0.030) **x +** 0.18 (±0.58)	0.71	1.63 ± 0.44
London N.K.	T < 10°C ; RH > 80 %	25	**y =** 0.561 (±0.046) **x -** 1.71 (±1.59)	0.83	2.06 ± 0.48
	T < 10°C ; RH < 80 % Ou T > 10°C ; RH > 80 %	148	**y =** 0.586 (±0.017) **x +** 0.85 (±0.47)	0.87	1.62 ± 0.29
	T > 10°C ; RH < 80 %	180	**y =** 0.709 (±0.022) **x +** 0.15 (±0.59)	0.83	1.43 ± 0.29
Marylebone Road	T < 10°C ; RH > 80 %	16	-	0.42	2.02 ± 1.18
	T < 10°C ; RH < 80 % ou T > 10°C ; RH > 80 %	79	-	0.12	2.02 ± 2.07
	T > 10°C ; RH < 80 %	55	**y =** 0.825 (±0.069) **x –** 3.40 (±3.13)	0.61	1.42 ± 0.42

Linear regressions TEOM vs.Partisol for $PM_{2.5}$ *(with in brackets, the confidence intervals for the slope and the intercept), the square of the Pearson correlation coefficients and the mean and the standard deviation for ratios Partisol/TEOM for different temperature and relative humidity bins.*

Site	**Temperature & relative humidity**	**N**	**RMA linear regression**	**Square Pearson correlation coefficient**	**Ratio Partisol/ TEOM**
Harwell	T < 10°C ; RH > 80 %	169	**y =** 0.459 (±0.023) **x +** 0.86 (±0.38)	0.58	2.00 ± 1.27
	T < 10°C ; RH < 80 % ou T > 10°C ; RH > 80 %	182	**y =** 0.372 (±0.014) **x +** 1.46 (±0.24)	0.73	2.41 ± 4.08
	T > 10°C ; RH < 80 %	110	**y =** 0.471 (±0.029) **x +** 1.21 (±0.42)	0.59	1.80 ± 0.71
Marylebone Road	T < 10°C ; RH > 80 %	18	**y =** 0.745 (±0.100) **x -** 2.48 (±3.43)	0.68	1.57 ± 0.38
	T < 10°C ; RH < 80 % Ou T > 10°C ; RH > 80 %	99	**y =** 0.810 (±0.048) **x -** 1.23 (±1.41)	0.66	1.35 ± 0.30
	T > 10°C ; RH < 80 %	153	**y =** 0.794 (±0.037) **x +** 0.27 (±1.10)	0.67	1.27 ± 0.26

Annex 8: Mean temperature and mean relative humidity associated with each bin

Site	Temperature & relative humidity	Mean temperature (°C)	Mean relative humidity (%)
Birmingham	T < 10°C ; RH > 80 %	5.7	90.6
	T < 10°C ; RH < 80 % ou T > 10°C ; RH > 80 %	10.6	79.5
	T > 10°C ; RH < 80 %	13.7	71.1
Glasgow	T < 10°C ; RH > 80 %	5.1	88.7
	T < 10°C ; RH < 80 % ou T > 10°C ; RH > 80 %	8.5	79.0
	T > 10°C ; RH < 80 %	13.0	74.0
Harwell	T < 10°C ; RH > 80 %	5.5 (PM_{10}) ; 5.1 ($PM_{2.5}$)	88.0 (PM_{10}) ; 88.2 ($PM_{2.5}$)
	T < 10°C ; RH < 80 % ou T > 10°C ; RH > 80 %	9.9 (PM_{10}) ; 10.2 ($PM_{2.5}$)	80.0 (PM_{10}) ; 80.5 ($PM_{2.5}$)
	T > 10°C ; RH < 80 %	15.0 (PM_{10}) ; 15.2 ($PM_{2.5}$)	71.9 (PM_{10}) ; 71.8 ($PM_{2.5}$)

Site	Temperature & relative humidity	Mean temperature (°C)	Mean relative humidity (%)
London N.K.	T < 10°C ; RH > 80 %	6.9	85.1
	T < 10°C ; RH < 80 % ou T > 10°C ; RH > 80 %	8.5	73.1
	T > 10°C ; RH < 80 %	15.0	65.0
Marylebone Road	T < 10°C ; RH > 80 %	7.4 (PM$_{10}$) ; 6.2 (PM$_{2.5}$)	84.5 (PM$_{10}$) ; 85.0 (PM$_{2.5}$)
	T < 10°C ; RH < 80 % ou T > 10°C ; RH > 80 %	8.8 (PM$_{10}$) ; 8.4 (PM$_{2.5}$)	74.0 (PM$_{10}$) ; 72.6 (PM$_{2.5}$)
	T > 10°C ; RH < 80 %	14.5 (PM$_{10}$) ; 15.4 (PM$_{2.5}$)	66.0 (PM$_{10}$) ; 63.2 (PM$_{2.5}$)