



Bureau Veritas HS&E Limited

**Analysis of Trends in Gravimetric
Particulate Mass Measurements in the
United Kingdom**

May 2008

DOCUMENT INFORMATION AND CONTROL SHEET

Client: Department for the Environment, Food and Rural Affairs (Defra)

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Document Status and Approval Schedule

Issue	Status	Description	Prepared by: Signed/Dated	Reviewed by: Signed/Dated
1	Draft 3	Sent by Email.	 28 th May 2008	 28 th May 2008

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Executive Summary

This report provides for an analysis of observed trends in filter based gravimetric PM₁₀ and PM_{2.5} concentrations in the United Kingdom as gathered through a network of samplers over the period 2001-2007. The use of gravimetric samplers in the UK provides for part of the UK implementation of monitoring requirements around compliance against legally binding limit values for particulate matter already in force (in the case of PM₁₀) or coming into force (in the case of PM_{2.5}).

European reference methods dictate the requirements for compliance around issues of uncertainty and the previous “*UK Equivalence Programme for Monitoring of Particulate Matter*” (2006) has shown which methods are currently commercially available in the UK market for monitoring of PM₁₀ equivalent to the EU reference method (EN12341), allowing for reporting against limit values. For PM_{2.5} work is ongoing in relation to determining the equivalence of available methods to the EU reference method EN14907.

Additional consideration to methods of monitoring of particulate matter is given in the UK to a number of practical issues such as ease of operation; available laboratory facilities; size of instrumentation; costs, etc, which provide for effective operation of deployed instrumentation into the network. Unlike a number of other EU Member States, the UK network is operated *via* private commercial companies on behalf of the UK Government and devolved administrations. Bureau Veritas HS&E Ltd is the Central Management and Co-ordination Unit of the network, whilst AEA Technology plc is the appointed QA/QC unit. Air Liquide is the appointed supplier of standard gases to the network.

For the provision of filter weighing services for undertaking the mass measurements for gravimetric analysis, the appointed sub-contractor is the UKAS accredited Bureau Veritas Laboratories. Other providers for filter mass measurements in the UK used in this work are the National Physical Laboratory and AEA Technology plc.

Particulate matter is directly emitted from many sources and is referred to as primary PM. However, chemical reactions in the atmosphere result in the formation of additional (secondary) PM giving rise to a wide variability in PM composition at local, regional and national levels. This provides for significant challenges in monitoring where uncertainty, precision and accuracy of monitoring methods are paramount for the reporting of robust data against legally binding standards. In the UK, there is no single dominant source of primary PM, though road transport accounts for around 22 % of the UK emissions of primary PM in 2006. Other significant sources include domestic combustion; electricity generation and industrial combustion and a number of industrial processes involving mineral products and agriculture. In most urban areas, road transport is likely to be the dominant source of primary PM, with possible exceptions in areas where significant solid fuel burning; construction or other PM generating activities take place. PM is emitted from vehicle exhausts but also arises as a consequence of wear of tyre material, brake and clutch pads and road surface, as well as through re-suspension of already deposited road dust.

Over the last 15 years, increasingly stringent vehicle emissions standards have resulted in significant reductions of primary exhaust PM (2008 Euro IV standards are 82% lower on PM than a Euro I standard car purchase between 1993 – 1996). The penetration of cleaner vehicles into the UK fleet has seen an overall decline in PM exhaust (26 % reduction over 2000 – 2006), in spite of growth in traffic levels. Current projections suggest a further decline of 27 % is anticipated between 2006 – 2010.

The decline in primary PM exhaust places more importance on the need for policy areas to look at non-exhaust and secondary PM levels. Current trends indicate increases in tyre and brake wear over the period 2000 – 2006 of 4.5 %. When taken into account, the overall trend in urban PM emissions from road transport over the period 2000 – 2006 is reduced from 26 % for exhaust-only emissions to 17 % overall. Issues of re-suspension give rise to increased uncertainty and are therefore likely to further reduce the estimated decline in urban PM emissions from road traffic over the period 2000 – 2006.

Beyond road traffic emissions of PM emissions arising as a result of industrial activities have been shown to be in decline as a result of tighter regulation. Consequently, over-riding factors in respect of overall trends in PM across the UK are those of the formation of secondary PM formation, which are dealt with through international agreements such as the National Emissions Ceiling Directive, the Large Combustion Plant Directive and the Solvent Emissions Directive to name but a few.

Whilst uncertainty therefore exists in relation to the impacts of some policy measures on PM emissions, the overall anticipated trend for the occurrence of PM in the UK is one of decline. Monitoring of resultant PM concentrations (PM₁₀ and PM_{2.5}) therefore provide a valuable evidence-base to support UK policy on whether declining trends in emissions results in concurrent improvements in PM concentrations. Analysis of annual mean PM₁₀ and PM_{2.5} trends over the period 2000 – 2007 indicates that this anticipated decline in PM levels is not arising, when based on gravimetric filter mass samplers. This observation conflicts with previous trends reported by the UK Air Quality Expert Group in their 2005 report entitled “*Particulate Matter in the United Kingdom*” based on previously reported TEOM methods.

Of particular note in the trend of gravimetric PM measurements is the apparent increase in PM concentrations in the last two years. This forms the primary focus of this report in relation to in-depth analysis.

Collocation of different monitoring methods at a number of sites provides for a comparison of gravimetric filter-based methods with EU reference method equivalent data acquired through non-gravimetric methods. Results at Auchencorth Moss in Scotland, where levels of PM are expected to be very low, indicate that an over-estimation in PM₁₀ levels in September 2007 in an order of three times. Elsewhere, comparisons of filter-based gravimetric methods show less discrepancy but support the notion that measurements undertaken by the Partisol 2025 method lead to an over-estimation of PM₁₀ levels during both summer (August 2007) and in winter (December 2006).

Potential discrepancies between filter-based gravimetric methods may arise for a wide range of reasons. A comparison of results between providers of filter mass measurements in the UK (in this case for PM_{2.5}) undertaken as part of further work at Teddington in 2007 has shown that discrepancies in results can arise as a consequence of filter media; differences in weighing protocols; and differences due to instrumentation. In this trial, collocation of the EU reference method (Low Volume Sampler) and the Partisol 2025 method was undertaken, which additionally included different filter media (quartz vs. Teflon coated glass fibre (Emfab)) and two different providers (Bureau Veritas Laboratories and the National Physical Laboratory). Results showed that differences in mean PM_{2.5} concentrations for the period June – August 2007 were strongly influenced by the provider (i.e. laboratory protocols) resulting in a difference in reported mean of 6.7 µg m⁻³. Interestingly, the choice of filter media was shown to influence reported concentrations with quartz filters providing for an over-estimation of PM_{2.5} concentrations of 3.8 µg m⁻³ when compared to Emfab filter measurements. Differences between instrumentation were lowest at 1.7 µg m⁻³ (with the Partisol consistently reading lower than the reference method)

Further analysis of quartz travel blank filters (filters that have been deployed into the day-to-day operations of the Partisol 2025 units but not actively sampled) show a strong influence in the over-estimation of reported mass concentrations for PM₁₀ and PM_{2.5} during 2006 and 2007. The impact on reported mass concentrations is statistically the same between PM₁₀ and PM_{2.5} highlighting that a common influence is driving the change in quartz travel blank mass. Analysis of Emfab travel blank filters provided by the same laboratory over the period 2003 – 2008 at a site in London (Earls Court Road) does not provide for the same trend in travel blanks. This indicates a strong influence of filter media on travel blank behaviour. Namely, Emfab filters appear to be less influenced by artefacts than quartz filters.

As way of re-assurance of quality in the provision of filter weighing services an audit was undertaken of the laboratory by representatives of CMCU and QA/QC units. Specifically, the audit focused on protocols and the variability in environmental conditions for the conditioning of filters pre- and post-weighing after exposure to sampling. Whilst historical problems in maintaining the temperature (20 °C and humidity conditions (5 0% RH) were highlighted, the impacts on mass measurements are

unlikely to be solely attributed to this aspect of operations. No single issue was identified in the audit as being responsible for the observed increase in travel blanks in 2006 and 2007.

Seasonal trend decomposition analysis has shown that a strong seasonal cycle occurs within the quartz travel blank data, which correlates well with ambient absolute humidity. Similar trends in seasonal effect on quartz blank filter mass and ambient absolute humidity is shown elsewhere in data gathered from The Netherlands, supporting this analysis.

Statistical analysis on the travel blank filter data (expressed as concentration equivalent) shows a statistically significant change-point in the data around April / May 2006 (95 % confidence interval in the timing of the change-point = December 2005 to May 2006). This indicates that there is a causal link between increases in quartz travel blanks reported PM concentrations.

Analysis of initial filter weights has provided for evidence of the possibility of two distinct nominally identical quartz filter types. The filters with a higher initial weight are associated with blank filters that have concentrations of $2.8 \pm 0.4 \mu\text{g m}^{-3}$ (95 % confidence interval in the mean) and the filters with a lower initial weight with concentrations of $0.3 \pm 0.3 \mu\text{g m}^{-3}$. Statistically, it can be shown that there is a clear difference in these two groups in their mean blank concentrations of $2.5 \mu\text{g m}^{-3}$. This is a potentially important finding as it shows that nominally identical filters have different characteristics in terms of their blank filter concentrations. The difference of $2.5 \mu\text{g m}^{-3}$ is also a considerable fraction of absolute blank filter weights. The manufacturing facility have been contacted, and confirmed that the tolerance for filter weight is from 127 mg to 161 mg (target 144 mg), and all of the filters used herein are within range. They confirmed these filter media are manufactured using a single machine. Although, all filter weights in any given batch will be very similar, the range of weights between batches would be much greater. This would explain the two separate distinct bands observed during 2005 but does not contribute significantly to explaining the significant change-point reported above.

Statistical analysis of ambient concentration data (PM_{10} and $\text{PM}_{2.5}$) highlights the occurrence of a different seasonal cycle when compared to travel filter blanks for quartz filters. This seasonal cycle peaks in spring as opposed to summer suggesting that different factors may influence travel filter blanks when compared to exposed filters. Trend analysis has shown that concentrations in ambient PM Levels have increased by around $9 \mu\text{g m}^{-3}$ over the period 2000 – 2007. Change-point analysis applied to monthly mean measurements of ambient PM_{10} and $\text{PM}_{2.5}$ concentrations has yielded no significant change-point over the time series. The result is not surprising as stronger influences on PM occurrence dominate. A refined analysis was therefore chosen to assess the likely extent of change-point in ambient PM concentrations. This approach considered the analysis of data at two sites (Harwell and North Kensington) on data determined through the subtraction of TEOM data from gravimetric concentrations. This data would account for mass concentrations not recorded by TEOM methods (due to the known under-estimation of particle mass) and include any artefact due to filter issues (*i.e.* travel blanks). The results of the refined approach confirmed the presence of a significant change-point in data at both sites, albeit at different times. At Harwell, the change-point occurrence was found in April/May 2006, whilst at North Kensington the change-point occurrence was found in December 2005. For both sites the uncertainty interval includes April/May 2006 change-point for travel filter blanks. Wider uncertainties are evident, which, in part, are likely to be attributed to increased variability in the data set due to it being reported ambient data, encompassing all the influences of emissions, meteorology, filter mass, etc that ambient data entails.

Current assessment methods used in the UK for determining compliance against limit values comprise of both monitoring and modelling methods. In recent years the Pollution Climate Mapping (PCM) model has used data acquired from gravimetric Partisol samplers to validate the approach. Thus, use of the Partisol data has since introduced a bias into the national assessment method, which has led to an over-estimation of exceedences of the limit values for PM_{10} , when compared to otherwise unbiased assessments. Comparison of the PCM model outputs against the FDMS method (a non-gravimetric method shown to be equivalent to the EU reference method) has highlighted the discrepancies of using Partisol 2025 gravimetric measurements to validate the model approach. Consequently, the bias introduced through the use of gravimetric data is required to be removed.

Regardless of the cause of increase in travel blank filter mass (whether it be seasonal or laboratory bias) correction of existing reported annual means is proposed through the application of the following:

Year	Annual Blank Average / $\mu\text{g m}^{-3}$	Standard Deviation	Annual Blank Count
2000	2.71	0.18	2
2001	1.08	1.36	124
2002	0.94	2.08	352
2003	2.23	2.47	210
2004	1.49	1.62	257
2005	1.46	2.42	402
2006	3.34	3.23	329
2007	4.51	2.83	238

Note that there are only 2 data points for the year 2000, and so confidence in the average concentration is very low. However, there are no valid annual averages for ambient data for 2000, and as such this correction factor is not in practice applied.

Initial consideration to the application of these values to annual means removes the apparent increasing trend in PM concentrations across the UK observed in recent years and significantly reduce the extent of [otherwise] reported exceedences of the PM₁₀ limit values.

In addition to the application of the above annual mean corrections to Partisol data, it is proposed that gravimetric sampling of PM mass in the UK move toward a filter media based on Emfab (Teflon coated glass fibre) or equivalent to reduce identified artefacts associated with filter media choice. The current EU reference method (EN12341) for PM₁₀ relies solely on the use of quartz filters. Consequently, it is recommended that the UK lobby the European Committee for Normalization (CEN) to review and update the existing standard as soon as possible, taking on board experiences across Member States of the practical implementation of gravimetric sampling.

CMCU and QA/QC have already reviewed the procedures for operating gravimetric samplers in the UK network, including routine travel blanks and providing for subtraction of travel blanks from filter mass measurements reported within each fortnightly batch.

1 Introduction

This report provides for an analysis of observed trends in gravimetric particulate matter occurrence in the United Kingdom over the period 2001 – 2007. It provides for a means of understanding the methods by which the UK has implemented provisions to comply with European Directives on particulate matter and to establish monitoring methods that comply with the European reference methods.

The primary focus of the report is gravimetric mass measurement of PM in order to convey the UK experience of implementing the European reference methods EN12341 and EN14907 – for PM₁₀ and PM_{2.5}, respectively – which has shown to lead to an apparent over-estimation of levels of both pollutants.

Other European reference method equivalent non-gravimetric methods are also deployed in the UK network and have been used in the current report as a means of providing further assurance on identification of issues associated with a number of apparent artifacts - laboratory, filter media, environmental variables used for filter conditioning – and comparisons with wider available datasets.

Consideration is made to the methods by which correction for apparent over-estimation of PM₁₀ and PM_{2.5} levels can be applied and the implications for UK compliance against the EU Directives for legally binding Limit Values on PM₁₀ (to be achieved by 31 December 2004).

The proposed methods for re-alignment of the UK Pollution Climate Mapping assessment are conveyed in order to build a consensus amongst UK expert groups and other interested parties on how best to achieve appropriate correction to historical data and to the procedures to be applied for future year assessments.

The report is structured in the following way:

- Chapter 2 provides for an understanding of the operational set-up of the UK compliance network for reporting against European Directives and the roles of various bodies and organizations;
- Chapter 3 undertakes the analysis of trends in reported levels of ambient gravimetric particulate matter levels, as observed from monitoring stations across the UK for PM₁₀ and PM_{2.5} metrics;
- Chapter 4 conveys the full details of in-depth analysis and statistical significance of apparent artifacts in the trends observed for PM₁₀ and PM_{2.5} as reported in Chapter 4;
- Chapter 5 provides for the proposed methods by which the UK may mitigate against the apparent over-estimation of PM levels and sets out the methods by which future year assessments on compliance against the Directive may be undertaken;
- Chapter 6 provides for a summary of key discussion areas;
- Appendix A sets out the policy context for UK compliance to European Directives and the harmonization of monitoring methods across Member States for reporting of ambient air pollution levels;
- Appendix B shows detailed graphs of the PM trends with and without correction for Partisol measurement offset;

Acknowledgments, a glossary and references are provided at the end of this report.

2 Implementation in the United Kingdom

2.1 The role of the Automatic Urban and Rural Network (AURN)

In the UK, the implementation of the EU legislation on ambient air quality is done through a number of contracts, awarded to commercial entities through open public tendering procedures. Further details of contracts awarded, the appointed contractors, and the key deliverables are provided at <http://www.airquality.co.uk>

The UK Automatic Urban and Rural Network (AURN) provides for the UK response to European legislation on the monitoring of the following pollutants:

- Particulate Matter – PM₁₀ and PM_{2.5}
- Gaseous pollutants – NO₂, O₃, CO, SO₂

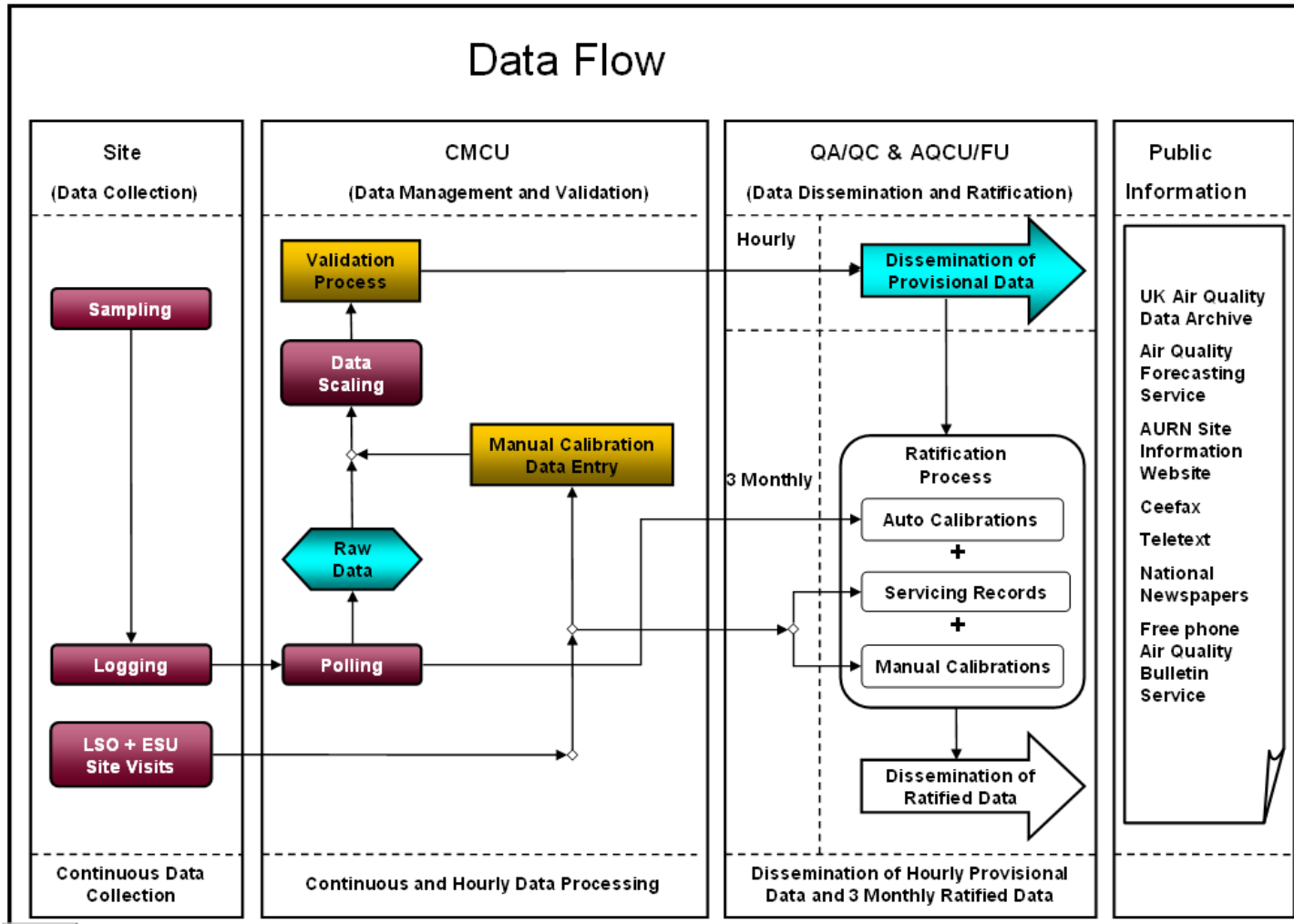
Requirements for a number of other pollutants included in the legislative framework of European legislation are fulfilled by a number of additional networks, due to technical reasons around methodologies and/or spatial coverage.

The AURN comprises a number of bodies and organizations involved in the day-to-day operations of the network. The following provides for a summary of these roles and provides for confirmation of the current appointed contractors (up to 2013):

- **Bureau Veritas HS&E Ltd** is the appointed Central Management and Co-ordination Unit (CMCU) for the AURN. The role of the CMCU is to manage the overall infrastructure of the network and to provide for preliminary analysis of data, its validation and onward dissemination to public information channels through the Air Quality Communications Unit. Once validated, the data is passed to the appointed QA/QC unit. For continuous monitoring, data is polled via telemetry and validated within the hour and published as “provisional data”. CMCU contractor is responsible for the appointment of local site operators – locally appointed organizations responsible for routine calibration procedures for equipment – and equipment support units. The equipment support units are appointed representatives of equipment manufacturers that maintain and service monitors. They respond to breakdown and poor performance of units as identified by CMCU through the polled diagnostic information.
- **AEA Technology plc (AEA)** is the appointed QA/QC unit for the network. The role of the QA/QC unit is to work closely with CMCU on the initial validation of data polled via telemetry. Provisional data is further ratified and published in its final format every three months, having taken into account further information available on the diagnostics and equipment performance, maintenance and servicing records and any localized events that may influence the validity of the data. AEA is also the appointed Air Quality Communications Unit, and remain responsible for the hosting and maintenance of the Air Quality Information Archive (at www.airquality.co.uk)
- **Air Liquide** is the appointed contractor for the supply of standard gases to the AURN.
- **The Department for the Environment, Food and Rural Affairs (Defra)** is the competent authority legally mandated to report on air quality compliance issues to the European Commission. It is the lead body in appointing contracts on air quality for UK Government associated with EU legislation applicable at the Member State level. The devolved administrations are the Scottish Government, the Department of the Environment Northern Ireland and the Welsh Assembly, which additional take lead roles in responding to air quality issues at the national and European levels.

Figure 2.1 provides for a summary of the data management process from sampling through to final dissemination of ratified data:

Figure 2.1: Summary of the data management process from sampling through to final dissemination of ratified data.



Further details on the UK network are available at the following website:

<http://www.bv-aurnsiteinfo.co.uk/>

The AURN is comprised of sites which are wholly funded by Government and those that are owned by local government. In the case of the latter, local authority owned sites in the UK have completed the necessary quality assurance and quality control audits for affiliation into the network. Broadly speaking, the sites in the AURN are therefore referred to as “Defra-owned” or “Affiliate” sites.

2.2 PM monitoring techniques used in the United Kingdom Network

The following section provides for a broad overview of the current methods deployed in the UK AURN. For filter-based measurement methods, automatic filter exchange methods have been chosen as preference above manual filter exchange methods in order to reduce overall costs and to remove impractical filter exchanges at midnight, in order to comply with the specified requirements of fixed 24-hour mass measurements stipulated in EU legislation.

Previously in the UK, a comprehensive study of cross-comparison of PM monitoring methods has been undertaken in order to comply with the need to seek equivalence with the EU reference method. This study largely focused on PM₁₀ and was undertaken in accordance with guidelines on demonstrating equivalence of monitoring methods with reference methods [1]. Consequently, where reference is made to PM Equivalence Trials, the reader is guided to the more detailed and in-depth study as published at the following website [2]:

http://www.airquality.co.uk/archive/reports/cat05/0606130952_UKPMEquivalence.pdf

Consideration is made to the outcome of the above study in relation to informing the UK methods for deployment on PM mass, whilst additionally flagging current short-falls in equivalence criteria due to further modifications made in equipment after the event. Where reference is made to Slope and Intercept, these are statistical parameters used in determining the relationship between the EU reference methods (x-axis) and the candidate method (y-axis). Further details of the analysis of datasets can be found in the UK PM Equivalence Trials.

The following provides for a brief overview of current methods deployed in the AURN:

- **PM₁₀ Reference Method**

Two AURN sites (Thurrock and Marylebone Road) operate units specified in the European Reference Method EN12341 – the Low Volume Sampler – in a PNS-X8 confirmation (the KFG (KleinfILTERgerat)). These units are operated with Whatman QMA quartz filters weighed by Bureau Veritas. The filters in these units are changed weekly.

Previously there were instruments in Harwell, Port Talbot, Glasgow and Belfast. These were removed from site in 2004 and were used operating Emfab filters in the UK Equivalence Trials.

Two SEQ47/50s are owned by Defra, and have recently been tested in further UK trials but are not as yet deployed into the AURN though these will be replacing the existing KFGs at Thurrock and Marylebone Road in due course. They differ from EN12341 in that there is sheath air cooling, and that filters are automatically exchanged daily.

- **PM_{2.5} Reference Method**

No UK sites operate the EN14907 reference method. UK experience is largely confined to their use in the UK PM Equivalence Trials [2,3], where prototypes of the final version were operated using Emfab filters.

- **Tapered Element Oscillating Microbalance (PM₁₀)**

The PM₁₀ TEOM is deployed widely around the UK. In the 2006 UK PM Equivalence Trials [2] the TEOM was shown to be not equivalent to the reference method, even with the application of a wide range of correction factors. The instrument was shown to underestimate PM mass, due to volatile species (such as ammonium nitrate and organic carbon aerosols) being lost at 50 °C, and the proportion of particles that are volatile varies in a non-linear fashion.

Current replacement and upgrade of TEOM units with PM₁₀ equivalent methodologies is being carried out in 2008.

- **Tapered Element Oscillating Microbalance (PM_{2.5})**

The PM_{2.5} TEOM was not originally included in the PM Equivalence Trials report in 2006 (PM₁₀ formed the emphasis of this trial). However, a single test was undertaken during the summer of 2007 at one site in the UK only [3]. Data acquired during this limited study was shown not to experience the loss of volatiles, although this is thought to be attributable to the low volatile fraction in PM observed in the UK during the generally wet summer of 2007. There are currently only 4 PM_{2.5} TEOMs in the AURN.

- **Filter Dynamic Measurement System Type B (FDMS) (PM₁₀)**

FDMS Type B PM₁₀ was tested in the UK PM Equivalence Trials [2] and was shown to be equivalent to EN12341 without the need for correction factors (Slope: 0.991; Intercept: 0.797 for “All Data” in the UK PM Equivalence Trials). This model is no longer commercially available and has been superseded by the Type C drier configuration. There are currently 21 PM₁₀ FDMS Bs in the AURN.

- **Filter Dynamic Measurement System Type B (FDMS) (PM_{2.5})**

FDMS Type B PM_{2.5} was tested in the UK PM Equivalence Trials [2] and was shown to be equivalent without the need for correction factors (Slope: 1.067; Intercept: -2.331 for “All Data” in the UK PM Equivalence Trials). This model is no longer commercially available and has been superseded by the Type C drier configuration. There are currently only 2 PM_{2.5} FDMS Bs in the UK network – the EMEP site in Auchencorth Moss, Scotland, and the other is located at an affiliate site in Swansea, Wales.

- **Filter Dynamic Measurement System Type C (PM₁₀)**

The Type C model FDMS differs from the Type B model in that it includes an improved drier that has a larger surface area. The instrument was tested during summer 2007 [3] for one dataset only and therefore is limited with regards to the extent to which it complies with EU equivalence criteria for PM measurements against the reference method. In this limited trial, the slope was the same as the FDMS Type B; however the instrument was shown to over read with an intercept of approximately 2 µg m⁻³, and as such did not meet the test for equivalence without the application of an intercept correction factor. Further tests are needed to assess whether a correction factor needs to be applied to those instruments deployed in the AURN. There are currently 2 PM₁₀ FDMS Cs in the National network and affiliate sites.

- **Filter Dynamic Measurement System Type C (PM_{2.5})**

The Type C model FDMS differs from the Type B model in that it includes an improved drier that has a larger surface area. The instrument was tested during summer 2007 [3] for one dataset only and therefore is limited with regards to the extent to which it complies with EU equivalence criteria for PM measurements against the reference method. In this limited trial, the slope was the same as the FDMS Type B; however the instrument was shown to over read with an intercept of approximately 2 µg m⁻³, and as such did not meet the test for equivalence without the application of an intercept correction factor. Further tests are needed to assess whether a correction factor needs to be applied to those instruments deployed in the National Network. Currently, there are no PM_{2.5} FDMS Cs deployed in the AURN.

- **Partisol 2025 (PM₁₀)**

This was tested in the UK PM Equivalence Trials and was shown to be equivalent without the need for correction factors [2]. Both reference method and Partisol were operating using Emfab filters, which deviates from the requirements of EN12341. The Partisol units operated in the AURN are done so with quartz filters (Whatman QMA weighed by Bureau Veritas) in order to comply with the requirements of EN12341. Currently, 9 sites monitor PM₁₀ using Partisol 2025 units.

- **Partisol 2025 (PM_{2.5})**

This was tested during summer 2007 for one dataset only [3]. As the PM_{2.5} Partisol is effectively a subset of the PM₁₀ Partisol, and the latter was shown to be equivalent, The PM_{2.5} Partisol was expected to agree closely with the standard. In practice, results from the limited 2007 trial indicated that it underestimated PM_{2.5} concentrations. Artefacts attributed to low PM concentrations in the summer of 2007, and the problems associated with regression calculations where there is significant scatter on data that are restricted to within a narrow range were additionally understood to provide for confounding effects in this analysis. There are currently 5 units measuring PM_{2.5} in the AURN, and they are operated with Whatman QMA quartz filters weighed by Bureau Veritas.

- **Met One Unheated Beta Attenuation Monitor (BAM) (PM₁₀)**

This was tested in the UK PM Equivalence Trials [2] and was shown to be equivalent with the application of a slope correction factor. There are currently no Met One BAMs in the AURN.

2.3 Links with AQUILA and JRC

In order to provide and maintain consistency across Member States various organisations provide assurance on measurements made within the AURN, covering issues related to precision, bias and accuracy and traceability to primary national standards. Within the UK, this function is undertaken by the QA/QC unit, but additionally through organisations such as the National Physical Laboratory and the AQUILA (the EU Network of Air Quality Reference Laboratories).

The European Reference Laboratory of Air Pollution (ERLAP) is responsible for the harmonization of air quality measurements across Member States in support of the current air quality directives. Quality assurance programmes are undertaken with the participation of national air quality reference laboratories. In the UK this function is taken by AEA and the National Physical Laboratory (NPL).

Meetings of ERLAP are normally held at the European Commission's Joint Research Centre (JRC) located at Ispra, Italy. Upon attendance at meetings, both NPL and AEA are tasked with informing Defra and the devolved administrations of any issues that may have consequences for the operation of the AURN. CMCU has previously attended AQUILA programme meeting at the Joint Research Council (JRC) premises in Ispra in May 2007 related to the monitoring of particulate matter for compliance against the EU Directives. The outcome of our work on the "*UK Particulate Matter Equivalence Programme (2006)*" was discussed by the Department's representative.

The JRC are currently running an inter-comparison of Member State routine network PM measurements against reference PM methods operated by the JRC within mobile laboratory facility. This programme covers all Member States of the EU and hence, will take several years to complete. The exercise in the UK is being undertaken at the Port Talbot AURN site during the period 21 Apr – 16 May 2008.

The JRC is running the following PM monitoring equipment:

- Two PM₁₀ sequential samplers (quartz Whatman QMA, 47 mm filters weighed by JRC);
- Topas LAP 320 aerosol particle size spectrometer counting particles >300nm;
- Sunset instruments semi continuous EC/OC analyzer (hourly values);
- One PM_{2.5} sequential sampler (quartz Whatman QMA, 47 mm filters weighed by JRC);
- Two PM₁ sequential sampler (quartz Whatman QMA, 47 mm filters weighed by JRC)
- PM₁₀ FDMS Type B instrument.

The routine AURN PM monitors at Port Talbot are:

- PM₁₀: FDMS Type C PM₁₀;
- PM_{2.5}: Partisol PM_{2.5} (quartz filter weighed by Bureau Veritas Laboratories).

However, to obtain additional value from the exercise the following additional equipment is being operated by Bureau Veritas and AEA:

- PM_{2.5} FDMS Type C;
- Partisol PM₁₀ (quartz filter weighed by Bureau Veritas Laboratories);
- Partisol PM₁₀ (Emfab filter weighed by Bureau Veritas Laboratories);
- Partisol PM_{2.5} (Emfab filter weighed by Bureau Veritas Laboratories);
- Partisol PM₁₀ (Emfab filter weighed by AEA).

Although this inter-comparison is necessarily of limited duration we anticipate that it will provide considerable additional information on the PM monitoring practices and procedures in the UK.

3 Trends in Gravimetric Particulate Matter: Emissions and Concentrations 2000 – 2007

This chapter provides an overview of the current analysis of PM trends in relation to both emissions and in relation to measured PM concentrations. Gravimetric filter based measurements provide for the focus of attention in relation to the latter, in order to highlight the apparent discrepancies between anticipated improvements in PM concentrations when compared to the trends in emissions.

3.1 Emissions of particulate matter in the UK

Particulate matter is directly emitted from many sources and is referred to as primary PM. However, chemical reactions in the atmosphere result in the formation of additional – secondary – PM giving rise to a wide variability in PM composition at local, regional and national levels. This provides for significant challenges in monitoring where uncertainty, precision and accuracy of monitoring methods are paramount for the reporting of robust data against legally binding standards.

The UK's National Atmospheric Emissions Inventory (NAEI) currently estimates that 152 kilotonnes of PM₁₀ were emitted in 2006 [4,5]. There is no single over-riding source of PM, though road transport is a major emitter, responsible for around 22 % of UK emissions of PM₁₀ in 2006. Other significant sources are domestic combustion, electricity generation and industrial combustion, various industrial processes involving mineral products and agriculture.

Due to technological measures to control emissions from road vehicles and industry processes driven by tighter emissions legislation and fuel switching from solid fuels to gas, PM emissions in the UK have been on a steady decline since 1980. Nationally, emissions of PM₁₀ are estimated to have declined by 18% since 2000. A similar trend is apparent for the finer PM size fractions; emissions of PM_{2.5} are estimated to have declined by 14 % since 2000. Road transport makes a larger contribution to emissions of the finer PM size fraction. Its contribution rises from 22 % for PM₁₀ to 27 % for PM_{2.5} and 44 % for PM_{0.1}.

In most urban areas, road transport is likely to be the most dominant source of directly emitted PM, except possibly in areas where there is a significant amount of solid fuel burning, construction or other activities of a dusty nature. PM is emitted directly from vehicle exhausts as a consequence of incomplete fuel combustion and burning of engine lubricants, but there are also significant amounts of PM emitted to air through mechanical processes such as wear of tyre material, brake and clutch pads and road surface and through re-suspension of already deposited road dust.

Emissions of PM from vehicle exhausts are dominated by diesel vehicles, but over the last 15 years diesel engine emissions have been regulated by increasingly strict European emission standards for PM. For example, a diesel car purchased in 2008 has to meet Euro 4 standards where limit values for PM are 82 % lower than for a new car purchased between 1993 and 1996 meeting Euro 1 standards. Table 3.1 shows the trend in PM urban exhaust emission factors in mg/km for successive Euro standards for different vehicle types. The reductions in emissions have been achieved through improved engine technology and fuel systems, improvements in the quality of diesel fuel (for example reductions in the sulphur content) and more recently by the introduction of exhaust after treatment systems such as oxidation catalysts and, more recently, diesel particulate filters.

As a consequence of the penetration of cleaner diesel vehicles (cars, vans and heavy duty vehicles) into the UK fleet and the retirement of older, high emitting vehicles, exhaust emissions of PM from road transport in urban areas have, overall, been declining in spite of the growth in traffic levels and the increased dieselisation of the car fleet. This can be seen in Figure 3.1 which shows urban PM exhaust emissions by vehicle type from the period 2000 to 2006 taken from the latest inventory. It indicates a 26 % reduction in urban exhaust PM

emissions over this period. The figure also demonstrates the increasing importance of diesel vans and cars as contributors of urban PM emissions; these were responsible for 78 % of urban exhaust PM emissions in 2006. Diesel vans (LGVs) are the single largest contributor responsible for 49 % of exhaust emissions.

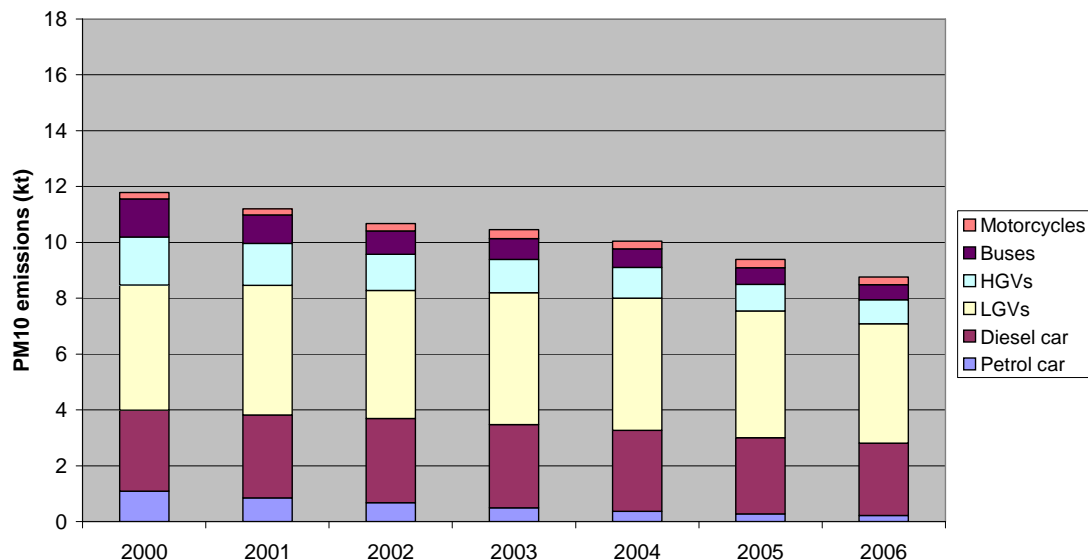
Table 3.1 PM exhaust emission factors in mg PM/km.

Petrol cars			Rigid HGVs		
	Exhaust	Tyre & brake		Exhaust	Tyre & brake
pre-Euro I	24	20	Pre-1988	890	72
Euro 1	3	20	88/77/EEC	426	72
Euro 2	1	20	Euro I	220	72
Euro 3	1	20	Euro II	153	72
Euro 4	1	20	Euro III	111	72
Euro 5	1	20	Euro IV	25	72
			Euro V	25	72

Diesel cars			Artic HGVs		
	Exhaust	Tyre & brake		Exhaust	Tyre & brake
pre-Euro I	154	20	Pre-1988	714	98
Euro 1	57	20	88/77/EEC	626	98
Euro 2	51	20	Euro I	577	98
Euro 3	32	20	Euro II	399	98
Euro 4	17	20	Euro III	288	98
Euro 5	2	20	Euro IV	64	98
Euro 6	2	20	Euro V	64	98

Diesel LGV			Buses		
	Exhaust	Tyre & brake		Exhaust	Tyre & brake
pre-Euro I	287	32	Pre-1988	1416	75
Euro 1	80	32	88/77/EEC	614	75
Euro 2	82	32	Euro I	311	75
Euro 3	57	32	Euro II	203	75
Euro 4	37	32	Euro III	147	75
Euro 5	4	32	Euro IV	44	75
Euro 6	4	32	Euro V	44	75

Figure 3.1 Urban UK exhaust emissions of PM₁₀ from road transport



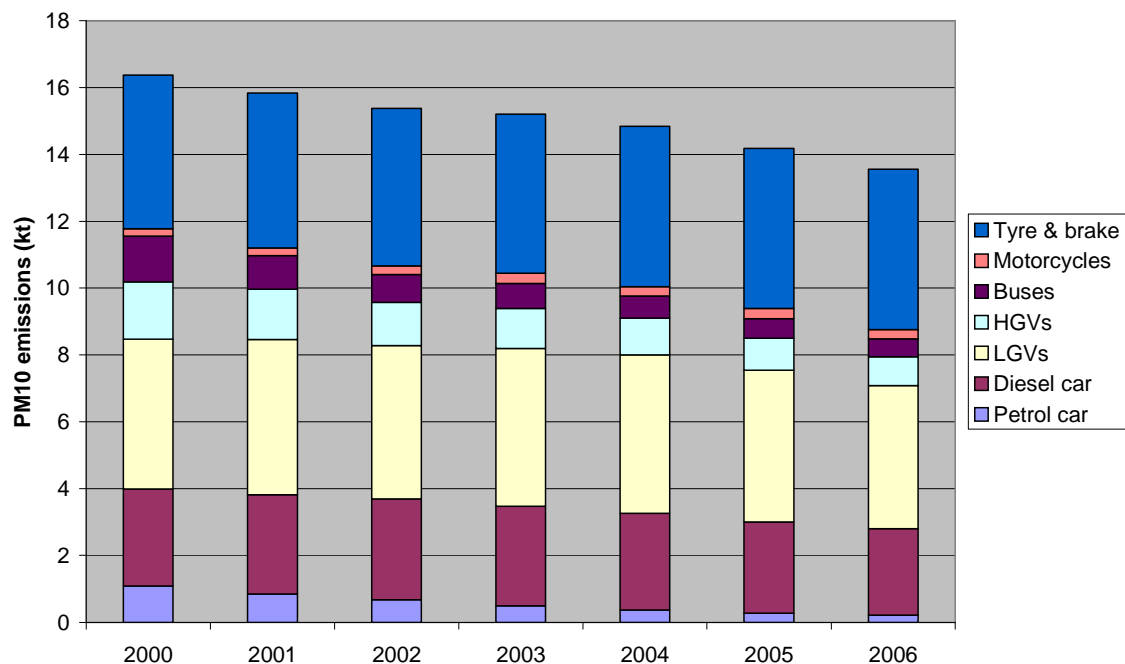
Current projections suggest the decline in urban exhaust emissions will continue; a further 27% reduction is anticipated between 2006 and 2010 due to the continued penetration of cleaner vehicles in the fleet offsetting the growth in traffic.

The decline in exhaust emissions from vehicles due to legislation has started to raise the importance of non-exhaust, mechanical sources of PM from traffic. The NAEI includes estimates of emissions from tyre wear and brake wear, but as yet does not include emissions from road surface wear. Emission factors for combined tyre and brake wear under urban traffic conditions can also be found in Table 4.1. This shows quite clearly how the emission factors for these sources were once relatively small compared with exhaust emissions from older generation diesel vehicles, but are now becoming similar or even larger than exhaust emission factors for more modern vehicles. A detailed description of the emission factors used in the NAEI and the effectiveness of abatement technologies for exhaust emission control can be found in AQEG (2005) [6].

Because emissions from tyre and brake wear cannot presently be controlled, their emissions have been steadily increasing as traffic levels have increased. In urban areas, tyre and brake wear emissions have increased by 4.5 % from 2000 to 2006 and are now 55% of exhaust emissions of PM₁₀.

Figure 3.2 shows urban PM₁₀ emissions from road transport from the period 2000 to 2006 with tyre and brake wear emissions included. When these sources are included the decline in urban PM emissions from road transport over the period 2000 to 2006 is reduced from 26% for exhaust-only emissions to 17 % overall.

Figure 3.2 Urban UK emissions of PM₁₀ from road transport including exhaust and tyre and brake wear sources.



The NAEI does not currently include PM emissions from road surface wear. Recent Defra research on non-exhaust PM carried out by TRL, the University of Birmingham and CERC indicated that emissions from this source are highly variable and depend on road surface conditions, but that emission factors could be as high as for tyre and brake wear emissions. Including this source in the inventory would further reduce the estimated decline in overall urban PM emissions from road transport.

Accounting for re-suspension as a source of non-exhaust PM in emission inventories is far more complex and this is another highly variable source. It may not be possible to represent re-suspension in terms of a simple emission factor and treated in a conventional emissions inventory approach, and instead may require a more sophisticated source apportionment modelling approach for a given receptor point. The Defra research led to implied emission factors for re-suspension by heavy duty and light duty vehicles by analysis of ambient monitoring data for the coarse PM fraction. The implied emission factors were much higher for heavy duty vehicles than for light duty vehicles and ranged from 1-140 mg/km. Including a re-suspension component to the non-exhaust PM emissions inventory on this basis would further reduce the estimated decline in urban PM emissions from traffic sources over the 2000 to 2006 period.

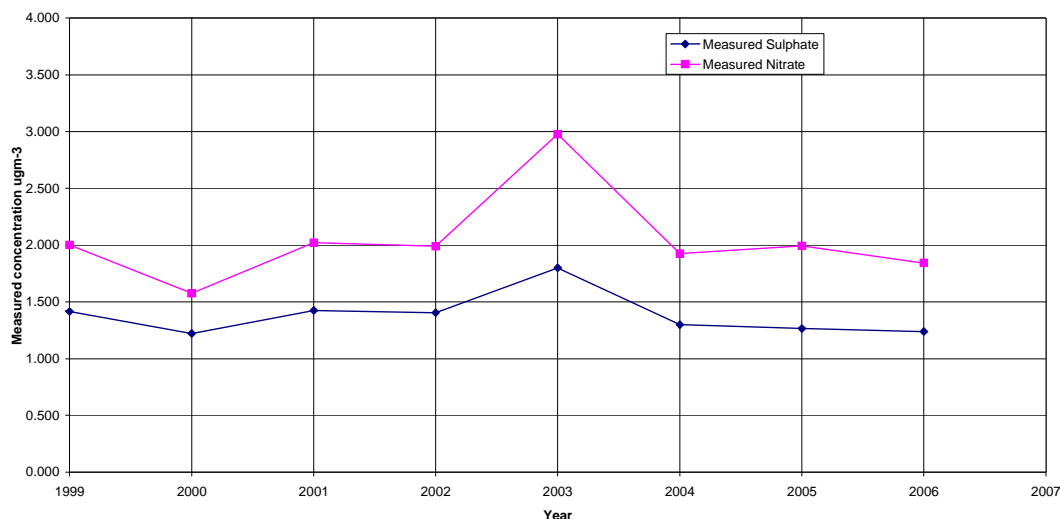
Finally, it should be pointed out that the PM emission trends described here are based on average urban road transport conditions. Any given location where ambient roadside PM data are monitored, analysed and interpreted will vary to different degrees from the urban UK average situation depending on local traffic conditions including the mix of vehicles such as proportion of cars, vans, HGVs, buses and taxis in the traffic flows, the petrol/diesel car mix, age and technology mix of vehicles (e.g. buses fitted with diesel particulate filters) and congestion. All these will vary around the country, and potentially with time of day and day of the week. Annual traffic levels over the time period from 2000 to 2006 will also have been changing at different rates around the country.

This means that emissions would have to be modelled using emission factors and activity data that reflect local conditions over the relevant period of time if trends in PM concentrations are to be truly interpreted in the context of primary PM emissions.

Beyond road traffic emissions of PM emissions arising as a result of industrial activities have been shown to be in decline as a result of tighter regulation. Consequently, over-riding factors in respect of overall trends in PM across the UK are those of the formation of secondary PM formation, which are dealt with through international agreements such as the National Emissions Ceiling Directive, the Large Combustion Plant Directive and the Solvent Emissions Directive to name but a few.

Local emissions of primary PM typically make up less than half of the measured PM mass. Other important sources include secondary PM, sea salt and dusts. Measured sulphate and nitrate concentrations (Figure 3.3) show no clear downward trend across the UK, although the strong influence of prevailing meteorology is shown in 2003 where higher levels of nitrate were recorded as a result of a long hot summer.

Figure 3.3 Annual mean UK average concentrations of sulphate and nitrate (1999 – 2006).



3.2 Trends in ambient PM₁₀ and PM_{2.5} concentrations

Long-term data sets on pollutant occurrence provide a means of measuring the success of national and international policy measures aimed at improving the quality of the air we breathe (Appendix A). Gravimetric monitoring for PM has now been undertaken in the UK for some 7 years (not at all sites), which provides for a means of assessing the likely extent to which existing policy measures may need to be reviewed.

The methods employed within the AURN have been reviewed in earlier sections. TEOMs are deployed widely; however, consideration of trends with this instrument should be treated with caution, as they are known to underestimate concentrations by a varied amount due to the loss of volatile species. Many TEOMs within the AURN have been/ undergoing conversion to FDMS; however, there are currently insufficient data to consider annual trends in detail. However, the collocation of FDMS instruments with gravimetric samplers has proved useful in relation to highlighting discrepancies in filter-based measurements, reported in the next chapter.

Table 3.2 shows Partisol units operated by Bureau Veritas as of 30th April 2008. PM₁₀ Partisol 2025 units have been introduced in to the AURN since 2000 at Bournemouth, Brighton, Dumfries, Northampton, Port Talbot, Westminster and Wrexham. Prior to early 2003, these instruments were operated using Whatman QMA filters weighed by AEA, before switching to the same filter media weighed BV Laboratories. In 2006 an EMEP site has been set up in Auchencorth Moss, near Edinburgh, and the Partisols at this site are incorporated in to the AURN. Partisols within the AURN are audited and the data are ratified, both by AEA, and all of these data have been uploaded on to airquality.co.uk.

A further network of Partisols were also running from 2000, and were introduced as part of a research project [7]. PM₁₀ and PM_{2.5} instruments were installed at Belfast, Birmingham, Glasgow Centre, Harwell, Manchester Piccadilly, London Marylebone Road, London North Kensington, and Port Talbot. The PM₁₀ Partisols were originally operating using Teflon filters weighed either by AEA or BV as a requirement of the biological assay work on PM required to fulfil the needs of the (then) programme. The PM_{2.5} Partisols have always operated using Whatman QMA filters, but they were in some cases originally weighed by AEA. Since early 2003, all 16 of these instruments have operated on Whatman QMA filters as weighed by BV. Four of the PM₁₀ Partisols were removed in 2004, and the remaining 12 PM₁₀ and PM_{2.5} instruments were switched off in 2007. Regardless of the laboratory or media, all the data have been uploaded on to airquality.co.uk, but it should be noted that Teflon data do not form part of the reference method in EN12341. These instruments have not been audited nor the data ratified.

A network of Scottish sites was introduced in order to collect one years worth of data using both PM₁₀ and PM_{2.5} instruments at Bush, Eskdalemuir and Fort William, and the addition of PM_{2.5} Partisols to the existing sites at Inverness and Dumfries. These Partisols have been audited, and the data ratified, both by AEA, but these instruments are not part of the AURN, and the data have been uploaded on to scottishairquality.co.uk.

Moving forward, new contracts were issued for the CMCU and QAQC of the AURN beginning April 2008, and this has lead to a reorganization of the Partisols network, and the requirement that all instruments will be incorporated in to the AURN and, as such, audited and the data ratified, both by AEA. Recently, the PM_{2.5} Port Talbot Partisol was relocated to a new site. The four Partisols at Marylebone Road and North Kensington were re-activated in May 2008. Harwell, Glasgow Centre and Glasgow Kerbside are due to return from June 2008 onwards. Brighton Roadside was relocated to Preston Park and converted to PM_{2.5} on 20th May 2008. Westminster and Bournemouth are due to be converted to PM_{2.5} during 2008, Northampton is due to be re-activated in 2008 and converted to PM_{2.5}, and Wrexham will have a co-located PM_{2.5} Partisol installed in 2008.

In order to provide for consistency in comparison in trends analysis it is important that such differences are considered. Consequently, for the purposes of this report concentrations are only considered if the filters were Whatman QMA Quartz filters weighed by Bureau Veritas Laboratories (and the previous names under which these laboratories have traded).

Figure 3.2 shows the trends in monthly averaged ambient PM₁₀ and PM_{2.5} concentrations as measured by Partisol units operating with Whatman QMA quartz filters weighed by BV for varying periods since 2000. Table 3.3 shows the valid annual average concentrations for all sites. A valid annual average is taken as at least 75 % data capture for the year. Many sites were discontinued in 2007, limiting the number of valid data for this year.

Figure 3.5 and Figure 3.6 show the trends in PM₁₀ and PM_{2.5} for sites where there are greater than two years of valid annual averages.

Specific issues to note are:

- 2003 is generally accepted to be an unusually high pollution year, and should be treated with caution.
- During 2007, relatively low levels of PM were experienced due to the dominance of low pressure and persistent rainfall over the UK. This weather event could explain the reduced concentrations observed in 2007. However, Westminster experienced rising concentrations during 2007. The only other London instrument to still be running for greater than 75 % of 2007 was the North Kensington PM_{2.5}, which shows falling concentrations for 2007 (Data availability for first 9 months only).

Overall, the analysis of data acquired over the period 2001 - 2007 at various sites across the UK indicates that, for gravimetric measurements made by Partisol 2025, there is an increasing trend in PM mass concentrations. The increase in mass is most notable in the last 2006 / 2007, which provides for a focal point of further attention in the following in-depth analysis of the trends reported here.

Table 3.2 Partisol units managed by Bureau Veritas as of 30th April 2008.

Site	Metric	Lab	Media	Start Date	Stop Date	Audited/Ratified
Auchencorth Moss	PM ₁₀	BV	QMA Quartz	14 Aug 2007	ongoing	yes
	PM _{2.5}	BV	QMA Quartz	1 Jan 2006	ongoing	yes
Belfast Centre	PM ₁₀	AEA	Teflon	2 Feb 2001	14 Mar 2002	no
		AEA	QMA Quartz	15 Mar 2002	16 Jan 2003	
		BV	QMA Quartz	17 Jan 2003	13 May 2004	
Birmingham Centre	PM ₁₀	BV	QMA Quartz	2 Feb 2001	8 Oct 2007	no
	PM _{2.5}	BV	QMA Quartz	26 Sep 2000	23 Apr 2002	no
Bournemouth	PM ₁₀	BV	QMA Quartz	24 Apr 2002	2 Oct 2007	no
	PM _{2.5}	BV	QMA Quartz	26 Sep 2000	2 Oct 2007	no
Brighton Roadside	PM ₁₀	AEA	QMA Quartz	18 Jul 2001	24 Jan 2003	yes
	PM _{2.5}	BV	QMA Quartz	25 Jan 2003	ongoing	yes
Bush (Midlothian)	PM ₁₀	BV	QMA Quartz	28 Feb 2003	ongoing	yes
	PM _{2.5}	BV	QMA Quartz	20 Oct 2006	30 Oct 2007	yes
Dumfries	PM ₁₀	AEA	QMA Quartz	20 Oct 2006	30 Oct 2007	yes
		BV	QMA Quartz	17 Aug 2001	18 Jan 2003	
		BV	QMA Quartz	24 Jan 2003	27 Mar 2007	
Eskdalemuir	PM _{2.5}	BV	QMA Quartz	16 Feb 2007	27 Mar 2007	yes
	PM ₁₀	BV	QMA Quartz	26 Feb 2007	6 Apr 2008	yes
Fort William	PM ₁₀	BV	QMA Quartz	26 Feb 2007	6 Apr 2008	yes
	PM _{2.5}	BV	QMA Quartz	27 Mar 2007	1 Apr 2008	yes
Glasgow Centre (St Enoch's)	PM ₁₀	AEA	Teflon	27 Mar 2007	1 Apr 2008	no
		AEA	QMA Quartz	11 Oct 2000	18 Jan 2001	
		BV	QMA Quartz	19 Jan 2001	28 Jan 2003	
Harwell	PM _{2.5}	BV	QMA Quartz	29 Jan 2003	11 May 2004	no
	PM ₁₀	BV	QMA Quartz	18 Oct 2000	9 Oct 2007	no
Inverness	PM ₁₀	BV	QMA Quartz	29 Sep 2000	25 Apr 2002	no
	PM _{2.5}	BV	QMA Quartz	26 Apr 2002	9 May 2004	no
Manchester Piccadilly	PM ₁₀	AEA	QMA Quartz	7 Sep 2000	6 Oct 2007	no
	PM _{2.5}	BV	QMA Quartz	11 Jul 2001	29 Jan 2003	yes
Marylebone Road	PM ₁₀	AEA	QMA Quartz	31 Jan 2003	ongoing	yes
		AEA	QMA Quartz	1 Dec 2006	ongoing	yes
		BV	QMA Quartz	21 Mar 2002	4 Oct 2007	no
North Kensington	PM _{2.5}	BV	QMA Quartz	28 Feb 2002	4 Oct 2007	no
	PM ₁₀	BV	QMA Quartz	28 Feb 2002	4 Oct 2007	no
Northampton	PM ₁₀	AEA	Teflon	21 Sep 2000	13 Mar 2002	no
		AEA	QMA Quartz	14 Mar 2002	15 Jan 2003	
		BV	QMA Quartz	16 Jan 2003	16 Oct 2007	
Port Talbot	PM _{2.5}	BV	QMA Quartz	7 Sep 2000	16 Oct 2007	no
	PM ₁₀	BV	QMA Quartz	27 Sep 2000	17 Apr 2002	no
Port Talbot Margam	PM ₁₀	BV	QMA Quartz	18 Apr 2002	24 Oct 2007	no
	PM _{2.5}	BV	QMA Quartz	7 Sep 2000	24 Oct 2007	no
Westminster Horseferry Road	PM ₁₀	AEA	QMA Quartz	5 Apr 2001	27 Jan 2003	yes
	PM _{2.5}	BV	QMA Quartz	28 Jan 2003	3 Oct 2007	yes
Wrexham	PM ₁₀	BV	QMA Quartz	28 Sep 2000	9 May 2002	no
	PM _{2.5}	BV	QMA Quartz	10 May 2002	9 May 2004	no
Wrexham	PM ₁₀	BV	QMA Quartz	14 Sep 2000	22 Jul 2007	no
	PM _{2.5}	BV	QMA Quartz	19 Oct 2007	ongoing	yes
Wrexham	PM ₁₀	BV	QMA Quartz	19 Feb 2003	ongoing	yes
	PM _{2.5}	BV	QMA Quartz	19 Feb 2003	ongoing	yes

Figure 3.4 Monthly time series of PM₁₀ and PM_{2.5} concentrations by site operating Bureau Veritas weighed Whatman QMA quartz filters only.

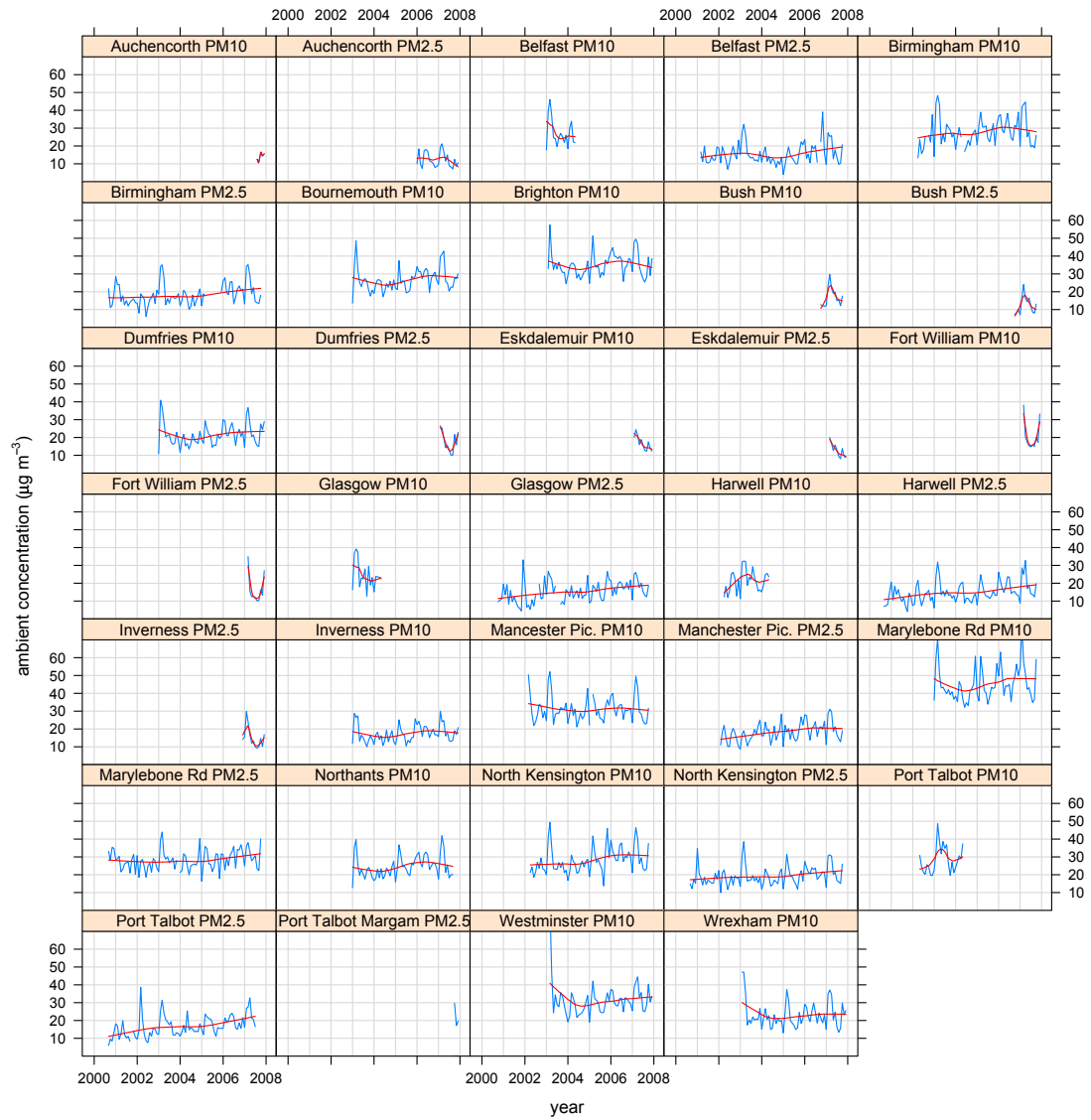


Table 3.3 Annual average concentrations for all sites where there is greater than 75 % collection in a calendar year. Averages are for sites operating Bureau Veritas weighed Whatman QMA quartz filters only.

	Auchencorth 10	Auchencorth 2.5	Belfast10	Belfast 2.5	Birmingham 10	Birmingham 2.5	Bournemouth 10	Brighton 10	Dumfries 10
2000									
2001						17.8			
2002				15.8		15.7			
2003			28.1	17.4	31.0	20.5	27.4	36.2	23.5
2004				12.4	23.7	16.0	23.4	32.0	17.5
2005				14.7			25.3	35.1	20.1
2006		12.2			32.2	22.4	29.4	37.9	23.8
2007		12.6					29.2	36.0	23.5

	Glasgow 2.5	Glasgow 10	Harwell 10	Harwell 2.5	Westminster 10	Inverness 10	North Kensington 10	North Kensington 2.5	Manchester Piccadilly 10
2000									
2001								17.9	
2002				12.7				18.0	
2003		26.6	22.9	16.7		17.1	28.1	20.8	33.6
2004	14.9			13.1	26.7	15.0	24.7	17.5	29.0
2005	16.2			14.6	29.7	16.7		19.2	30.1
2006	18.5			17.7	31.3	19.5	31.5	21.9	32.0
2007					33.5	18.8		21.7	

	Manchester Piccadilly 2.5	Marylebone 10	Marylebone 2.5	Northampton 10	Port Talbot 10	Port Talbot 2.5	Port Talbot Margam 2.5	Wrexham 10	Bush 10
2000									
2001			25.8						
2002			25.5			13.4			
2003	16.6	45.3	30.0		31.8	18.4		26.7	
2004	18.4	41.5	27.1	21.0		15.5		19.8	
2005	18.3	43.9	27.5	24.9		17.5		21.7	
2006	21.3	47.4	31.2	27.7		19.5		23.5	
2007								24.0	18.7

	Bush 2.5	Inverness 2.5	Dumfries 2.5	Eskdalemuir 10	Eskdalemuir 2.5	Fort William 10	Fort William 2.5
2000							
2001							
2002							
2003							
2004							
2005							
2006							
2007	13.8	15.1	17.2	16.7	12.7		

Figure 3.5 Trend of annual average PM₁₀ concentrations.

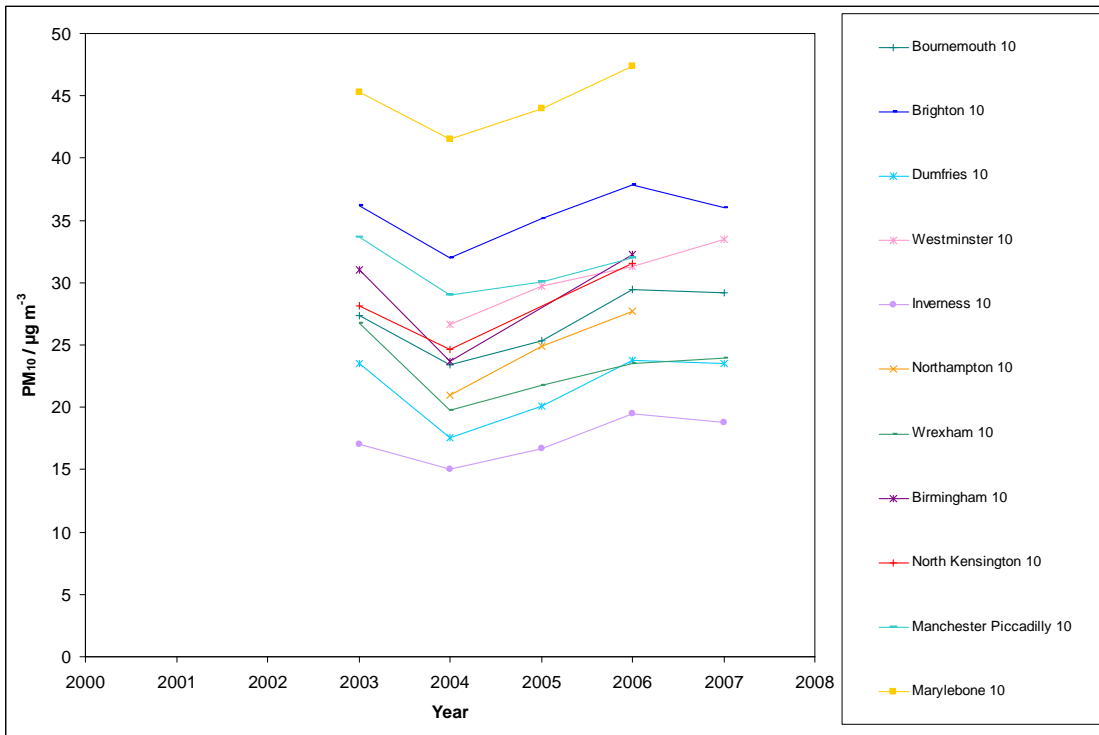
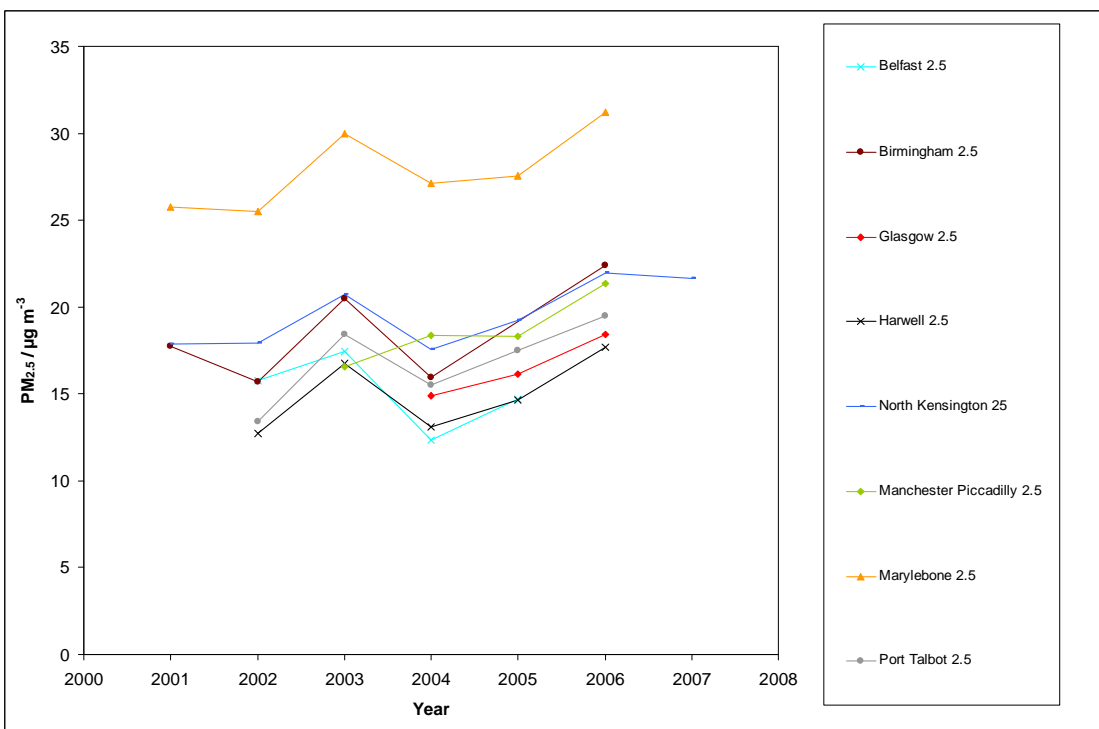


Figure 3.6 Trend of annual average PM_{2.5} concentrations.



4 Analysis of Trends

This section discusses evidence from three separate sources which suggest that Whatman QMA 47mm quartz filters weighed by Bureau Veritas Laboratories are reading higher than expected. A laboratory audit has been carried out in order to try to identify the cause of the overestimation and trend analysis has been used in order to try and identify the source of the problem

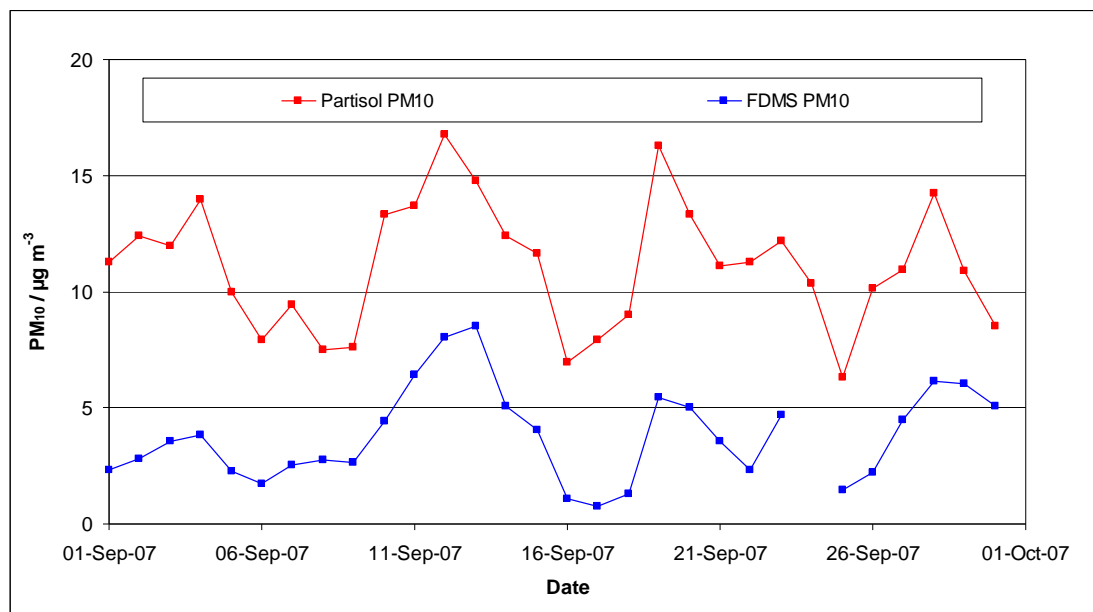
4.1 Evidence for the overestimation of gravimetric measurements

4.1.1 Partisol 2025, KFG and FDMS Ambient Data

The UK PM equivalence Trial tested several candidate methods against the EN12341 and EN14907 reference methods both operating with Emfab filters. Two of the candidate methods tested were the PM₁₀ Partisol 2025 (also with Emfab filters) and the PM₁₀ FDMS B. In both cases, the slope of the candidate method against the reference method was very close to one (1.003 and 0.991 respectively), and the intercept was very close to zero (0.530 and 0.797 $\mu\text{g m}^{-3}$ respectively). Such, the collocation of Partisols with FDMS and KFG instruments would be expected to yield similar agreement.

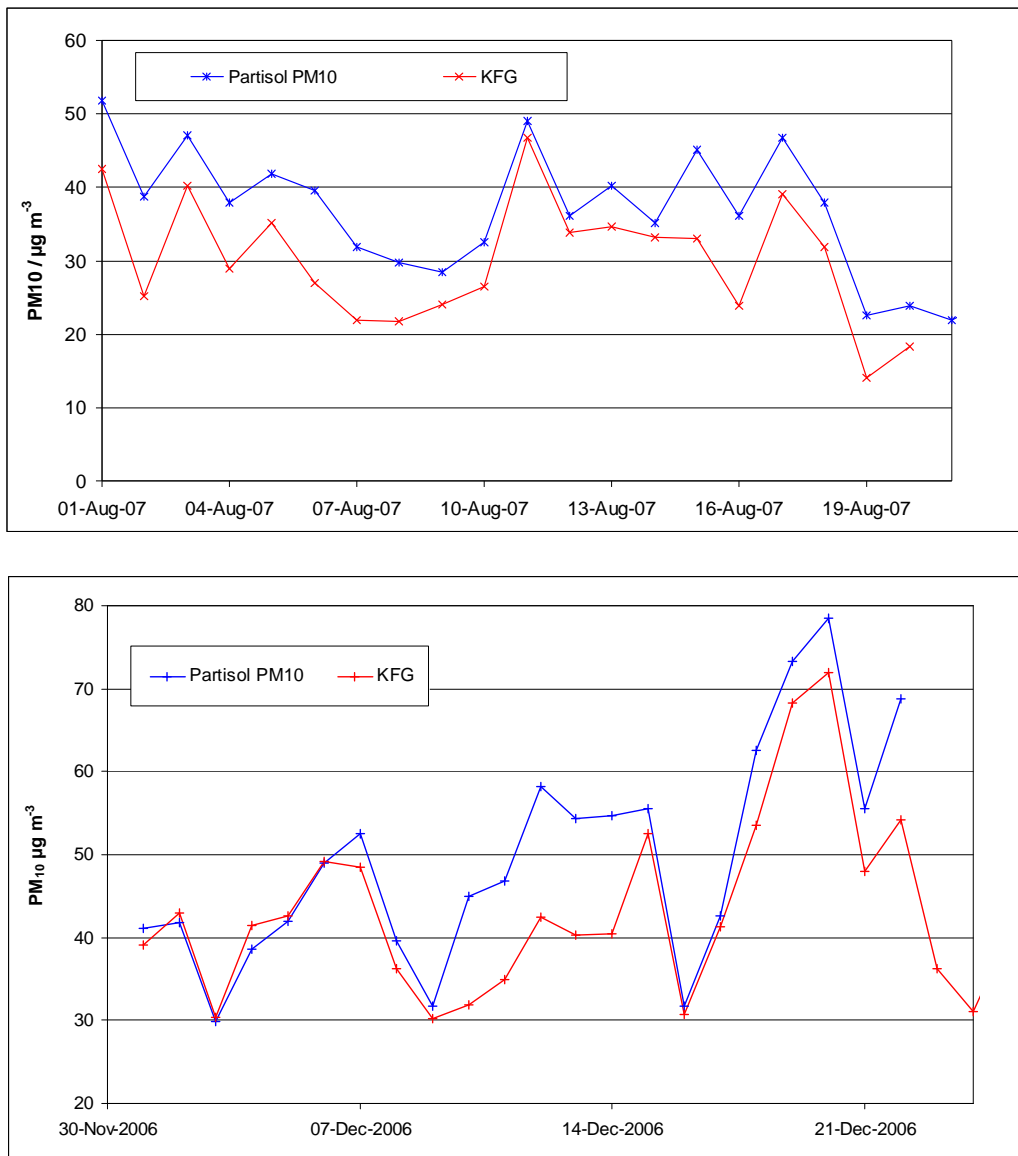
FDMS Type B instruments are collocated with Partisol 2025s at a number of sites throughout the UK including: Manchester Piccadilly; Birmingham Centre; London Marylebone Road and Auchencorth Moss. At all sites there is evidence that the Partisol is reading significantly higher than the FDMS B. This is most evident at Auchencorth Moss where ambient PM concentrations are low (Figure 4.1 below). The averages of the September 2007 data shown in Figure 4.1 is 11.2 $\mu\text{g m}^{-3}$ for the PM₁₀ Partisol, and 3.8 $\mu\text{g m}^{-3}$ for the PM₁₀ FDMS (considering paired days only).

Figure 4.1 Comparison of PM₁₀ monitoring at Auchencorth.



At Marylebone Road, a Partisol PM₁₀ reads significantly higher than a collocated PM₁₀ KFG PNS-X8 sampler, both utilising Whatman QMA quartz filters weighed by Bureau Veritas Laboratories (Figure 4.2. Datasets are shown for both the summer and winter periods. The PNS-X8 KFG filters are more exposed to radiative heating from the sun than the Partisol filters, and so there may be an anticipated reduction of concentrations measured by the PNS-X8 KFG during the summer, though in practice this is not always observed [8]. The averages of the December 2006 data shown in Figure 4.2 is 49.7 $\mu\text{g m}^{-3}$ for the PM₁₀ Partisol, and 44.1 $\mu\text{g m}^{-3}$ for the PM₁₀ KFG (considering paired days only). The averages of the August 2007 data shown in Figure 4.2 is 37.6 $\mu\text{g m}^{-3}$ for the PM₁₀ Partisol, and 30.1 $\mu\text{g m}^{-3}$ for the PM₁₀ KFG (considering paired days only).

Figure 4.2 Comparison of PM₁₀ monitoring at London Marylebone Road in both a summer and winter period.



4.1.2 Comparison of PM data for different weighing laboratories

Recent further studies have been undertaken to provide a means by which comparison can be made between laboratories providing gravimetric filter mass measurements. Participating laboratories include that of the appointed gravimetric provider for AURN samplers: Bureau Veritas (Bureau Veritas) Laboratories; and that of the National Physical Laboratory (NPL). The study included the following instruments:

- PM_{2.5} Bureau Veritas weighed Whatman QMA quartz Partisol 2025 to EN12341;
- PM_{2.5} NPL weighed Whatman QMA quartz Partisol 2025 to EN14907;
- PM_{2.5} NPL weighed Emfab Partisol 2025 to EN14907;
- PM_{2.5} NPL weighed Emfab Leckel (PM_{2.5} reference method) to EN14907.

This gives the opportunity to test the effects of filter media, laboratory, weighing method and instrument based on the average difference of paired data only. The results (Figure 4.3 and Figure 4.4) are as follows:

- PM_{2.5} difference due to Filter Media = 3.8 µg m⁻³; Count = 65; Standard Deviation = 1.7; Calculated as NPL weighed quartz Partisol minus NPL weighed Emfab Partisol.
- PM_{2.5} difference due to Laboratory and weighing protocol = 6.7 µg m⁻³; Count = 47; Standard Deviation = 3.1; Calculated as BV weighed quartz Partisol minus NPL weighed quartz Partisol.
- PM_{2.5} difference due to Instrument = -1.7 µg m⁻³; Count = 64; Standard Deviation = 1.2; Calculated as NPL weighed Emfab Partisol minus NPL weighed Emfab Leckel.

The quartz filters weighed by NPL (to EN14907) were on average 6.7 µg m⁻³ lower than the same filters weighed to EN12341 by Bureau Veritas Laboratories, which suggests that the laboratory and/or weighing method are contributing significantly to measured concentrations. The occasional negative concentrations measured by the NPL weighed Emfab Partisol have been checked, and the results and maths are all correct.

Figure 4.3 PM_{2.5} Concentrations measured in Teddington 2007.

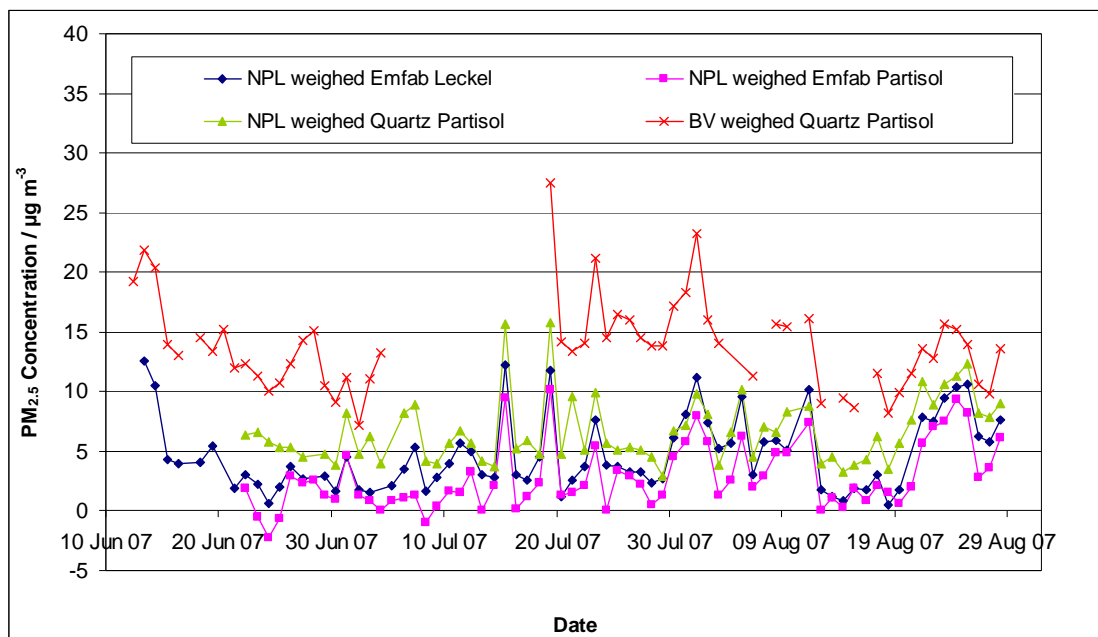
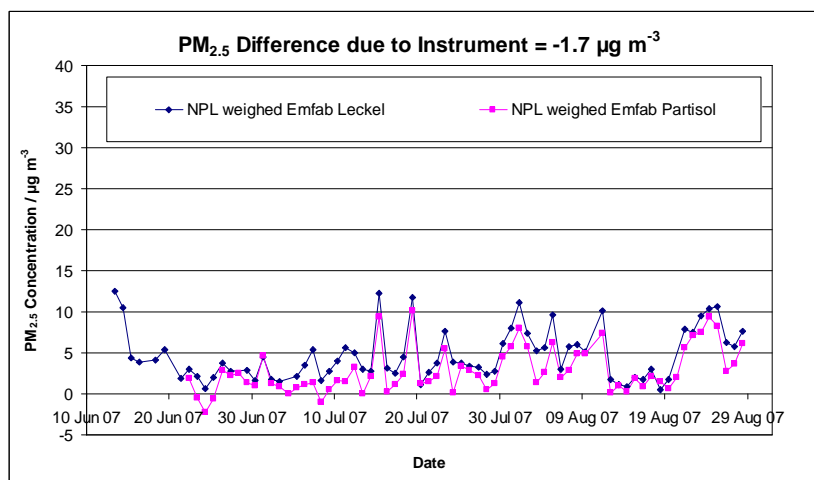
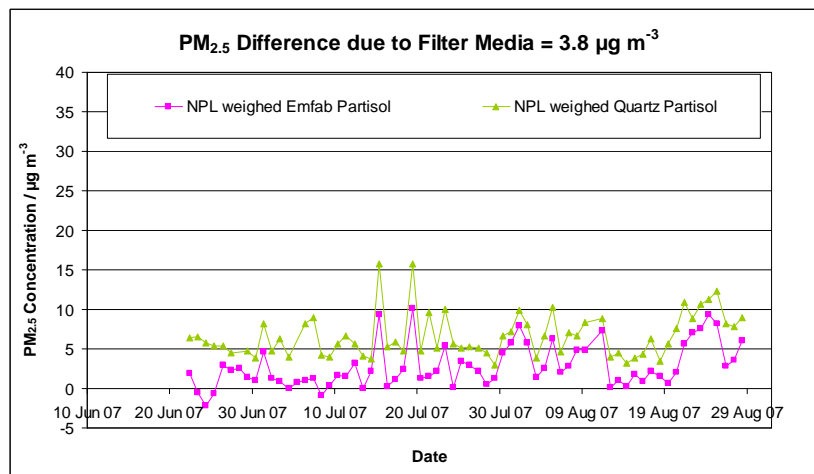
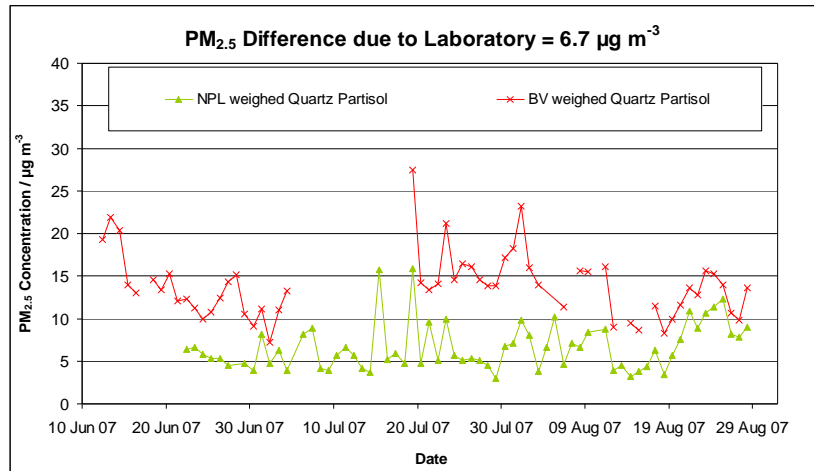
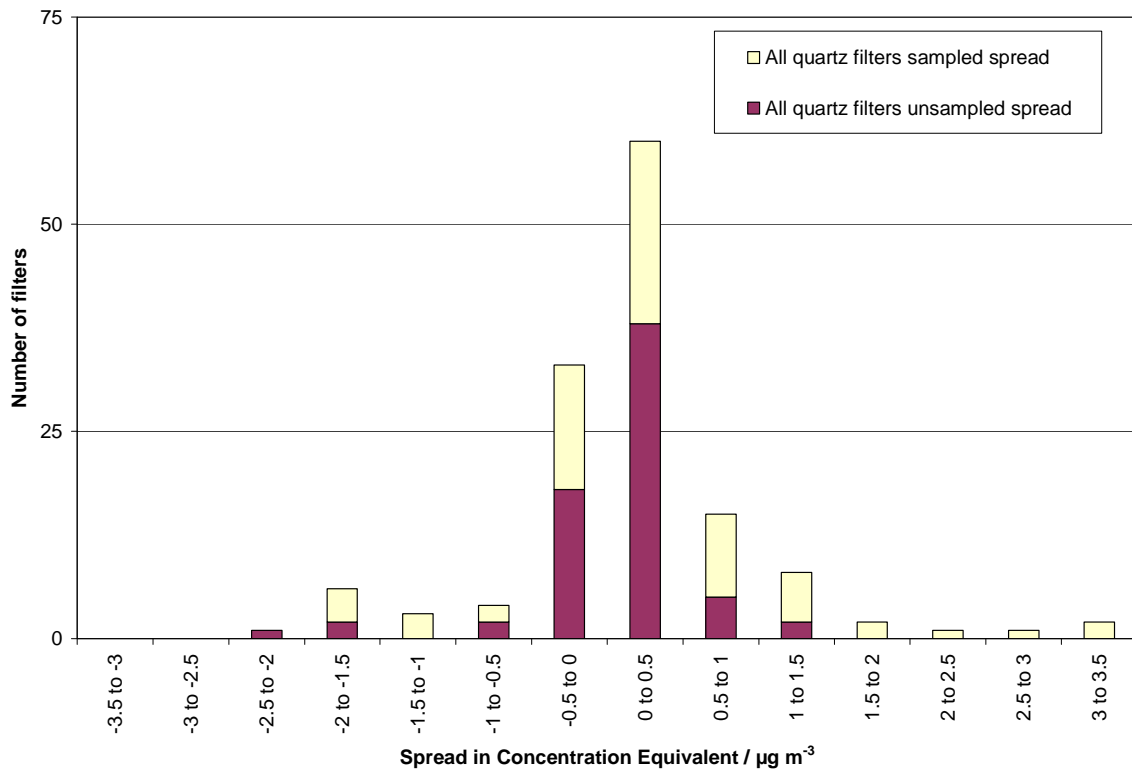


Figure 4.4 PM_{2.5} Difference due to Laboratory, Filter Media and Instrument.



The PM_{2.5} difference due to Laboratory and weighing protocol was shown to be 6.7 µg m⁻³. Under EN12341, filters are conditioned for 48 hours, and then weighed. The weighing protocols in EN14907 differ in that filters are conditioned first for 48 hours, then weighed, then conditioned for a further 24 hours before reweighing. The graph below (Figure 4.5) shows the shift in concentration equivalent between the two weighings of unsampled and sampled filters. This shift alone cannot account for the 6.7 µg m⁻³ difference due to both the weighing methodology and the laboratory. This indicates that differences in laboratory procedures were largely responsible for the discrepancies in reported concentrations.

Figure 4.5 PM_{2.5} Spread in concentration equivalent due to repeat weighing of Whatman QMA quartz filters weighed by NPL.



4.1.3 Travel Blank Filters

Day-to-day operation of the Partisol 2025 units deployed in the network requires that pre-conditioned and weighed filters are loaded into filter cassettes. Fortnightly dispatch of filters is made through the supply of 14 loaded filter cassettes into a filter magazine, sent to the local site operator. Occasionally filters are not sampled (*i.e.* do not have ambient air drawn through them for any period of time) due to over supply or instrument failure, and these are returned to the weighing facility as field or travel blanks. It is not possible to say definitively which travel blanks have been through the sampling mechanism, and which have not, only that none of the filters have had ambient air drawn through them, and that the vast majority will have remained in the unsampled filter magazine within the instrument, and will never have been through the sampling mechanism. For the two instruments located at Auchencorth Moss (PM₁₀ and PM_{2.5}), and a non AURN site in Derby, 15 filters have been supplied routinely with one being designated as a “travel blank” per fortnight dispatch. As the filters from Derby are treated in an identical fashion to those for the Defra sites, and there is a good coverage of travel blank filters, these filters are covered in the statistical analyses presented herein.

Figure 4.6 shows the variation in travel blanks for all the Partisols operating Bureau Veritas weighed Whatman QMA Quartz filters. The blanks are weighed and reported as PM mass concentrations, by dividing the volume that would have been sampled had they not been blanks. Partisols run at 16.7 l min⁻¹ for 24 hours, which gives a volume of 24 m³ for a 24 hour sample. There is evidence of an increased travel blank in 2006 and 2007. Figure 4.7 shows the monthly average variation for PM₁₀ and PM_{2.5} Partisols separated. There is no clear difference for the two size fractions except during February 2007. This month had only one filter for PM_{2.5} which was post weighed just before the laboratory move from Glasgow to Runcorn. The implications of the move are discussed in Section 4.2.2.7.

Figure 4.8 shows the variation of the travel blank concentration equivalent for Emfab filters weighed by Bureau Veritas Laboratories and deployed in a Partisol 2025 located Earls Court Road in London. In contrast to the quartz filters there is no evidence for an increased travel blank concentration equivalent to that shown above in recent years.

Figure 4.9 shows the variation for the travel blank concentration equivalent for Whatman quartz QMA filters weighed by Bureau Veritas Laboratories and deployed in a KFG. Note that the KFG has a flow rate 2.3 times greater than the Partisol, though is assumed to have the same flow rate when calculating the blank concentration equivalent for ease of comparison. There is limited evidence for increased travel blank mass in recent years, although there are a very limited number of travel blanks and it is hard to draw definitive conclusion from this comparison.

Figure 4.10 shows the variation for the blank concentration equivalent for Whatman quartz QMA filters weighed by AEA and deployed in Partisols. These are largely laboratory blanks rather than field blanks. The protocols employed by AEA have changed over time. Initially, there was a laboratory blank, and all filters were weighed relative to this blank. Later, there was no laboratory blank, and absolute weights are reported. Both laboratory blanks (45 filters) and field blanks (33 filters) were available for 2001-2 for research Partisols in London Marylebone Road, Glasgow, Belfast, Northants, Bournemouth, Inverness, Wrexham and Dumfries. It is interesting to note that the field blanks weight more than the laboratory blanks (1.7 vs. 0.1 µg m⁻³). However, in some cases, the travel blanks have been weighed relative to the lab blanks, and in some cases the travel blanks are based on absolute weights. As such, these data should be treated with caution.

Figure 4.6 Variability of travel blank concentration equivalent as a function of date for all Whatman quartz filters for Partisols weighed by Bureau Veritas Laboratories for the Defra sites and Derby. The line of best fit is a locally-weighted regression smooth, and the uncertainty intervals are shaded

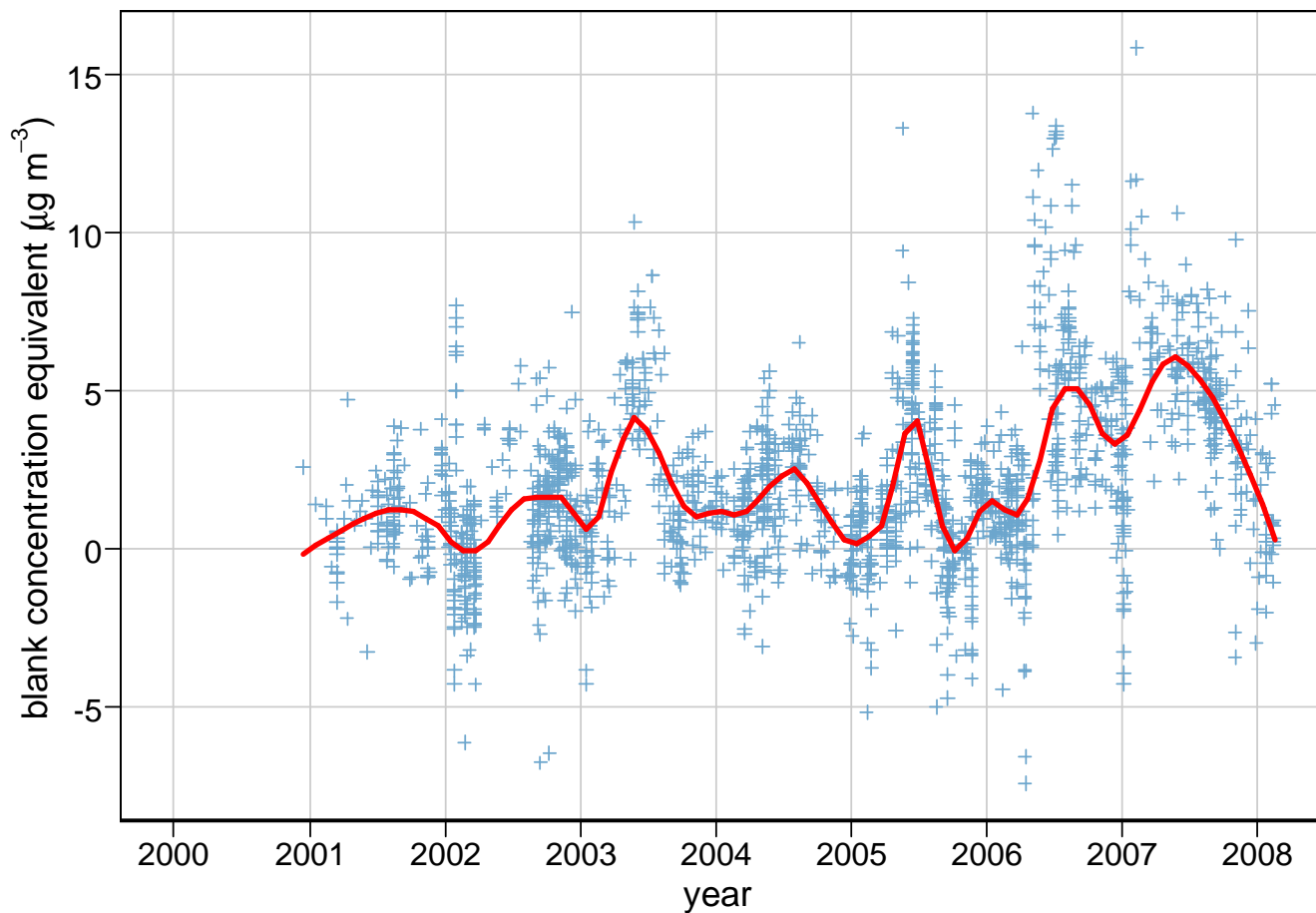


Figure 4.7 Variability of the PM₁₀ and PM_{2.5} travel blank concentration equivalent as a function of date for all Whatman quartz filters for Partisols weighed by Bureau Veritas Laboratories for the Defra sites and Derby.

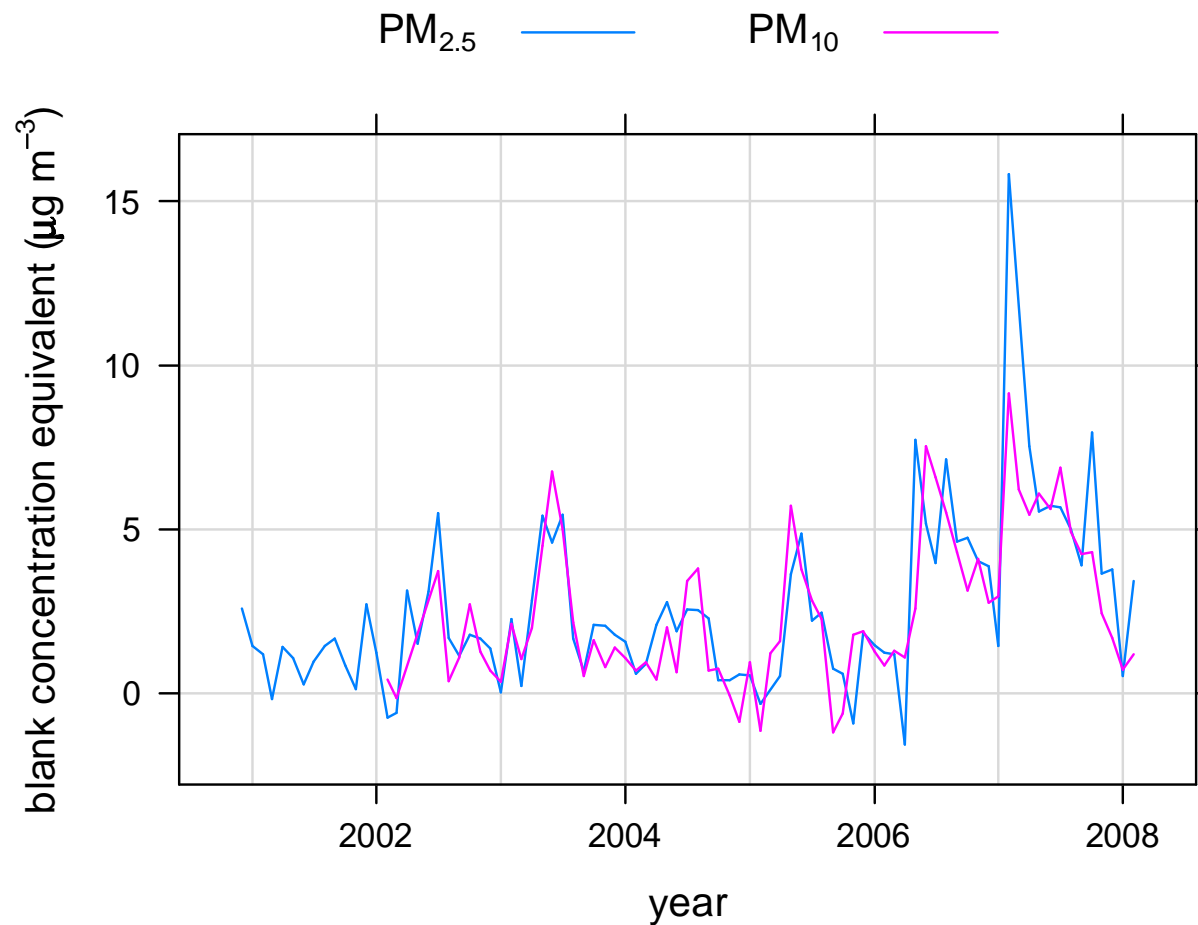


Figure 4.8 Variability of the travel blank concentration equivalent for Emfab filters weighed by Bureau Veritas and deployed in a Partisol in Earls Court Road in London

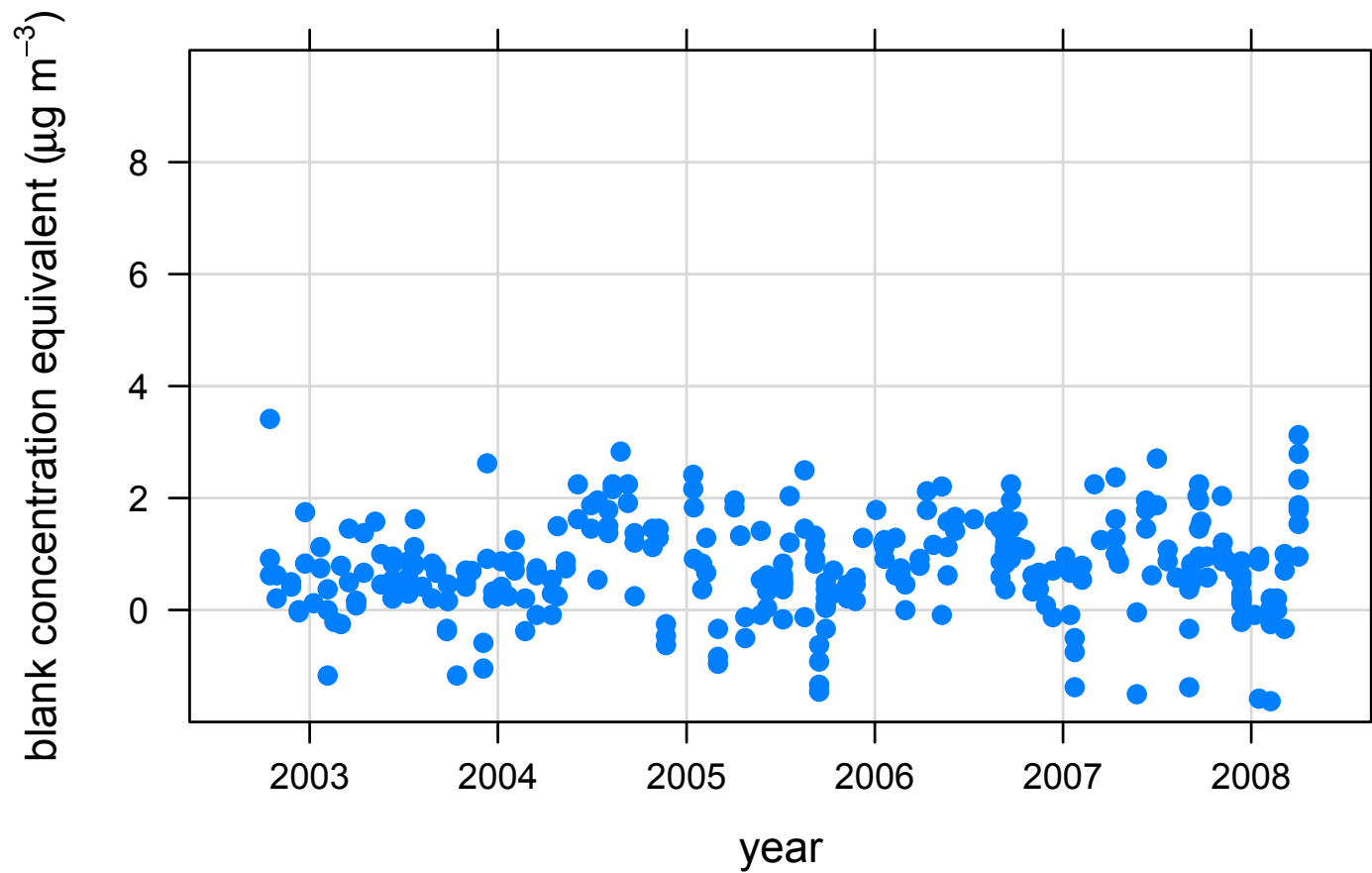


Figure 4.9 Variability of the travel blank concentration equivalent for PNS-X8 KFG filters weighed by Bureau Veritas assuming the same flow rate as a Partisol 2025.

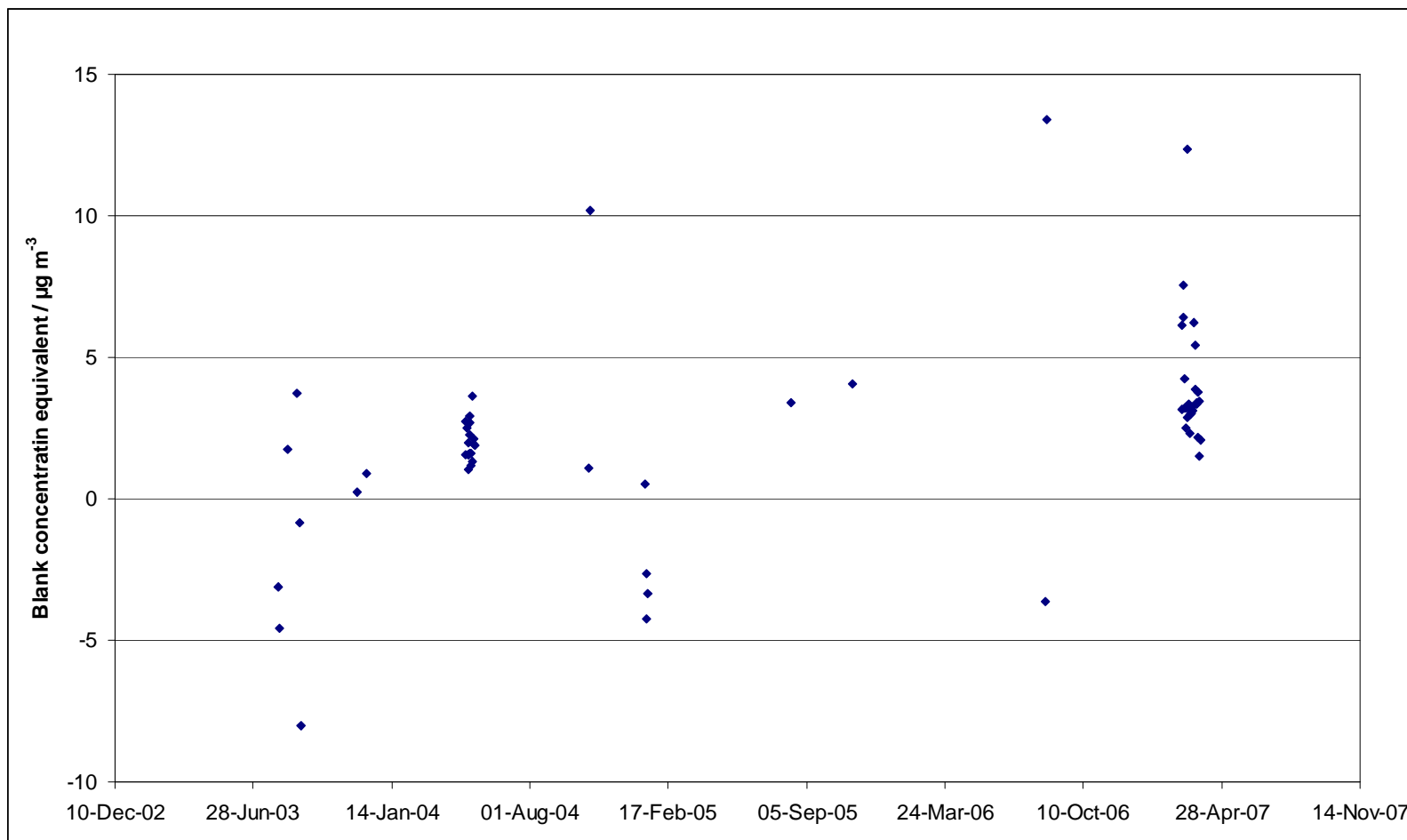
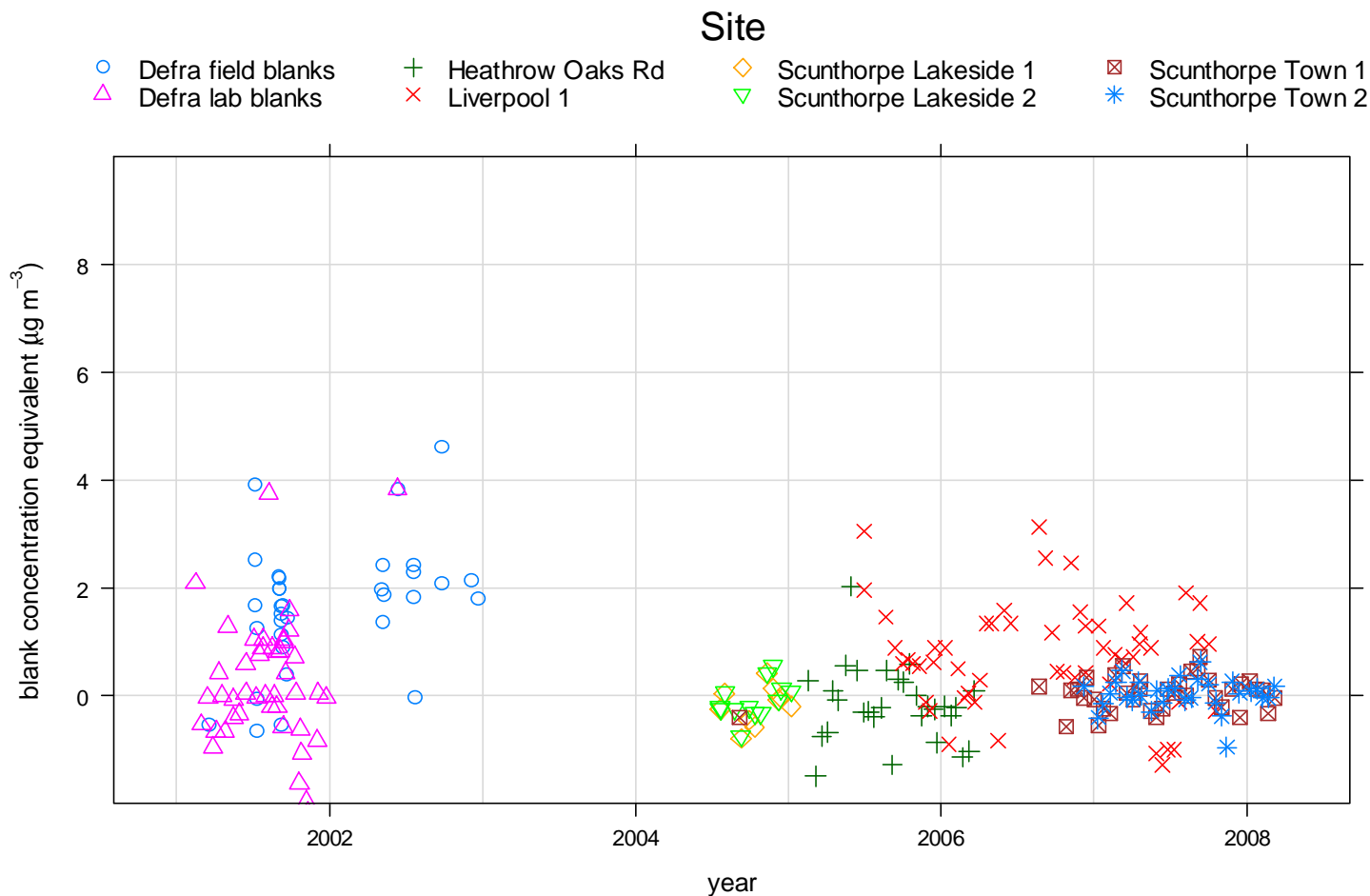


Figure 4.10 Variability of the laboratory blank concentration equivalent for Whatman QMA quartz Partisol 2025 filters weighed by AEA. Travel (field) blank concentration equivalents are also shown for the Defra research sites.



4.1.4 Summary of evidence for an overestimation

Ambient PM_{2.5} concentrations measured using Whatman QMA quartz filters weighed to EN14907 by NPL show significantly lower concentrations than those weighed to EN12341 by BV. The only significant difference between the EN14907 and EN12341 protocols is that in the former the filters are weighed twice. The reweighing of filters was shown to have little effect on concentrations, and as such, this indicates that quartz filters may be affected by the weighing protocols employed by BV.

This overestimation appears to be associated with mass increases in travel blanks and this is independent of particulate size fraction. The collective evidence suggests that there is an overestimation primarily in 2006 and 2007 of PM concentrations measured by Partisols operating with Whatman QMA quartz filters as weighed by Bureau Veritas Laboratories.

There is limited evidence to suggest that there is an increase in travel blank concentration equivalent for Bureau Veritas Laboratories weighed Whatman QMA quartz filters deployed in the PNS-X8 KFG (Figure 4.9). This impacts the concentration measured by the KFG to a lesser extent than the Partisol 2025, as the KFG has a flow rate 2.3 times greater. This may account for the discrepancies observed in Figure 4.2.

Emfab travel blank filters weighed by Bureau Veritas Laboratories show no evidence of increased concentration equivalent. NPL have previously studied the effect of humidity on different filter media [9], and showed that Emfab was much less susceptible to humidity effects than quartz. This points to the hydrophilic nature of quartz, and the humidity within the Bureau Veritas Laboratories as the potential problem.

For filters weighed by Bureau Veritas Laboratories, concentrations reported on the national database have not previously been corrected for the travel blank or laboratory blank mass. For filters weighed by AEA, concentrations reported on the national database have never been corrected for travel blanks, but have occasionally been corrected for laboratory blanks.

4.2 Bureau Veritas Laboratories Audit

Preliminary analysis has shown that differences in filter weighing protocols between Bureau Veritas Laboratories and another laboratory may be responsible for the apparent over-estimation of PM mass in recent years. To explore this fully an audit of the Bureau Veritas Laboratories was carried out in Glasgow by David Harrison (Bureau Veritas HS&E Ltd) and Ken Stevenson (AEA) on 22nd January 2008. Also present was the following Bureau Veritas Laboratories staff: Gillian Dick; John Carrington and Janet Hutchinson.

Bureau Veritas Laboratories are located in Glasgow. The filter weighing facility was previously in Runcorn and re-located in Glasgow in the week commencing 16th February 2007. An UKAS audit was scheduled immediately after this re-location and UKAS were satisfied that appropriate laboratory procedures, consistent with previously accreditations, were being continued at the new facility. To this end, any temporary suspension of dissemination of laboratory results (in force whilst re-location and UKAS audit were undertaken) was removed and normal operations were resumed.

Since 2000, the filter weighing facility has undergone a number of changes in ownership. Previous trading names for the filter weighing facility are: CRE Energy and Environment; EMC Environment Engineering; and Casella CRE Air. Throughout these changes staff competency in operating the facility has been maintained and shown to comply with the requirements of the UKAS body. This ensured consistency in laboratory procedures and reporting mechanisms.

EN12341 specifies that both unused and sampled filters "*shall be exposed for 48 h on open but dust-protected sieve trays in an air-conditioned weighing room with a temperature of (20 ± 1) °C and a relative humidity of (50 ± 5) %*". The filter weighing facility is located within a controlled environment room, which attempts to comply with these requirements.

4.2.1 Results of the Audit

The following provides for a summary outcome of the observations made by CMCU and QA/QC in their undertaking of the audit.

The laboratory has a documented quality system and is accredited by UKAS to ISO 17025 2005 for a range of determinations. Filters are conditioned and analysed according to documented procedure no 54 "*Determination of Particulate Matter on Filters by Gravimetric Analysis*".

The laboratory was clean and tidy, and everyone involved in the weighing had a dedicated attitude. The environmental conditions in the weighing room are set to 50 % RH and 20 °C. Humidity and temperature readings are taken beside the balance and since the laboratory move in February 2007, are additionally taken outside the balance enclosure in the weighing room. Out of specification conditions are reported to the Quality Manager, if this should occur then filters are reconditioned for 48 hours. On the day of the audit, both RH readings were observed to be identical and within range. The records of humidity going back to 2003 were studied, and it was noted that there was some variability.

The procedures and methods are checked periodically as part of the UKAS audit procedure. The balance, temperature probe and external humidity probe are all checked approximately annually using externally traceable equipment. The calibration and service records are kept with the Equipment Records File.

Un-sampled filters are conditioned on trays with a slight overlap due to space constraints (Figure 4.11). However, they are continually turned in order to give those areas covered a chance to equilibrate.

Un-sampled filters are assigned a unique internal ID that the computerised system associates with a particular filter based upon its position in the weighing tray. An AH60 AutoHandler (MTL Corporation, Minnesota, USA) (Figure 4.12) is used. The balance is tared (zeroed) before each and every mass determination is performed. A filter or check-weight will remain on the balance until a stable reading

is obtained (typically 30 seconds) or until 2 minutes has elapsed in which case an immediate reading is taken which will be flagged as “unstable” in the database.

Figure 4.11 Photo of conditioning of unsampled filters showing slight overlap.



Figure 4.12 Photo of balance and automated filter handler.



The balance contains a polonium 210 source to remove static. The source should be replaced annually, though was not replaced for the first four years. A corona discharge blower is occasionally used for Teflon filters. The system is password protected. Settings cannot be changed without authorisation from the Technical Manager. A weekly check is made to ensure that data is being correctly transferred between the balance and the data system, the automated weighing of a filter is observed and the recorded weight checked with that observed.

For each tray of filters weighed:

- The AutoHandler will “home” and position itself over the balance in the tare position and run a balance internal calibration;
- The balance will weigh the 100 mg and 200 mg check-weights four times to ensure that the balance is stable and fully exercised. All check weight data is written directly to the check weight database. NIST certified check weights are used. The certified values are used, along with the balance uncertainty to set tolerances for check weights;
- Three laboratory blank filters are then weighed (47mm QMA, 47 mm Emfab, 25 mm glass fibre). These are replaced every week and weighed every time a tray of filters is weighed. Each week a new blank/QC filter of each type is selected and weighed with every tray that week. Used blank/QC filters are archived to enable blank correction of filter weights if requested by the client at a future date;
- The system will then reweigh both of the check weights once;
- The first row of ten field filters are then weighed. All field filter data is written directly to a “Filters” database which includes date, time, analyst, environmental conditions and balance serial number. At the end of the row the first filter is reweighed;
- The check weights are weighed again followed by the next row of ten field filters, and the process continues until all of the filters have been weighed.

If any of the check-weights or laboratory blanks deviate by more than 20 µg from expected, then the entire batch is reweighed. If the reweigh of every 10th filter deviates by more than 20 µg from expected, then that row of 10 filters is reweighed. A list of labels is printed in the correct order by the system and these are applied to Petri dishes (Partisol) and the base portion of Analyslides (PNS-X8 KFG) in which the correct filters are placed. The labels contain unique bar codes which are read by a bar code reader. All filters are dispatched to end users by Special Mail Service on a next day delivery to enable the dispatch to be tracked should they fail to be delivered.

PNS-X8 filters are sent to the local site operators for weekly installation. Sampled filters are removed and replaced in the Analyslide in which they were initially dispatched and returned to Bureau Veritas Laboratories for post weighing. Filters are conditioned for 48 hours by removing the lids from the Analyslides. This leaves the filter identification label on the base and still associated with the correct filter.

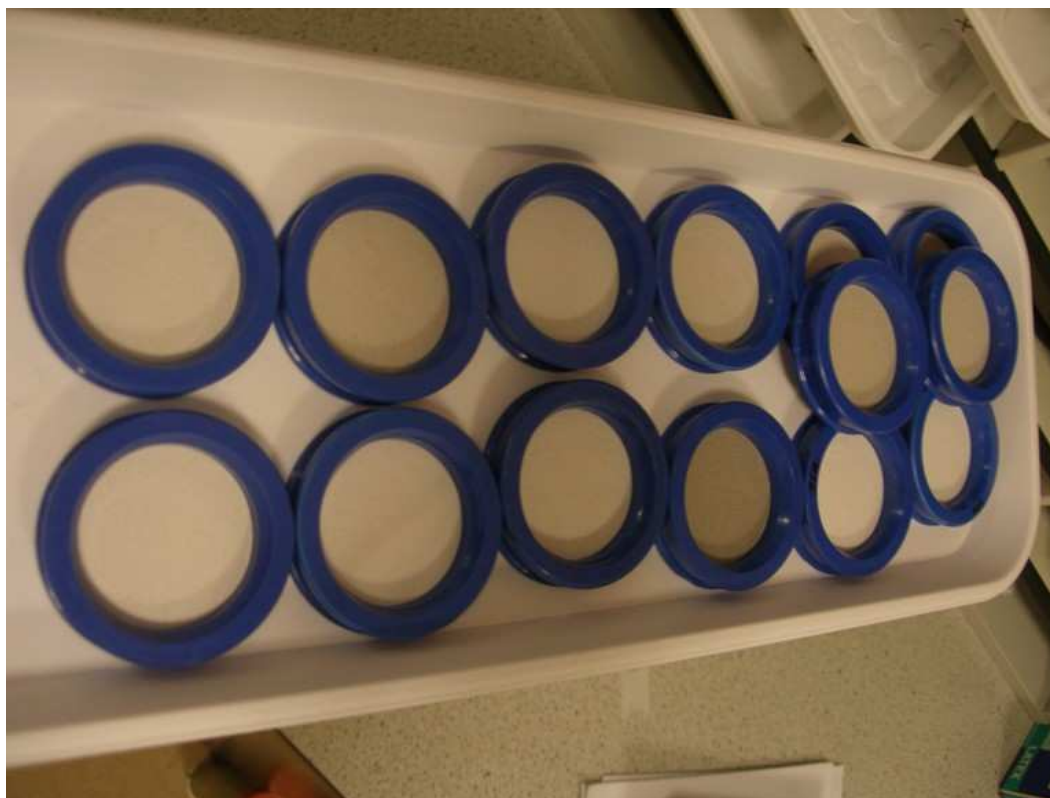
Partisol 2025 filters are removed from the Petri dishes and placed in the filter holders used by the instrument. Filters are dispatched to the LSO for installation in to the Partisol 2025 on a fortnightly basis along with a dispatch sheet containing the batch number, Internal IDs, Filter Numbers and RP codes (a unique number stamped on the back of each filter screen). Contrary to EN12341, exposed Filters are conditioned with the metal screen in the blue filter holders with the lids still on (Figure 4.13). Between uses the filter holders are cleaned with lint free wipes, though this has only occurred since the relocation of weighing facilities in February 2007.

Regardless of sampling method, the sampled filters are automatically weighed using the same criteria as the blank filters. The filters are examined visually when they are removed from the magazine to ensure that they were returned in the correct order and any damaged or missing filters have comments recorded on the corresponding dispatch sheet. The analyst identity, date, time, number of filters, client name, filter condition (clean/used) and tray number is recorded in the filter weighing log book. New Petri dishes are used to store the sampled filters, whereas Petri dishes previously used for clean filters are reused for further clean filters.

Mass gains are calculated by the software from the weighing data in the database and a report of analysis is generated, the report is checked for errors then emailed or faxed to the project co-ordinator at Bureau Veritas HS&E Ltd. Sample concentration is calculated as the sample mass

divided by the volume, and these data are sent to AEA for auditing and inclusion on the National Database. As discussed in Section 4.1.4, for filters weighed by Bureau Veritas, concentrations reported on the National database have not previously been corrected for the travel blank or laboratory blank mass.

Figure 4.13 Photo of conditioning of sampled Partisol filters in filter holders.



The audit highlighted certain procedures which were tasked for further action, namely:

- Variability of humidity;
- Conditioning of un-sampled filters with overlap;
- Reuse of Petri dishes;
- Conditioning of exposed Partisol filters in filter holders;
- Cleanliness of Partisol filter holders;
- Deposited dust in weighing facility;
- Laboratory move.
- The age of the Polonium 210 source.

These are discussed in the following section.

4.2.2 Experiments to ascertain the source of the high blank values.

4.2.2.1 Humidity

When the filter weighing facility was located at Runcorn there were occasional problems with maintaining the weighing room humidity and temperature settings. This has improved considerably since the facility was moved to Glasgow in February 2007. As there are still problems with the blank values since February 2007, it is anticipated that this is unlikely to be the root cause of the increased blank weights shown in recent years.

The affect of humidity on travel blanks is discussed in Section 4.3.4.

4.2.2.2 Conditioning of un-sampled filters

Filters are conditioned with a slight overlap contrary to EN12341. In order to test this, filters conditioned with a slight overlap were alternated in a Partisol magazine with those conditioned individually. This was sent to a site near Cheltenham where each filter was passed through a Partisol 2025 for four hours a piece with no flow. As described in Section 4.1.3, travel blank filters have typically not been in the sampling mechanism of a Partisol, though some have. Four hours in the sampling position was chosen as at the time of the experiment there was a very tight deadline for an earlier draft of the present report. Sampled filters were conditioned in the blue filter holders as per normal operation. Results are shown in Table 4.1 assuming a 24 hour sampling period in order to be consistent with the treatment of travel blanks elsewhere in this report. None of the filters had a significantly high concentration equivalent, and most were in fact negative rather than positive. As such, it was not possible to recreate the high baselines normally observed.

Table 4.1 Equivalent Concentration of blank filters conditioned with overlap and on their own.

Concentration Equivalent / $\mu\text{g m}^{-3}$	Conditioned with a slight overlap	Conditioned on their own
Average	-0.18	-1.38
Max	0.58	0.38
Min	-1.29	-3.04

4.2.2.3 Re-use of Petri Dishes

New Petri dishes are used to store sampled filters, whereas Petri dishes previously used for clean filters are reused for further clean filters. If a Petri dish is contaminating an un-sampled filter after it has been first weighed, but before it is reweighed after sampling, then this would lead to a mass and therefore a concentration equivalent gain. It is not known how many times Petri dishes have been reused, though this could be considerable. New Petri dishes should be used for clean filters, and these should be reused for sampled filters.

4.2.2.4 Conditioning of Exposed Partisol filters in Filter Holders

The sampled Partisol filters (and field blanks) are conditioned in Partisol 2025 filter holders which do not allow the full filter to be in contact with the controlled atmosphere. In order to test the impact of this, the laboratory was instructed to perform the following test:

Partisol filters ($\text{PM}_{2.5}$ filters sampled in January 2008 at Fort William) were conditioned and weighed as usual. Afterwards these filters were conditioned for a further 2 days separately on a tray and reweighed in order to see if the masses of the filters decreased significantly.

Table 4.2 Increase in concentration of PM on filters after weighing; conditioning for a further 48 hours then weighing again relative to PM concentration.

Concentration at Weighing 1 / $\mu\text{g m}^{-3}$	Concentration at Weighing 2 / $\mu\text{g m}^{-3}$	Increase in Concentration between Weighings / $\mu\text{g m}^{-3}$	Description of Deposit
3.21	4.13	0.92	Unexposed
6.92	7.54	0.62	Light grey particulate
8.04	8.71	0.67	Very light grey particulate
8.29	8.79	0.50	Very light grey particulate
9.38	10.29	0.92	Light grey particulate
10.46	11.25	0.79	Grey particulate
11.71	12.88	1.17	Grey particulate
12.67	12.83	0.17	Grey particulate
15.13	17.04	1.92	Grey particulate
17.00	16.92	-0.08	Grey particulate
17.04	17.88	0.83	Grey particulate
22.13	23.58	1.46	Dark grey particulate
24.04	24.71	0.67	Dark grey particulate
38.17	37.33	-0.83	Very dark grey particulate
Average		0.77	

In general, filters actually gained rather than lost mass; an average $0.77 \mu\text{g m}^{-3}$ was added to the concentration by conditioning for a further 48 hours. These results are contrary to those expected. These filters are ordered in Table 4.2 from an unexposed filter to a filter with $38.17 \mu\text{g m}^{-3}$ equivalent of PM, which is moderate by UK standards. While the unexposed filter gained weight, and the most exposed filter lost weight, there is no overall pattern in the results. Similarly, when ordered by maximum sampling relative humidity, there is no overall pattern as to which filters gained or lost mass due to conditioning for a further 48 hours.

Table 4.3 Increase in concentration of PM on filters after weighing; conditioning for a further 48 hours then weighing again relative to Maximum RH.

Increase in Concentration between Weighings / $\mu\text{g m}^{-3}$	RH Maximum / %	RH Minimum / %	RH Average / %
1.46	75.3	43.9	62.7
0.62	77.8	46.4	64.3
0.67	79.2	38.6	58.7
1.17	80.6	50.9	69.5
1.92	80.6	53.7	66.5
-0.08	81.3	48	66.3
0.17	81.5	40.4	61.9
-0.83	83.4	53.3	70.7
0.79	84.1	50.9	67.9
0.50	85.5	43.3	62.8
0.67	86.5	62.9	76.9
0.92	87.2	50.9	69.4
0.83	94.3	54	81.7

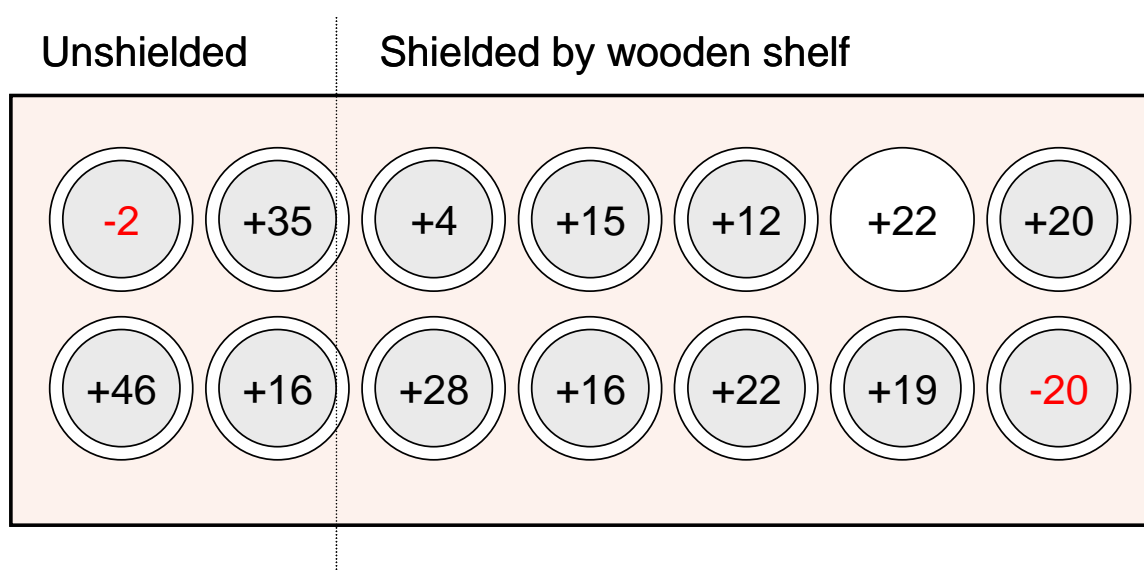
4.2.2.5 Cleanliness of Partisol Filter Holders

Partisol filter holders are cleaned prior to reuse, which was not practiced prior to the relocation of the laboratory to Glasgow in February 2007. Cleaning of the holders could result in a net mass gain or mass loss for the filters, dependent upon whether there is a decrease of increase in deposits on the holders due to the cleaning process. As there are high blank concentration equivalents both before and after February 2007, this is unlikely to be the current cause of the high blank problems.

4.2.2.6 Deposited dust in weighing facility.

The weighing facilities were continually kept clean, but historically, there have occasions when deposited dust was observed that has originated from the ceiling tiles. Figure 4.11 shows that filters are conditioned with the majority kept under protection from dust by a wooden shelf, but a few filters are not protected. The results from the filters conditioned and weighed twice in Section 4.2.2.4 were analysed based on the position of the filters on the conditioning tray and the results are shown in Figure 4.14. The average mass gain of the four unshielded filters is 24 μg , whereas the average mass gain of the eight shielded filters is 14 μg . However, the two filters to have lost weight were located both in the most exposed and most shielded areas (shown in red below). While the deposited dust is a potential contamination issue, as there is no evidence of a shift in the blank mass problem when the facility was moved from Runcorn to Glasgow, deposition of dust seems unlikely to be the cause of increased blank masses.

Figure 4.14 Increase in mass (μg) of filters based on their position for conditioning on the tray.



4.2.2.7 Laboratory relocation

The re-location of the laboratory occurred at a time when there were very significant travel blank concentration equivalents, as the largest single travel blank concentration equivalent was a filter weighed for the $\text{PM}_{2.5}$ Partisol at Auchencorth that was both pre and post weighed at Runcorn, just before the laboratory move. A total of 22 of the travel blank Whatman QMA quartz filters were pre weighed in Runcorn, and post weighed in Glasgow. These had an average concentration equivalent to $6.18 \mu\text{g m}^{-3}$, the average of the last 22 blank filters (based on date in sampler) to be both pre and post weighed in Runcorn was $4.76 \mu\text{g m}^{-3}$, and the average of the first 22 both pre and post weighed in Glasgow was $5.98 \mu\text{g m}^{-3}$. This would suggest that the laboratory move had a temporary effect on travel blanks but is not the route cause of the ongoing problem.

4.2.2.8 The age of the Polonium 210 source.

The polonium 210 source was not initially changed for four years. The source is used to eliminate static from the filters. Teflon filters are particularly prone, though quartz filters are less so. The implications for not frequently changing the source are that filters could take longer for the mass to stabilise. As the system waits until the readings are stable before moving on to the next filter, there is not thought to be any impact on the validity of the filter weights collected during this period. It is possible that the magnitude of static effect is dependent on whether the filter has been sampled. However, as there is an observed increase in mass for both sample and travel blank filters, this is not considered to be an issue.

4.2.3 Conclusions of Laboratory Audit

Tests performed in response to an audit of the laboratories were unable to identify a clear possible cause for the increase filter blanks in recent years. The following two issues were identified that should be rectified. However, it is not recommended that the methodology is changed at this point until the cause of the problem is identified:

- Sampled Partisol filters should be removed from the filter holders prior to conditioning.
- New Petri dishes should be used for un-sampled filters.

4.3 Travel blank trend analysis

David Carslaw (Institute of Transport Studies, University of Leeds) was commissioned to use sophisticated analysis techniques to look for trends in the datasets. A full description of the techniques used can be found in [10], and key findings of this work are reproduced here. The present report deals primarily with the date the blank filters were placed in the sampler, as it is not easily possible to correct any sampled data by any other date. Dates can be categorised by the date the blank filter was first weighed, the date of the final weighing, or the date which it was placed in to the sampler. The significance of these three dates is discussed in detail in David Carslaw's report [10]. No correlation was seen between both the time taken between weighings or the personnel involved, to the magnitude of the travel blank concentration equivalent.

4.3.1 Statistics of the trend in Bureau Veritas weighed Whatman QMA quartz filters

Figure 4.15, Table 4.4 and Table 4.5 show statistical analyses in Bureau Veritas Laboratories weighed Whatman QMA quartz filters used in Partisol 2025s. Data are sorted in to year or month by date placed in sampler. These statistics show that there are a variable number of travel blanks on a monthly basis since November 2000, and as such any analysis based on monthly data should be treated with caution. For the annual averages, there is sufficient number of travel blank filters in order to have confidence in the averages for all years except 2000, when there were only 2 travel blank filters. For both the monthly and annual averages, the standard deviation is often greater than the average blank concentration equivalent, though this is not unexpected when considering averages close to zero.

Figure 4.15 Box and whisker plot of Bureau Veritas weighed Whatman QMA Quartz filters filter weights used in Partisol 2025s by month. The filled circles show the median concentrations and the shaded boxes show the 25th and 75th percentile concentrations.

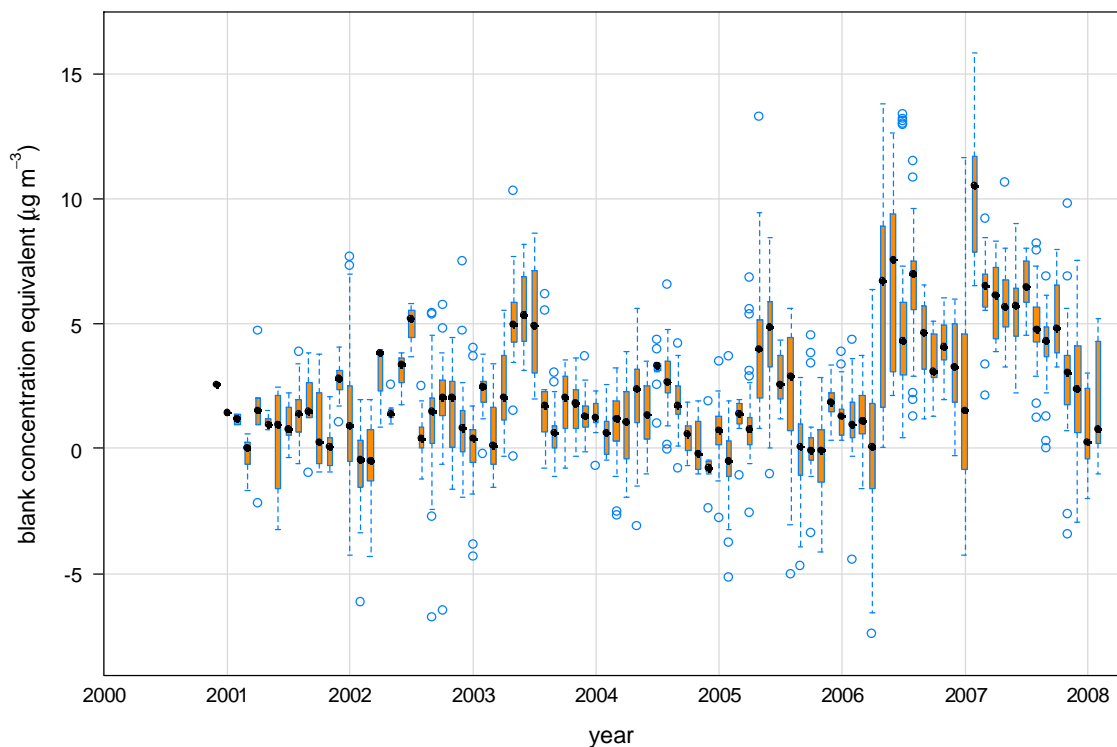




Table 4.4 Annual average blank concentration equivalent.

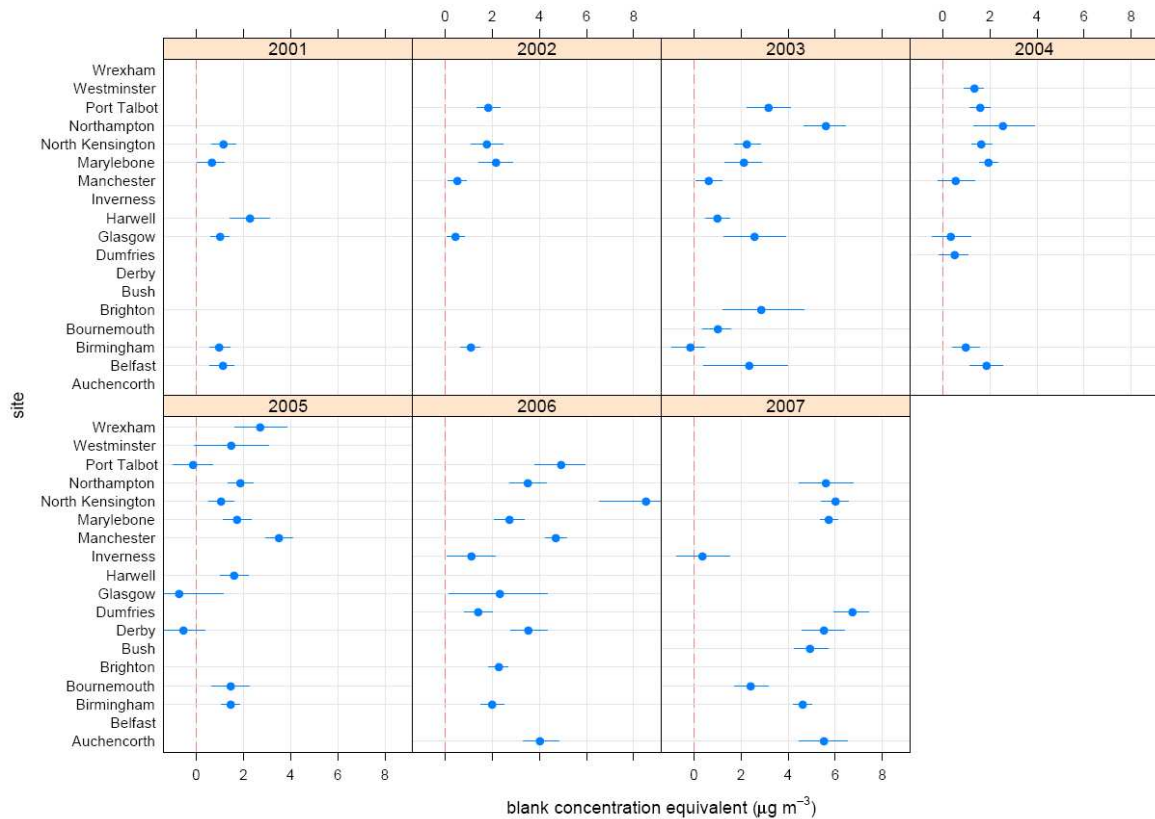
Year	Annual Blank Average / $\mu\text{g m}^{-3}$	Standard Deviation	Annual Blank Count
2000	2.71	0.18	2
2001	1.08	1.36	124
2002	0.94	2.08	352
2003	2.23	2.47	210
2004	1.49	1.62	257
2005	1.46	2.42	402
2006	3.34	3.23	329
2007	4.51	2.83	238

Table 4.5 Variation in Bureau Veritas weighed Whatman QMA Quartz filters filter weights used in Partisol 2025s by month placed in sampler.

Month	Count	Mean	Minimum	Maximum	Standard Deviation
December 2000	1	2.58	2.58	2.58	
January 2001	1	1.42	1.42	1.42	
February 2001	2	1.17	0.96	1.38	0.30
March 2001	15	-0.19	-1.67	0.58	0.64
April 2001	5	1.40	-2.21	4.71	2.48
May 2001	5	1.08	0.75	1.54	0.31
June 2001	4	0.27	-3.25	2.46	2.56
July 2001	19	0.96	-0.38	2.21	0.76
August 2001	35	1.43	-0.58	3.88	1.05
September 2001	5	1.65	-0.96	3.83	1.79
October 2001	4	0.83	-0.92	3.79	2.08
November 2001	15	0.11	-0.92	2.08	0.90
December 2001	14	2.69	1.04	4.08	0.72
January 2002	50	1.23	-4.25	7.71	2.88
February 2002	42	-0.65	-6.13	1.96	1.44
March 2002	48	-0.45	-4.29	1.96	1.39
April 2002	4	3.12	0.88	3.96	1.49
May 2002	7	1.52	1.00	2.58	0.51
June 2002	8	3.10	1.75	3.83	0.71
July 2002	3	4.90	3.71	5.79	1.07
August 2002	17	0.51	-1.21	2.50	0.98
September 2002	49	1.11	-6.75	5.42	2.03
October 2002	48	1.93	-6.46	5.75	1.69
November 2002	42	1.58	-1.63	4.46	1.57
December 2002	34	0.95	-1.96	7.50	1.77
January 2003	34	0.15	-4.29	4.04	1.60
February 2003	13	2.21	-0.21	3.79	1.00
March 2003	12	0.48	-1.54	3.42	1.49
April 2003	9	2.54	-0.29	5.50	1.88
May 2003	22	4.91	-0.33	10.33	2.03
June 2003	21	5.42	3.13	8.17	1.55
July 2003	15	5.13	2.00	8.63	2.35
August 2003	15	1.82	-0.79	6.17	1.91
September 2003	30	0.56	-1.13	3.04	1.00
October 2003	17	1.73	-0.79	3.54	1.32
November 2003	11	1.60	-0.33	3.63	1.18
December 2003	11	1.46	-0.13	3.71	1.04
January 2004	17	1.33	-0.67	2.33	0.75
February 2004	10	0.68	-0.46	2.54	0.91
March 2004	38	0.93	-2.67	3.21	1.35
April 2004	26	1.06	-1.96	3.88	1.60
May 2004	53	2.11	-3.08	5.63	1.77
June 2004	24	1.37	-1.04	3.50	1.37
July 2004	11	3.18	1.00	4.33	0.85
August 2004	28	2.80	-0.04	6.54	1.38
September 2004	16	1.89	-0.79	4.21	1.28
October 2004	13	0.55	-0.67	1.87	0.73
November 2004	10	0.15	-1.04	1.92	1.17
December 2004	11	-0.63	-2.37	1.92	1.00
January 2005	52	0.68	-2.75	3.50	1.08
February 2005	25	-0.63	-5.17	3.67	1.85
March 2005	11	1.22	-1.08	1.96	0.86
April 2005	44	1.08	-2.58	6.83	1.65
May 2005	19	4.28	0.83	13.29	3.09
June 2005	56	4.48	-1.04	8.42	2.02
July 2005	18	2.80	1.21	4.33	1.00
August 2005	30	2.27	-5.00	5.63	2.63
September 2005	51	-0.10	-4.71	2.83	1.57
October 2005	22	0.31	-3.38	4.54	1.70
November 2005	39	-0.23	-4.12	2.83	1.85
December 2005	35	1.84	0.33	3.38	0.71
January 2006	26	1.37	0.33	3.88	0.91
February 2006	28	1.05	-4.46	4.33	1.54
March 2006	50	1.24	-1.58	3.75	1.27
April 2006	28	-0.24	-7.42	6.38	2.94
May 2006	24	6.01	0.08	13.79	4.09
June 2006	14	6.85	2.13	12.62	3.52
July 2006	38	5.20	0.46	13.37	3.51
August 2006	31	6.55	1.29	11.50	2.40
September 2006	26	4.35	1.21	6.54	1.56
October 2006	13	3.49	1.29	5.08	1.29
November 2006	12	4.08	1.96	6.04	1.19
December 2006	39	3.33	-0.25	6.00	1.70
January 2007	38	2.23	-4.25	11.62	3.89
February 2007	5	10.48	6.50	15.83	3.63
March 2007	15	6.20	2.13	9.17	1.74
April 2007	8	5.97	3.88	8.29	1.63
May 2007	22	5.92	3.25	10.63	1.69
June 2007	19	5.64	2.21	9.00	1.69
July 2007	14	6.52	4.54	8.04	1.17
August 2007	41	4.94	1.25	8.21	1.37
September 2007	34	4.08	0.00	6.88	1.43
October 2007	4	5.20	3.25	7.96	2.00
November 2007	28	2.86	-3.42	9.79	2.47
December 2007	10	2.51	-2.96	7.54	3.14
January 2008	17	0.67	-2.00	3.04	1.71
February 2008	13	1.69	-1.04	5.21	2.24

Figure 4.16 shows the annual average blank equivalent concentration for sites where there are at least 6 blank filters in a year. There is some scatter particularly for 2006 and 2007. This is because the blanks are not evenly distributed by site and by month, and as there is a significant monthly variation in the blank particularly during 2006 and 2007. Section 4.1.3 discussed how there was no difference between blanks for PM₁₀ and PM_{2.5}, and as such, both PM₁₀ and PM_{2.5} Partisols are grouped together in Figure 4.16. It is possible that the overestimation of PM on sampled filters is dependent on site location, though there is no way of identifying this, at least until the cause of the laboratory offset is identified.

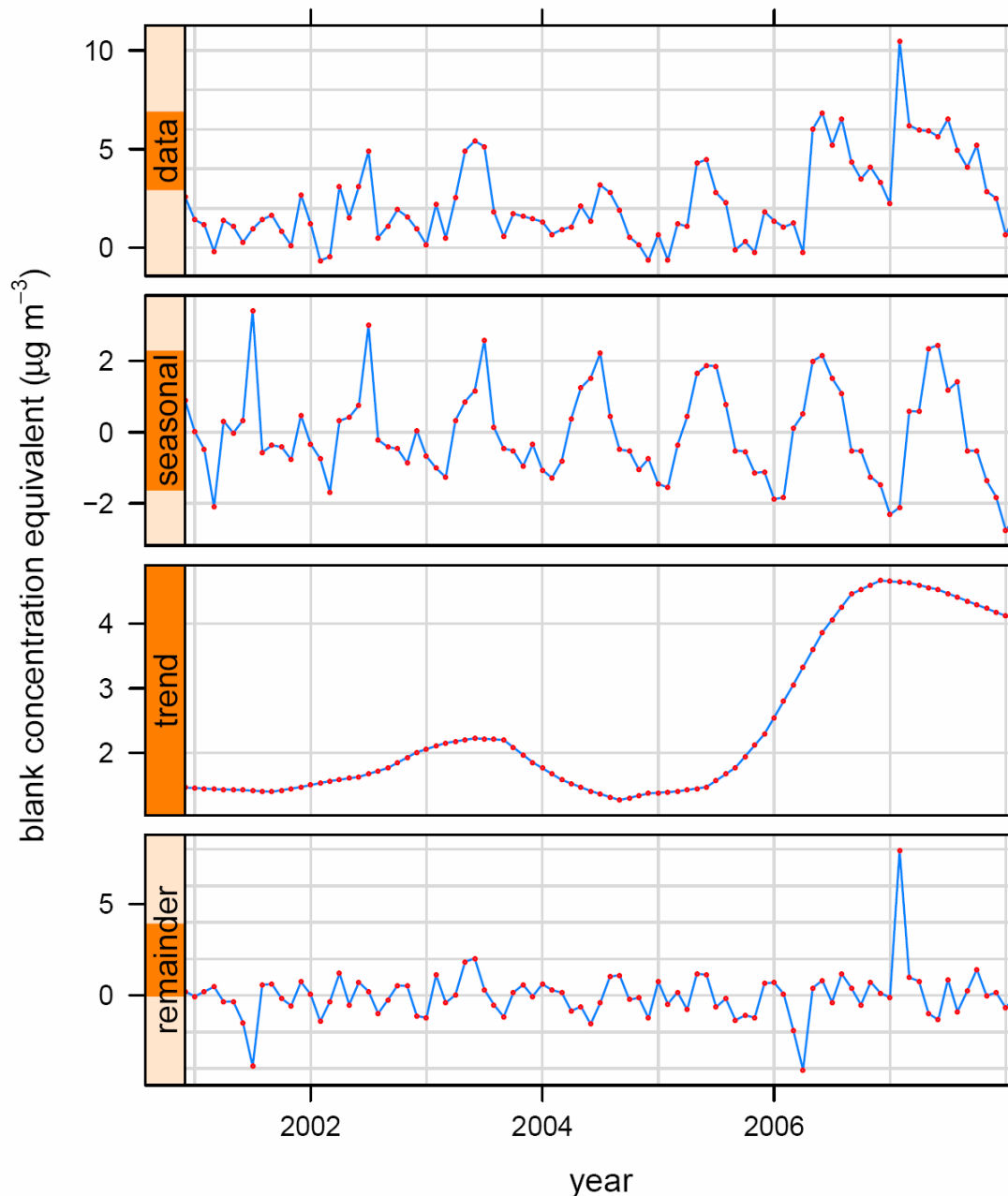
Figure 4.16 Dependency of site on annual average field blank concentration equivalent.



4.3.2 Trend Analysis and seasonal affects

A seasonal trend decomposition technique based on locally weighted regression (STL) [11] was used to determine whether there is evidence of a seasonal cycle in the blank filter weights. Figure 4.17 shows the seasonal decomposition applied to the entire data set. The top panel shows the raw data and the subsequent panels show the extracted components (trend, seasonal and remainder). The orange bar adjacent to the y-axis in each plot covers the same range of concentrations in each plot and helps to show component variation.

Figure 4.17 Monthly time series of Bureau Veritas weighed Whatman QMA blank filter weights for Partisol 2025s decomposed into trend, seasonal and remainder components using the STL technique.



The trend report [10] compares the seasonal trends to meteorological parameters, and concludes that the best correlation is for the ambient absolute humidity and the final filter weigh date. In the Netherlands [12], a plot has been produced of locally weighed and deployed Whatman QMA quartz travel blank filter weights against ambient absolute humidity (Figure 4.18), showing evidence of correlation. All filters were preconditioned in a humid atmosphere before weighing, and the preconditioning time was increased from 1st January 2008.

Seasonal affects were not seen in either the Bureau Veritas weighed quartz filters for PNS-X8 KFGs, or the AEA weighed quartz filters, however, these are size-limited datasets, and the AEA filters were

laboratory not field blanks. A slight seasonal affect was observed in Emfab filters weighed by Bureau Veritas Laboratories for Partisols (Figure 4.19).

Figure 4.18 Variation of Whatman QMA travel filter blank mass against ambient absolute humidity. Data were collected in the Netherlands.

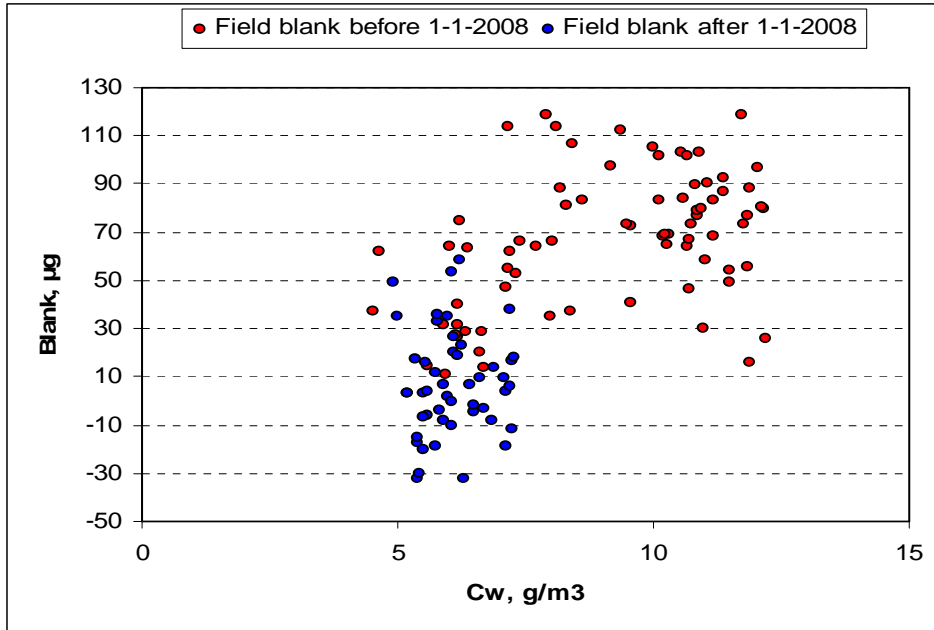
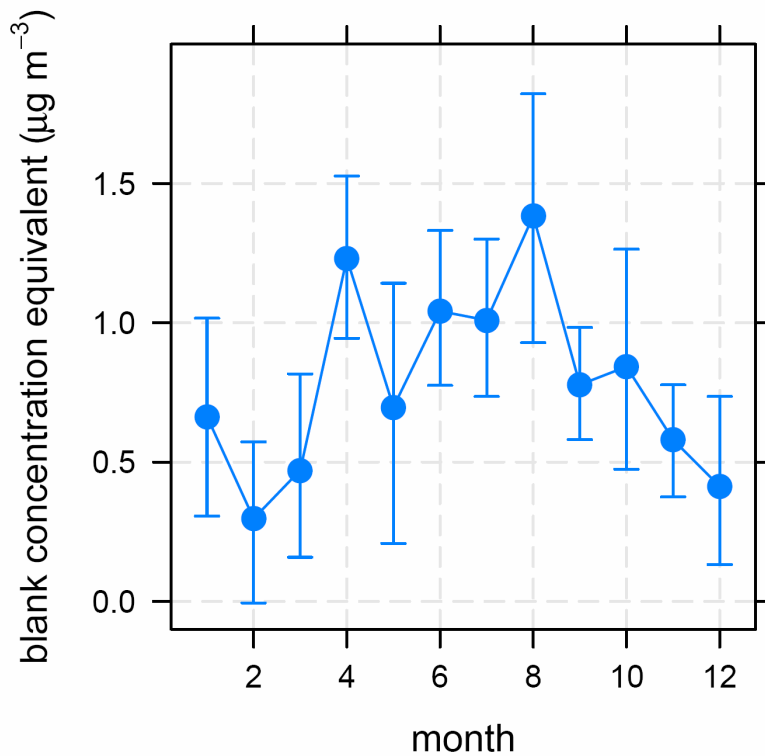


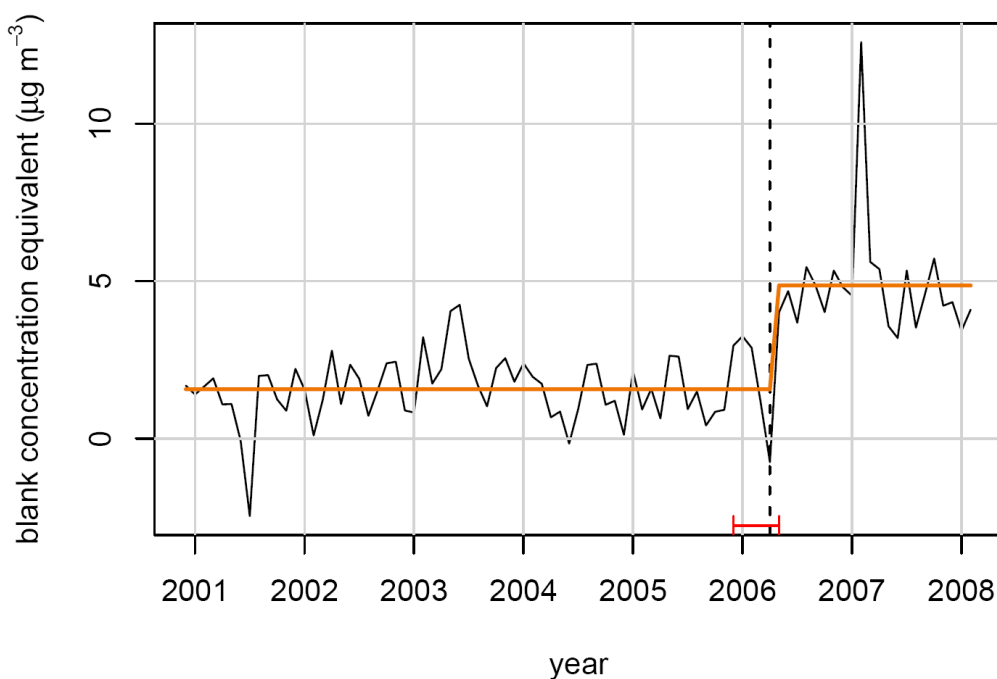
Figure 4.19 Seasonal affect in Emfab filters weighed by Bureau Veritas for Partisols.



4.3.3 Change Point analysis

Change-point analysis was used on the de-seasonalised data, which correspond to the trend plus remainder shown in Figure 4.17 [13,14]. Figure 4.20 shows the results. The vertical dashed line shows the location of the best estimate of the detected (single) change-point in April 2006 (where May 2006 represents the first month after the change). The error bar adjacent to the x-axis show the 95 % confidence intervals in the timing of the change-point (December 2005 – May 2006). The thick line shows the mean level filter weights before and after the change-point. These results provide strong evidence that there was significant change in the mean blank filter weight around April/May 2006, when concentrations increased by approximately $3 \mu\text{g m}^{-3}$.

Figure 4.20 Change-point analysis of de-seasonalised monthly mean Bureau Veritas weighed Whatman QMA blank filter weights for Partisol 2025s.



The laboratory was consulted in order to establish if anything had change around May 2006. There were problems in March 2006 with an intermittent fault which caused the automatic filter tray to stop in mid run with the error message "an error has occurred - contact vendor". This was diagnosed as a problem either with the interface box, between the PC and the robot, or the RocketPort interface card in the PC; possibly due to humidity induced corrosion. The old PC was replaced and a new bar-code reader purchased along with a USB interface for the controller. This is not thought to be a potential cause for the high blank values, and does not give any indication as to a significant change around May 2006.

4.3.4 Affect of Humidity

Data were available giving the 24 hour average relative humidity and temperature of the laboratory at the time of pre and post weighing. Figure 5.20 summarises these effects for all Bureau Veritas weighed Whatman QMA Partisol blank quartz filters. The plots show the number of counts in each 'bin' to highlight the overall distribution. Plots are split by initial and final conditions *i.e.* laboratory conditions when blank filters were first weighed and the conditions when filters were weighed after exposure. The solid line shows a smooth fit to the data. The dashed lines show the tolerances allowed under EN12341. There is no clear affect on the data.

Figure 4.21 Relationship between blank filter weight and laboratory temperature and humidity.

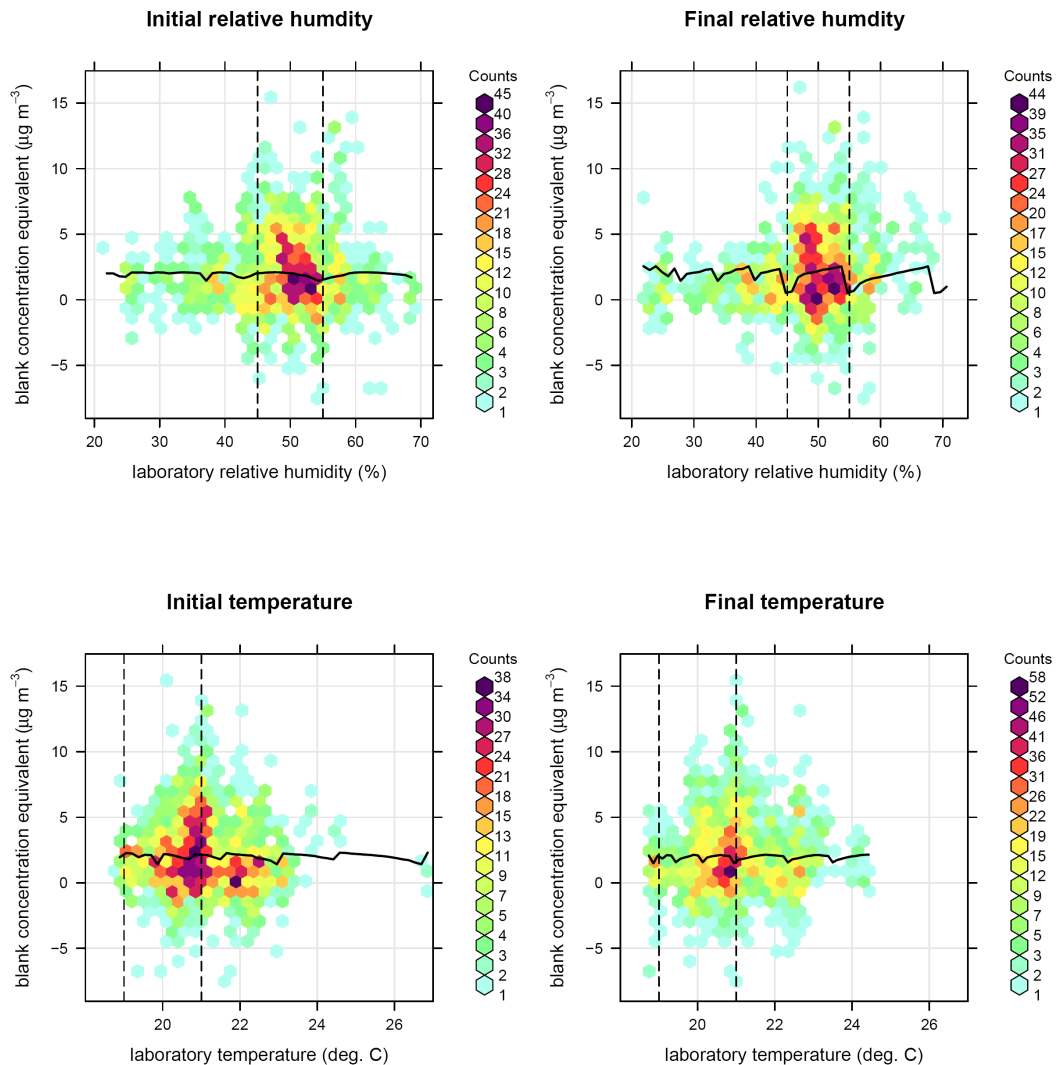


Figure 4.22 shows the laboratory RH as a time series. It is clear that there was a seasonal pattern from August 2002 to August 2004. Figure 5.22 splits the data from Figure 4.21 to highlight the period when there was a laboratory seasonal affect, and the period since May 2006 where there was a step increase in blank concentration equivalent. There is some evidence to suggest that the laboratory RH problems from August 2002 to August 2004 contributed to the seasonal affect seen in the blank data in Figure 4.17. It is possible that this may have the seasonal trend decomposition technique to see trends in subsequent years, and that this may partially explain the spike for February 2007 in Figure 4.20 (which also corresponds with the laboratory move discussed in Section 4.2.2.7).

During the comparison of filters weighed by Bureau Veritas and NPL (Section 4.1.2), all Bureau Veritas filters were weighed well within the RH and temperature tolerances set down in EN12341. The humidity measured by NPL was occasionally very slightly out of range. These findings would suggest that the laboratory conditions are not the cause of the discrepancy in filter weights between the two laboratories.

RH is measured in two separate places in the Bureau Veritas laboratory, and both agree and have been UKAS accredited. As such, it is highly unlikely that the true RH in the Bureau Veritas laboratory is anything other than that recorded in the filter weighing records and used in the analyses herein.

Figure 4.22 Time series of laboratory humidity at the time of initial filter weighing. The shaded area shows the tolerances allowed under EN12341.

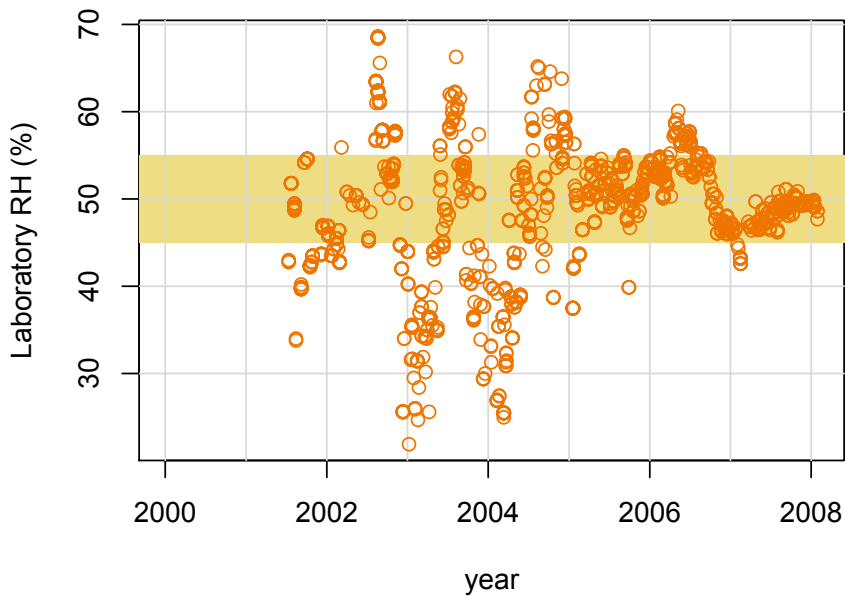
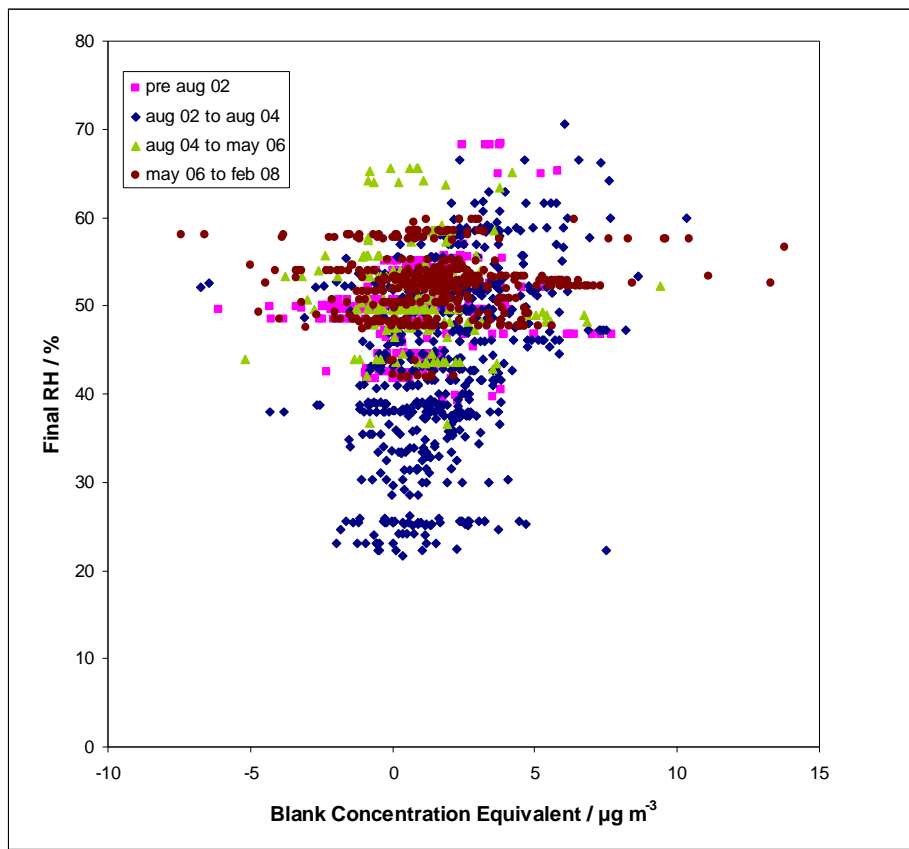


Figure 4.23 Scatter plot of laboratory relative humidity for travel blanks at time of post weighing of Bureau Veritas weighed Whatman QMA quartz filters for Patrisols



4.3.5 Filter Weight

The time series of initial filter weight shows evidence of two distinct bands and these were weighed concurrently during 2005 (Figure 4.24). During this period, Partisol magazines of 14 filters would often include both types of filter.

Figure 4.24 Time series of initial filter weight.

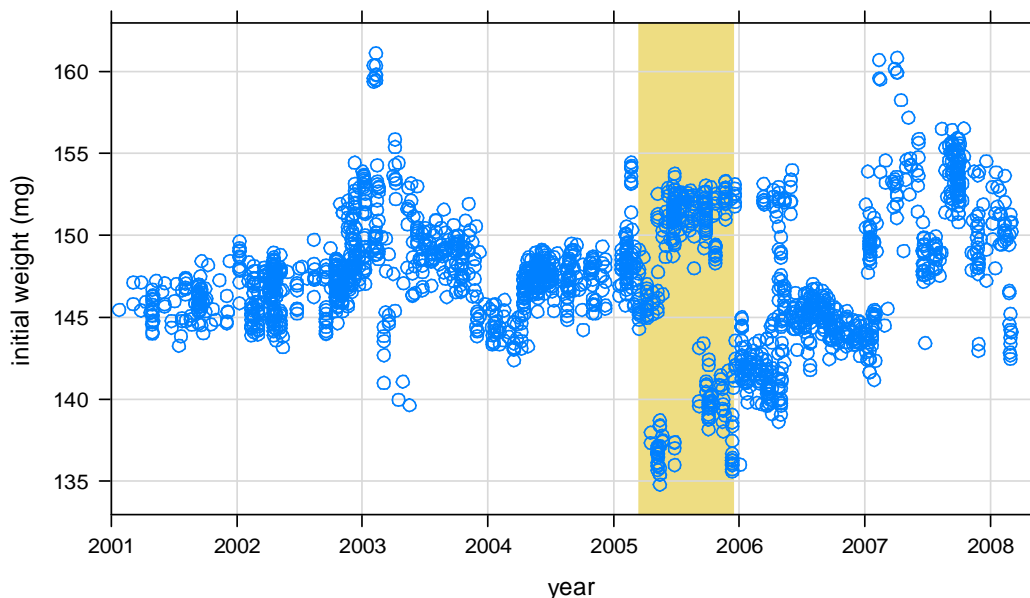


Figure 4.25 shows that for the highlighted period in Figure 4.24, the two distinct types of nominally identical filter possessed very different travel blank concentration equivalents. The filters with a higher initial weight are associated with blank filters that have concentrations of $2.8 \pm 0.4 \mu\text{g m}^{-3}$ (95 % confidence interval in the mean) and the filters with a lower initial weight with concentrations of $0.3 \pm 0.3 \mu\text{g m}^{-3}$. Statistically, it can be shown that there is a clear difference in these two groups in their mean blank concentrations of $2.5 \mu\text{g m}^{-3}$. This is a potentially important finding as it shows that nominally identical filters have different characteristics in terms of their blank filter concentrations. The difference of $2.5 \mu\text{g m}^{-3}$ is also a considerable fraction of travel blank filter concentration equivalents.

The Whatman manufacturing facility (Maidstone, UK) have been contacted, and confirmed that the tolerance for filter weight is from 127 mg to 161 mg (Target 144 mg), and all of the filters used herein are within range [15]. They confirmed these filter media are manufactured using a single machine. Although, all filter weights in any given batch will be very similar, the range of weights between batches would be much greater. This would explain the two separate distinct bands observed during 2005. Examples of blanks from both weight ranges in 2005 will be sent to the manufacturing facility for further investigation.

Section 4.1.2 discussed the comparison of $\text{PM}_{2.5}$ datasets weighed to EN14907 by NPL and EN12341 by Bureau Veritas. Figure 4.25 shows the variation of initial filter mass for the $\text{PM}_{2.5}$ Partisols operated using Whatman QMA Quartz filters weighed by both NPL and BV. All filters weighed by NPL were approximately 150 mg, as were all but one of those sampled prior to 5th July 2007 and weighed by Bureau Veritas. The Partisol in which the BV filters were installed was broken for 2 weeks, and all Bureau Veritas weighed filters sampled after that point were approximately 155 mg. Figure 4.27 shows that the heavier filters tended to result in the over estimate PM concentrations by a greater amount than the lighter filters. This is consistent with the findings that the heavier filters have a more significant blank problem.

Figure 4.25 Relationship between initial filter weight and blank filter concentrations. The period covered is shown by the shaded area in Figure 4.24

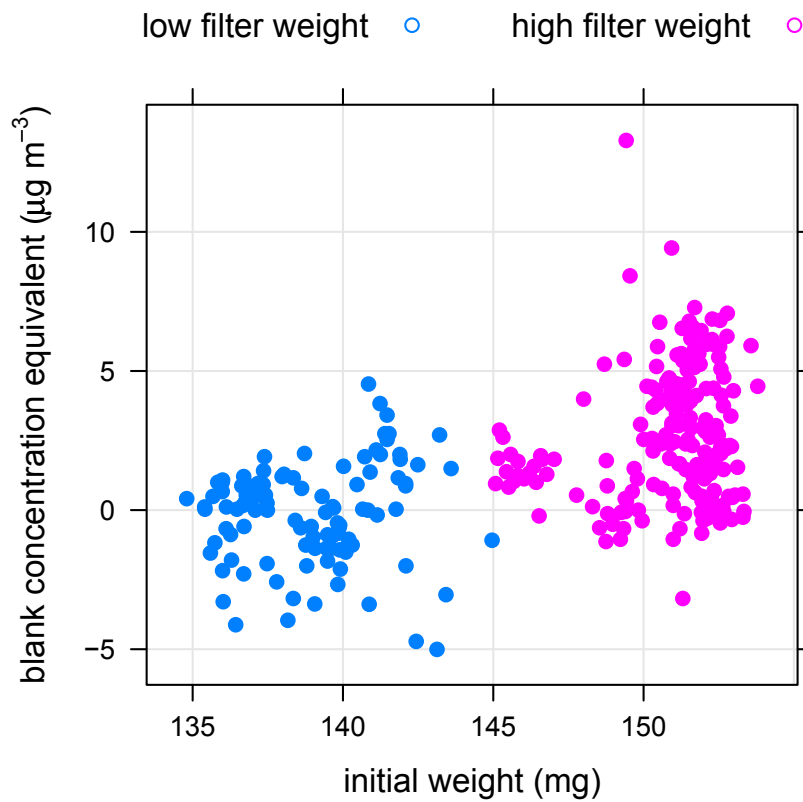


Figure 4.26 Variation of Initial Filter Mass for Whatman QMA filters weighed by BV and NPL for the 2007 Teddington Field Trials.

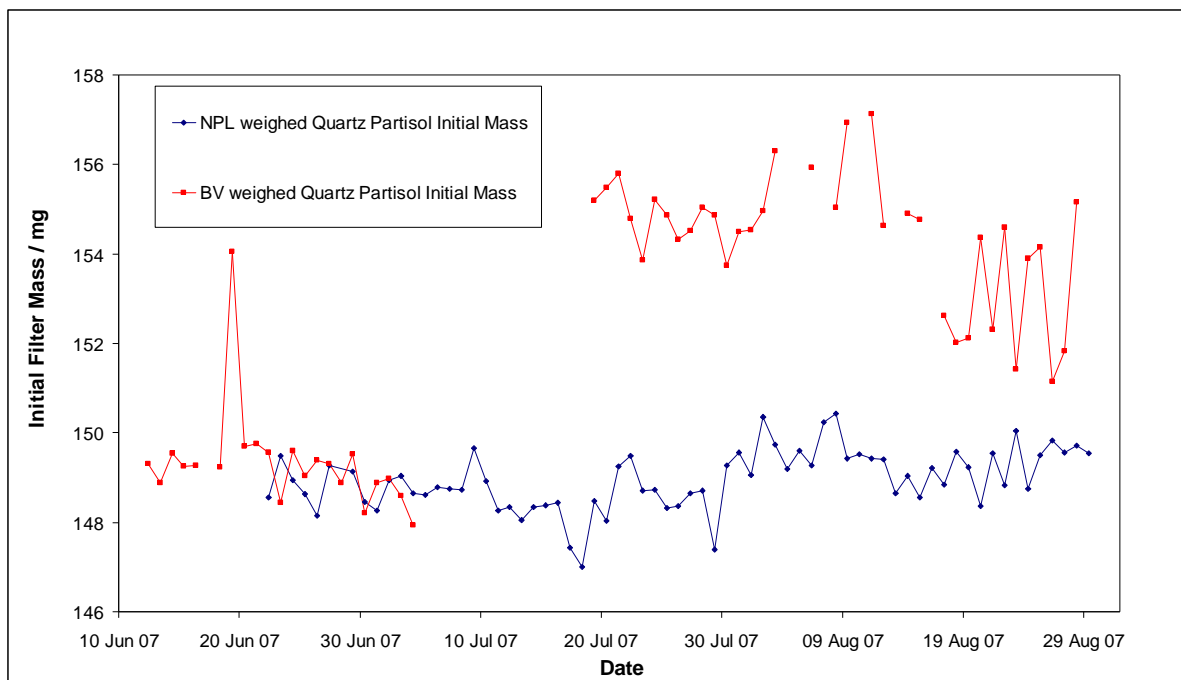
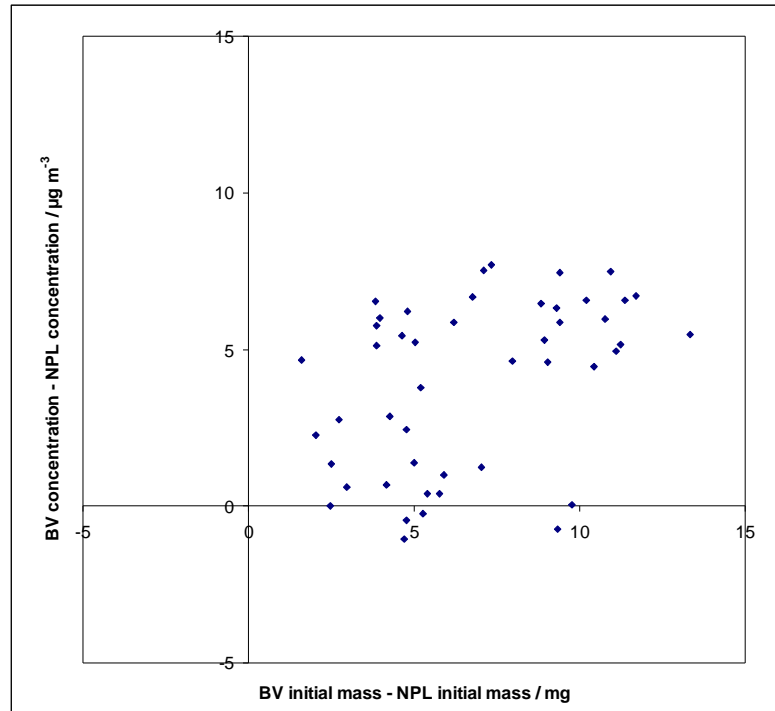


Figure 4.27 PM_{2.5} Scatter plot of the initial mass difference of Whatman QMA quartz filters weighed by BV and NPL versus the difference in measured PM_{2.5} concentration.

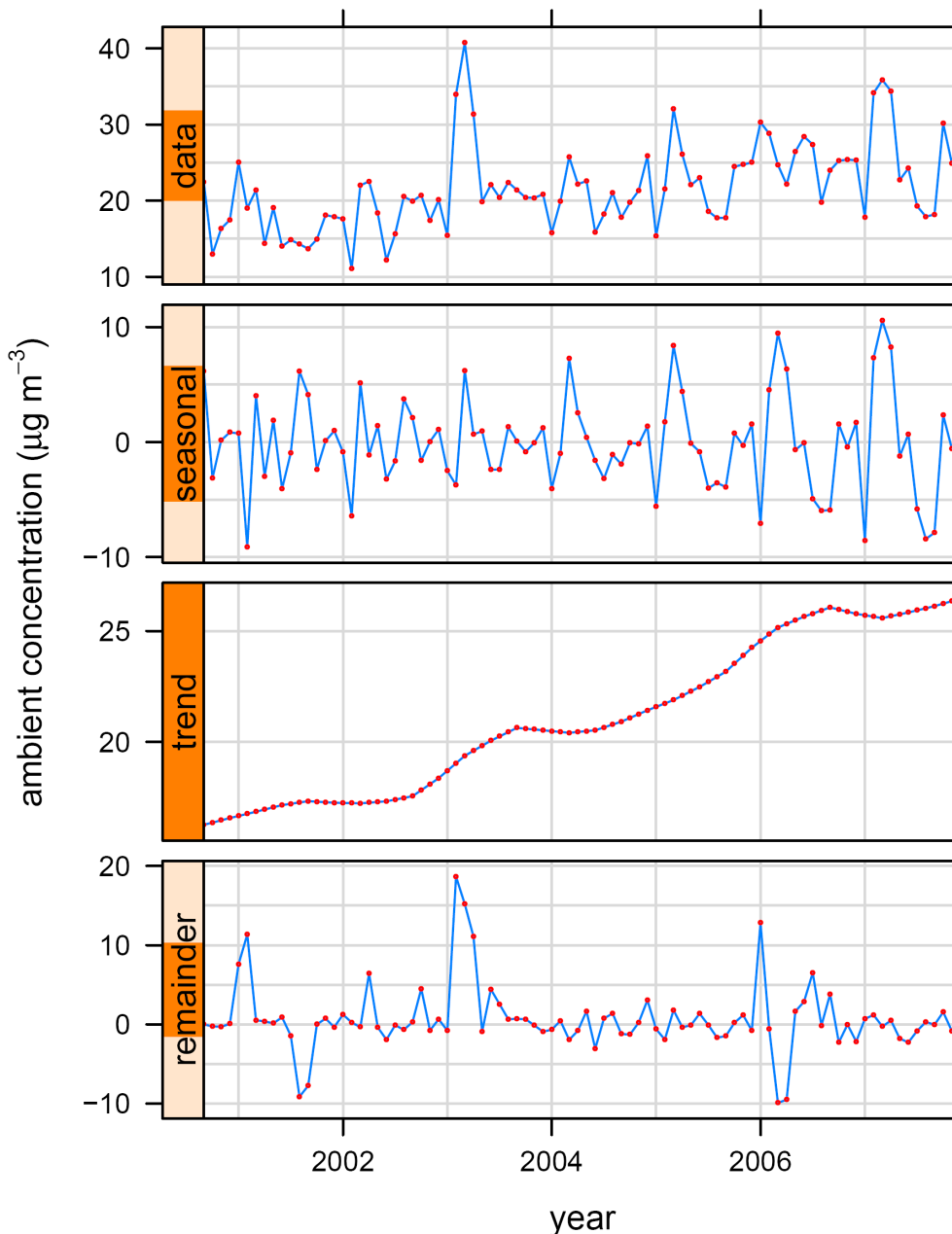


4.3.6 Trends and change-point in ambient data

The trend analysis performed in Section 4.3.2 for travel blank data can also be applied to ambient concentration data (Figure 4.28). Only sites with greater than 1500 days of measurements were used (i.e. 17 of the 34 sites discussed in Section 3). The 17 instruments used were PM_{2.5} Belfast; PM₁₀ Birmingham; PM_{2.5} Birmingham; PM₁₀ Bournemouth, PM₁₀ Brighton, PM₁₀ Dumfries; PM_{2.5} Glasgow; PM_{2.5} Harwell; PM₁₀ Westminster; PM₁₀ Inverness; PM₁₀ North Kensington; PM_{2.5} North Kensington; PM₁₀ Manchester Piccadilly; PM_{2.5} Manchester Piccadilly; PM_{2.5} Marylebone Road; PM_{2.5} Port Talbot; and PM₁₀ Wrexham.

The measured data show a different seasonal cycle compared with the filter blanks; peaking in the spring as opposed to the summer. These results suggest that different factors may affect the blank and exposed filters. The peak in ambient concentration in March is consistent with long-range transport of secondary aerosol. An exception appears to be 2006 where concentrations were not elevated during the spring. The trend component shown in Figure 4.28 confirms that at these sites concentrations increased from 2000-2007 by about 9 µg m⁻³.

Figure 4.28 Monthly time series of mean PM₁₀ and PM_{2.5} concentrations decomposed into trend, seasonal and remainder components using the STL technique. Data are for the 17 sites where there were at least 1500 days of valid measurements.



Change point analysis was applied to the site-averaged monthly measurements of PM₁₀ and PM_{2.5} for all sites, though no significant change points could be detected. This finding is not unexpected because measured particle concentrations are affected by a wide range of sources and "real" effects tend to dominate. The analysis was therefore refined to individual sites; namely: PM_{2.5} concentrations at Harwell and at North Kensington. The subtraction of TEOM data from gravimetric concentrations were used to account for a large fraction of particle mass concentration. The remainder would thus consist of particle mass not detected by TEOMs (Section 2.2) and any artefact due to filter issues.

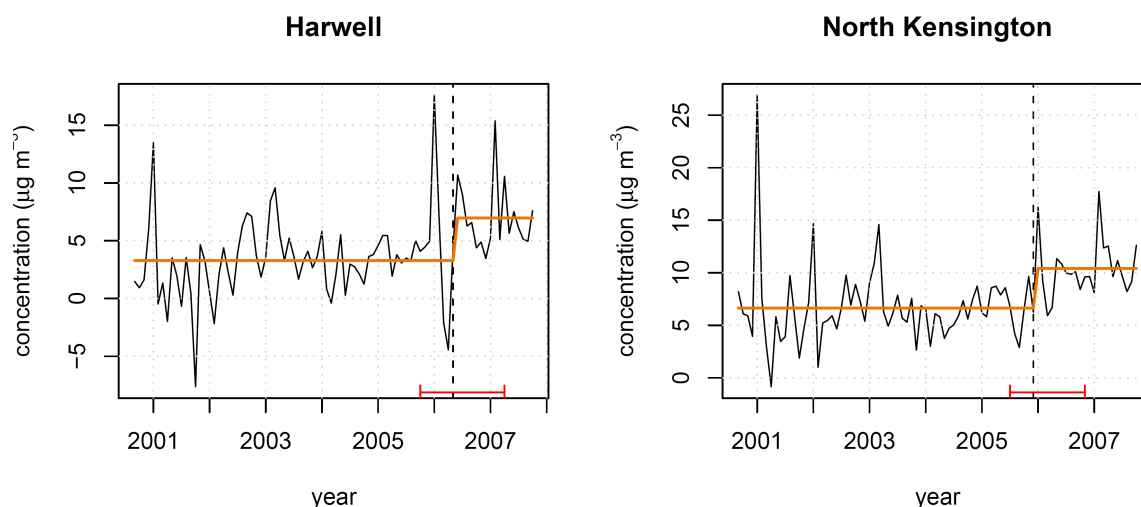
The Harwell site was chosen as it is rural, has no dominant local particle sources and has good data capture for both gravimetric and TEOM concentration measurements. The greatest difference in

TEOM and gravimetric PM_{2.5} concentrations at Harwell occurs during springtime conditions *i.e.* the time of year that appears to be consistently dominated by long-range transport. This is probably due to ammonium nitrate aerosols which form a significant mass fraction at Harwell. The results of the analysis are shown in Figure 4.29. A statistically significant change-point was detected in April/May 2006 for Harwell PM_{2.5} concentrations, although the 95 % confidence interval in the timing of it is wide (February 2006 – April 2007).

For North Kensington there are no measurements of PM_{2.5} made by TEOM. Therefore, PM_{2.5} data were obtained from the Bexley 2 LAQN suburban site, which should provide reasonably representative urban background PM_{2.5} concentrations. Six months data from the Bexley 2 site were missing during 2000/2001. These data were replaced by the mean values over the entire time series from 2000 – 2007. The results of the analysis are shown in Figure 4.29. A different change-point to Harwell was detected (December 2005, 95 % confidence interval from July 2005 to November 2006).

For both sites the uncertainty interval for the change-point includes the April/May 2006 change point identified for the travel blank filters (Section 4.3.3). The wider uncertainties are in part due to the noisier ambient data compared with that for the travel blank filter weights. Taken together there is some evidence therefore that the measured particle concentrations reflect the patterns shown in the blank filter weights. This evidence is not definitive, but it appears likely that the problems that affect the blank filter weights in 2006/7 also affect the exposed filters.

Figure 4.29 Change-point analysis of PM_{2.5} concentrations at Harwell and North Kensington. The black line shows the de-seasonalised data, the thick line shows the mean level filter weights before and after the change-point, the dashed line shows the best estimate of the change-point timing and the error bars adjacent to the x-axis show the 95 % confidence intervals in the timing of the change-point.



4.4 Organic Carbon Artifacts

Whatman QMA filters are 95% quartz with a 5 % borosilicate as binder and are heat treated for several hours at 500°C [8, 15]. Quartz is known to have a high affinity for gas phase VOCs and SVOCs, and filters that have previously been heat treated will have an increased affinity [16, 17]. Once a saturation point has been reached, all of the active sites are filled, and a filter will not gain any extra total SVOC or VOC mass, though the specific makeup will change with the changing air mass [16].

NPL have used a Sunset Instrument's organic and elemental carbon analyser on fresh un-sampled Whatman QMA filters and have found that they range between 0.7 and 2.9 µg m⁻³ concentration equivalent, and that this can be reduced to around 25 % of the original value by heat treating at 500 °C [18]. This would suggest that although the filters are initially heat treated, they are relatively

saturated with VOCs and SVOCs once they reach the point of sale. NPL have additionally analysed travel blank filters from Auchencorth Moss, these have an average concentration equivalent of $2 \mu\text{g m}^{-3}$ (Standard deviation = $1.2 \mu\text{g m}^{-3}$; $n = 33$), which is comparable to that of fresh un-sampled filters [18]. This would suggest that there is no significant contribution of gas phase VOCs and SVOCs to the mass of particles measured using Whatman QMA quartz filters. Further, as the travel blank filters from Auchencorth Moss were from a period where there was a significant blank concentration equivalent issue, this indicates that there is no contamination of filters with VOCs or SVOCs through the weighing protocols employed at Bureau Veritas Laboratories.

4.5 Summary of main findings

In depth analysis of trends in PM data acquired from gravimetric samplers has shown discrepancies between the measured concentrations of PM_{10} undertaken using quartz filters in Partisol equipment, when compared to the EU reference method. The comparison is particularly stark at a rural site in Scotland (Auchencorth Moss) where low levels of PM_{10} are expected to occur.

Investigation of the influencing factors of filter media and laboratory weighing procedures (between two key providers in the UK) show that both have a contributing influence to the apparent over-estimation of $\text{PM}_{2.5}$ concentrations. It is therefore anticipated that similar impacts would be observed for PM_{10} measurements based on the same filter media and using the same laboratory filter weighing procedures.

Increases in the mass of travel blanks appears to be the strongest influencing factor in discrepancies between filter-based methods with non-filter based methods for PM measurements. Specifically, a significant increase in the mass of travel blank filters appears evident in the last two years (2006/2007).

An audit of the current UKAS accredited provider on filter mass measurements to the UK network has considered issues around the stability of the environmental conditions in which filters are conditioned; the procedures for conditioning filters; the re-use of storage containers (*i.e.* cleanliness); the potential for deposited dust occurring within the filter conditioning room and the impact of the re-location of the facility from Runcorn to Glasgow. The audit has shown areas of minor improvement in procedures associated with the provision of filter weighing services, but nothing substantial that may otherwise provide for assurance that an impact on travel blank filter weights is expected.

Statistical analysis of the trends in filter blank mass have considered hidden trends within the data set, which appear to highlight the presence of a strong seasonal affect within the overall trend in filter blanks over 2001 – 2007. This seasonal affect is shown to correlate well with ambient absolute humidity. Change-point analysis on de-seasonalised data has confirmed the presence of a statistically significant step change in the data set around April 2006, when measured concentrations appeared to increase by approximately $3 \mu\text{g m}^{-3}$. Consultation with the laboratory and the previous laboratory audit have been unable to define the precise reasons for such a change.

Analysis of initial blank filter weights has shown that there appears to be two distinct types of nominally identical filters within the dataset, providing for a difference of approximately $2.5 \mu\text{g m}^{-3}$, although it would appear that these filters comply with the margins of tolerance (127 mg to 144 mg) in weight to comply with the equipment manufacturers quality criteria.

Statistical analysis of the trends in ambient concentrations confirms that a seasonal cycle exists within the reported concentrations data, albeit with a different pattern of occurrence. The peak in ambient concentrations of PM in March is consistent with long-range transport of secondary aerosol. Considering all instruments for which there are greater than 1500 days of data, no significant change-point was found within the trend analysis, although concentrations were shown to increase from 2000 – 2007 by approximately $9 \mu\text{g m}^{-3}$. It is thought the lack of significant change-point in the ambient data is attributed to over-riding impacts of real effects – such as peak occurrence in March. Further analysis on ambient data (through subtraction of TEOM data from the Partisol data) has confirmed that significant change-points are found, albeit at differing times (April/May 2006 at Harwell and December 2005 at North Kensington). This suggests that the increase in travel blank mass is having an effect on ambient concentrations.

5 Implications for compliance with EU Directives

Within the UK, compliance with the EU Air Quality Directive for PM is based on both modelling (the Pollution Climate Mapping (PCM) model) and monitoring within the AURN.

The PCM model uses monitoring data and the UK disaggregated emission inventory along with measurements and models for other PM components, including secondary PM to map estimated ambient pollutant concentrations on a 1x1km scale throughout the UK. Up to 2003, the PCM model was based on TEOMx1.3 measurements – as these were the best available measurements of gravimetric PM at the time.

However since the results of the PM Equivalence Programme showed that TEOM measurements were not equivalent to the EU reference method (even when multiplied by 1.3) a new approach was needed. Although Partisol measurement was limited to relatively few locations, these were the only data measured by an EU Equivalent methodology in the UK and hence, the PCM maps were based on these Partisol measurements.

Therefore, it follows that if there is a bias in the Partisol data, this is reflected in the PCM model data for the whole of the UK and, if the bias is positive this may be leading to the UK reporting more exceedences of the Directive than would be the case for unbiased data.

For 2007, a body of FDMS B PM₁₀ data are also available and provisional PCM maps based on these data have been produced. Figure 5.1 and Figure 5.2 show how the PCM model and AURN data compare at background and roadside sites respectively. Agreement for the FDMS is, of course, good as the model used was scaled to this dataset. The plot shows how the Partisol data appears to be higher than the corresponding TEOM FDMS data. Much better agreement between Partisol and FDMS data is achieved if the Partisol data has a bias of 7.8 µg m⁻³ removed. The figure of 7.8 µg m⁻³ is derived from the initial study in to the present report [19]. This analysis should be reconsidered based on the findings of the present report.

Figure 5.1 Anticipated changes in PM₁₀ verification with provisional correction of measured gravimetric data for background locations and agreement with FDMS data (2007) (µg m⁻³)

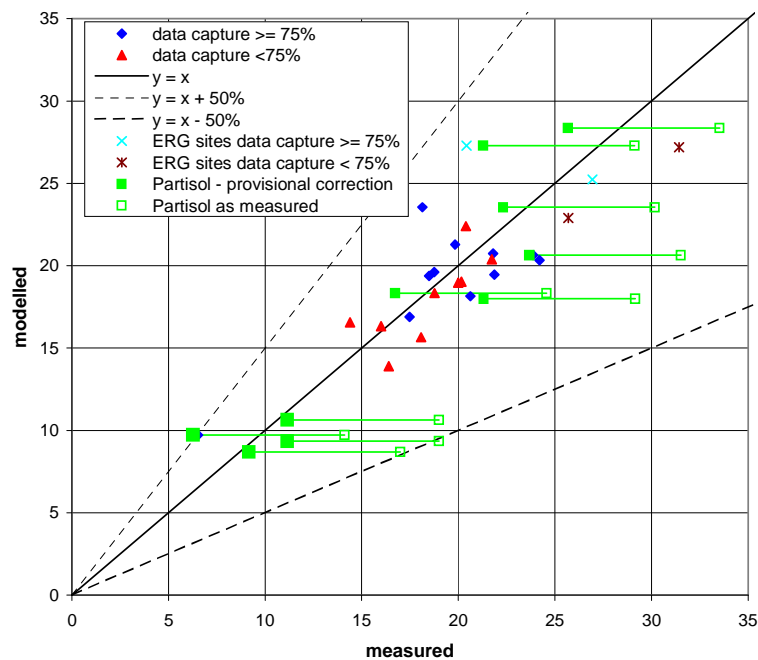
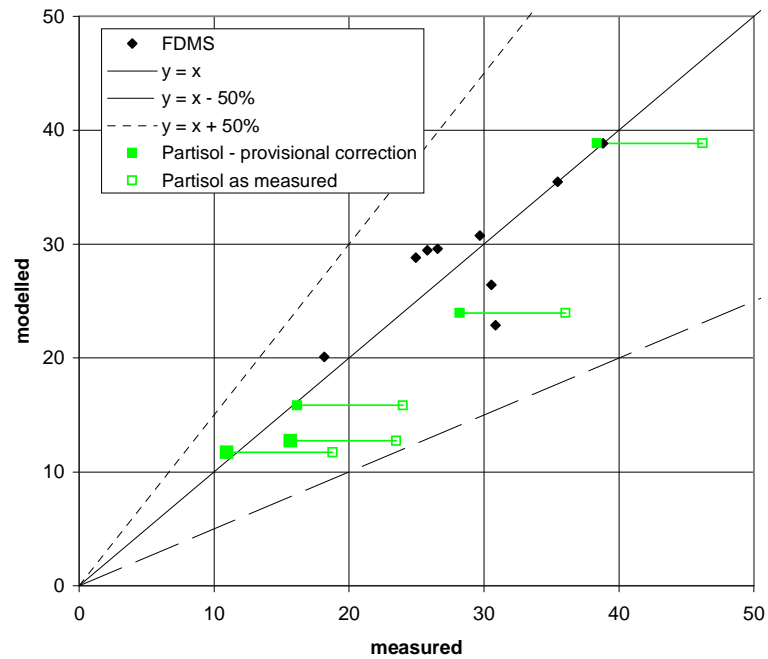


Figure 5.2 Anticipated changes in PM₁₀ verification with provisional correction of measured gravimetric data for roadside locations and agreement with FDMS data (2007) ($\mu\text{g m}^{-3}$)



This analysis indicates that there could be significant discontinuity between the 2006 and earlier maps based on Partisol data and the 2007 map based on FDMS data, unless the appropriate annual Partisol bias is removed. This is particularly important for 2005 as this is defined, by the EU, as the base year for Member States applying for a time extension for compliance with the Directive limit values for PM₁₀.

6 Future Considerations and Mitigation Plans

Section 3 discussed trends in the annual average PM_{10} and $PM_{2.5}$ concentrations for Partisols operating with Bureau Veritas Laboratories weighed Whatman QMA quartz filters. It is desired to correct these data for a more accurate interpretation of trends. Regardless of the cause of filters overestimating concentrations (whether it be a seasonal affect or laboratory bias), correction by subtracting the average blank concentration could be applied to the annual mean data. It should be noted that the blank filters were only travel blanks, and have not sampled filtered air.

As there is increased confidence in the blank concentration for a larger number of blank filters, it is proposed to correct the data by the annual average blank filter concentration equivalent for all sites (Table 4.4). These values have to be calculated using the date that the blank filter was placed in to the sampler, as it is not possible to match up historical sampled filters by the date they were pre or post weighed. Note that on Table 4.4, there are only 2 data points for the year 2000, and so confidence in the average concentration is very low. However, there are no valid annual averages for ambient data for 2000, and as such this correction factor is not in practice applied. Section 4.3.1 discussed that it is possible that the overestimation of PM on sampled filters is dependent on site location, though there is no way of identifying this, at least until the cause of the laboratory offset is identified. Section 4.1.3 discussed how there was no difference between blanks for PM_{10} and $PM_{2.5}$, and as such, both PM_{10} and $PM_{2.5}$ instruments are corrected by an identical factor.

Table 6.1 shows the valid annual average concentrations after the application of these correction factors. Figure 6.1 and Figure 6.2 show the corrected trends in PM_{10} and $PM_{2.5}$ for sites where there are more than two years worth of data (as previously shown uncorrected in Figure 3.5 and Figure 3.6). Appendix B shows each site individually; with error bars corresponding to one standard deviation of the annual mean travel blank (Table 4.4). After correction, there is increased evidence for reducing concentrations, though PM_{10} concentrations are still rising at Westminster.

Correction of data on a daily basis is not possible, as the variation in blanks is too great. It may be possible to correct on a monthly basis, however, as Air Quality Objectives relate only to daily and annual averages, this may not be required. Should monthly correction be required, then correction factors are given in Table 4.5. It may be possible to correct for only the laboratory bias contribution to concentration over estimation, and not for the seasonal affect. However, this would not be advised until the cause of the laboratory bias is identified.

Clearly, going forward, filter weighing issues need to be more tightly controlled. Bureau Veritas have already initiated the use of a blank filter with every cassette of 14 filters used at all sites. This will mean that, in future, there will be a blank value associated with every filter batch. This will provide much better data on the magnitude of the blank value and quickly highlight any seasonal change, drift or sudden change in this value. The decisions on how and whether to correct for this blank will be informed by the outcome of the discussion on the historical blank situation set out in this paper.

The issue of laboratory blanks in addition to "travel" blanks also needs to be assessed and possibly trialled to see if this provides additional useful information.

In addition, we plan to investigate a system of regular laboratory weighing inter-comparisons to monitor laboratory weighing performance. However, the detailed methodology for this will need to be carefully thought out.

The present report proposes a correction factor for Partisol 2025 data collected using Whatman QMA quartz filters weighed by Bureau Veritas Laboratories. It is important to reiterate that this report does not propose a correction factor for Partisol 2025 data collected prior to February 2003 where the filters were Teflon (as weighed by Bureau Veritas or AEA) or quartz (as weighed by AEA). Distinction in the data set in relation to the use of Teflon and quartz filters is therefore recommended in order to inform users of the end data that differences exist.

Previously, not all of the instruments discussed in this report were incorporated in to the AURN. Those that were part of a research project were not audited to the same high standards associated

with the AURN. As part of the CMCU and QAQC contract renewals beginning April 2008, all Partisols are incorporated into the AURN and the same quality standards apply.

It is proposed that regular comparison with results reported by FDMS analysers will be more easily facilitated and will become a routine quality check on both monitoring methods.

Table 6.1 Corrected annual average concentrations for all sites where there is greater than 75 % collection in a calendar year. Averages are for sites operating Bureau Veritas weighed Whatman QMA quartz filters only.

	Auchencorth 10	Auchencorth 2.5	Belfast10	Belfast 2.5	Birmingham 10	Birmingham 2.5	Bournemouth 10	Brighton 10	Dumfries 10
2000									
2001						16.69			
2002				14.85		14.76			
2003			25.84	15.18	28.81	18.22	25.17	33.97	21.28
2004				10.87	22.24	14.46	21.91	30.54	16.04
2005				13.25			23.87	33.68	18.62
2006		8.82			28.88	19.05	26.10	34.53	20.48
2007		8.13					24.64	31.52	18.98

	Glasgow 2.5	Glasgow 10	Harwell 10	Harwell 2.5	Westminster 10	Inverness 10	North Kensington 10	North Kensington 25	Manchester Piccadilly 10
2000									
2001								16.78	
2002				11.79				17.02	
2003		24.41	20.67	14.51		14.83	25.88	18.52	31.40
2004	13.40			11.62	25.17	13.53	23.19	16.05	27.49
2005	14.69			13.15	28.28	15.19		17.77	28.62
2006	15.12			14.35	27.98	16.15	28.21	18.60	28.63
2007					29.00	14.26		17.18	

	Manchester Piccadilly 2.5	Marylebone 10	Marylebone 2.5	Northampton 10	Port Talbot 10	Port Talbot 2.5	Port Talbot Margam 2.5	Wrexham 10	Bush 10
2000									
2001			24.69						
2002			24.57			12.49			
2003	14.33	43.08	27.77		29.58	16.17		24.52	
2004	16.87	40.00	25.62	19.51		14.05		18.30	
2005	16.85	42.47	26.06	23.44		16.01		20.26	
2006	17.98	44.05	27.90	24.39		16.17		20.18	
2007								19.47	14.18

	Bush 2.5	Inverness 2.5	Dumfries 2.5	Eskdalemuir 10	Eskdalemuir 2.5	Fort William 10	Fort William 2.5
2000							
2001							
2002							
2003							
2004							
2005							
2006							
2007	9.27	10.61	12.71	12.18	8.15		

Figure 6.1 Trend of corrected annual average PM₁₀ concentrations.

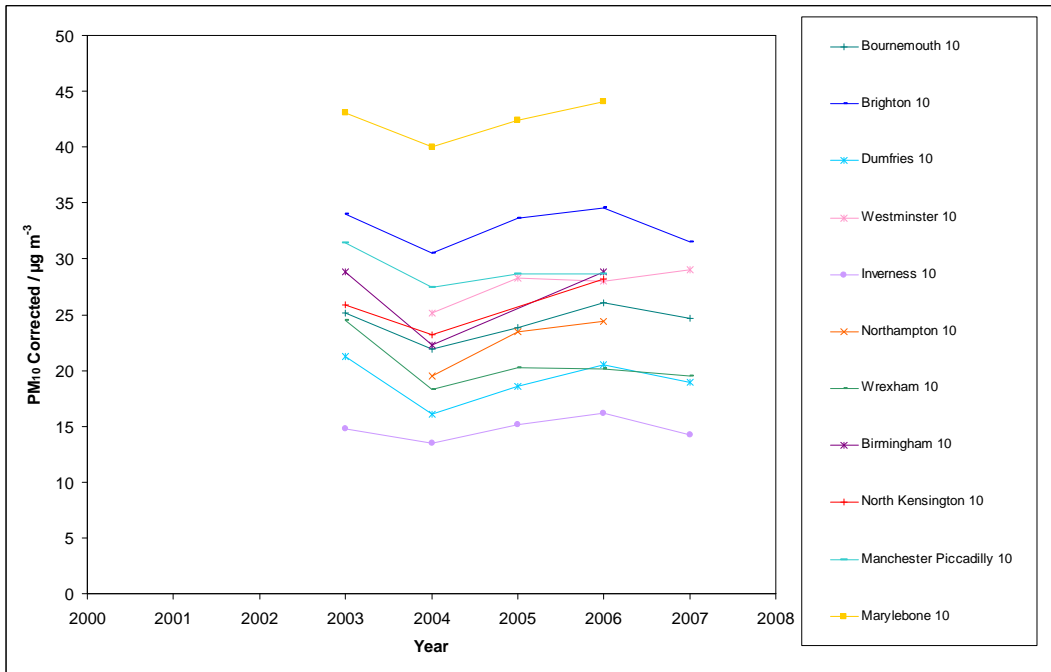
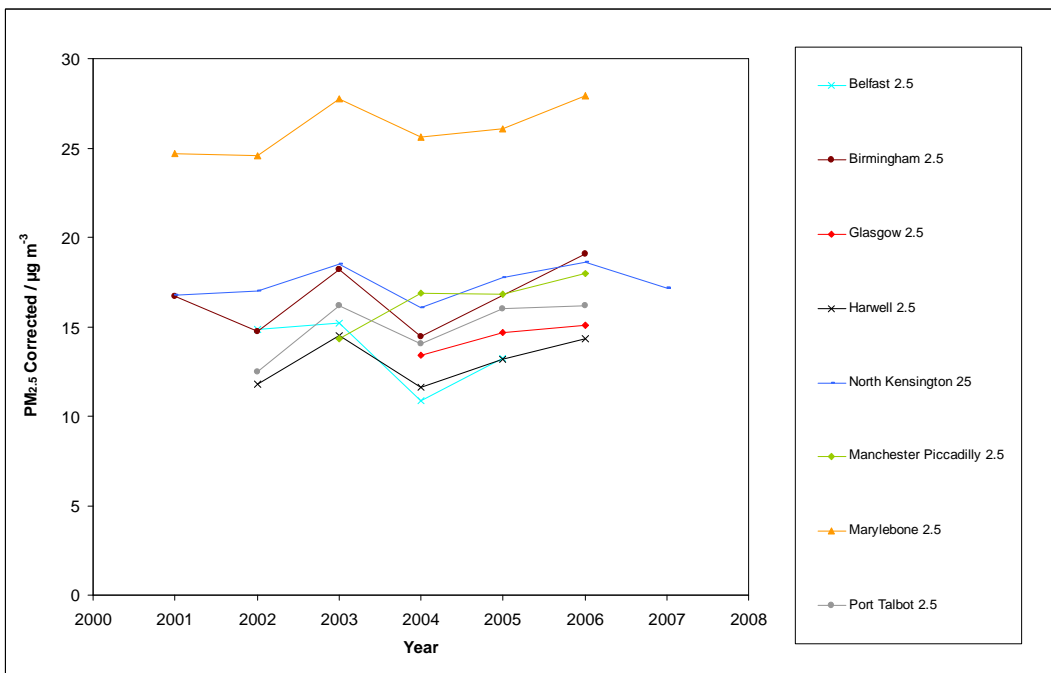


Figure 6.2 Trend of corrected annual average PM_{2.5} concentrations.



Acknowledgements

The authors are grateful to a large number of people, bodies and organisations for their cooperation during the course of this work, including the following:

Members of the Government Air Quality Expert Group for their consideration to the preliminary outcomes of the work and for their guidance on further work included here, including: Prof. Roy Harrison, Dr Paul Quincey, Dr Mathew Heal, Prof. Duncan Laxen, and Dr Dick Derwent.

Special thanks to Dr Tim Murrells, from AEA for his contribution to trends in emissions. To David Djonge of the Municipal Health Service, Amsterdam, The Netherlands, for his provision of data and to Tony Clark and David Butterfield for their comments and suggestions throughout the formulation of this analysis.

Thanks to Gary Fuller and David Green for their comments and provision of Emfab filter data.

Additional thanks go to the following local authorities for the provision of additional data on field blanks through gravimetric measurements made via locally operated networks: Derby City Council; BAA; North Lincolnshire Council; and Liverpool City Council.

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Glossary

AEA	Atomic Energy authority
AQEG	Air Quality Expert Group
AQUILA	Air QUality Laboratories
AURN	Automated Urban and Rural Network
BAM	Beta Attenuation Monitor
CEN	European Committee for Normalization
CERC	Cambridge Environmental Research Consultants
CMCU	Central Management and Co-ordination Unit of the AURN
CRE	Previous trading name for the Bureau Veritas filter weighing facility
Defra	Department for the Environment, Food and Rural Affairs
EMC	Previous trading name for the Bureau Veritas filter weighing facility
EMEP	European Monitoring and Evaluation Programme
ERLAP	European Reference Laboratory of Air Pollution
EU	European Union
FDMS	Filter Dynamics Measurement System
HGV	Heavy Goods Vehicle
ISO	International Organization for Standardization
ITS	Institute of Transport Studies
JRC	Joint Research Centre
KFG	Klein Filtergerät
LAQN	London Air Quality Network
LGV	Light Goods Vehicle
NAEI	National Atmospheric Emissions Inventory
NIST	National Institute of Standards and Technology
NPL	National Physical Laboratory
PC	Personal Computer
PCM	Pollution Climate Mapping
PM	Particulate Matter
PM ₁₀	Concentration of particles less than 10 microns in diameter
PM _{2.5}	Concentration of particles less than 2.5 microns in diameter
PNS-X8	The European PM ₁₀ reference method
QA	Quality Assurance
QC	Quality Control
QMA	Quartz filter material manufactured by Whatman
RH	Relative Humidity
RP	Rupprecht & Patashnick
STL	a Seasonal Trend decomposition procedure based on Loess
SVOC	Semi Volatile Organic Compound
TEOM	Tapered Element Oscillating Microbalance
TRL	Transport Research Laboratory
UK	United Kingdom
UKAS	United Kingdom Accreditation service
USA	United states of America
USB	Universal Serial Bus
VOC	Volatile Organic Compound

Appendix A - Policy Context

The Air Quality Framework Directive (96/62/EC) and its four daughter directives (1999/30/EC, 2000/69/EC, 2002/3/EC, and 2004/107/EC) set concentration limit values or target values for a range of air pollutants such as sulphur dioxide; nitrogen oxides; particulate matter (PM₁₀); carbon monoxide; ozone; benzene; lead; and polycyclic aromatic hydrocarbons. These laws require the monitoring of a number of air pollutants. If monitoring shows that the target values are exceeded, Member States are obliged to set up, implement and report on abatement plans. The set of laws has been developed over time in response to emerging scientific knowledge. Some of the limit values have already entered into force – such as those on particulate matter – while others will only come into effect in 2010 (e.g. nitrogen dioxide).

The Directives require that Member States report to the Commission each year whether or not the limit values set in the Directive have been achieved. Council Decision 97/101/EC introduces a Community-wide procedure for the exchange of information and data on ambient air quality, whilst the Public Participation Directive (2003/35/EC) sets the legislative framework to ensure that the public is given early and effective opportunity to participate in the preparation and modification or review of the plans or programmes drawn up under the Air Quality Framework Directive and the daughter directives.

Whilst overall air quality trends in the European Community are encouraging, continued efforts and vigilance are still required. To this end, air pollution remains the focus of attention under a new Thematic Strategy – a new generation of environmental policy with focus on the medium term requirements for environmental improvement up to 2020. The policy areas work around themes rather than specific pollutants under the Thematic Strategy approach and, to this end, the Thematic Strategy on Air Pollution was adopted by the Commission in September 2005, jointly with a proposal for a new Ambient Air Quality Directive.

The need for a new directive arose as a consequence of Thematic Strategy on Air Pollution identifying the requirement to set new objectives for fine particles (PM_{2.5}). Additionally, experience with implementation of existing regulations – such as those around PM₁₀ and NO₂ – has shown that there is a need for increased flexibility around achieving environmental standards. Consequently, the existing statutes have been merged into a single legal text and the reporting requirements have been modernised in line with the Commission's initiatives on better regulation.

Existing limit values set down in previously individual directives remain unchanged in the new consolidated directive. For PM₁₀, these include the following:

- Annual mean limit value of 40 µg/m³ to be achieved by 31 December 2004;
- Daily mean limit value of 50 µg/m³ (not to be exceeded more than 35 days in a year) to be achieved by 31 December 2004.

In the case of the existing adopted limit values for PM₁₀, the primary focus on compliance relates to assessment of the UK in 2005, which is discussed in Section 5.

The key elements of the new directive are:

- the introduction of a limit value of 25µg/m³ to be met everywhere by 2015 (with a target date of 2010), with a second stage 'indicative' limit value of 20 µg/m³ to be met by 2020.
- The driver for reductions in PM_{2.5} is intended to be the Exposure Reduction target for urban background areas to be achieved by 2020. The percentage reduction required is expected to depend upon the baseline concentration established by Member States at urban background locations (expressed as an average). For the UK it is currently expected to be 15% based on current figures.
- an Exposure Concentration obligation of 20µg/m³ to be met as an average across urban background by 2015.

- compliance flexibilities for PM₁₀ (3 years from coming into force, i.e. to 2011) and NO₂ (5 years from coming into force, i.e. 2015) subject to Member States putting forward detailed plans set out on how the limit values will be achieved with the extended time frames.
- clarification that only man-made sources of pollution can be addressed, through allowing reductions for natural sources
- compliance with the limit values will not need to be assessed where the public does not have access and there is no fixed habitation, or on a carriageway and central reservation;

On the 14th April the European Commission welcomed the final adoption of the new Ambient Air Quality directive. The directive will be published in the EU's official journal in May 2008.

The monitoring of PM metric is therefore an essential element of establishing compliance against the existing and forthcoming legislation on pollutant levels. Specifically, this report provides for a clearer understanding of the key challenges facing Member States in relation to the measurement of particulate matter (PM), which varies considerably across Europe and the difficulties in adherence to harmonized methods.

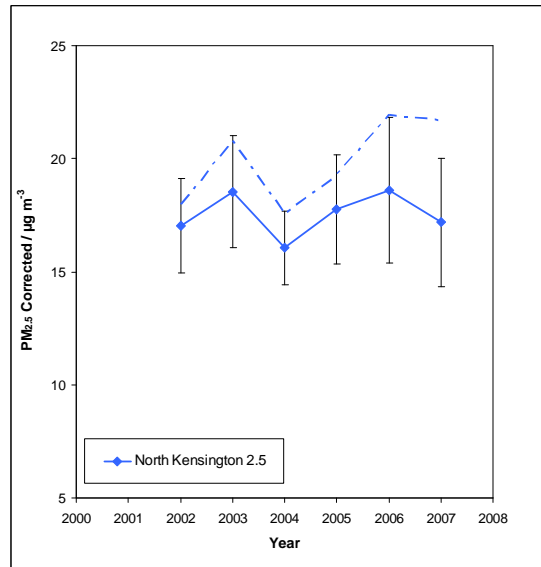
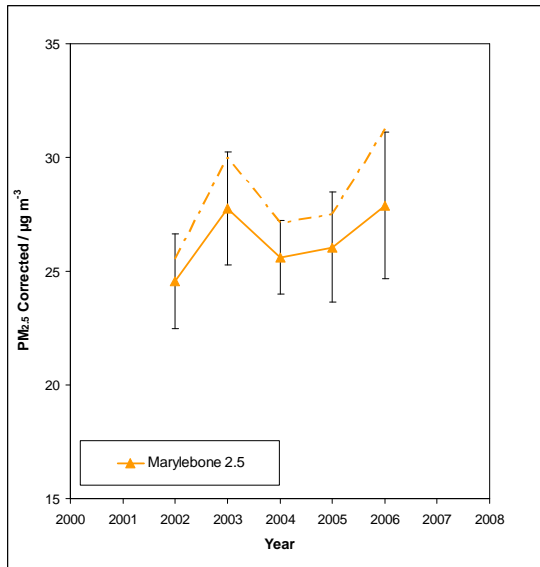
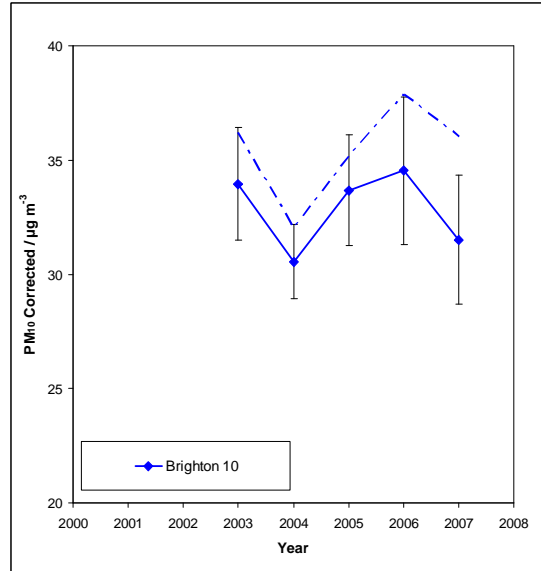
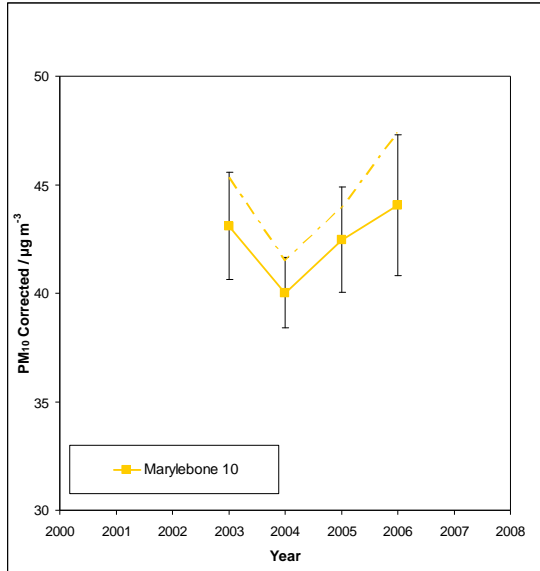
Elsewhere in Europe the following instruments are anticipated to bring about significant improvements in ambient air quality in future years:

- the Auto-Oil Programme which sets tightening emissions standards for vehicles in future years and the banning of leaded petrol from 1 Jan 2000;
- the Acidification Strategy which aims to reduce emissions of SO₂, NO_x and ammonia in order to reduce the risk to ecosystems;
- the Sulphur Content of Certain Liquid Fuels Directive, which sets a maximum value of sulphur content of heavy fuel oil and for gas;
- the EC Large Combustion Plant Directive, which sets emissions limit values from new large combustion plants, taking in to account technological advances in future years;
- the National Emissions Ceiling Directive which sets ceilings for national emissions of a number of pollutants to be attained by 2010;
- the Solvents Directive aims to reduce emissions of volatile organic compounds, which are involved as a precursor to the formation of tropospheric ozone;
- the Integrated Pollution Prevention and Control Directive which requires specific permits for industrial sites and limit their emissions to air, and;
- We understand that a Commission statement, to be published at the same time as the new Directive, sets out Commission proposals that are expected to be published in 2008.

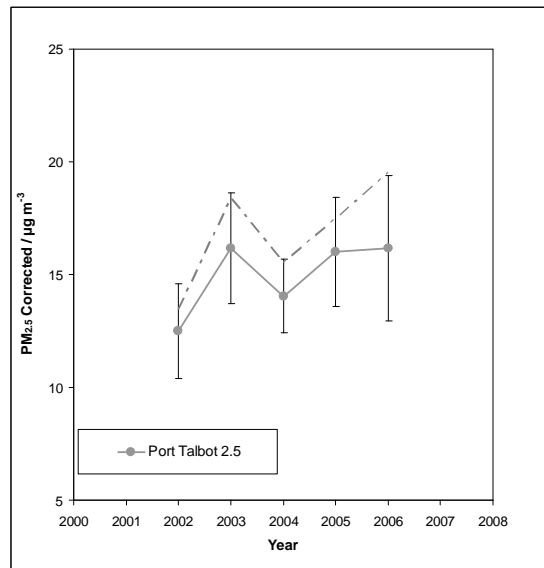
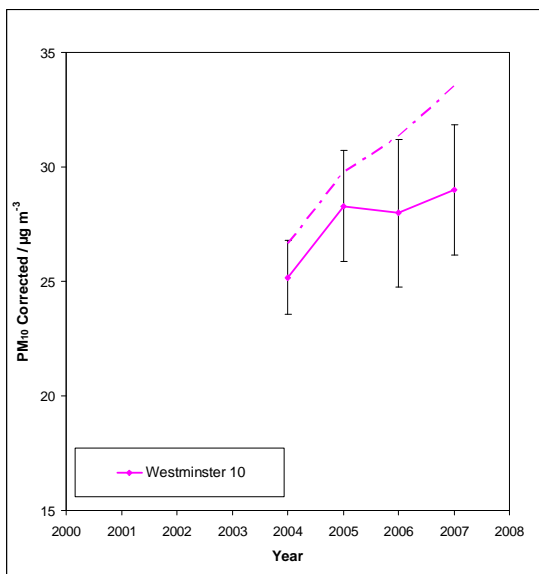
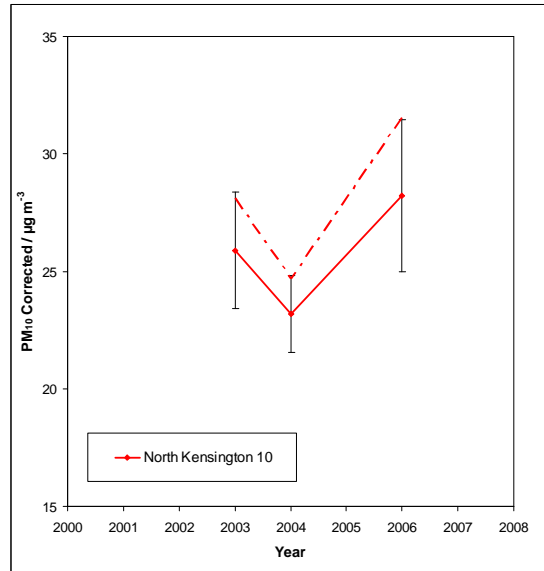
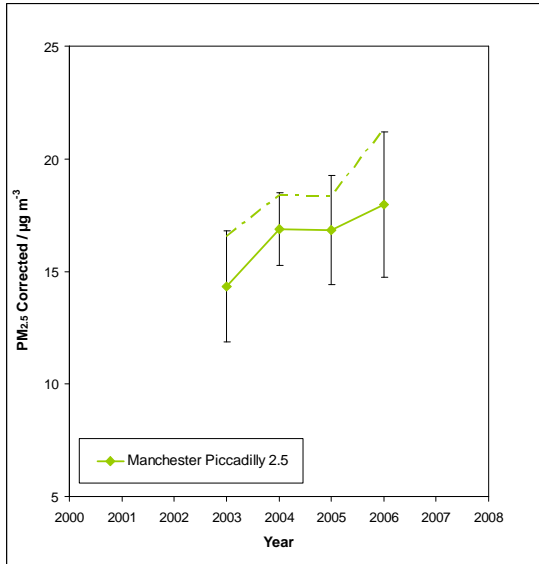
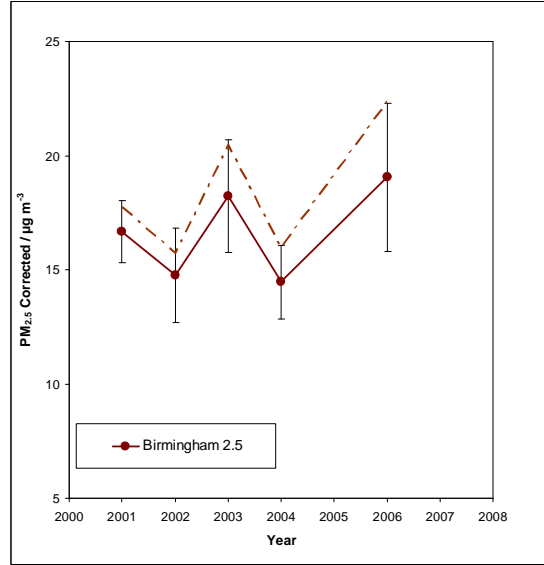
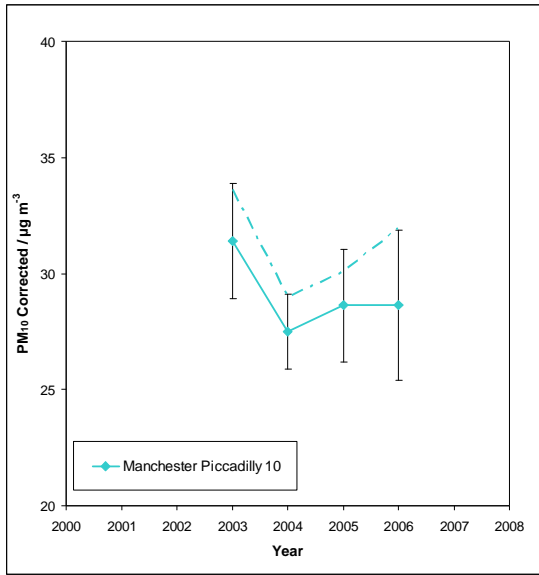
Analysis of long-term trends in monitored data provides for a means of understanding whether overall environmental policy improvements such as those listed above, are working, whilst additionally providing a means by which additional policy formulation may be required.

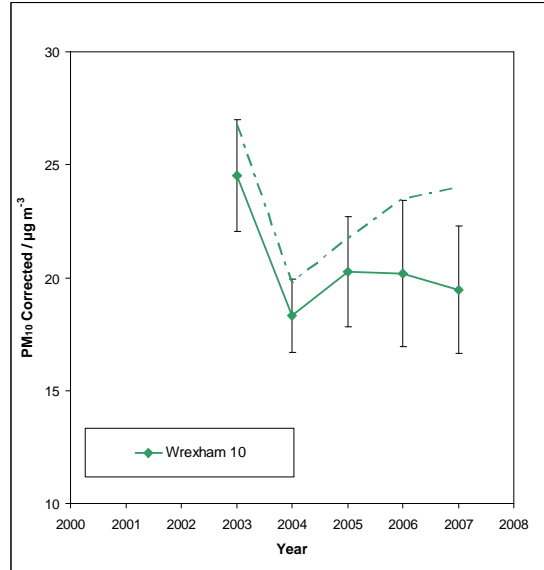
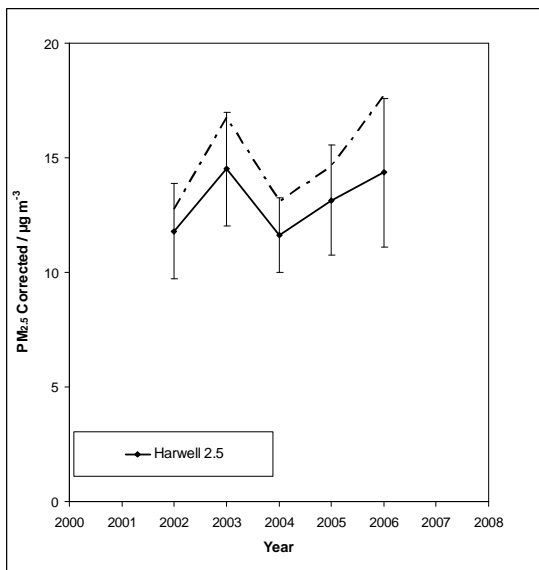
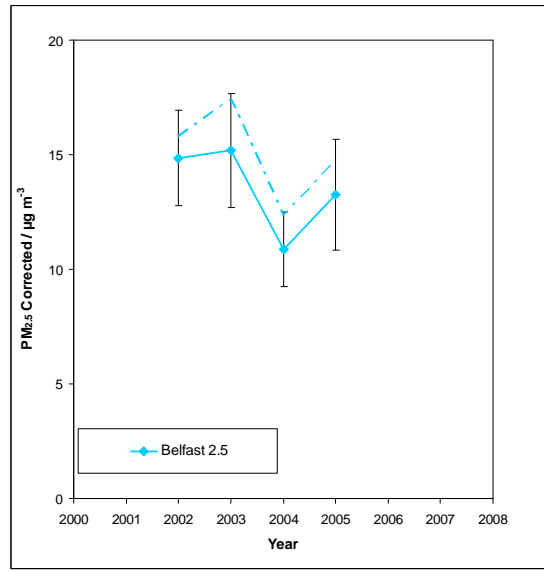
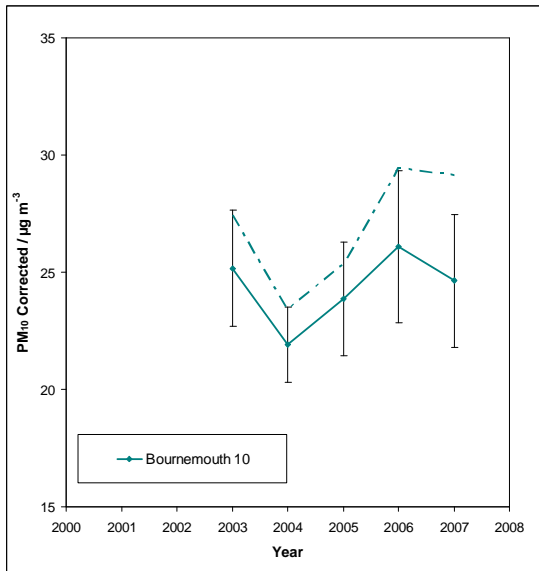
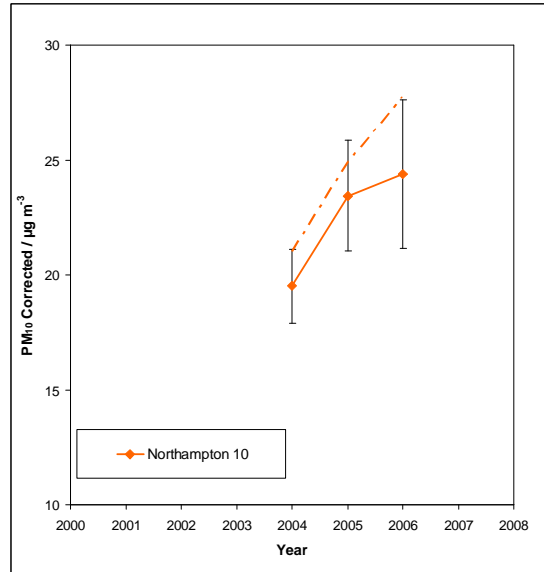
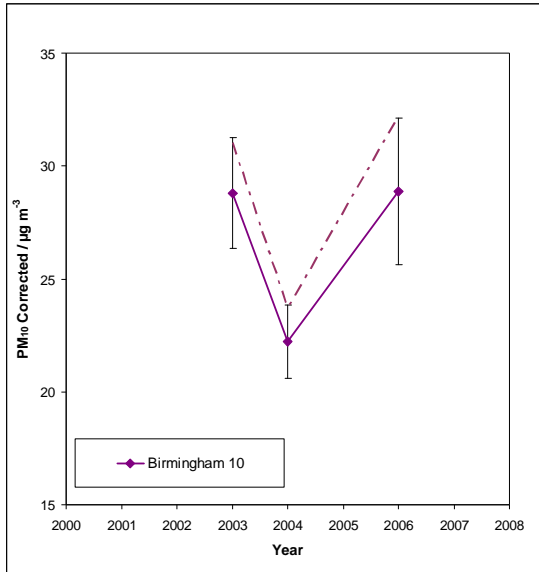
Appendix B - Graphs of Annual Trends in PM

The following graphs show uncorrected trends in PM (dashed line) and corrected trends in PM (solid line) with error bars corresponding to one standard deviation of the annual average travel blank. The y axis of all the graphs is standardised to cover $20 \mu\text{g m}^{-3}$.



Analysis of Trends in Gravimetric Particulate Mass Measurements in the UK







Analysis of Trends in Gravimetric Particulate Mass Measurements in the UK

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