NPL

National Physical Laboratory

Report

**NPL REPORT**

**DQL-AS 020**

# CPEA 28: Airborne Particulate Concentrations and Numbers in the United Kingdom (Phase 2)

## Strategic Network Review

**Prof. Dick Derwent, rdscientific,**
**Prof Roy Harrison, Birmingham University,**
**Peter Woods, National Physical Laboratory,**
**Paul Quincey, National Physical Laboratory,**
**Melanie Williams, National Physical Laboratory.**

**NOT RESTRICTED**

**NOVEMBER 2005**

# CPEA 28: AIRBORNE PARTICULATE CONCENTRATIONS AND NUMBERS IN THE UNITED KINGDOM (PHASE 2)

## STRATEGIC NETWORK REVIEW

**Prof. Dick Derwent, rdscientific**
**Prof. Roy Harrison, Birmingham University**
**Peter Woods, National Physical Laboratory**
**Paul Quincey, National Physical Laboratory**
**Melanie Williams, National Physical Laboratory**

ISSN 1744-0602

National Physical Laboratory
Teddington, Middlesex TW11 0LW



Approved on behalf of Managing Director, NPL, by Dr S. Windsor,
authorised by the Director, Quality of Life Division.

**Contents**

# 1 Summary

This strategic review of the equipment in the Network, has been undertaken by Prof Dick Derwent, Prof Roy Harrison and the National Physical Laboratory, the manager of the Network. This review proposes both the optimum configuration for existing instruments, to ensure that the Network addresses current research priorities, and prioritised developments to the Network. The monitoring recommendations from the Report of the UK Air Quality Expert Group (AQEG) 'Particulate Monitoring in the United Kingdom' 2005, have been taken into account.

The strategic review starts from the position that the Network has two distinct aims. The first is to provide information on the chemical composition of particulate matter, ideally at the hourly level of time resolution, on a continuous basis. The need for this information was highlighted in the AQEG report, to allow the relevant chemical processes to be modelled more reliably. Ultimately the aim is mass closure, accounting for the total mass, measured as $PM_{10}$ or $PM_{2.5}$, in terms of the masses of its chemical components. However, the more immediate aim is to provide selected speciation of particulate matter at strategically important sites within the Network.

This entails continuous measurements of the sulphate, nitrate, organic carbon and elemental carbon concentrations in particulate matter. Priority is given to the London conurbation. A proposed new site at Rochester will characterize the particulate loadings in air masses entering the London conurbation from continental Europe. Further recommendations cover paired urban background and rural sites in Northern Ireland, Scotland and Wales, to characterise particulate matter in the different environments across the United Kingdom. These Network developments will also facilitate characterisation of long-range transport of particulate matter into the United Kingdom from the Atlantic Ocean through the recirculation of European pollution.

The second aim is to extend reliable datasets of airborne particle number and size at selected sites. Long time series measurements of particle number are important for epidemiological studies, while size distributions provide important additional information on the processes involved in particle formation and evolution. In this context, it is recommended that obsolete particle sizing equipment should be replaced to permit monitoring of the effects of any future curbs on diesel particulate emissions.

Further recommendations cover the evaluation of available equipment to inform future purchase, and measurements of sodium, calcium, ammonium and iron concentrations at selected sites to provide additional information on chemical composition.

Potential cost savings from the closure of certain sites are identified, although data from certain of these sites have been, or may be, used for other local purposes, eg epidemiological studies, and these should be considered before a decision to remove them is taken.

Indicative costs for developing the network are supplied separately.

# 2 Policy Context

## 2.1 National Air Quality Strategy

At a national level, the policy to control the concentrations of certain pollutants (including $PM_{10}$ particulates in ambient air) is set out in 'The United Kingdom Air Quality Strategy, CM3587, 1997 and 'The Air Quality Strategy for England, Scotland, Wales and Northern Ireland CM4548, 2000'. These two closely related documents arose from the Environment Act of 1995, which required UK Government to produce a national air quality strategy containing specific standards relating to the quality of ambient air, to define objectives for restricting the levels of particular substances in air, to develop measures to achieve these, and to establish a system for local air quality management. This UK Strategy was supplemented by new targets for $PM_{10}$ for England and London in 2002 (see www.defra.gov.uk/new/2002) and an Addendum prepared by Defra and the devolved administrations in 2003, which includes revised objectives for particulates ($PM_{10}$). The Air Quality Strategy, and its Addendum, established the framework for achieving improved ambient air quality, from 2003 and beyond, by:

- setting health-based standards for eight main air pollutants with dates for their achievement in the short-to-medium timescale;
- providing objectives for the protection of vegetation and ecosystems;
- identifying actions to be carried out at local, national and international levels to achieve these.

These standards are based on recommendations made by the Government's Expert Panel on Air Quality Standards (EPAQS). It is useful here to distinguish between 'standards' and 'objectives' as used in the Air Quality Strategy. Standards are intended to be the concentrations of the pollutants that enable an acceptable level of air quality to be achieved, based on assessments of the effects of each pollutant on human health, including the effects on sensitive sub-groups of the population. Objectives are policy targets, expressed as the maximum concentration of the pollutant to be achieved, either without exception, or with an allowed number of exceedences within a specified timescale. A summary of the current Air Quality Strategy Objectives, which generally match the requirements of the EU first Daughter Directive (99/30/EC), are given in Table 1 overleaf.

Table 1: EU limit values and Air Quality Strategy (AQS) objectives for $PM_{10}$.

| Legislation | 24-hourly values | Annual values ($\mu g\ m^{-3}$) | Achieve by |
|---|---|---|---|
| EU First Daughter Directive (99/30/EC) Stage I limit value | 50 $\mu g\ m^{-3}$ with up to 35 exceedences per year | 40 | 1 January 2005 |
| EU First Daughter Directive (99/30/EC) Stage II indicative limit value | 50 $\mu g\ m^{-3}$ with up to 7 exceedences per year | 20 | 1 January 2010 |
| AQS (2000) statutory objectives | 50 $\mu g\ m^{-3}$ with up to 35 exceedences per year | 40 | 31 December 2004 |
| AQS Addendum (2003) – all parts of UK except London and Scotland provisional objectives | 50 $\mu g\ m^{-3}$ with up to 7 exceedences per year | 20 | 31 December 2010 |
| AQS Addendum (2003) – Scotland provisional objectives | 50 $\mu g\ m^{-3}$ with up to 7 exceedences per year | 18 | 31 December 2010 |
| AQS Addendum (2003) – London provisional objectives | 50 $\mu g\ m^{-3}$ with up to 10 exceedences per year | 23 | 31 December 2010 |

There are no UK strategy objectives or standards for fine or ultra-fine particles, or for the specific chemical species within them that are covered by this Network.

The aims of this Network are to carry out an effective research programme and provide valid data to improve our scientific knowledge of the sources, chemical transformation, transport etc of airborne particulate matter (PM). This will improve understanding of the complex, multidimensional issue of the impacts of particulate matter in the atmosphere on human health and the environment, to guide *future* regulatory initiatives.

## 2.2 Local Air Quality Management

One of the more important measures set out in the UK Air Quality Strategy to achieve its objectives is through the implementation of a system for local air quality management (LAQM). This requires local authorities in the UK to periodically review and assess current and future air quality in their areas. A local authority (LA) must designate an air quality management area (AQMA) if any of the objectives set out in regulations are not likely to be met for the relevant period. LAs carry out this review and assessment in three stages. Work on this commenced December 1997 and is still ongoing. The high-quality data produced by Defra's national Networks, including the data obtained for $PM_{10}$ particulate matter that form part of this Network, are essential in underpinning these assessments and are also important in identifying, where required, AQMAs.

It is also worth noting that the devolved administrations of Scotland and Wales took over most of the policy and legislative work affecting their countries, including air quality, in 1999. However, these devolved administrations (DAs) recognise the trans-boundary nature of many of the air pollutants and it was therefore decided to continue with a joint

UK Air Quality Strategy with common objectives. Scotland, Wales and Northern Ireland will continue to contribute to UK policy on air quality issues to the EU and other international negotiations, and they will also be responsible for implementing EU and other international commitments (e.g. EU Directives) in their respective countries. In addition, the Greater London Act also gives the Mayor of London duties relating to air quality, which need to be operated coherently with the National Air Quality Strategy.

### 2.3 UK Scientific Advisory Groups

Government is guided in its policy by several groups of independent experts from the UK. For example, the standards and objectives for each pollutant were based on the recommendations of Defra's Expert Panel on Air Quality Standards (EPAQS), who assess the available evidence on the effects of exposure, as mentioned above. A further evaluation of health effects is provided by the UK Department of Health's Committee on the Medical Effects of Air Pollutants (COMEAP), which for example produced a report 'Quantification of the Effects of Air Pollution on Health in the UK, COMEAP, 1998'.

COMEAP estimated, for example, that in 1996 in the UK, $PM_{10}$ pollution was associated with around 8,000 deaths brought forward, and 10,000 hospital admissions for short term exposures, and that over the lifetime of the current population of England and Wales a reduction of 1 $\mu g\ m^{-3}$ of $PM_{2.5}$ would lead to a gain of about 0.3 million life years.

EPAQS produced a report on Particles in 1995, with a second report entitled 'Airborne Particles - What is the appropriate measurement on which to base a standard?' in 2001. The UK's standards for each pollutant are closely linked to health-effect research evaluated by the World Health Organisation (WHO). The WHO produces periodic scientifically-independent reviews of the health aspects of air quality in Europe (see below), which are used as inputs into UK standards.

Guidance on atmospheric chemistry and practical aspects of air quality monitoring and control has in the past been provided to Defra by several specialist groups such as the Photochemical Oxidants Review Group (PORG) and the Airborne Particles Expert Group (APEG). Currently, Defra has established the Air Quality Expert Group (AQEG) as a high-level overarching Expert Group, which has already produced reports on Nitrogen Dioxide, and Particulate Matter. The latter represents a comprehensive review of most aspects of the scientific, technical and policy issues that are relevant to this Network. AQEG's recommendations and conclusions most relevant to this Network have been summarised below. The AQEG PM Report goes into detail on certain specific research activities and interpretational requirements for this Network, and these include:

- Contributions to urban PM levels from the regional scale;
- Better characterisation of long-range transport;
- Correlations between PM nitrate and sulphate;
- Future PM sulphate trends;
- Representation of sulphate in the Defra source receptor model;
- Development of improved mass closure modelling.
- Improved source apportionment to inform policy

In addition, the AQEG Report makes some detailed and specific recommendations on monitoring and siting of the instrumentation in this Network, and these are summarized below:

Table 2 Summary of AQEG Monitoring Recommendations

| Measurement | Recommendation |
|---|---|
| Continuous $PM_{2.5}$ nitrate | Expand existing network to provide paired urban background/rural data at 4 locations, throughout the UK including London |
| Continuous $PM_{coarse}$ nitrate | Expand existing network to include measurements at the 4 urban background/rural locations identified above |
| Continuous EC/OC | Expand existing network to provide paired roadside /urban background data at 4 locations throughout the UK including London |
| Continuous $PM_{2.5}$ sulphate | Expand existing network to provide paired urban background/rural data at 4 locations, throughout the UK including London |
| Daily iron ($PM_{10}$) | Expand existing Network to include all Defra Site- Specific Receptor Model sites |

Wider input to policy making is provided by Defra's Air Quality Forum, which brings together numerous stakeholders such as industry, conservation organisations, and other government departments. The Environment Agency, industrial stakeholders, and others with an interest in Local Authority Pollution Control, also meet at the Air Quality Forum. In forming their conclusions, all of the above Groups rely on data from Defra Networks being demonstrably valid.

## 3 Aims of the Review

This Network is unusual in providing information primarily for research rather than regulatory purposes. Regulatory monitoring of Particulate Matter is carried out within the Automated Urban and Rural Networks. The deployment of equipment within this Network has evolved since the first instruments were operated in 1998 and needs to be regularly reviewed to optimise the benefits to current research and policy priorities.

It is important to note that the Network has two distinct purposes. Firstly, to provide chemical composition data that is directly helpful to understanding present and future concentrations of $PM_{10}$ and $PM_{2.5}$, the mass-based current and likely future parameters for ambient particulate legislation; and secondly, to provide information about particle numbers and sizes, which are of great interest in the areas of health effects and atmospheric science, including climate change, and which may be regulated in the more distant future.

The history can be summarised as:

| | |
|---|---|
| From 1998 | 3 scanning mobility particle sizing instruments (SMPS): particle number concentration by size in the range ~ 11 to 450 nm |
| From 1999 | 7 condensation particle counters (CPC): total particle number concentration in the size range ~7 to 1000 nm |
| From 2001 | 3 hourly $PM_{2.5}$ nitrate analysers<br>4 hourly $PM_{10}$ organic and elemental carbon analysers<br>4 daily Partisol $PM_{10}$ samplers for sulphate analysis |

A Strategic Network review of the equipment and its deployment was a key part of NPL's successful bid to operate this Network. This review aims to propose:

- the optimum configuration for existing instruments (including those purchased but not deployed), to ensure that the Network addresses current research priorities, as far as possible; and

- prioritised developments to the Network that would provide additional data, bearing in mind both research priorities and the fact that the SMPS instruments are at the end of their useful lives.

Indicative costs are supplied separately.

# 4 Background to the Review

In response to the December 1991 air pollution episode and the requirement to inform the public on air quality issues, the then Department of the Environment established an urban monitoring Network based on continuously recording instruments. The continuous monitoring of $PM_{10}$ began using TEOMs during 1992, with the result that the UK has now the longest records of urban $PM_{10}$ monitoring of any EU Member State. Over the periods of these records, $PM_{10}$ trends have been largely downwards up to the year 2000, followed by a period with no trend or a slightly increasing trend.

In reviewing these trends, Defra's Air Quality Expert Group AQEG) was unable to offer a satisfactory explanation for the observed behaviour and as a consequence, had limited confidence in the projections of future exceedences of $PM_{10}$ limit and target values. For example, the Stage 1 Limit Value of the EU First Daughter Directive (99/30/EC) for $PM_{10}$ has been exceeded at the Marylebone Road site in London during 2005. These difficulties arise because of the complex nature of $PM_{10}$ and because of the many sources that contribute to each daily exceedence.

The inherent problem is that there are many components making up $PM_{10}$ and $PM_{2.5}$, all with their own geographical distributions and future trends. AQEG proposed that the current $PM_{10}$ and $PM_{2.5}$ monitoring should be supplemented with some continuous particulate composition monitoring. The focus was given in the AQEG recommendations to achieving mass closure and an emphasis was given to the co-location of continuously recording instruments. Without mass closure for $PM_{10}$ and $PM_{2.5}$, AQEG felt that the scientific underpinning of air quality policy for airborne particulate matter would continue to be weak. However, the ultimate aim of complete mass closure brings in the problem that $PM_{10}$ and $PM_{2.5}$ are themselves poorly defined through standard manual gravimetric measurement methods. In the short term context of this Network, therefore, it is best to concentrate on a set of key components.

## 4.1 Chemical composition of $PM_{10}$ and $PM_{2.5}$

One of the immediate difficulties associated with any monitoring of suspended particulate matter is that particulate matter is not a single, well-defined chemical substance such as ozone or nitrogen dioxide. Particulate matter is a complex mixture of substances, which is characterized by its physical properties. Particulate matter in air is defined solely by its method of measurement (QUARG 1993; EPAQS 2001).

Previous studies of particulate matter in the United Kingdom (QUARG 1996; APEG 1999) have identified a number of important components that contribute to the mass concentrations of both $PM_{10}$ and $PM_{2.5}$. Separate measurements can, in principle, be made of each of these components. Mass closure is said to be achieved when, within experimental error, the sum of the mass concentrations of all identified components adds up to the total mass concentrations of $PM_{10}$ and $PM_{2.5}$.

Achieving mass closure is important for scientific underpinning and for policy purposes because it signifies that all the major PM components have been identified and quantified. Projections into the future may then be more robust as the opportunity for surprises is dramatically reduced.

Mass closure studies for the United Kingdom have been carried out as research activities and have been described in some detail by APEG (1999). A major study in and around Leeds addressed the annual average situation during the period from March 1995 to March 1996 (Clarke et al. 1996). Mass closure has been attempted during the TRAMAQ study at a range of roadside and background sites (Harrison et al. 2003). However, mass closure studies have not been attempted for the locations employed in the Site Specific Receptor Model of $PM_{10}$ concentrations (Stedman et al. 2001) used by DEFRA for the purposes of air quality assessment. Hence, there is no independent means of verifying the interpolations, extrapolations and assumptions inherent in the current receptor modelling, which is used to estimate future exceedences of air quality targets.

Whilst further annual mass closure studies would be valuable for UK air quality policy development, AQEG identified the importance of achieving mass closure at a significantly higher temporal resolution down to the hourly level. In this way, detailed attribution would be provided for all episodes of poor PM air quality, for episodes of long-range transport and episodes associated with particular air pollution sources, such as traffic, open burning, construction and natural sources such as Saharan dust outbreaks and the photochemical oxidation of biogenic VOCs.

In this report, a case is made for more continuous monitoring of particulate composition based on the deployment of established monitoring equipment for particulate sulphate, nitrate, elemental carbon and organic carbon. Together, these instruments monitor a substantial fraction of the mass concentration of $PM_{10}$ and $PM_{2.5}$ as identified by APEG (1996; 1999). The difference between the total loadings from the components and the total mass concentrations is anticipated to come from crustal material, wind-blown dusts, Saharan dust, construction activities, vehicle re-suspension and agricultural activities. The composition of these components of particulate matter are not properly understood and the main method of characterization is slow. However quantification of certain key components, namely iron, sodium, calcium and ammonium, even on a daily basis, would provide very valuable additional information. It would be an important step forward to have some continuous monitoring of this residual component to replace the assumptions employed in current receptor modelling studies.

### 4.2 Particle Counting and Sizing

$PM_{10}$ or $PM_{2.5}$ is a mass measurement of particles below a certain size. The contribution of particles less than 100nm in size to the total airborne particulate mass is very small, but they are dominant in terms of number density in the atmosphere. They are believed to have potential adverse health effects because of their high surface area and their ability to penetrate biological material. It is for this reason that the numbers of particles within different size ranges is a very important metric for epidemiological studies.

To quote from the WHO Working Group report "Health Aspects of Air Pollution with Particulate Matter, Ozone and Nitrogen Dioxide" in 2003:

"The number of ultra-fine (< 100 nm) particles in air has been subject to research in recent years, following suggestions that such particles may in particular be involved in the cardiovascular effects often seen to be associated with PM… More research is needed to establish the possible links between ultra-fine PM sources, exposures and health more accurately and precisely."

Diesel engines are one of the major sources of particles measured at roadside locations and it is probable that EU emission standards for vehicles (e.g. EURO V) will be based on particle number concentrations, in addition to, or instead of, mass measurements. Particle counting and sizing will therefore be needed into the future, at roadside locations, to provide a benchmark against which to evaluate the effectiveness of future vehicle standards. The measurements at Marylebone Road will also be needed to evaluate fully any additional measures put into place in London, as a response to actual and expected particulate exceedences.

### 4.3 Current Network Equipment

The deployment of the existing equipment is shown in Appendices 1 and 2. Spare equipment, bought but not deployed is also listed. The equipment has been purchased and deployed in stages since 1998. The first instruments to be deployed were the particle sizing instruments (SMPSs) which measure numbers of particles in size ranges from ~11nm to ~450nm. The particle counting equipment (CPCs) was deployed the following year. They measure total number of particles in the size range ~7nm to ~1000nm.

The three SMPSs have now reached the end of their useful life, and they will not be supported by the manufacturer after the end of 2005. Any new equipment should be chosen to provide data that is demonstrably consistent with the previous data. The seven CPCs are mainly located in urban background sites, apart from Port Talbot and recently Marylebone Road, but there is no similar instrument at a rural site. Although SMPSs and CPCs both measure particle number, the different size ranges measured means that the results from the two instruments are not directly comparable.

The hourly carbon instruments at Harwell, Kensington and Marylebone Road provide the rural, urban background, kerbside set to calculate urban and kerbside increments for organic and elemental carbon in the $PM_{10}$ fraction in South East England. The carbon instrument in Belfast has no rural comparison. Data capture rates over the past two years have been disappointing. Measures have been put in place to improve data capture rates but these instruments need to be thoroughly evaluated to provide a sound basis for data interpretation.

The hourly nitrate instruments at Marylebone Road, Harwell and Belfast measure nitrate concentrations in the $PM_{2.5}$ fraction. They have demonstrated better data capture rates but there is no instrument at an urban background site in London to allow the rural/urban background/kerbside comparison. The instrument in Belfast again has no rural comparison. These instruments also need to be fully evaluated to clarify instrumental and sampling issues described later in 5.2.

Sulphate concentrations in the $PM_{10}$ fraction are currently made with daily filter measurements using Partisol 2025s. The available continuous sulphate instrument has not been deployed, and we propose that it should be evaluated, before being deployed, to inform future purchases. For example, the continuous instrument must be shown to be comparable to the daily method.

While carbon and sulphate concentrations are measured in the $PM_{10}$ fraction, nitrate is measured in the $PM_{2.5}$ fraction at present, due to a $PM_{2.5}$ cyclone internal to the instrument. This complicates any analysis of the data, though in practice most carbon and sulphate particles are expected to be in the $PM_{2.5}$ fraction.

From the point of view of particle composition, the sites in the Network are of differing importance. Harwell is the only rural site in the Network. It is important due to its rural location to the west of London, co-location of other equipment and its possible use as an EMEP super-site. Marylebone Road is important for its roadside location and its profile in the media. There is a duplication of urban background sites in London, ie Kensington and Bloomsbury. Bloomsbury has drawbacks as a site as the equipment is situated under trees. The trees cause significant equipment maintenance problems, they will capture a fraction of the ambient particulate matter and the data is also likely to be unduly affected by high levels of tree pollen.

Port Talbot is a key industrial site, with significant profile in Wales. Glasgow and Belfast sites, together with Port Talbot, also satisfy the need to have data from the Devolved Administrations. Manchester, Birmingham, Belfast and Glasgow are classed as urban background as they are all situated in pedestrianised areas. There is scope for taking equipment out of some of these sites to deploy elsewhere, or to direct resources at priority sites.

The one rural site (Harwell) in the Network is not sufficient to characterize the rural background throughout the UK, with any certainty. There is also only one kerbside location, Marylebone Road. There are also no Network sites on the eastern coast of the UK, so there is currently no direct measure of particulate matter arriving from the continent.

Some of the sites in the Network are already at full capacity in terms of physical space and the installation of extra equipment would necessitate a new enclosure. The alternative, to install the equipment at another site, would not answer the need for co-location of measuring equipment, which is considered vital for valid interpretation of the data.

# 5 Scientific and Policy Messages

## 5.1 Continuous particulate sulphate monitoring

Analysis of the $PM_{10}$ monitoring data in the south east of England shows the presence of an important regional background contribution, upon which urban and traffic increments are superimposed. Figure 1 shows the $PM_{10}$ concentrations during 2002 along an east-west transect across London through Westminster. The presence of a regional background concentration of about 16 µg $m^{-3}$ is evident with urban and traffic increments superimposed upon it.

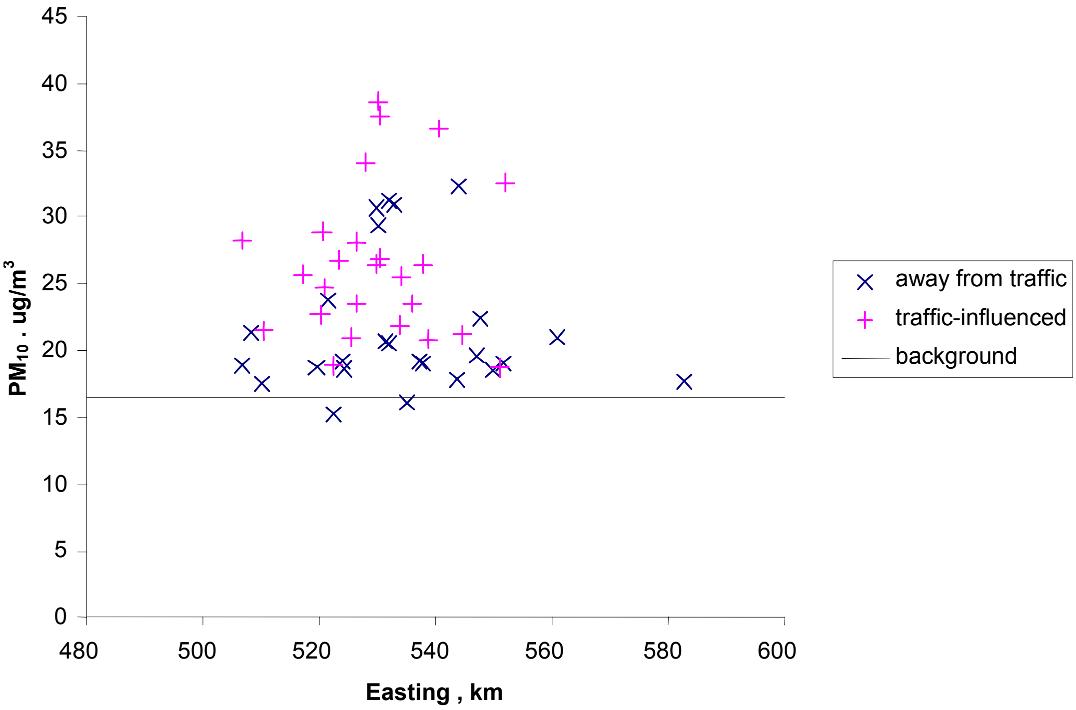


**Figure 1. Annual mean $PM_{10}$ concentrations along an east-west transect across London through Westminster showing the presence of a regional background.**

Particulate sulphate and its import from the continent of Europe makes a substantial contribution to regional background levels over the south and east of the United Kingdom as is evidenced by the particulate sulphate levels found at Barcombe Mills, see Figure 2. In addition, there is a wider scale background of particulate sulphate that results from the recirculation of European regionally-polluted air masses that enter the British Isles from the North Atlantic Ocean as shown by the monitoring at Lough Navar (Northern Ireland) and Strathvaich Dam (Scotland), see Figure 2. Continuous monitoring of particulate sulphate is required to assess the importance of short term variations in these contributions and to ensure that they are adequately represented in the Site Specific Receptor Model used by DEFRA for the purposes of air quality policy assessment.

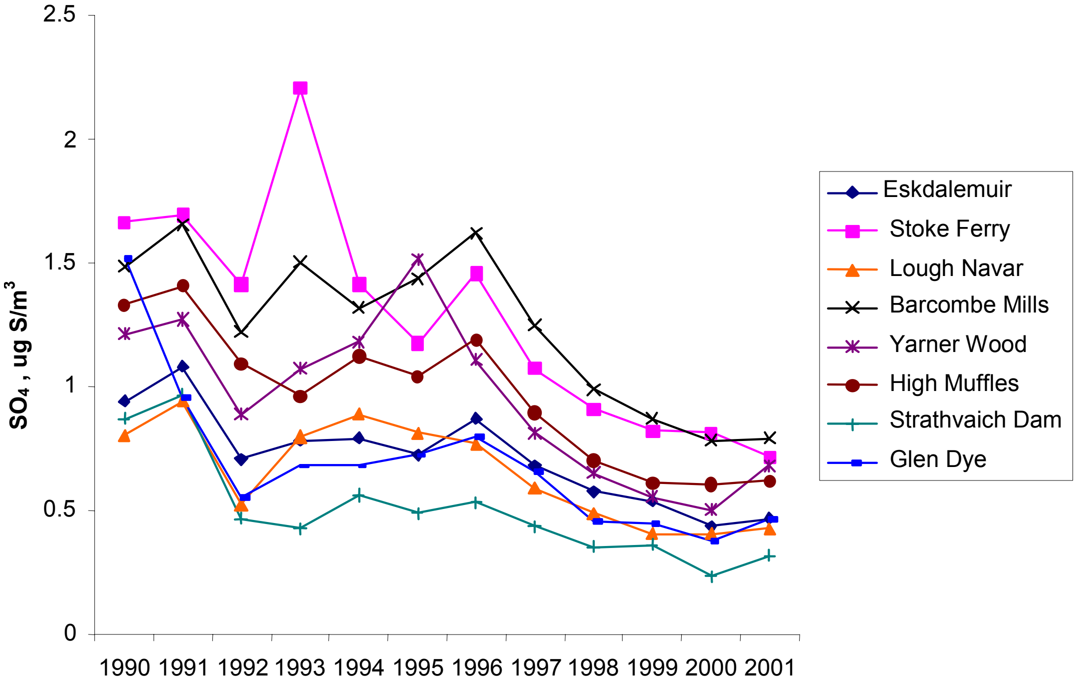


**Figure 2. Annual mean levels of particulate sulphate from 1990-2001.**

Particulate sulphate also exerts an important controlling influence on the distribution of ammonia and its compounds between the gas and particulate phases. Much of the particulate sulphate is present in the particulate phase as ammonium sulphate and some as sulphuric acid. Only when there is excess ammonia present in the atmosphere will all the particulate sulphate be present as ammonium sulphate, and formation of ammonium nitrate will occur. Any ammonium nitrate so formed is thermally unstable, and will tend to decompose in the presence of any un-reacted sulphuric acid, to form ammonium sulphate (Adams et al. 1999). There is therefore a strong coupling between particulate ammonium, sulphate and nitrate. Continuous monitoring is required to assess the importance of short-term variations in the coupling between particulate sulphate and nitrate.

Without an understanding of this coupling between particulate ammonium, sulphate and nitrate, it is difficult to be certain about future trends and the response of $PM_{10}$ and $PM_{2.5}$ levels to European regional pollution controls on $SO_2$ and $NO_x$ (Erisman and Schaap 2004). This is a major uncertainty in policy assessments addressing airborne particulate matter.

There is little current understanding of whether there are any urban or traffic increments in particulate sulphate concentrations. The mass closure study for Leeds (Clarke et al. 1996) pointed to the presence of a significant urban enhancement of particulate sulphate over rural levels of about 15%. However, there is no information about how such enhancements have changed more recently due to the introduction of low-sulphur fuels.

### 5.2 Continuous particulate nitrate monitoring

Because of the important instrumental and sampling issues connected with the monitoring of particulate nitrate, which is often in semi-volatile form, it is difficult to have confidence in current understanding of particulate nitrate in Europe. There are issues about the distribution of particulate nitrate between the coarse and fine particle size fractions. There are issues between the semi-volatile and non-volatile particulate phases. There are also issues concerning whether any of the monthly and daily filter-based observations made in the UK and rest of Europe have been artefact-free. Any proposal for additional continuous particulate nitrate monitoring needs to be firmly based on an understanding of these instrumental and sampling issues which should contribute to the resolution of these monitoring issues.

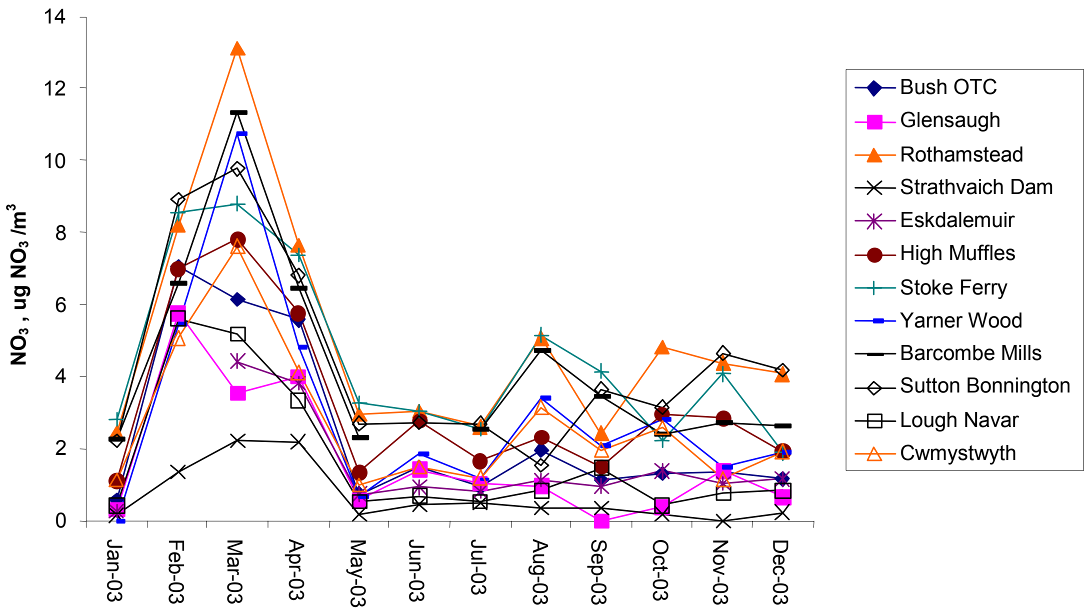


**Figure 3. Monthly mean levels of particulate nitrate during 2003.**

Figure 3 presents the monthly mean levels of particulate nitrate observed during 2003. The presence of a strong spring-time peak in particulate nitrate is clearly evident in the observed levels from February through to April. The levels reached during the spring of 2003 were about double those generally observed in previous years. However, the peak episodic levels were not captured because of the monthly mean time resolution of the filter samples. The origins of the elevated nitrate are presumably from long-range transport from the European continent. These nitrate episodes during the spring of 2003 contributed to a reversal in the previous downwards trends in $PM_{10}$, producing a slight increase in $PM_{10}$ levels between 2002 and 2003 across much of the United Kingdom.

Continuous particulate nitrate monitoring is required to establish and quantify the presence of a regional background of particulate nitrate and its origins in continental Europe, together with its variations under episodic conditions. Coupling with particulate ammonium and sulphate is an important feature of the fate and behaviour of particulate nitrate (Erisman and Schaap 2004). Continuous particulate nitrate monitoring is required to understand this coupling, with a view to quantifying future trends in $PM_{10}$ and $PM_{2.5}$.

There is little current understanding of whether there are any urban or traffic contributions to particulate nitrate concentrations. The mass closure study for Leeds (Clarke et al. 1996) pointed to there being an enhancement of urban over rural levels that varied from about 15% to 100%. However, traffic emissions of $NO_x$ have decreased significantly since that period to the present date and so the current position on urban enhancements of particulate nitrate is uncertain.

### 5.3 Continuous elemental carbon monitoring

Monitoring studies to date have confirmed that there are both traffic and urban increments in both $PM_{10}$ and $PM_{2.5}$ levels (APEG 1999). These studies have employed air quality data from the paired roadside and urban background sites in Marylebone Road and Bloomsbury in London. A study of the elemental and organic carbon data obtained from this Network was carried out recently (Harrison and Jones 2004). The observed increments appear to be significantly larger than those expected on the basis of diesel exhaust emission inventories. Several hypotheses have been put forward to explain this discrepancy and each have their different ramifications for air quality policy. Continuous monitoring of elemental carbon at paired traffic-influenced and urban background sites should allow direct comparisons of traffic increments with the diesel emission inventories. Furthermore, if these measurements continue with time, they should be suitable for the monitoring of compliance with the proposed future diesel exhaust emission standards.

Few measurements have been made of elemental carbon in the United Kingdom. Measurements were made every eighth day at Bush Estate, Midlothian during the EMEP EC/OC campaign during the period from July 2002 to June 2003, see Figure 4. From this limited dataset, there appears to be evidence of a significant regional background component from continental Europe because the slightly elevated levels observed during the spring of 2003 coincided with elevated levels of particulate nitrate. Continuous monitoring is required to assess the importance of this contribution in southeast England.

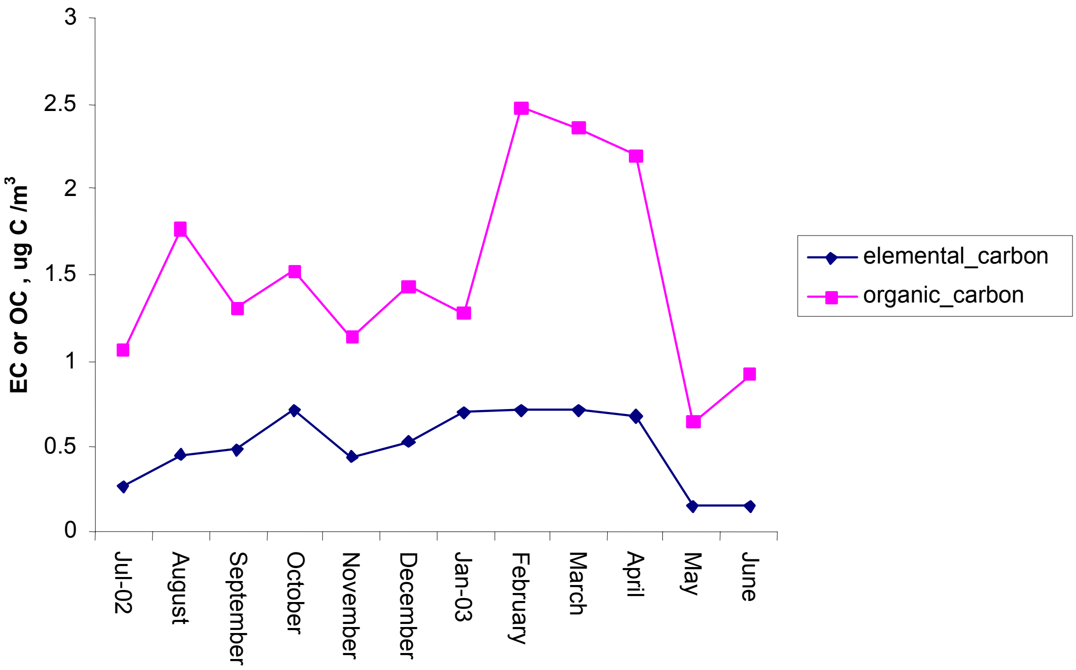


**Figure 4. Results from the EMEP EC/OC measurement campaign at Bush Estate, Midlothian during July 2002 to June 2003.**

## 5.4 Continuous organic carbon monitoring

A major shortcoming identified in the AQEG report was current understanding of the organic carbon fraction of particulate matter. In principle, there are primary and secondary sources of organic carbon to consider, together with man-made and natural biogenic sources. Each will have local, regional and long-range transport contributions. Organic carbon was monitored during the EMEP EC/OC campaign at Bush Estate, Midlothian as shown in Figure 4 above. The elevation in organic carbon levels during the spring of 2003, in this dataset, coincides with the elevated levels of particulate nitrate shown in Figure 3 and may be attributed to long-range transport from continental Europe. This elevation indicates the possible presence of secondary organic particulate matter, which may be biogenic in origin. However, these monthly mean averaged results do not allow the link to be made definitively.

A study of the elemental and organic carbon data from this Network highlighted the importance of non-traffic sources of particulate organic carbon at the Marylebone Road site. (Harrison and Jones 2004). Continuous monitoring of particulate organic carbon at paired traffic-influenced and urban background sites should allow the identification of any traffic contribution to primary organic carbon particulate matter. Such contributions are anticipated from un-burnt fuels and lubricants associated with diesel vehicular traffic.

Continuous monitoring of organic carbon at rural sites could establish the magnitude of any regional background from continental Europe. Co-location with ozone monitoring should help identify any photochemical contribution from secondary organic carbon particulates.

## 5.5 Particle Counting and Sizing

Particle counting equipment is currently deployed mainly at urban centres. Results from these instruments have been used to investigate seasonal, diurnal and directional variations in particle number for source apportionment purposes (Harrison and Jones 2004). As more attention is focused on the importance of particle size for health effects then the long-term datasets from particle counting equipment will be useful for epidemiological studies. For this purpose they are best located at background sites in the centres of large conurbations. However there are currently no similar instruments in related rural locations to provide a measure of the urban increment in terms of particle number. The different measurement properties of the CPCs and the SMPSs limit the extent to which their results can be cross-compared.

Particle sizing /counting equipment is currently deployed at kerbside (Marylebone Road), urban background (Bloomsbury) and a rural site (Harwell). Results from the two SMPSs in London have been compared with those from Harwell to deduct rural and urban increments from kerbside data for source apportionment. In particular, data from the SMPSs has provided valuable information on the contribution of different classes of vehicles to kerbside measurements, when compared with data from vehicle exhausts. Continuous datasets from this equipment will allow monitoring of the effects of any future curbs on diesel particulate emissions.

# 6 Proposals for Particulate Composition Monitoring, Counting and Sizing

## 6.1 Particulate Composition Monitoring

The proposals for the monitoring of particulate composition take the form of recommendations covering a minimum set of continuously recording instruments and a prioritised set of locations for the deployment of the sets of instrumentation. Because the aim is to provide chemical composition measurements that will improve national modelling of $PM_{10}$ and $PM_{2.5}$, the minimum set of instrumentation is the same for each site across the proposed Network. The aim is to provide composition data with hourly time resolution, on a continuous basis.

The set of instruments recommended for continuous particulate composition monitoring is as follows:

- continuous elemental and organic carbon ($PM_{10}$ and $PM_{2.5}$)
- continuous sulphate ($PM_{10}$ and $PM_{2.5}$)
- continuous nitrate ($PM_{10}$ and $PM_{2.5}$)
- continuous $PM_{10}$ and $PM_{2.5}$ by TEOM – FDMS

The priorities for implementing the requirement for $PM_{10}$ and $PM_{2.5}$ are discussed later in this section.

Each set of instruments should be located at the same site to maximise knowledge of interrelationships. The continuous particulate composition monitoring should also be collocated, as far as possible, with AURN measurements of $O_3$, $NO_x$ and $SO_2$.

The monitoring locations proposed, in our order of priority, are as shown below. Those in italics are not currently part of this Network. The ownership of the existing site is shown in brackets.

1. *Rochester (Medway Council – affiliated to AURN)*
2. Marylebone Road
3. North Kensington
4. Harwell
5. Belfast
6. *Lough Navar (AURN)*
7. *Bush Estate (AURN)*
8. Glasgow
9. Port Talbot
10. *Narberth (Pembrokeshire Council – affiliated to AURN)*

The order of priority for the monitoring locations gives the highest priority to the London conurbation. The Rochester and Harwell sites have been chosen to characterize the particulate loadings in air masses entering the London conurbation from continental Europe and in those leaving the London conurbation and influencing southern England.

The Marylebone Road and North Kensington sites have been chosen because they are paired traffic and urban background sites that have been widely used to characterize traffic increments. The paired sites at Rochester and North Kensington are well suited to monitor the London urban increment.

The focus on the London conurbation stems from the attention given by AQEG to the levels of $PM_{10}$ observed in London, which in turn reflects its position as the major urban conurbation in the UK. Furthermore, as noted previously, the Marylebone Road site has exceeded the Stage 1 limit Value of the EU First Daughter Directive (99/30/EC) for $PM_{10}$ during 2005. Without better composition data, it is going to be difficult to elucidate the steps to be taken to ensure that such an occurrence does not happen in subsequent years.

We propose that the highest priority is given to composition of the $PM_{10}$ fraction rather than $PM_{2.5}$, subject to confirmation by Defra. Looking to the future, the new proposal for revision of the Framework Directive and the three Daughter Directives requires, in its current form, measurement of the chemical species in this Network in the $PM_{2.5}$ fraction at 'background' locations. Measurements of $PM_{2.5}$ composition could be made at a later date either by the purchase of additional new instruments, or by changing the size selection head on existing instruments.

After the London conurbation, the next highest priority is seen as Northern Ireland. Paired urban background and rural locations in Belfast and Lough Navar are proposed. This recognizes the importance of solid fuel combustion in Northern Ireland and the requirement to characterize particulate matter in the different environments across the United Kingdom. The Lough Navar site is well-suited to the monitoring of the long-range transport of particulate matter into the United Kingdom from the Atlantic Ocean through the recirculation of European pollution. Paired sites are then proposed in the other Devolved Administrations to complete the requirements.

The understanding of $PM_{10}$ also requires measurements of particulates containing iron, sodium, calcium and ammonium, in addition to the species measured in this Network. Iron is particularly important at roadside locations as it represents re-suspended particles from vehicle (non-exhaust) emissions, as discussed in the AQEG Report 2005.

It is also recommended that the rural particulate composition monitoring sites should be collocated with EMEP monitoring activities. Collocation with the proposed EMEP super-site activities involving the deployment of particle-into-liquid aerosol samplers would be advantageous to both activities by providing field inter-comparisons.

It is recommended that these instruments should be fully evaluated in the laboratory before further purchases are made. The programme of work should include comparison with manual methods.

### 6.2 Particle Counting and Sizing

It is recommended that the particle counting/sizing equipment should remain in place at the existing Network sites included in the priority sites listed above. ie Marylebone Road Kensington, Harwell, Glasgow, Belfast and Port Talbot, to provide continuity of data sets and supplementary information about the particles. Data from the urban background sites, Kensington, Glasgow and Belfast, could support epidemiological studies. Particle counters in Birmingham and Manchester could either remain in place, to provide extended time series results for more epidemiological studies, be moved to the new priority sites, i.e. Rochester, Lough Navar and Bush Estate, or removed from operation to save costs. As noted previously, measurements at the Bloomsbury site are compromised by the proximity of trees and this site is a strong candidate for re-location. The sizing equipment (SMPS) at Marylebone Road provides information on vehicle emissions when allowance is made for the urban and rural backgrounds. This equipment has now reached the end of its life and it is recommended that new equipment should be purchased for Marylebone Road, Kensington and Harwell, to provide the necessary roadside, urban background and rural comparison.

# 7 Options for Network optimization and further development

Based on the rationale presented above, proposals are outlined below. Indicative costs are supplied separately.

## 7.1 Rochester - composition

The Rochester site has been chosen to characterize the particulate loadings in air masses entering the London conurbation from continental Europe and in those leaving the London conurbation and influencing southern England. The sites at Rochester and North Kensington are well suited to monitor London increments.

Rochester is believed to be an essential, uniquely placed site, new to this Network, which is also part of the Defra Site Receptor Model. It should be developed to provide a new multi-technique monitoring site, with automatic nitrate, carbon and sulphate analysers, monitoring the $PM_{10}$ fraction initially. Upgrading of the existing TEOM (R&P 1400AB) to FDMS instruments (R&P 8500) is also recommended, although these instruments belong to the local authority rather than Defra. The existing enclosure will not accommodate all of the recommended equipment, therefore installation and operation of a new, separate enclosure would be necessary. The site owner and operator have indicated their agreement to this. However existing, non-deployed automatic nitrate, carbon and sulphate analysers could be used.

## 7.2 Instrument Evaluation

Further development of the Network after the proposed new site at Rochester requires purchase of new automatic nitrate, carbon and sulphate analysers. There is evidence that the reliability of these analysers, particularly the automatic carbon and sulphate analysers, is less than that required for continuous network operation. It is therefore recommended that this equipment should be fully evaluated in the laboratory for six months. Such a study would also compare these instruments with gravimetric measurements.

## 7.3 London and Harwell - composition

The Harwell site in the Network has been prioritised to enable characterization of particulate loadings in air masses leaving the London conurbation to the west and influencing southern England. The existing Marylebone Road and North Kensington sites have been prioritised for expansion because they are paired traffic and urban background sites that have been widely used to characterize traffic increments. Harwell also has the advantage that it is the proposed location for extended EMEP monitoring activities. Collocation with the proposed EMEP super-site activities involving the deployment of particle-into-liquid aerosol samplers would be advantageous to both activities by providing field inter-comparisons.

As stated previously, the focus on the London conurbation stems from the attention given by AQEG to the levels of $PM_{10}$ observed in London. Furthermore, the Marylebone Road site has exceeded the Stage 1 limit Value of the EU First Daughter Directive (99/30/EC) for $PM_{10}$ during 2005. Without better composition data, it is going to be difficult to elucidate the steps to be taken to ensure that such an occurrence does not happen in subsequent years.

The two London sites, together with Harwell and Rochester should be considered as London roadside, urban background and (complementary) rural sites. Marylebone Road and Harwell already contain automatic carbon and nitrate equipment. Kensington contains an automatic carbon instrument and the second non-deployed automatic nitrate (in addition to that to be deployed at Rochester) could be installed. The filter based sulphate equipment would then be replaced with new automatic sulphate instruments (when these have been fully evaluated) at all three sites. These instruments should all monitor the $PM_{10}$ fraction initially. Upgrading of the existing TEOM (R&P 1400AB) to FDMS instruments R&P 8500) is recommended, although these instruments are operated under the AURN contract. Modifications to the enclosure at Kensington would be needed to accommodate the extra equipment.

### 7.4 London and Harwell – particle sizing

Particle sizing equipment installed at these sites has now reached the end of its life and it is recommended that new equipment should be purchased for Marylebone Road, Kensington and Harwell, to provide the necessary roadside, urban background, rural comparison. Data from the SMPSs has provided valuable information on the contribution of different classes of vehicles to kerbside measurements, when compared with data from vehicle exhausts.

### 7.5 Northern Ireland

As noted above, after developing the Network in the London conurbation, Northern Ireland is the next priority location for expanding the continuous particulate monitoring. Paired urban background and rural locations in Belfast, an existing site in the Network, and Lough Navar, a new site to the Network, are proposed. This recognizes the importance of solid fuel combustion in Northern Ireland and the requirement to characterize particulate matter in the different environments across the United Kingdom. The Lough Navar site is well-suited to the monitoring of the long-range transport of particulate matter into the United Kingdom from the Atlantic Ocean through the recirculation of European pollution.

Belfast and Lough Navar should be upgraded to provide the full range of speciation equipment, which would sample the $PM_{10}$ fraction initially. Upgrading of the existing TEOM (R&P 1400AB) to FDMS instruments (R&P 8500) is recommended, although these instruments are operated under the AURN contract.

### 7.6 Scotland and Wales

The existing urban background sites at Glasgow and Port Talbot should be paired with new rural sites at Bush Estate and Narberth respectively, to characterize particulate matter in different environments across the United Kingdom. Port Talbot is predominantly an industrial area, and it not only provides information on a different type of environment, but it also has a high profile in Wales. All four sites should be upgraded to provide the full range of speciation equipment, which would sample the $PM_{10}$ fraction initially. Upgrading of the existing TEOM (R&P 1400AB) to FDMS instruments (R&P 8500) is recommended, although these instruments are operated under the AURN contract. New enclosures would be needed at Glasgow, Port Talbot and Narberth to accommodate the extra equipment.

### 7.7 Other composition measurements

The automatic carbon, nitrate and sulphate instruments together monitor a substantial fraction of the mass concentration of $PM_{10}$ and $PM_{2.5}$ as identified by APEG (1996; 1999). The difference between the total loadings from the components and the total mass concentrations is anticipated to come from crustal material, wind-blown dusts, Saharan dust, construction activities, vehicle re-suspension and agricultural activities. The composition of these components of particulate matter are not properly understood and the main methods of characterization are slow. However quantification of certain key components, namely iron, sodium, calcium and ammonium, even on a daily basis, would provide very valuable additional information. It would be an important step forward to have some continuous monitoring of this residual component to replace the assumptions employed in current receptor modelling studies. This could be accomplished using the spare Partisols and ion chromatography for sodium and ammonium measurements at selected sites. Iron and calcium measurements may be carried out using inductively coupled plasma mass spectrometry (ICPMS) and these measurements could readily be assimilated into an existing Network.

### 7.8 Cost Savings

Withdrawing particle counting/sizing equipment from Birmingham, Manchester and Bloomsbury would provide a cost saving as running costs would no longer be incurred. These are not priority sites and the urban background sites of Belfast, Glasgow and Kensington will provide similar data. However it should be recognized that some of these sites have provided long continuous valid datasets, which have been or may be, useful e.g. for epidemiological studies, and this should be considered before a decision to remove them is taken.

Further costs savings could be made after initial validation of the automatic sulphate analysers against the non-automatic Partisol equipment, when the latter equipment could be withdrawn from service.

## 8 References

Adams, P.J., Seinfeld, K.H., and Koch, D.M. (1999). Global concentrations of tropospheric sulphate, nitrate and ammonium aerosol simulated in a general circulation model. J. Geophysical Research **104**, 791-813.

APEG (1999). Source apportionment of airborne particulate matter in the United Kingdom. DETR, London.

Clarke, A.G., Andrews, G.E., Azadi-Bougar, G.A., Bartle, K.D., Tolebi, M. and Askey, S.A. (1996). The sources and chemistry of atmospheric particles. Report to DoE EPG 1/5/44.

Erisman, J.W. and Schaap, M. (2004). The need for ammonia abatement with respect to secondary PM reductions in Europe. Environmental Pollution **129**, 159-163.

EPAQS (2001). Airborne particles. Stationery Office, London.

Harrison, R.M., Jones, A.M., and Lawrence, R.G. (2003). A pragmatic mass closure model for airborne particulate matter at urban background and roadside sites. Atmospheric Environment **37**, 4927-4933.

Harrison, R.M., Jones, A.M. (2004). Interpretation of particulate elemental and organic carbon concentrations at rural, urban and kerbside locations. Submitted for publication.

QUARG (1993). Urban air quality in the United Kingdom. DoE, London.

QUARG (1996). Airborne particulate matter in the United Kingdom. DoE, London.

# Appendix 1: Network monitoring instruments

| Site | Type | Hourly $PM_{2.5}$ nitrate | Hourly $PM_{10}$ organic and elemental carbon | Daily $PM_{10}$ filter (sulphate) | CPC | SMPS |
|---|---|---|---|---|---|---|
| Belfast Centre | Urban centre | x | x | x | x | |
| Birmingham Centre | Urban centre | | | | x | |
| Glasgow Centre | Urban centre | | | | x | |
| Harwell | Rural | x | x | x | | x |
| London Bloomsbury | Urban centre | | | | | x |
| London Kensington | Urban background | | x | x | x | |
| London Marylebone Road | Kerbside | x[1] | x | x | x | x |
| Manchester Piccadilly | Urban centre | | | | x | |
| Port Talbot | Urban background | | | | x | |

1 – owned by the Network but operated by King's College London

Equipment owned but not deployed:

1 hourly carbon; 2 hourly nitrate; 1 hourly sulphate; 1 CPC

Equipment models:

| | |
|---|---|
| CPC | TSI model 3022A |
| SMPS | TSI model 3071 |
| Hourly nitrate | Rupprecht and Patashnick 8400N |
| Hourly carbon | Rupprecht and Patashnick 5400 |
| Hourly sulphate | Rupprecht and Patashnick 8400S |
| Daily sulphate | Rupprecht and Patashnick Partisol 2025 |

# Appendix 2: Maps
Current Network

Proposed New Network