AIR QUALITY EXPERT GROUP

Fine Particulate Matter ($PM_{2.5}$) in the United Kingdom

Prepared for:
Department for Environment, Food and Rural Affairs;
Scottish Executive; Welsh Government; and
Department of the Environment in Northern Ireland

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This is a report from the Air Quality Expert Group to the Department for Environment, Food and Rural Affairs; Scottish Government; Welsh Government; and Department of the Environment in Northern Ireland, on Fine Particulate Matter ($PM_{2.5}$) in the United Kingdom.

United Kingdom air quality information received from the automatic monitoring sites and forecasts may be accessed via the following media:

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Terms of reference

AQEG is an expert committee of Defra and considers current knowledge on air pollution and provides advice on such things as the levels, sources and characteristics of air pollutants in the UK. AQEG reports to Defra's Chief Scientific Adviser, Defra Ministers, Scottish Ministers, the Welsh Government and the Department of the Environment in Northern Ireland (the Government and Devolved Administrations). Members of the Group are drawn from those with a proven track record in the fields of air pollution research and practice.

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- Give advice on current and future levels, trends, sources and characteristics of air pollutants in the UK;

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Executive Summary

1. Particulate matter (PM) is the term used to describe condensed phase (solid or liquid) particles suspended in the atmosphere. Their potential for causing health problems is directly linked to the size of the particles. A growing body of research has pointed towards the smaller particles, in particular PM less than 2.5 μm in diameter ($PM_{2.5}$), as a metric more closely associated with adverse health effects than other metrics such as PM_{10} (particles with a diameter less than 10 μm).

2. The EU's Air Quality Directive, the Directive on Ambient Air Quality and Cleaner Air for Europe (2008/50/EC), defines standards by which air pollution can be assessed and establishes specific air quality objectives. To achieve these objectives there are a number of other legislative instruments which aim to reduce air pollution by controlling emission sources. In the Directive a new approach for $PM_{2.5}$ was introduced in recognition of the lack of evidence to indicate that there is a concentration of particulate matter below which health effects do not occur. This new approach aims to achieve a reduction in the overall exposure of the population to $PM_{2.5}$ based on the concept that greater public health benefits could be obtained from a general reduction in exposure than from a policy aimed at reducing exposure in hot spots only. The focus of legislation for $PM_{2.5}$ is on limiting long-term exposure through the use of annual standards, coupled to a reduction of $PM_{2.5}$ background concentration in urban areas across the UK over the period 2010-2020. The National Emission Ceilings Directive (2001/81/EC) and the recent revision of the UNECE Convention on Long Range Transboundary Air Pollution's Gothenburg Protocol both aim to reduce transboundary transport of a number of air pollutants which affect the concentrations of background $PM_{2.5}$ by setting limits on their emission from member states.

3. This report, prepared by the Air Quality Expert Group (AQEG) for Defra and the Devolved Administrations gives an overview of the evidence base for $PM_{2.5}$ in the UK. The report challenges the robustness of the evidence for making future policy decisions in respect of $PM_{2.5}$ in the UK context. There is an analysis of the evidence concerning key relevant aspects including $PM_{2.5}$ measurement and the composition and current concentrations of $PM_{2.5}$ across the UK, as well as source emissions and receptor modelling for $PM_{2.5}$. Finally, AQEG evaluates the methods for modelling $PM_{2.5}$ and what can be said about future concentrations. The report concludes with an assessment of the key uncertainties and gaps in the evidence base that require action.

I.1 Measurement

4. The measurement of $PM_{2.5}$ mass concentration is a demanding task, as the metric does not correspond to a definite physical or chemical component of the air but is in effect defined by the measurement method itself. The reference method for legislative purposes is declared in the Air Quality Directive to be that described in the CEN European standard EN 14907.

5. $PM_{2.5}$ contains a large proportion of semi-volatile and hygroscopic material which means that the $PM_{2.5}$ mass is subject to variation due to environmental conditions during and after sampling. The difficulties of PM measurement are reflected in the fact that the required measurement uncertainty for PM in the

Air Quality Directive is ±25%, with a 95% level of confidence, at concentrations close to the limit value; for most other gaseous pollutants the comparable value is ±15%.

6. There are three aspects to the question 'Do we have robust measurements of PM2.5?';

   a) whether the AURN (Automated Urban and Rural Network) measurements meet the reporting requirements of the Directive. The data capture (the percentage of time for which data meeting the uncertainty requirement are available) currently (2009 and 2010) falls slightly short of the Directive requirements.

   b) whether conclusions about small changes in concentration (typically smaller than the ±25% uncertainty required by the Directive) can be drawn from UK data. Data obtained using the same type of instrument and the same quality assurance/quality control (QA/QC) procedures are expected to be comparable with each other such that the relative uncertainty is significantly less than 25%. Relative uncertainties should be even less when longer term averages are taken, reducing the total impact of random variations. However, operational problems with the monitoring instruments on the UK network have made relative uncertainties hard to quantify.

   c) whether the measurements are robust enough to improve our understanding of the sources of $PM_{2.5}$ and $PM_{2.5}$ precursors. At the current time, uncertainties in $PM_{2.5}$ measurement data make them far from ideal for comparison with models. The lack of robustness is due to a combination of $PM_{2.5}$ being defined operationally, the relatively large uncertainties in the measurement of $PM_{2.5}$ concentrations and the inherent complexities of airborne particle formation and evolution.

7. The current analysers most widely used to measure $PM_{2.5}$ (FDMS, Filter Dynamics Measurement System, see Chapter 2 for full details) are based on new and relatively complex technology. Significant work is required to fully understand and characterise this technology. In particular, it is recommended that issues concerning long-term reliability and the handling of semi-volatile components are further investigated.

I.1.1 Measurement recommendations

8. At present the measurement of $PM_{2.5}$ remains a challenge, with current measurements falling just below the data capture requirements of the EU Air Quality Directive. **AQEG recommends a focused working group is assembled to address the achievement of Directive requirements using current measurement methods.**

9. High quality and comprehensive measurements of the chemical components of $PM_{2.5}$ are an important future goal. Chemically-speciated measurements have twofold benefits, in terms of the attribution of composition of $PM_{2.5}$ for control purposes and their ability to be used for source apportionment. To date, the measurements of some components of a non-volatile nature have a lower uncertainty than the overall mass concentration, but some methods still have

significant uncertainty. The area of measurement of the chemical components of $PM_{2.5}$ needs review and the evidence requirements need clearly stating. **AQEG recommends a comprehensive review and rationalisation of the requirements for PM chemical composition measurements in the UK.**

I.2 Concentrations and composition of $PM_{2.5}$

10. A new measurement network was established in 2009 for $PM_{2.5}$ using reference equivalent instrumentation. Data are now becoming available from this network to evaluate $PM_{2.5}$ distribution and legislative compliance. However, there is a requirement to define the important rural background contribution to $PM_{2.5}$ across the UK. The relative lack of rural background sites, there are only three, restricts our ability to quantify sources of $PM_{2.5}$. Additionally, there are limited measurements of $PM_{2.5}$ composition in different types of location and in different areas of the UK.

11. Evidence from urban sites and the limited number of rural background measurement sites indicates that regional (rural) background concentrations make a considerable contribution to the overall mass of $PM_{2.5}$ in urban areas, accounting for around 60-80% of the background concentrations in the major urban areas of southern England. The regional background concentrations are dominated by secondary $PM_{2.5}$, primarily as ammonium nitrate and ammonium sulphate, but also as organic particles. In the central and southern UK around 60% of the urban background mass $PM_{2.5}$ is made up of secondary particles. Sulphate particles remain important, despite the large reductions in sulphur dioxide emissions since the 1980s.

12. High $PM_{2.5}$ concentrations are frequently associated with air transported into the UK from continental Europe. There is evidence that PM_{10} episodes associated with air arriving from continental Europe, especially during the spring, are composed of fine particles ($PM_{2.5}$) and not coarse particles ($PM_{2.5-10}$), with nitrate playing a particularly important role. This nitrate is largely associated with ammonium, derived from ammonia emissions.

13. Emissions of the gaseous pollutants ammonia, oxides of nitrogen and sulphur dioxide from sources in the UK and Europe contribute to the formation of secondary PM over a large area. Black carbon is a major component of the $PM_{2.5}$ associated with road traffic emissions and domestic (oil and solid fuel) combustion. Primary emissions from road traffic, including the non-exhaust component, make a significant (about 30-50%) contribution to the urban background increment of $PM_{2.5}$ above rural concentrations. Road traffic can make substantial contributions to $PM_{2.5}$ concentrations at the kerbside (within 1 m of the kerb) of around a third of total concentrations, but at the roadside (a few metres from the kerb) the contributions are more limited (~1-2 $\mu g\ m^{-3}$ out of a total concentration of ~7-8 $\mu g\ m^{-3}$ alongside busy roads) except in street canyons.

14. There is evidence to suggest that domestic and commercial sources make a contribution to concentrations of $PM_{2.5}$ during the evening period, which may be due to solid fuel combustion and to particles released during cooking. Based on the limited evidence available, primary particles from industrial sources do not appear to make a major contribution to urban background concentrations.

I.2.1 Concentration and composition recommendations

15. Resources should be made available to ensure that the results from the $PM_{2.5}$ monitoring network now in place are fully analysed to extract as much information as possible about the sources contributing to $PM_{2.5}$ in different parts of the UK.

16. **The rural $PM_{2.5}$ monitoring network should be expanded to allow a better quantification of the rural background**. This recommendation should be given urgent consideration. Additional sites will help verify modelled background concentrations and confirm the modelled spatial pattern of decreasing rural background concentrations from the south-east of England to the north-west of Scotland. They will also allow the urban increment to be determined more precisely.

17. Further work should be carried out to characterise the organic component of particles, in particular to improve our understanding of the contribution from secondary organic particles with respect to what is controllable under future policy measures.

I.3 Emissions and receptor modelling

18. The major sources of primary $PM_{2.5}$ are combustion in the energy industries, road transport (both exhaust and non-exhaust emissions), off-road transport, residential sources and small-scale waste burning. Total $PM_{2.5}$ emissions in the UK are predicted to decrease by 25% relative to 2009 levels by 2020, with an especially large contribution from reductions in road traffic exhaust emissions.

19. The main traffic sources of $PM_{2.5}$ are exhaust emissions from diesel vehicles (cars, light goods vehicles and heavy goods vehicles), together with tyre wear, brake wear and road surface abrasion from all vehicles. A broadly similar picture prevails across the European Union. There are significant uncertainties attached to some of these emissions estimates and particularly to the estimates of $PM_{2.5}$ from non-exhaust traffic sources. With reductions in exhaust emissions of PM, the non-exhaust components of traffic emissions will become much more important, emphasising the need to develop measures to control emissions from these sources.

20. With respect to $PM_{2.5}$ secondary organic and inorganic precursor species, UK total emissions of nitrogen oxides (NO_x) have declined by 59% between 1990 and 2009 and are set to decline by a further 37% relative to 2009 levels by 2020. There is some uncertainty in inventories of road transport emissions for NO_x, with evidence to suggest that "real world" emissions of NO_x from Euro III-IV diesel vehicles are higher than previously thought and have not been declining as anticipated. While future road transport emissions of NO_x are expected to decrease, the rate of reduction may, therefore, not be as fast as current inventory projections indicate. UK emissions of sulphur dioxide (SO_2) and non-methane volatile organic compounds (NMVOCs) also fell between 1990 and 2009, by 89% and 70% respectively. Much smaller reductions of just 40% and 8% are anticipated between 2009 and 2020 for these two pollutants respectively. For ammonia (NH_3), UK emissions have fallen by only 21% between 1990 and 2009 and are not predicted to fall any further up to 2020. According to a recent estimate of past and future trends in EU-27 emissions of PM

precursors, the changes between 2005 and 2010 have been similar to those for the UK. The predicted changes in emissions between 2010 and 2020 for EU-27 are also similar to those predicted for the UK for NO_x, SO_2 and NH_3, although rather larger reductions are predicted for NMVOC emissions in EU-27 compared with the UK. Different changes in emissions would be expected where the contributions of different sources to precursor emissions vary between countries, but caution should also be taken when making comparisons because different emission factors may have been used in the inventories compiled for the UK and EU-27 countries.

21. Emissions from shipping are not well quantified. Emissions of SO_2 from shipping in Europe are predicted to decrease by just 3% in the next decade, although SO_2 emissions in Sulphur Emission Control Areas around the UK coast are expected to fall significantly. NO_x emissions from shipping in Europe are predicted to increase by 16% over the next decade.

22. Comparisons between the results of receptor and dispersion models have highlighted significant differences in relation to industrial/commercial/residential emissions of primary particles and the model predictions of secondary organic aerosol particles. Receptor modelling results highlight the weaknesses in current knowledge of a number of sources including wood smoke and cooking aerosol, and also suggest that the UK National Atmospheric Emissions Inventory (NAEI) emission factors for gas combustion may be rather high.

23. Use of carbon-14 as a tracer allows a distinction to be drawn between carbon derived from contemporary sources, such as wood burning or emissions from vegetation, and from fossil fuel sources. Analysis of carbon-14 in airborne particulate matter collected in Birmingham indicates a major contribution to secondary organic carbon from biogenic precursors.

24. Formulation of abatement strategies is made difficult by inadequacies in knowledge of the contribution of certain sources and weaknesses in understanding precursor–secondary particle dependencies for the major secondary components.

I.3.1 Emissions and receptor modelling recommendations

25. **AQEG recommends that the enhancement of emissions inventories is essential if numerical models of atmospheric $PM_{2.5}$ are to be improved.** The key areas for improvement are:

- non-exhaust vehicle emissions including tyre and brake wear, road abrasion and road dust resuspension;
- fugitive dust emissions from construction, demolition, quarrying, mineral handling, industrial and agricultural processes, and methods for quantifying them nationally and locally;
- $PM_{2.5}$ emissions from domestic and commercial cooking;
- $PM_{2.5}$ emissions from small-scale waste burning and bonfires;

- $PM_{2.5}$ emissions from domestic wood burning, accounting for the effectiveness of control measures;
- biogenic emissions of NMVOCs;
- emissions of NH_3 from agriculture, with their temporal as well as spatial variability;
- exhaust emissions from off-road machinery used in construction and industry;
- emissions of SO_2 and NO_x from shipping, in particular their spatial distribution around ports and harbours, the temporal variability and future emissions; and
- exhaust emissions of $PM_{2.5}$ from diesel vehicles under real world driving conditions and the factors and technologies affecting them.

26. Inventories should be developed to provide a quantification of the spatial and temporal variability in emissions of primary $PM_{2.5}$ and its precursors from all contributing sources, including those not covered in national inventories, or provide the means for calculating them in air quality models. Developments should include spatially-gridded inventories with high resolution temporal profiles for different source sectors.

27. Further urgent research on the emissions and atmospheric chemistry of biogenic volatile organic compounds (VOCs) in the context of secondary organic aerosol formation in the UK is required, as this may have significant impact on the options for mitigation measures. Examples of critical areas have been recently evaluated.[1]

I.4 Modelling and the future

28. Models are an important tool for understanding the links between emissions and observations data and making predictions of ambient concentrations in a self-consistent framework. **Modelling of $PM_{2.5}$ remains a substantial challenge** owing to uncertainties in and lack of measured data, uncertainties/ lack of understanding of some aspects of the dynamic, physical and chemical processes which need to be described within the models, and uncertainties in the emission data and their projections.

29. Several PM models covering urban to regional scales are used to predict UK air quality. They are based on a range of modelling systems (e.g. Eulerian, Lagrangian and Gaussian plume). Models are useful for quantifying the different contributions to PM, e.g. local urban emissions, and the contribution made by the long-range transport of pollutants.

30. Modelling results have shown that $PM_{2.5}$ concentrations exhibit localised peaks in urban areas, owing to local sources of primary $PM_{2.5}$, superimposed on a regional background. These local sources are generally well represented by models, except when close to roads with complex street geometries. An

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[1] EPRI and A&WMA Workshop on *Future Air Quality Model Development Needs*, 12-13 September 2011, Washington, D.C., USA.

important limiting factor in estimating concentrations and human exposure in urban areas is likely to be uncertainty in the emissions, including missing sources.

31. The largest contribution to $PM_{2.5}$ concentrations overall is the secondary inorganic aerosol (SIA). The relatively slow formation of SIA (hours to days) means that concentrations tend to be smoothly distributed over large areas. Models show the nitrate component of SIA over the UK is now larger than that of sulphate, and is more variable in space and time, depending on the variability in ammonia emissions and concentrations owing to major reductions in sulphur dioxide (SO_2) emissions in the UK and elsewhere in Europe in recent decades.

32. The relatively small urban increment above regional background points to the need to consider control strategies for the regional background where secondary inorganic aerosol is by far the largest component according to models. Indeed, if nothing was being done to address the regional background the removal of the whole of the urban increment would be required to meet the targets set for $PM_{2.5}$ exposure reduction.

33. Source apportionment from modelling shows how further reductions in SIA depend on control of emissions of SO_2, NO_x and NH_3 in other countries and from shipping, as well as from sources in the UK. **Modelling indicates a complex non-linear response of SIA concentrations to reductions in precursor emissions due to chemical interactions between pollutants, in particular the high dependence on the availability of NH_3, and the reversibility and temperature dependence of the formation of ammonium nitrate. The effectiveness of further SO_2 and NO_x reductions is uncertain given that overall emissions of NH_3 are likely to remain more constant as well as showing high spatial and temporal variation**.

34. Modelling of the secondary organic aerosol component, SOA, is uncertain both in terms of precursor emissions and chemical processes. It may be more difficult to control SOA and its precursors, of which biogenic emissions are a large component, than SIA. It is worth noting that the oxidants for the biogenic VOC precursors are all controlled by atmospheric chemistry and will respond to further reductions in anthropogenic emissions. It is not clear whether SOA levels will remain constant in the future if man-made emissions of VOCs and NO_x change significantly.

35. The semi-volatile components of organic aerosols and ammonium salts comprise a substantial fraction of $PM_{2.5}$ and present a substantial modelling and measurement challenge. Other components, such as sea salt, rural and urban dusts, and water content, also need to be included in models in order to explain total $PM_{2.5}$ concentrations and achieve mass closure. These components make a substantial contribution to overall $PM_{2.5}$ concentrations.

36. **There is significant uncertainty in predicting $PM_{2.5}$ concentrations into the future, owing to uncertainty in future European precursor emissions, particularly with respect to the secondary organic and secondary inorganic aerosol.**

I.4.1 Modelling recommendations

37. **AQEG recommends the more extensive and consistent evaluation of $PM_{2.5}$ models in the UK**, considering for example, similar time periods and the speciated components of $PM_{2.5}$. Such an evaluation should also consider the temporal and spatial characteristics of the key components of $PM_{2.5}$. Furthermore, the evaluation would provide a more robust assessment of model performance beyond meeting the Air Quality Directive requirements for model performance. **Verification of models, particularly source attribution, remains challenging largely because of the lack of availability of chemically-speciated measurements.** There is also a need to develop methodologies for quantifying uncertainties in modelled values.

38. Further work on sea salt, rural/urban dusts and water content is required to investigate how they may be represented in modelling, including, for example, the response of the water content associated with the $PM_{2.5}$ fraction to reductions in pollutant emissions.

39. With respect to mitigation, substantial further reductions in SO_2 emissions from 2006-2008 levels of around 50% across Europe will be required to achieve an appreciable reduction of about 1 $\mu g\ m^{-3}$ in sulphate in $PM_{2.5}$ in the southern UK. Similarly, a 1 $\mu g\ m^{-3}$ reduction in nitrate would require a reduction of about 50% in European NO_x emissions from 2007 levels if SO_2 and NH_3 emissions remain constant. However, reductions of both SO_2 and NO_x emissions would necessitate a greater NO_x reduction to achieve the same improvement in nitrate, as reduced sulphate formation is accompanied by an increase in nitrate.

40. **Further consideration should be given to assessing the effectiveness of ammonia abatement as a way of reducing UK secondary inorganic $PM_{2.5}$,** in concert with any requirement for wider transboundary abatement.

41. Modelling of the secondary organic aerosol component of $PM_{2.5}$ is uncertain both in terms of precursor emissions and chemical processes; further work is required in this area, in particular on the fundamentals of the mechanisms of formation and incorporation of precursors into the aerosol.

Chapter 1

Introduction

1. Particulate matter (PM) is the term used to describe condensed phase (solid or liquid) particles suspended in the atmosphere. It includes materials referred to as dust, smoke and soot, as well as pollen and soil particles. Particulate matter may be directly emitted into the atmosphere (termed primary particles) or formed by the reaction of atmospheric gases (secondary particles). Airborne particles range in size from a few nanometres to several hundred micrometres. By convention, those smaller than (<) 2.5 µm diameter are referred to as fine particles and those greater than (>) 2.5 µm diameter as coarse. Particulate matter is effectively defined by the measurement method rather than as some unambiguous chemical or physical component of the air (see Chapter 2). It is a complex mixture consisting of many different components from a range of sources. The composition of PM varies depending on emissions, weather conditions, local and regional contributions, and temporal variations (see Chapter 3).

2. The size of particles is directly linked to their potential for causing health problems (Harrison *et al*., 2010). The requirement to control atmospheric concentrations of particulate matter derives from its well recognised and quantified effects upon human health, including premature mortality, hospital admissions, allergic reactions, lung dysfunction and cardiovascular diseases. A growing body of research has pointed towards the smaller particles within the PM_{10}[1] metric as being the most significant in relation to health outcomes. In particular, attention has focused on PM less than 2.5 µm in diameter ($PM_{2.5}$) as a metric more closely associated with adverse health effects than PM_{10},[2] although there is still debate as to whether it is actually the ultrafine fraction ($PM_{0.1}$) (or indeed a non-mass metric, such as particle number[3]) that is primarily responsible for the effects.

1.1 Purpose of this report

3. In this report the Air Quality Expert Group (AQEG) aims to give an overview of the evidence base describing the $PM_{2.5}$ environment in the UK. The report challenges the robustness of the evidence for making future policy decisions concerning $PM_{2.5}$ in the UK context. There is an analysis of the evidence on the key aspects of $PM_{2.5}$, including $PM_{2.5}$ measurement and the composition and current concentrations of $PM_{2.5}$ across the UK, and source emissions and receptor modelling for $PM_{2.5}$. Finally, AQEG evaluates the methods for modelling $PM_{2.5}$ and what can be said about future concentrations. The report concludes with an assessment of the key uncertainties and gaps in the evidence base that require action.

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[1] PM_{10} has a technical definition based on measurement parameters, but in general terms it is particulate matter less than 10 µm in aerodynamic diameter.

[2] $PM_{2.5}$ is a part of the PM_{10} metric, so the two metrics are not independent.

[3] Particle number is the total number of particles measured per unit volume; particle mass concentration is the mass of particles per unit volume (for example, µg m^{-3}).

4. In broad terms, the report responds to the following questions:

   (a) How well can we understand the $PM_{2.5}$ environment in the UK in terms of emissions, modelling and measurement? Where are the key uncertainties in these and what can be done to address them?

   (b) What is the current state of knowledge on $PM_{2.5}$ in the UK? What does this tell us about the best way to reduce concentrations, and thus exposure, in terms of the scale at which controls should operate, the components which should be addressed and the sectors which may need to be controlled?

   (c) What are the key challenges of a legislative target based on change over time (the exposure reduction target), in particular in terms of the consistency of assessment, uncertainty in forecasts and the variability of concentrations due to, for example, meteorology?

1.2 Policy approach

5. The European Union's (EU's) Air Quality Directive, the Directive on Ambient Air Quality and Cleaner Air for Europe (2008/50/EC), transposed into UK law through the Air Quality Standards Regulations 2010, is one of the key legislative instruments in place to address air pollution under the European Commission's Thematic Strategy on Air Pollution. It was the first EU directive to include limits on ambient concentrations of $PM_{2.5}$. In the Directive a new approach for $PM_{2.5}$ was introduced in recognition of evidence suggesting that there is no clear concentration of particulate matter below which health effects do not occur. This new approach aims to achieve a reduction in the overall exposure of the population to $PM_{2.5}$, based on the concept that greater benefits could be obtained from a general reduction in exposure than by a policy aimed at reducing concentrations in geographically-limited "hot spots". Exposure is assessed through the average concentration measured at urban background locations across the country.

6. In response to this general reduction approach, the focus of legislation for $PM_{2.5}$ is on limiting long-term exposure through the use of annual standards, coupled to a reduction in $PM_{2.5}$ background concentration in urban areas across the UK over the period 2010-2020. Table 1.1 shows various relevant air quality standards for $PM_{2.5}$, including the newly-introduced average exposure indicator (AEI) and exposure reduction target (see also Table 1.2).

7. A number of legislative approaches are being taken to control exposure to PM in order to achieve the standards in Table 1.1. These include controls on motor vehicle emissions, controls on industrial sources and controls introduced by local authorities to address individual hot spots. The National Emission Ceilings (NEC) Directive (2001/81/EC) underpins the controls at the national level. The Directive sets national limits on emissions with a date by which they are to be achieved. In relation to PM, the key controls have been on emissions of nitrogen oxides (NO_x), sulphur dioxide (SO_2) and ammonia (NH_3), as these are precursors of secondary inorganic PM (largely ammonium nitrate (NH_4NO_3) and ammonium sulphate ($(NH_4)_2SO_4$)). Emissions of volatile organic compounds (VOCs) are covered by the NEC Directive as precursors of ozone, rather than as precursors of secondary organic PM.

8. A review of the European Commission's Thematic Strategy on Air Pollution and the legislative framework for air pollution in Europe is currently underway, and may result in a revision of the NEC and Ambient Air Quality Directives.

Table 1.1: Air quality standards for $PM_{2.5}$ and PM_{10}.

	Pollutant	Time period	Standard	To be achieved by
UK	$PM_{2.5}$	annual mean	Objective of 25 µg m^{-3}	2020
		three-year running annual mean	15% reduction in average urban background concentrations against a 2010 baseline	2020
	PM_{10}	24-hour mean	Objective of 50 µg m^{-3} not to be exceeded more than 35 times a year	2005
		annual mean	Objective of 40 µg m^{-3}	2005
Scotland	$PM_{2.5}$	annual mean	Objective of 12 µg m^{-3}	2020
		three-year running annual mean	15% reduction in average urban background concentrations against a 2010 baseline	2020
	PM_{10}	24-hour mean	Objective of 50 µg m^{-3} not to be exceeded more than seven times a year	2005
		annual mean	Objective of 18 µg m^{-3}	2005
EU	$PM_{2.5}$	annual mean	Target value of 25 µg m^{-3}	2010
		annual mean	Limit value of 25 µg m^{-3}	2015
		annual mean	Stage 2 indicative limit value of 20 µg m^{-3}	2020
		three-year average exposure indicator (AEI)	See Table 1.2	2020
		exposure concentration obligation (ECO)	20 µg m^{-3} at urban background stations (measured as a three-year average)	2015
	PM_{10}	24-hour mean	Limit value of 50 µg m^{-3} not to be exceeded more than 35 times a year	2005
		annual mean	Limit value of 40 µg m^{-3}	2005

Table 1.2: National exposure reduction targets for $PM_{2.5}$.

Exposure reduction target relative to the AEI (average exposure indicator)[1] in 2010[2]		Year by which the exposure reduction target shouldbe met
Initial concentration, µg m^{-3}	**Reduction target, %**	
less than or equal to 8.5	0	2020
more than 8.5 but less than 13	10	
13 to less than 18	15	
18 to less than 22	20	
22 or more	All appropriate measures to achieve 18 µg m^{-3}	

1 The AEI is derived from three-year average urban background measurements (i.e. 2009, 2010, 2011 for 2010) as defined in the EU Ambient Air Quality Directive (2008/50/EC).

2 Where the AEI in the reference year is 8.5 µg m^{-3} or less, the exposure reduction target is zero. The reduction target is also zero in cases where the AEI reaches the level of 8.5 µg m^{-3} at any point of time during the period 2010 to 2020 and is maintained at or below that level.

1.3 Effects of $PM_{2.5}$ and links to climate change

9. Airborne particulate matter has consequences for human health, the environment and climate change. An overview of the impacts is offered here to demonstrate the importance of reducing levels of $PM_{2.5}$ and the linkages between different impact areas; further review of effects is beyond the scope of this current report.

1.3.1 Health effects of $PM_{2.5}$

10. The Committee on the Medical Effects of Air Pollutants (COMEAP) reports *Long-Term Exposure to Air Pollution: Effect on Mortality* (COMEAP, 2009) and *The Mortality Effects of Long-Term Exposure to Particulate Air Pollution in the United Kingdom* (COMEAP, 2010) provide an excellent synthesis of the current evidence on the impact of particulate matter on mortality. There is clear evidence that particulate matter has a significant contributory role in human all-cause mortality and in particular in cardiopulmonary mortality.

11. $PM_{2.5}$ penetrates deeply into the human respiratory system. The acute effects of particle exposure include increases in hospital admissions and premature death of the old and sick due to diseases of the respiratory and cardiovascular systems. The evidence is that both $PM_{2.5}$ and PM_{10} cause additional hospital admissions and deaths on high pollution days. Less severe effects of short-term particle exposure also occur during pollution episodes, including worsening of asthma symptoms and even a general feeling of being unwell leading to a lower level of activity.

12. Long-term exposure to particles is associated with increased levels of fatal cardiovascular and respiratory diseases, including lung cancer, which reveal themselves as increased rates of death in cities with higher concentrations of airborne particles. COMEAP (2009) expressed the view that the best estimate of the chronic health impacts of particulate matter exposure was a 6% increase in death rates per 10 µg m^{-3} $PM_{2.5}$ concentration. As with the acute effects of particle exposure no wholly safe level has been identified.

13. However, these conclusions relate to PM as measured by mass as opposed to different sources or components of PM. Airborne particles differ greatly from place to place in size and chemical composition. There is currently no clear understanding of which particle properties, such as their size or the presence of specific chemical substances, are most responsible for the toxic effects. COMEAP (2009), mirroring the position of the World Health Organization (WHO), states that:

> 'Our view is that particulate matter represented by $PM_{2.5}$ is a complex and possibly interacting mixture of many components, including sulphate, and though these components may differ from one another in terms of their toxicity, such data as we have do not allow confident separation of their effects on health. In the absence of clear evidence to the contrary we consider that the recommended coefficient should apply equally to all components of $PM_{2.5}$, including particulate matter measured as sulphate and nitrate. This is not to say that all components of $PM_{2.5}$ do have the same toxicity – but, rather, that there is not, at present, evidence to quantify different components differently, in a way that would gain wide consensus.'

14. Additionally, the composition of PM will change over time as further mitigation measures are introduced and as new technologies (and therefore sources) emerge. An improved understanding of the behaviour and composition of PM will in turn help improve the understanding of its impacts on health.

1.3.2 Ecosystem impacts of $PM_{2.5}$ in the UK

15. $PM_{2.5}$ may have both direct and indirect effects on ecosystems. In terms of direct effects, aerosols are hygroscopic, often deliquescent, and can exist in liquid form on transpiring leaves. Burkhardt (2010) has proposed the concept of "hydraulic activation of stomata", whereby aerosols deposited on leaf surfaces enable the efficient bi-directional transport of water and solutes between leaf interior and leaf surface. If air pollution led to large accumulations of particulates on leaves, the drought tolerance of trees might be affected, leading to regional tree die-back. Aerosols may also have an indirect effect by modifying plant exposure to sunlight. Both theoretical and observational studies have demonstrated that photosynthesis is more efficient under diffuse light conditions. Mercado *et al.* (2009) used a global model to estimate that "global dimming" caused by increased global aerosol in the atmosphere enhanced the land carbon sink by one quarter between 1960 and 1999.

16. The largest effects of man-made aerosols on ecosystems are likely to be indirect, through their role as long-range vectors of air pollutants. Ammonium sulphate and ammonium nitrate aerosol are formed by the atmospheric oxidation and reaction of precursor gases (SO_2, NO_x) with NH_3 (Seinfield and Pandis, 1998) and comprise a major component of fine particulate matter. In this form, $PM_{2.5}$ makes an important contribution to sulphur and nitrogen deposition leading to the acidification and eutrophication of natural ecosystems. Surface deposition of $PM_{2.5}$ may occur via two different pathways: dry deposition and wet deposition.

17. Dry deposition is the direct deposition of aerosol to vegetation driven by turbulent fluxes. This may be as 'dry' particles or as cloud droplets formed by activation of the aerosols. Aerosol particles act as cloud condensation nuclei and are efficiently incorporated into cloud water at the point of droplet formation (Pruppacher and Klett, 2010). In upland forests the concentrations of sulphur and nitrogen in cloud water may be much higher than in precipitation. Concentrations of particulate sulphur in the range 1-3 $\mu g\ m^{-3}$ incorporated into cloud water may result in damage to foliage through the direct deposition of cloud droplets (Cape, 1993). However, there appear to be no direct effects of dry particles on vegetation except where leaf surfaces are covered, e.g. by dust from industrial or agricultural activity.

18. Estimates of the direct dry deposition of particulate nitrogen and sulphate in the UK have been made using the Concentration Based Estimated Deposition (CBED) technique (Smith *et al.*, 2000; RoTAP, 2012), which combines measurements from the Acid Gases and Aerosols Monitoring Network (AGANet) with vegetation-specific deposition velocities. Annual dry deposition of particulate sulphate, nitrate and ammonium to the UK was estimated at 3 Gg sulphur (S), 7 Gg N-NO_y (nitrogen as oxides of nitrogen) and 8 Gg N-NH_x (nitrogen as ammonia and ammonium) respectively, averaged over the period 2006-2010. This represents only a modest contribution to the total deposition of 39 Gg S, 77 Gg N-NO_y and 76 Gg N-NH_x in the UK averaged over the period 2006-2010.

19. Particulate matter is efficiently removed from the atmosphere by the mechanism of wet deposition. Wet deposition is the removal of matter from the atmosphere by precipitation. The growth of cloud droplets leads to the formation of raindrops which will deposit particulate matter contained in solution to the earth's surface. Due to the solubility of gases (SO_2, nitric acid (HNO_3), NH_3, etc.) in rainwater, it is not possible to distinguish the relative contributions of gases and particulates by measurement of concentrations in precipitation. Atmospheric transport models are able to demonstrate that wash-out of particulate matter is the dominant mechanism for wet deposition of sulphur and nitrogen, in particular in remote upland regions with sensitive ecosystems. Fine PM is an air pollutant which is associated with long-range transboundary transport. The EMEP model generates source–receptor matrices of the contribution to deposition of sulphur and nitrogen in each European country from emissions from all other countries. These modelling results show that emissions of primary pollutants from non-UK sources (including other countries and international shipping) contribute 43% of total sulphur deposition and 46% of nitrogen deposition in the UK (Nyri *et al.*, 2010) in the form of long-range particulate transport. The particulate phase of nitrogen and sulphur pollutants therefore represents an important link between primary gaseous emissions, long-range transport and eventual deposition in precipitation to ecosystems in the UK.

20. The indirect effects of PM on ecosystems through wet and dry deposition can be assessed by the impact of total deposition on soil processes, and therefore on ecosystems, expressed as a "critical load". A critical load is defined as "A quantitative estimate of an exposure to one or more pollutants below which significant harmful effects on specified sensitive elements of the environment do not occur according to present knowledge" (UBA, 2004), and is the main

criterion used in the UK to assess the risk of ecosystem impacts. For terrestrial habitats, 54% of natural ecosystem area in the UK is currently estimated to exceed critical loads for acidity. Critical loads for effects of nitrogen deposition on sensitive habitats are calculated to be exceeded for 58% of their area in the UK (RoTAP, 2012).

1.3.3 Climate change impacts of $PM_{2.5}$ in the UK

21. The report *Air Quality and Climate Change: A UK Perspective* (AQEG, 2007) provides a thorough overview of air quality and climate interactions.

Impact of PM on climate change

22. Ammonia, SO_2, NO_x and volatile organic compounds (VOCs) are all precursors of secondary aerosols. These aerosols are reflective, so that they scatter solar radiation back to space and exert a negative (cooling) radiative forcing effect on climate. They also influence the radiative properties of clouds. Thus, reductions in the precursors of secondary aerosols, and therefore in secondary aerosols themselves, are likely to lead to increases in temperature. There is evidence that the cooling effects of sulphate aerosol may have partly masked the warming effects of greenhouse gases.

23. Black carbon absorbs solar radiation and black carbon aerosols, or mixtures of aerosols containing a relatively large fraction of black carbon, exert a positive (warming) radiative forcing effect on climate. This effect is especially marked when the black carbon aerosol is located above reflective surfaces such as clouds or snow and ice. While black carbon emissions have decreased significantly in the UK over recent years, substantially increased emissions have been observed from China and India.

24. Aerosols also act indirectly by modifying the radiative properties of clouds. They act as cloud condensation nuclei, increasing droplet number concentrations and decreasing the average droplet size in clouds. This process affects the ability of the clouds to scatter radiation. The precipitation efficiency from the clouds is also reduced, so that their lifetime is increased. Overall, the aerosol indirect effect is cooling; its magnitude is highly uncertain.

25. Air pollutants may also have significant effects on concentrations of carbon dioxide and methane through their impacts on ecosystem sources and sinks. These include the effects of nitrogen deposition in increasing plant growth and thus carbon uptake, and the effects of sulphate deposition in reducing methane emissions from major natural sources.

Impacts of climate on PM

26. It is difficult to predict the effects of climate change on regional air quality. Temporal variations, surface temperature and soil dryness are keys to understanding the likely severity of future summers. Climate change will have the greatest impact on ozone concentrations. VOCs are precursors of ozone and so have indirect effects on climate. Increases in temperature as the climate changes will lead to changes in the chemistry of ozone formation. The greatest effect will be on the concentration of water vapour, which will lead to decreases

in ozone in the background troposphere but increases in more polluted regions where there are higher concentrations of NO_x. There could also be an increase in the flux of ozone from the stratosphere to the troposphere. Hot summers, like that of 2003 when there was a substantial photochemical smog episode in Europe, including the south-east of England, are likely to become 'typical' by the 2040s, leading to a higher frequency of summer pollution episodes. There was evidence that emissions of volatile organic compounds from vegetation played a role in the 2003 episode; increases in temperature led to increases in emissions of biogenic compounds such as isoprene.

Future challenges

27. Several challenges remain in understanding the impacts of PM on climate change and of climate change on air quality:

    (a) Modelling of air quality–climate interactions has tended to focus on time-averaged responses rather than responses under meteorological conditions that are more relevant for air quality episodes. For example, global modelling studies have calculated the response of ozone to various global warming scenarios averaged over seasons and at low resolution. There is a need to examine air quality–climate interactions on much finer time and space scales and during episodic conditions relevant to winter and summer pollution events. For example, arguments about the dominant effect of increasing precipitation on pollutants are irrelevant for anticyclonic pollution episodes in which precipitation plays no role.

    (b) Our understanding of air quality–climate interactions involving aerosols needs to be updated and reappraised to provide a UK or European picture. Our current simplistic view of how decreases in PM would cause positive radiative forcing (through direct and indirect effects) is a global mean picture that may not be applicable in a UK context. Developments in our understanding of aerosol microphysics from models, combined with new intensive aerosol observations over Europe, have provided a much better picture of how PM and aerosol microphysics are related. There are several examples of how our understanding of aerosol air quality–climate effects has changed, including: (i) changes in surface aerosol (e.g. on a daily or seasonal timescale) do not always correspond to changes at cloud level (which would be needed to drive an indirect forcing). Nitrate aerosol over Europe has also been observed to be much more prevalent at cloud level than at the surface, due to the effect of temperature; (ii) there is evidence that carbonaceous combustion aerosol may form a large fraction of cloud condensation nuclei, which might make arguments about mitigation of black carbon too simplistic. Overall, a more sophisticated approach to appraising climate versus air quality impacts of aerosols needs to be considered, rather than just relying on generic model results.

(c) The importance of secondary organic aerosol in assessments of air quality–climate interactions has become more apparent since the 2007 AQEG report. However, there are now open questions concerning biogenic versus anthropogenic sources. For example, there is some evidence that a major fraction of organic aerosol (OA) may be derived from anthropogenically modified biogenic volatile organic compounds (i.e. biogenic secondary OA is formed preferentially in polluted environments). Understanding such links is highly relevant to policy measures because it means that changes in gas phase pollutants (NO_x, ozone, etc.) might impact PM and aerosol forcing. The impact of climate on biogenic emissions is still an open question.

(d) It is important to review our understanding of how the aerosol system will respond to changes in anthropogenic emissions and to integrate our knowledge about PM and climate-relevant particles. It is important to understand how PM concentrations and climate-relevant particles might respond differently to changing emissions. The future trajectory of anthropogenic secondary organic aerosol (SOA) is very uncertain because of changes in the nature of the emissions as well as the response of SOA to atmospheric chemistry changes (NO_x, ozone, etc.). Changes in some emissions are likely to have a large effect on particle mass but a small effect on number (e.g. non-nucleating semi-volatile species or large primary particles), while for some emissions the opposite may be true (e.g. emissions of numerous small particles from combustion that may affect climate but not PM). These climate and air quality issues should be considered in an integrated way.

(e) Climate change will exert a potentially important upward pressure on PM for many reasons that are not well understood. The effects of climate change on PM and climate-relevant particle number concentrations should be assessed, recognising that these parameters may behave differently. Also, it would be useful to understand the importance of:

(i) changes in atmospheric circulation patterns which will affect the occurrence of blocking anticyclonic weather (and the build-up of PM extremes);

(ii) temperature increases causing greater biogenic VOC emissions and consequently increased biogenic SOA;

(iii) changes in removal processes, primarily wet scavenging. This is likely to dominate future changes in PM, but maybe only on a long-term average basis with little effect on PM extremes; and

(iv) changes in atmospheric chemistry affecting oxidants, nitrate formation and SOA chemistry.

Chapter 2

Measuring $PM_{2.5}$ and its components

2.1 Introduction

1. Most measurements of $PM_{2.5}$ are made to check compliance with air quality legislation. Measurement data are also critical for understanding the chemical and physical processes that affect particulate matter (PM), and so they also support the development of models, and decisions about measures to reduce PM concentrations. This chapter discusses the measurement techniques for monitoring $PM_{2.5}$ and components of $PM_{2.5}$ that are referred to in this report, and highlights the difficulties of obtaining reliable measurements. Data quality issues are also discussed. Techniques such as aerosol mass spectrometry, which provide valuable information in other contexts, are not described because they do not provide data used in this report.

2. $PM_{2.5}$, along with PM_{10}, is unusual among regulated air quality metrics in being effectively defined by the measurement method rather than as some unambiguous chemical or physical component of the air. This was not the original intention, and it is, to a large extent, the consequence of the metric featuring in legislation before a good scientific understanding of airborne particles was available. As a better understanding has emerged, it has proved difficult to modify the definition of $PM_{2.5}$ (or PM_{10}) accordingly, because of the implications for the legislation.

2.1.1 Challenges with $PM_{2.5}$ measurement

3. In principle, $PM_{2.5}$ is the mass concentration of airborne particles with an aerodynamic diameter of less than 2.5 µm, expressed in $\mu g\ m^{-3}$, where the volume of air is its volume at ambient conditions (rather than at standardised temperature and pressure). The size of 2.5 µm was chosen because of its significance for the penetration of human lungs, set out by the high risk respirable convention in the document ISO 7708:1983, *Air quality – Particle size fraction definitions for health-related sampling*. For comparison, PM_{10} corresponds to the thoracic convention in the same document, i.e. the size of inhaled particles that penetrate beyond the larynx.

4. There is a long history of particle mass concentration measurements based on the removal of unwanted large particles (in this case > 2.5 µm) using a size-selective inlet such as an impactor, followed by the weighing of the particles that remain in the airstream. This is done by passing the airstream through a particle filter that is weighed before and after sampling. The key measurement issue is that the process of collecting particles onto a filter prior to mass determination can lead to significantly different results depending on the partial or total loss of semi-volatile particles (i.e. those that may evaporate during collection), and because variable amounts of water can remain bound to the particles.

5. The exact form of the inlet collection efficiency curve for different particle sizes, typically determined by an impactor that removes the larger particles through a combination of drag and inertia, is another variable whose effects are generally smaller. Figure 2.1 illustrates an indicative size-selection curve for $PM_{2.5}$. The curve has a midpoint rather than a step change at 2.5 µm, and variations in the curve can allow through a larger or smaller fraction of particles with a diameter of say 3 µm, with a consequent change to the result. The correct form of the collection efficiency curve for regulatory purposes is the one obtained from the reference method inlet system described within European Standardisation body CEN standard EN 14907:2005.

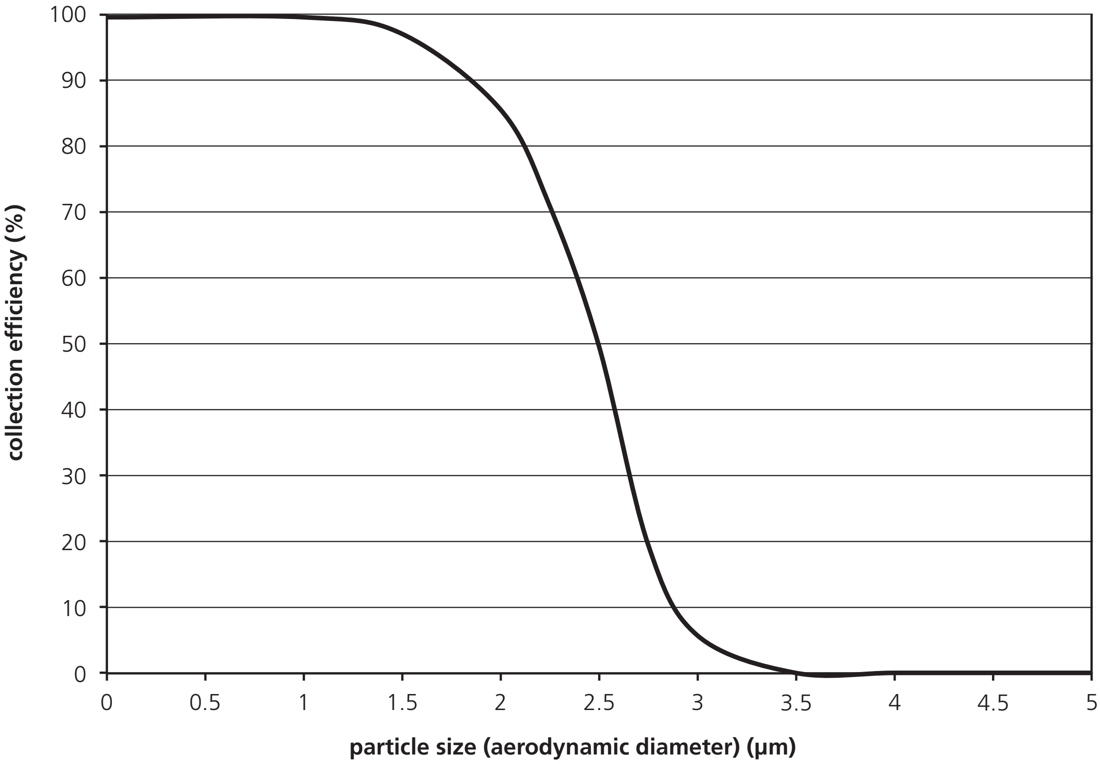

Figure 2.1: Indicative size-selection curve for a $PM_{2.5}$ inlet.

6. It is worth noting that fibrous filters downstream of the size-selective inlet are in practice highly efficient at collecting all the airborne particles that reach them. Small particles that might be expected to pass through gaps between the fibres adhere to them by diffusive processes.

7. Further measurement problems have arisen as PM concentrations have decreased in recent decades. The filters used to collect the particles are themselves susceptible to changes in mass due to, for example, absorption of water or loss of fibres, and these changes have become more significant as PM concentrations have become lower. It is difficult to correct for these effects as they can vary between different filter types and batches in ways that are not fully understood. Other artefacts such as the absorption of reactive gases onto the filter or the PM are also possible.

8. Similar problems exist for PM_{10}, which is, in principle, the same measurement but with a size cut-off at 10 µm instead of 2.5 µm. Unfortunately, the problems are proportionately greater for $PM_{2.5}$ both because the absolute PM mass is smaller, and because in general the particles will contain a larger proportion of semi-volatile and hygroscopic material.

9. The approach for regulatory purposes in Europe has been to standardise a reference measurement method through the European standardisation body CEN. The standard for $PM_{2.5}$ (EN 14907) was published in 2005 and is a modified and improved version of the earlier standard for PM_{10} (EN 12341:1999).

10. These methods are manual gravimetric methods, based on the weighing of filters. Because of the issues outlined above and variations allowed within the reference method as described in Section 2.2, such as the use of different filter materials, it is, for example, possible for two operators to follow the procedures within the standard and obtain results that differ by 10%. As the metric is effectively defined by convention to be the result obtained by the standard method, it is not possible to say that one result is more correct than the other, and this must be borne in mind when comparing:

    - measurements made in different places (especially in different countries), as the methods used may have systematic differences;
    - measurements made at different times, as the methods used may have changed in a subtle way that has a significant effect on the results; and
    - measurements with modelled concentrations, as the semi-volatile loss and water content in measured samples is not well defined.

11. Undesirable effects can have a positive or negative influence on the weighed filter mass, and these are briefly summarised in Table 2.1.

Table 2.1: A summary of factors affecting the reliability of filter weighing as the basis for determining PM.

Effects causing undesirable filter mass increase	Effects causing undesirable filter mass decrease
Sorption of water vapour by the filter material over time (highly dependent on filter material)	Physical loss of filter material, especially fibres, or PM due to poor handling
Sorption of reactive gases by the filter material or PM on the filter during sampling	Excessive loss of semi-volatile PM due to overheating of the filter during sampling
Filter conditioning at the post-sampling weighing being carried out at a higher end of the allowed range for temperature or relative humidity*	Filter conditioning at the post-sampling weighing being carried out at a lower end of the allowed range for temperature or relative humidity*

* the conditioning parameters are given in Section 2.2.1.

12. These difficulties apply even when only the reference method is being used. In practice, monitoring networks mostly use automatic methods, differing significantly from the reference method but designed to give results that are equivalent, introducing other uncertainties that make the situation more complicated. This chapter will outline:

- the principles of the reference method for measuring $PM_{2.5}$ and the process used to determine whether other methods are equivalent to the reference method (Section 2.2);
- the principles and operation of the methods used to produce the $PM_{2.5}$ data used within the report (Section 2.3); and
- the methods used to produce data for related metrics such as anion concentration and elemental and organic carbon (Section 2.4).

2.2 The reference method for measuring $PM_{2.5}$ and the determination of equivalence

2.2.1 The reference method

13. As explained above, the reference method for measuring $PM_{2.5}$ described by CEN within EN 14907 effectively defines what is meant by $PM_{2.5}$ for regulatory monitoring purposes within the European Union. The method is a manual gravimetric method for daily concentrations. Samples of PM are taken by pumping ambient air through a size-selective inlet followed by a filter; the concentration of PM is determined by measuring the change in mass of the filter in a specialised weighing laboratory at prescribed temperature and humidity conditions, and combining the result with the volume of air sampled.

14. The desired cut-off curve for airborne particles close to 2.5 µm is defined by the design of the standard inlets and the control of the flow through them. The size-selective inlets are impactors. They force the airstream along a convoluted path so that a combination of inertia and aerodynamic drag forces the larger particles to collide with a greased plate and be removed. Cyclones are a different design of size-selective inlet, but are based on the same general principle. The retention of semi-volatile material is constrained by restrictions on the temperature near the filter during and after sampling. The quantity of water in the collected PM is constrained by limits on the temperature and humidity during a conditioning period before the filters are weighed: currently 19-21°C and 45-55% relative humidity. In an experiment involving the weighing of 20 UK PM filter samples at different humidities, the allowed range of relative humidity led to variations in measured $PM_{2.5}$ of 4-9% (Butterfield and Quincey, 2009). Examples of other relevant experimental work can be found in Brown *et al.* (2006) and Rasmussen *et al*. (2010).

15. Two versions of the method are described in EN 14907, a low volume method with a sampling flow of 2.3 $m^3\ hr^{-1}$ and filters of 47 mm diameter, and a high volume method with a sampling flow of 30 $m^3\ hr^{-1}$ and filters of 150 mm diameter.

16. The filter material used for sampling can influence the result, primarily because the filter mass can vary over time. This mass change can be in response to

humidity changes or the slow accumulation of water or other material, such as semi-volatile organic matter or reactive gases, unrelated to the pumped sampling, and this will be interpreted as changes to the PM mass. There is no ideal filter material, and the mass change can vary between different batches of the same filter material. EN 14907 allows filters made from quartz fibres, glass fibres, PTFE-coated glass fibre and PTFE membrane to be used.

2.2.2 Equivalent methods

17. The reference methods for $PM_{2.5}$ are not capable of producing real-time data, and neither the low volume or high volume version has been used to produce the data used in this report. The EU allows the use of equivalent methods for regulatory purposes, where equivalence is defined within the Guide to the Demonstration of Equivalence (2010). This sets out a procedure for quantifying the agreement between reference and non-reference methods over a series of parallel field measurements. The objective is that equivalent instruments should produce daily data with a measurement uncertainty less than that required in the Ambient Air Quality Directive (±25% with a 95% level of confidence) at concentrations close to the limit value. Given the nature of the definition of $PM_{2.5}$, these equivalent methods will in general have the same limitations as the reference method (which they must agree with), together with further limitations specific to the equivalent methods.

18. A major exercise within the UK in 2006 (Harrison *et al.*, 2006) found that the automatic instruments Filter Dynamic Measurement System (FDMS) (made by Thermo) and Beta Attenuation Monitor (BAM) (made by Met-One) could be used as equivalent instruments for $PM_{2.5}$ measurement. Virtually all of the automatic data within this report are from FDMS instruments (described in Section 2.3.2).

19. Other $PM_{2.5}$ data are presented from non-reference manual gravimetric samplers known as Partisols. These have a lower sampling flow than the low volume reference method, at 1 m^3 hr^{-1}, but the same sized 47 mm diameter filters. These have not been shown to be equivalent for $PM_{2.5}$ data, although they have for PM_{10}.

2.2.3 Current developments relating to the reference method

20. In view of the regulatory requirements and the experience gained with PM measurement issues in recent years, CEN is currently producing two new standards. The first is a revised version of the standard methods for both $PM_{2.5}$ and PM_{10}, so that EN 14907 and EN 12341 will be combined. The aim of this is to reduce the scope for variations in results allowed within the methods, without causing any significant discontinuity with earlier results. The second is a new standard covering automatic methods. In effect this will bring the procedures in the Guide to the Demonstration of Equivalence (2010) into a formal standard, and also set out requirements for ongoing quality assurance and quality control, bringing PM CEN standards more in line with those for gaseous pollutants.

2.3 Methods used to produce the $PM_{2.5}$ data in this report

21. Most of the $PM_{2.5}$ data used in this report were produced by the Automatic Urban and Rural Network (AURN), the UK's national compliance monitoring network which has extensive quality assurance and quality control checks to comply with European reporting requirements. The network and methods used are described in the following sections.

2.3.1 Current $PM_{2.5}$ monitoring sites in the Automatic Urban and Rural Network (AURN)

22. Table A1.1 in Annex 1 provides a summary of $PM_{2.5}$ monitoring sites in the UK AURN in 2010. All but one of these sites uses either Filter Dynamic Measurement System (FDMS) or Partisol instruments, described in more detail below. The sites are shown on a map of the United Kingdom in Figure 2.2.

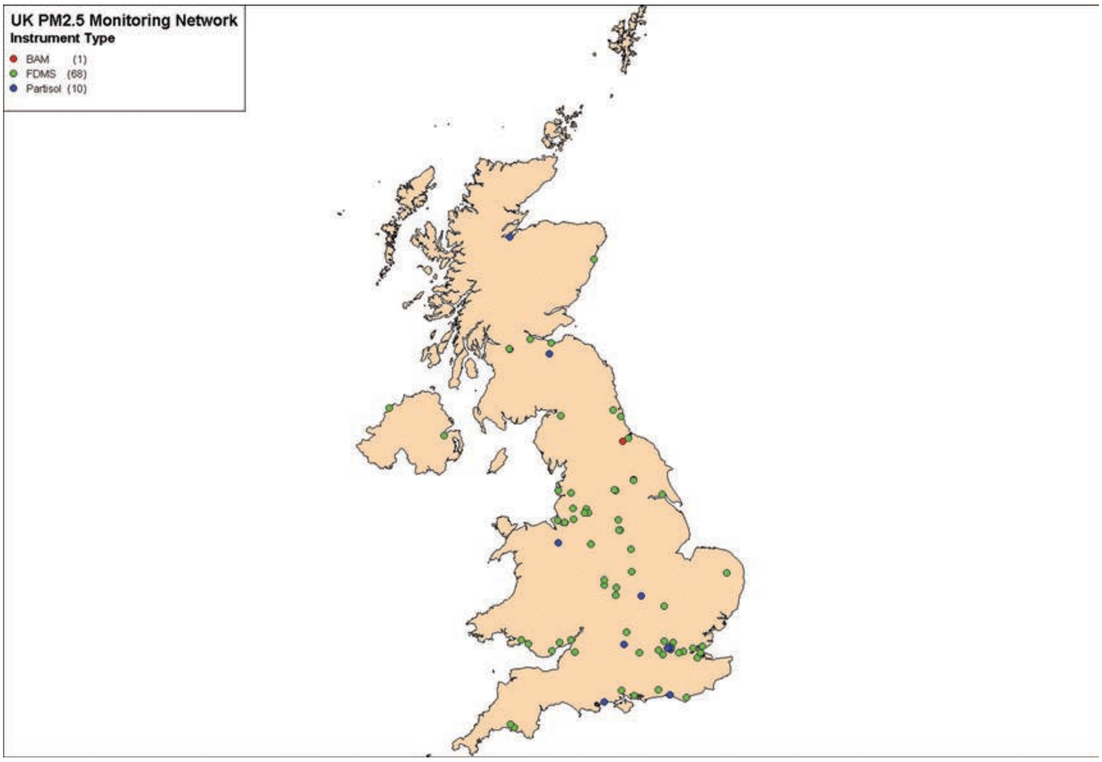

Figure 2.2: $PM_{2.5}$ monitoring sites in the Automatic Urban and Rural Network (AURN).

2.3.2 The Filter Dynamic Measurement System (FDMS) instrument

23. The FDMS provides particulate matter measurements that are equivalent to the EU reference method. It is based on a Tapered Element Oscillating Microbalance (TEOM). TEOMs work on the principle that the frequency of oscillation of a tapered glass tube (element) is highly sensitive to the mass attached to the end of the tube, so that small changes to the mass of a filter mounted on the end of the tube can be quantified by accurate measurements of the tube's resonant frequency. The FDMS accounts for semi-volatile PM that would not be detected by earlier TEOM models. The device provides high-sensitivity PM mass concentration readings for both short-term averages (over one hour) as well as 24-hour averages. The system's basic output consists of one-hour average mass concentrations (in $\mu g\ m^{-3}$) of PM updated every six minutes, together with corresponding "non-volatile" ("base") and "volatile" ("reference") concentrations, as described below.

24. The FDMS instrument calculates PM mass concentrations based upon independent measurements of "non-volatile" and "volatile" mass concentrations (see c and d below). The analyser constantly samples ambient air using a switch valve to change the path of the main flow every six minutes. The sampling process consists of alternate sample and reference (filtered) airstreams passing through the exchangeable filter in the TEOM mass sensor. The measurement sequence is as follows:

    (a) The analyser draws air through the PM_{10} head in the same way as a basic TEOM and then splits the excess flow through the Auxiliary Mass Flow Controller.

    (b) The main flow then passes through a new module (a permeation dryer) which removes water from the airstream. The air then reaches a switching valve.

    (c) For six minutes, the air passes directly into the sensor unit, where PM is collected on the filter and weighed. This is identical to the method used in the TEOM 1400AB, except that the air is dried and the FDMS operates at 30°C, rather than 50°C. The flow of air for this part of the cycle is marked on the Base Cycle diagram in Figure 2.3. The average concentration over this six minute period is the "non-volatile" or "base" measurement of the 12-minute cycle.

    (d) The switching valve then diverts the air through to a purge filter. The main flow of air passes through the dryer as before, but then passes into a cooled chamber, which is held at 4°C. The air then passes through a filter, which retains all the PM in the airstream, but allows any gases to pass through. This scrubbed, zero air is then returned to the sensor unit, where it is sampled normally, to provide a baseline measurement. The flow of air for this part of the cycle is marked on the Purge Cycle diagram in Figure 2.3. The average concentration over this six minute period is the "volatile" or "reference" measurement of the 12-minute cycle.

(e) During the "volatile"/"reference" cycle, any semi-volatile particulates that were collected during the "non-volatile"/"base" measurement cycle can evaporate from the sensor filter. This means that the "volatile" cycle average is usually a small negative value, as material is being lost from the filter. The "volatile" cycle measurement can also, on occasion, be slightly positive, if gases are absorbed by PM on the filter cartridge. The FDMS uses the average "non-volatile" and "volatile" concentrations to calculate an overall mass concentration for the 12-minute cycle, according to the following example equation:

Mass Concentration = "Non-volatile" Concentration – "Volatile" Concentration
Example:
"Non-volatile" = 25 µg m^{-3}, *"Volatile" = -2.6 µg* m^{-3}
Mass Concentration = 25 – (-2.6) = 27.6 µg m^{-3}

The exchangeable purge filter can provide a time-integrated particulate matter sample that can be used for subsequent chemical analysis.

25. It should be recognised that the loss of semi-volatile particles from the filter occurs relatively slowly, so that the loss during a particular cycle will include semi-volatile material collected in previous cycles. This is evident as a time shift of a few hours in the "volatile" concentration. This can affect the interpretation of PM changes happening over a timescale of a few hours, though daily average concentrations will not be significantly affected.

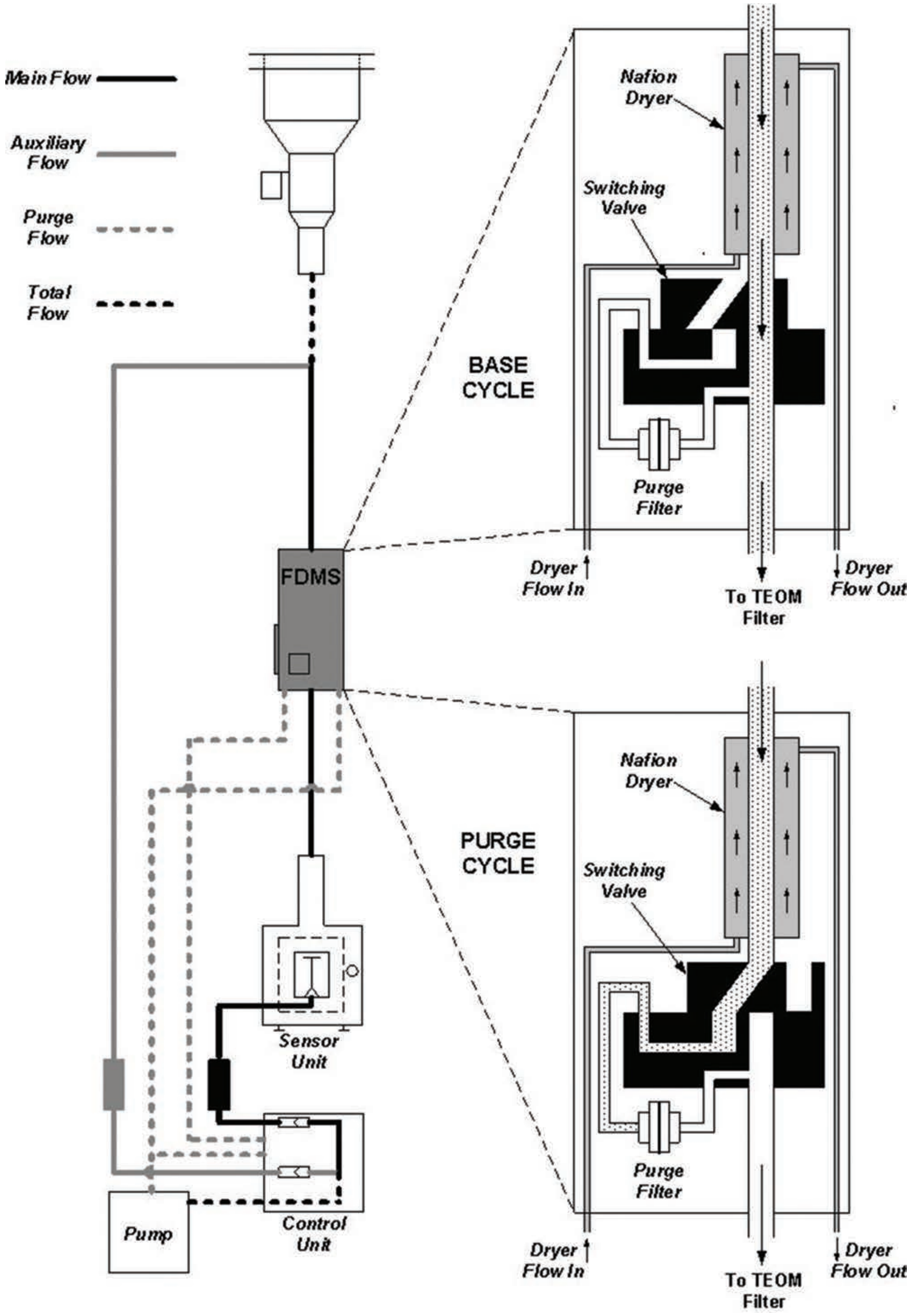

Figure 2.3: FDMS design (diagram courtesy of Dr David Green, King's College London).

2.3.3 The Partisol 2025 instrument

26. The Partisol 2025 is a gravimetric sampler which employs a sequential sampling system of uniquely identified filters that enables up to 16 fixed 24-hour period particulate samples (00:00-00:00 hours GMT) to be undertaken between routine site visits. For the purposes of the UK AURN operations site attendance is required every 14 days to exchange filter cassette magazines from the storage and supply positions within the unit. The results from this method have not been shown to be equivalent to the reference method.

27. The provision of gravimetric sampling, where PM is pulled through a filter via a vacuum pump, requires that pre- and post-exposed filters are weighed in standardised environmental conditions. The increase in mass between the two weighings provides for a measurement of the mass in PM captured on the filter during the course of the specified sampling period. The calculation of PM concentration (mass per unit volume of air) is determined by the division of the mass (in µg) by the total volume of air sampled (in m^3 at ambient temperature and pressure conditions). The volumetric flow rate is controlled internally using a mass flow meter linked to ambient temperature and pressure measurements, and this flow is checked periodically using an external, calibrated flow meter.

28. Pre- and post-conditioning of filters is carried out in accordance with the requirements of EN14907, the CEN reference method for $PM_{2.5}$ measurements. Conditioned filters are provided in pre-loaded filter cassettes via the filter cassette magazine. The magazine is loaded into the supply position within the Partisol 2025 unit and unique filter identifiers are loaded into the software programme to enable identification of each filter exposed during each sampling period. Sampling of air takes place via an initial PM_{10} size-selective impactor combined with a $PM_{2.5}$ Sharp Cut Cyclone (SCC).

2.3.4 Quality assurance/quality control procedures

29. Data from specific types of instrument must be evaluated in the wider context of the checks and calibrations employed during their use and in the production of published data, a process usually known as quality assurance and quality control (QA/QC). In the case of the AURN, this is the role of the QA/QC Unit. All $PM_{2.5}$ measurements, whether from automatic monitors or manual samplers, are subject to a rigorous procedure of validation and ratification before they are published on the UK-AIR website[1], in part to meet the legal obligations of the Air Quality Directive (2008/50/EC).

30. QA/QC checks are employed to specifically ensure that AURN data are:

    - genuinely representative of ambient concentrations existing in the various areas under investigation;
    - sufficiently accurate and precise to meet monitoring objectives;
    - comparable and reproducible. Results must be internally consistent and comparable with international or other accepted standards, if these exist;
    - consistent over time. This is particularly important if long-term trend analysis of the data is to be undertaken; and

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[1] http://uk-air.defra.gov.uk

- representative over the period of measurement; for most purposes, a yearly data capture rate of not less than 90% is required for determining compliance with EU limit values. Data capture rates actually achieved are described later in this chapter.

The main aspects of QA/QC are site inter-calibrations and data ratification.

2.3.5 Network inter-calibration and site audits

31. Within the UK, a system of routine site audit and network inter-calibration has been in place for many years. The primary aims and objectives of the site audit and network inter-comparison exercise can be summarised as follows:

- to check and evaluate a wide range of analyser key functions via a comprehensive set of tests and calibrations; and

- to carry out on-site instrument calibrations using standards that are directly traceable to the QA/QC Unit Calibration Laboratory and national metrology standards.

32. This network inter-calibration is undertaken by the QA/QC Unit at six-monthly intervals and includes every site and every analyser in the network. The inter-calibration therefore provides detailed and quantified information on overall network performance. The aim of each audit exercise is to provide the following information:

- leak and flow checks to ensure that ambient air reaches the analysers without being compromised in any way;
- TEOM k_o evaluation (the stiffness of the glass tapered element). The analyser uses this factor (k_o) to calculate mass concentrations, so the value is calculated with test masses to determine its accuracy;
- particulate analyser flow rate checks to ensure that the flow rates through critical parts of the analyser are within specified limits; and
- site infrastructure and environment checks to ensure that metadata on the station remains accurate and up to date, and that any site safety issues are noted for action.

33. In principle these tests are performed to meet the requirements for QA/QC set out in CEN Standard Methods so as to comply with the Air Quality Directive. In the case of $PM_{2.5}$, the standard is only available in draft form, but UK participation in the CEN Working Group ensures that UK procedures are very similar to draft procedures. The QA/QC Unit is also accredited by the United Kingdom Accreditation Service under BS EN17025 to perform these tests; accreditation involves annual assessment by an external expert.

34. The site audit and inter-calibration results provide vital information for the data ratification process. For example, if the TEOM k_0 or flow rate checks are outside acceptable limits (2.5% and 10% respectively) then data may need to be re-scaled or rejected depending on both the reason for the outlier and severity of the discrepancy.

35. For non-automatic $PM_{2.5}$ monitoring, QA/QC may also include auditing of the filter weighing facilities to ensure that all documented procedures are being followed correctly, that the lab is managed and operated effectively, and that all staff are suitably trained for the tasks required of them.

2.3.6 Particulate data ratification

36. Initial data validation checks carried out by the Central Management and Control Unit (CMCU) and QA/QC units to allow "provisional" data to be reported to the public are followed by more thorough checking at three-month intervals. This latter process is called data "ratification". These checks ensure that the final reported data are reliable and consistent.

37. Ratification takes into account all the available information on the operation of the particulate monitors as outlined in the following paragraphs. The first step of ratification is to go back to the "raw" unvalidated data from the analyser; this allows traceability of all operations on the data within the ratification process to be maintained.

38. In general, the ratification of $PM_{2.5}$ monitoring data should follow similar procedures and allow the same full traceability as applies to other particulate and gaseous monitoring data. General procedures should include:

- ratification of the basic reporting averages (e.g. hourly or 15-minute data) in order to maximise data quality, not of the composite daily means which may mask instrument operating problems; and
- taking account of all information about the monitoring site and its surrounding location during the ratification process.

39. FDMS instruments require ratification of both base (non-volatile) and reference or purge (volatile) measurement channels. These parameters are used to calculate the total $PM_{2.5}$ concentration in ambient air on an hour-by-hour basis.

40. Since for an FDMS instrument, total $PM_{2.5}$ mass concentration is the sum of the volatile and non-volatile parts, the data processing and reporting of these three concentrations are inextricably linked. A total $PM_{2.5}$ concentration can only be reported if valid volatile and non-volatile measurements were made. Similarly, if the total $PM_{2.5}$ mass concentration is judged to be unreliable (e.g. excessive noise), then both the volatile and non-volatile parts are deleted. Figure 2.4 presents FDMS concentrations for a problematical AURN monitoring site where we are trying to measure especially low concentrations. There are several features to note here:

- The volatile concentrations during this period were low so that the total mass concentration is only slightly greater than the non-volatile concentration.
- Unfortunately, all air quality instruments are affected by signal noise. This noise becomes more apparent as sensitivity is increased to detect the lower concentrations. The FDMS instrument at this site appears to be producing noisy data throughout, believed to be related to difficulties in controlling the enclosure temperature.

- There are long periods of negative concentrations both for the volatile and non-volatile components of the $PM_{2.5}$ at this location, which cannot be exactly correct. However, this feature is particularly apparent because of the low concentrations, and the measurements still fall within the uncertainties of the method and based on current reporting rules would pass as ratified.

- In some cases FDMS instruments are prone to reporting negative data after a filter change but in this case it is clearly a more general problem. Instrument filter changes are however recommended to be undertaken only when essential, and the AURN QA/QC Unit has worked closely with the FDMS instrument supplier to develop upgraded filter changing procedures.

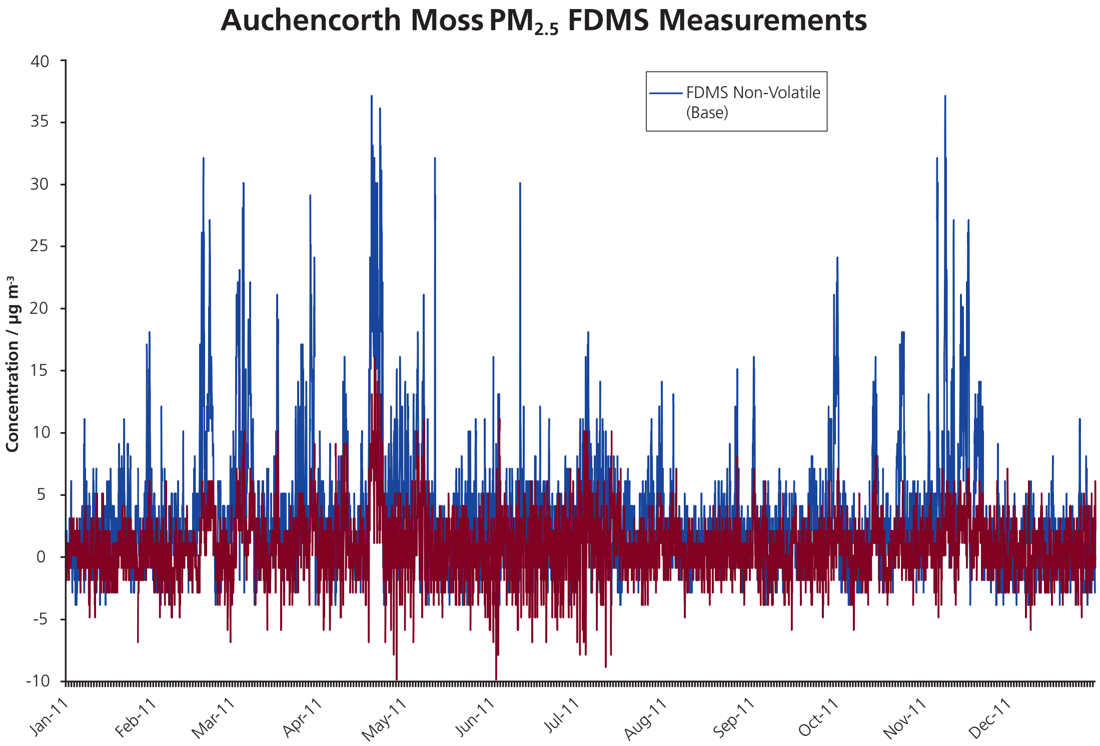

Figure 2.4: Example FDMS data. The y-axis shows the volatile and non-volatile components of $PM_{2.5}$ in µg m^{-3}.

41. For correct operation, FDMS instruments must operate within certain temperature and humidity tolerances. Hence, the ratification process also closely inspects these data. As a general rule there must always be at least 4°C separation between the internal and external dew points to prevent moisture condensation on the filter.

42. Provisional non-automatic (Partisol) $PM_{2.5}$ daily mean measurements are calculated by the CMCU from the change in mass of weighed filters following exposure to ambient air. The relevant instrument flow rates, filter exposure period, instrument alarms and diagnostics are all required for data ratification by the QA/QC Unit.

43. Ratification of the data will include checking that all instrument operating parameters are within specification and that the resulting measurements compare sensibly with other monitoring data at this site or from nearby locations (explained in more detail in Section 2.3.7).

2.3.7 Comparison with other data

44. In the case of $PM_{2.5}$ monitoring one of the most important data ratification checks is comparison with other data, both other pollutants monitored at the same site and $PM_{2.5}$ monitored on a regional basis. The two key criteria are as follows:

- Are $PM_{2.5}$ measurements at a site generally less than co-located PM_{10} concentrations as you would expect (allowing for occasional excursions within instrument uncertainties)?
- Are the volatile $PM_{2.5}$ measurements at a site consistent with regional concentrations?

QA/QC checks can easily be put in place to review instrument performance against these criteria.

45. Firstly, calculation and plotting of the daily difference between PM_{10} and $PM_{2.5}$ measurements from co-located instruments will show if there is any substantial bias towards $PM_{2.5}$ concentrations exceeding PM_{10}. Of course this will not identify in itself whether there is a problem with the $PM_{2.5}$ instrument over-reading or PM_{10} instrument under-reading. This decision will need to be made through interpretation of audit results, instrument servicing reports and using the experience of the QA/QC Unit.

46. Secondly, plotting regional volatile $PM_{2.5}$ data, together with statistical analysis, can enable the identification of any monitoring sites that may be operating as outliers. If outliers are detected then it may be that such data are invalid, depending of course on the number and quality of the other measurements in the region against which they are being compared. An example of regional volatile $PM_{2.5}$ data is shown in Figure 2.5. In this case further investigation would be required for London Harlington and Camden Kerbside which appear to be high and low respectively compared to the regional mean.

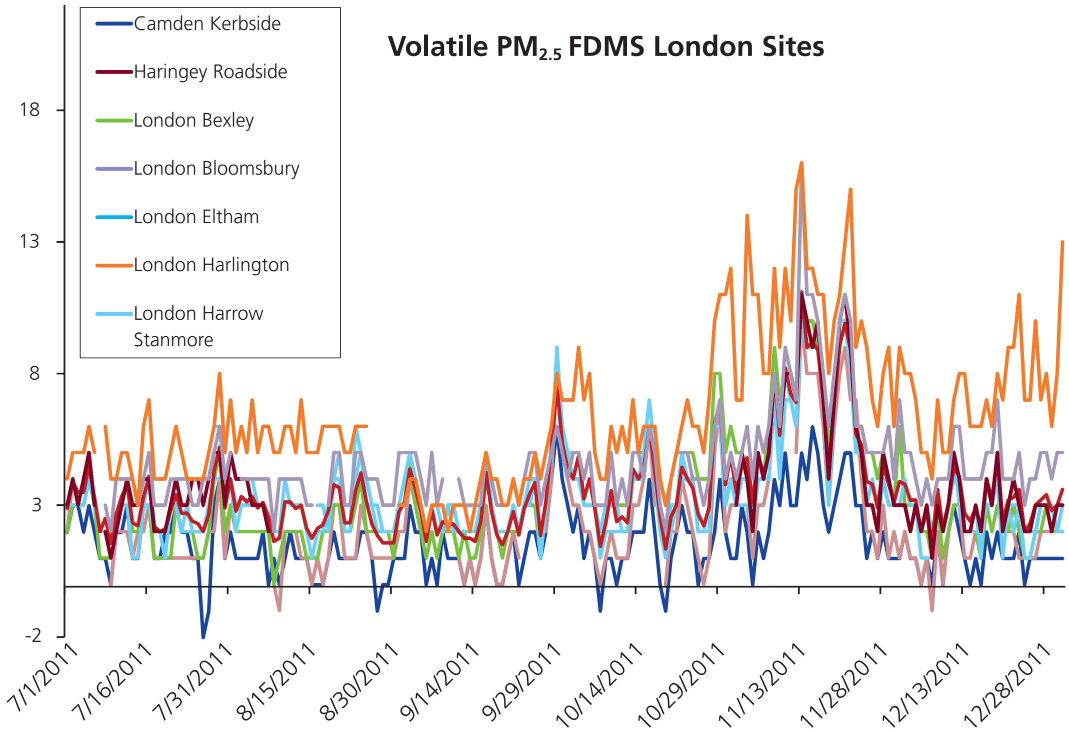

Figure 2.5: Regional volatile FDMS data. The y-axis shows $PM_{2.5}$ concentrations in µg m^{-3}.

2.3.8 Identification of poor data quality due to instrument failure

47. $PM_{2.5}$ monitoring instruments may fail for numerous reasons. The equipment is serviced at the regular six-monthly ESU (equipment support unit) visits but malfunctions can arise between services. Some faults are minor, such as sample flows just below optimum, but flow blockages can prevent the instrument from sampling ambient air. Ratification uses all available information, such as raw measurements, calibrations, alarms, engineer reports, etc., to decide if the data can be corrected or need to be rejected.

2.3.9 Main FDMS instrument problems and their effects

48. The FDMS analyser, used almost exclusively in the UK AURN for PM monitoring since 2009, presents many challenges for data processing and ratification. The challenges centre on response anomalies and mismatches, which can result in significant data rejection. This is in contrast to the earlier TEOM analysers, which, although not immune to problems themselves, tended not to experience such extended periods of unacceptable data quality and therefore generally met the 90% annual data capture requirement.

49. Many of the issues with FDMS data quality have been perceived to be related to the performance of the instruments' dryer units. Whilst any specific problem with the dryer unit is often difficult to identify, the following symptoms have often been observed:

- $PM_{2.5}$ higher than PM_{10} at locations where the two parameters are being measured in parallel;
- an increasing baseline offset on either $PM_{2.5}$ or PM_{10} measurements over an extended duration of months or even years. This is usually most evident in the volatile fraction but not exclusively so;
- a sudden (usually downwards) step change in the measured concentrations following the replacement of a dryer unit. Again this is usually most evident in the volatile fraction but not exclusively so;
- the volatile measurements at an individual site being consistently higher than those at other locations within a radius of 130 km; and
- poor comparison with other co-located or nearby reference equivalent measurements.

50. Whilst the dryer-related issues are still not fully understood, further research is ongoing to determine whether the baseline offset can be routinely quantified and therefore corrected for during data ratification. This will enable data of previously unacceptable quality to be recovered in future and thereby improve the overall ratified data capture of FDMS instruments.

51. Data capture refers to the amount of data meeting the uncertainty requirement compared with the largest achievable set of data for the year. In 2009, the network mean data capture for $PM_{2.5}$ was 85.8%, with 34 out of 76 sites falling below 90%. This compares with an average of 93.6%, with 13 out of 81 sites falling below 90% for the relatively simple ozone measurement, and 89.6%, with 34 out of 115 sites falling below 90% for the more complicated nitrogen dioxide (NO_2) measurements. In 2010, the corresponding numbers were 82.6% for $PM_{2.5}$ (40/78); 92.7% for ozone (15/80); and 90.5% for NO_2 (26/117). The data capture for $PM_{2.5}$ has therefore fallen short of Air Quality Directive requirements (90%), and is significantly less than that achieved for other pollutants. Further details about data capture at individual sites are available at http://uk-air.defra.gov.uk.

2.4 Methods used to produce data for other metrics in this report

2.4.1 $PM_{2.5}$ black carbon (aethalometry)

52. The black carbon data in Chapter 3 of this report were obtained from the UK's Black Carbon Network. Black carbon is measured by aethalometers, with size selection of the sampled aerosol being made by a $PM_{2.5}$ cyclone placed close to the inlet of the aethalometer. The Network has only been producing data since 2008, when aethalometers were installed to replace the earlier black smoke instruments.[2]

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[2] Further details about the Black Carbon Network are available at http://uk-air.defra.gov.uk.

53. Aethalometers quantify black carbon on filter samples based on the transmission of light through a sample. The sample is collected on a quartz tape, and the change in absorption coefficient of the sample is measured by a single pass transmission of light through the sample measured relative to a clean piece of filter. The system evaluates changes in two optical sensors (sample and reference), with the light source both on and off, such that independent measurements of the change in attenuation of the sample are produced for averaging periods of typically five minutes. The absorption coefficient for material added during the period, α (in m^{-1}), is calculated from the attenuation change combined with the area and volume of the sample, and converted to a black carbon concentration for the period, as a first approximation, using a mass extinction coefficient for the sample (16.6 $m^2\ g^{-1}$) chosen by the manufacturer to give a good match to elemental carbon (described in Section 2.4.3). In practice this mass extinction coefficient will vary with factors such as particle size, sample composition and quantity of material already on the filter, as discussed below. The reporting of black carbon in $\mu g\ m^{-3}$ should therefore be seen as a convention for scaling the optical absorption coefficient of the PM, rather than as an accurate measure of the concentration of some specific chemical component.

54. The aethalometers on the Network operate at two wavelengths, 880 nm and 370 nm. The 880 nm wavelength is used to measure the black carbon (BC) concentration of the aerosol, while the 370 nm wavelength gives a measure of the "UV component" of the aerosol. At wavelengths shorter than about 400 nm, certain classes of organic compounds (such as polycyclic aromatic hydrocarbons and also certain compounds present in tobacco smoke and fresh diesel exhaust) start to show strong UV absorbance. The UV component can therefore in principle be used as an indicator of oil and solid fuel emissions.

55. The UV component concentration presented in this report is obtained by subtracting the measured BC concentration from the concentration measured by the 370 nm source. The UV component is not a real physical or chemical material, but a parameter based on UV absorption due to the mix of organic compounds measured at this wavelength. This fictional material 'UVPM' is expressed in units of 'BC Equivalent'.

56. It is well known that the assumption of constant mass extinction coefficient does not hold as the filter spot darkens, leading to non-linearity in the aethalometer response. The effect of this non-linearity is that the aethalometer under-reads at high filter tape loadings. To correct for non-linearity, the model developed by Virkkula *et al.* (2007) has been used to correct for increased attenuation due to spot darkening during sampling. This uses a simple equation $BC_{corrected} = (1+k.ATN)\ BC_{uncorrected}$, where ATN is the light attenuation by the filter spot, and k is a parameter determined for each filter spot such that continuity between adjacent filter spots is greatly improved. All of the black carbon and UV component results in this report have been corrected by this method. Inevitably uncertainties are connected with this correction, but these have not yet been fully evaluated.

57. Black carbon data have the advantages of sensitivity, high time resolution and high data capture, because of the relatively simple physical principles of the instrument. However, interpretation of the data should take into account the fact that the measurement does not correspond to a specific chemical component of the PM. The measured parameter is similar to elemental carbon, but this metric itself is not precisely defined, as described below. Also, standardisation and QA/QC procedures for black carbon are at a less advanced stage than for regulated pollutants, so that comparisons with data from outside the Network will have limitations.

2.4.2 PM_{10} nitrate, sulphate and chloride

58. Daily measurements of the inorganic components of PM_{10} (sulphate, nitrate and chloride) are made within the Particle Numbers and Concentrations Research Network,[3] which uses a Thermo Partisol 2025 sequential air sampler. Since 2007, ultrapure quartz filters (Pallflex Tissuquartz) have been used and cut in half to allow for the analysis of both elemental carbon/organic carbon and inorganic components. Further details about the Network are available at http://uk-air.defra.gov.uk.

59. The Partisol 2025 sampler, as described in Section 2.3.3, provides uninterrupted sampling of ambient air and automatic exchange of filters for up to 16 days. The instrument uses an airflow of 1 $m^3\ hr^{-1}$ through a PM_{10} inlet and the filter temperature is maintained to within ±5°C of ambient temperature. The exposed filters are stored in small polypropylene filter bags and kept in a cold room until analysis to prevent further loss of semi-volatile components such as ammonium nitrate. Extracts from the filters are dissolved in an eluent of 3.5 mM sodium carbonate and 1 mM sodium hydrogen carbonate and analysed in the laboratory by ion chromatography for sulphate, nitrate and chloride content. Ambient concentrations are derived from the mass measured on the filter and the airflow during the sampling period. Calibration is via gravimetrically-prepared solutions.

60. CEN has produced a Technical Report standardising these measurements, TR 16269:2011 *Ambient air: Guide for the measurement of anions and cations in* $PM_{2.5}$. In practice, although standardisation is less advanced than for other regulated pollutants, the analytical process is relatively simple, and analytical results should be relatively robust. Comparisons with other data are likely to be more compromised by losses of semi-volatile material before analysis, especially of ammonium nitrate, which can be a substantial fraction of the nitrate and the $PM_{2.5}$, as described in Chapter 3.

2.4.3 PM_{10} elemental carbon/organic carbon

61. Daily measurements of the elemental carbon/organic carbon (EC/OC) components of PM_{10} are made within the Particle Numbers and Concentrations Research Network. A Thermo Partisol 2025 sequential air sampler is used, as for the sulphate, nitrate and chloride components above. Ultrapure quartz filters (Pallflex Tissuquartz) are used.

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[3] Operated by the National Physical Laboratory on behalf of Defra and the Devolved Administrations.

62. In the laboratory, a 1.5 cm^2 punch is taken from each filter and analysed for elemental and organic carbon in a thermo-optical procedure in which the metrics are method-defined. It involves heating the sample to remove the PM from the filter, and conversion of the carbon to methane, followed by detection by flame ionisation in a Sunset Laboratories instrument. In a helium atmosphere, the sample is gradually heated to 870°C to remove organic carbon on the filter. During this first phase there are usually some organic compounds that are pyrolytically converted to elemental carbon. Measuring the transmission and reflection of a laser beam through the filter continuously monitors this pyrolytic conversion and allows a correction to be made for it. Elemental carbon is detected in the same way after heating to 870°C in the presence of oxygen and helium. The protocol used is termed Quartz, a close variant of the NIOSH (US National Institute for Occupational Safety and Health) protocol. Other protocols, based on different temperatures and timings, are used by other groups in the UK, Europe and elsewhere, as described below. The optical correction can be made using either the transmitted or reflected signal.

63. In essence the method provides a measurement of total carbon (TC), the accumulation of all carbon atoms released from the filter during all phases of heating, which is divided into EC and OC (TC = EC + OC) according to the time at which the carbon was released. The laser signal is used to determine when the time division is made, based on the assumption that when the laser signal returns to its initial value, any pyrolytically converted material has been removed. In practice the TC value can be calibrated accurately using standard solutions of organic material on clean filters, but the EC/OC split can vary significantly depending on the laser signal used (transmittance or reflectance), as the underlying assumption is not strictly valid. The chemical significance of the EC/OC split will also depend on the broader composition of the particulate matter and the temperature protocols used, and is complicated further by the consideration of carbonates, which can be significant components of the TC that do not rightly belong in either the EC or OC categories.

64. Broadly speaking, the use of a reflectance signal for the pyrolysis correction leads to significantly higher EC values than when a transmittance signal is used (by up to around a factor of two), with correspondingly less OC. Protocols that have a lower maximum temperature during the inert gas heating phase, such as the EUSAAR 2 protocol with a maximum of 650°C, tend to record significantly higher EC values than protocols such as NIOSH and Quartz (again by up to around a factor of two), with correspondingly less OC (see for example Watson *et al*., 2005, and Cavalli *et al*., 2010).

65. Comparisons of EC and OC data therefore need to take into account the method used for their analysis. Standardisation of EC/OC methods for European regulation is at an early stage. A Technical Report TR 16243:2011 *Ambient air quality – Guide for the measurement of elemental carbon (EC) and organic carbon (OC) deposited on filters* has been produced by CEN, but this is aimed at reducing variations within several prescribed methods, each of which will produce different results, rather than defining a single method.

66. The Birmingham EC/OC data used in Chapters 3 and 4 were obtained using a protocol similar to EUSAAR II, as described in the references given in those chapters.

2.4.4 $PM_{2.5}$ elemental carbon/organic carbon

67. Daily EC/OC measurements of the $PM_{2.5}$ size fraction, using the same analysis methods as for the PM_{10} fraction described above, started at Harwell and Auchencorth Moss in late 2011. However, no ratified results are yet available to include in this report.

2.4.5 $PM_{2.5}$ anion and cation measurements using the MARGA

68. Two MARGA instruments (manufactured by Metrohm Applikon) are operated as part of the UK Eutrophying and Acidifying Atmospheric Pollutants Network at the rural sites Auchencorth Moss and Harwell. These provide hourly measurements of ionic components in $PM_{2.5}$ (NH_4^+, Na^+, K^+, Ca^{2+}, Mg^{2+}, Cl^-, NO_3^-, and SO_4^{2-}), together with similar analysis of PM_{10}, and measurement of the water-soluble gases NH_3, HCl, HNO_3, HNO_2 and SO_2.

69. The instrument contains an automated continuous-flow wet rotating denuder and steam-jet aerosol samplers. The denuder removes gases from the sampled airstream before the residual particles (which pass through the denuder) are converted by steam into droplets which are subsequently captured and analysed. The solutions of dissolved gases and dissolved particles are analysed online by ion chromatography, using parallel systems for cations and anions. Dual samplers are installed at the UK EMEP Supersites (Harwell and Auchencorth Moss), with separate analysis of PM_{10} and $PM_{2.5}$ aerosols. Internal standards of Li^+ (lithium cations) and Br^- (bromide anions) are used for calibration checks.

70. The steam-jet aerosol collector measures only water-soluble aerosol, with parallel and simultaneous ion chromatography for anions and cations. Some discrepancies have been noted at Auchencorth Moss, with $PM_{2.5}$ occasionally giving higher readings than PM_{10}. At least part of this is attributed to lack of flow control leading to uncertainty in the volume of air sampled. Data submitted to EMEP are flagged as uncertain. This problem has been rectified on later models (such as the one installed in 2009 at Harwell) and the Auchencorth instrument was upgraded to include mass flow control during autumn 2011. The MARGA has been operating at Auchencorth since June 2006 with varying reliability in terms of data capture. Recent upgrades to software have improved data capture and the latest planned upgrade should improve matters further.

71. As described in Chapter 3 later, concerns about the quality of the MARGA data have meant that their analysis has not been included in the report.

2.4.6 Acid Gases and Aerosols Monitoring Network (AGANet) measurements using the DELTA system

72. The DELTA system uses a long-time integrated measurement (four weeks) of trace gases and particles. Gases are removed on a series of acid- and alkali-coated cylindrical denuders prior to trapping particles on an alkali-impregnated filter. The alkali decomposes any trapped ammonium nitrate (NH_4NO_3) to release ammonia (NH_3) which is subsequently trapped on an acid-washed filter. Sampling is done with no size-selective inlet to avoid losses of gases such as nitric acid (HNO_3). Measurements at CEH have shown that the effective

cut-off for particle sampling is around 4.5 µm (Tang *et al*., 2009). Denuder and filter samples are analysed at CEH Lancaster using ion chromatography (for the anions), flow injection permeation/conductivity (for ammonium ions) and ICP-OES (for the metals).

2.5 Summary

2.5.1 What does the $PM_{2.5}$ metric measure?

73. $PM_{2.5}$ data show, in principle, the mass concentration of airborne particles with an aerodynamic diameter less than 2.5 µm, the size range being based on the high risk respirable convention for the human lung, and the size-selection curve being set by the reference inlet system in EN 14907. In practice, measurement of the mass is complicated by the presence of semi-volatile particles, variations in water content and other factors, such that the $PM_{2.5}$ metric does not correspond to definite physical or chemical components of the air, but is in effect defined by the measurement method. Within the United Kingdom AURN, the relevant measurement method is that set out in CEN standard EN 14907, the method referred to by the Ambient Air Quality Directive.

74. The difficulties of PM measurement are reflected in the fact that the required measurement uncertainty for PM in the Directive is ±25% with a 95% level of confidence, at concentrations close to the limit value, while for most gaseous pollutants the comparable value is ±15%.

75. Considerable effort is spent ensuring that reported AURN $PM_{2.5}$ data are both internally consistent and comparable with reference method data. It should be appreciated, however, that the most widely used instrumentation (FDMS) is based on relatively new and complex technology designed to provide an automatic equivalent to the reference method, which is not directly amenable to automation.

2.5.2 How do PM_{10} and $PM_{2.5}$ measurement issues compare?

76. The uncertainties in $PM_{2.5}$ data, expressed as percentages, are inherently larger than for PM_{10} data. This is because the absolute $PM_{2.5}$ mass is smaller, making variations in the mass of the filter (required by the reference method) more significant, and also because in general the $PM_{2.5}$ fraction will contain a larger proportion of semi-volatile and hygroscopic material, which means that the $PM_{2.5}$ mass is subject to more variation due to environmental conditions during and after sampling. Conclusions drawn from $PM_{2.5}$ data must therefore be qualified by these inherent measurement limitations.

2.5.3 Do we have robust measurements of $PM_{2.5}$?

77. There are at least three aspects to this question. First, we need to consider whether the AURN measurements meet the reporting requirements of the Directive, specifically in terms of measurement uncertainty (±25%) and data capture (required to be greater than 90%). Data capture refers to the amount of data meeting the uncertainty requirement compared with the largest achievable set of data for the year. In 2009, the network mean data capture for $PM_{2.5}$ was 85.8%, with 34 out of 76 sites falling below 90%. This compares with an

average of 93.6%, with 13 out of 81 sites falling below 90% for the relatively simple ozone measurement, and 89.6%, with 34 out of 115 sites falling below 90% for the more complicated NO_2 measurements. In 2010, the corresponding numbers were 82.6% for $PM_{2.5}$ (40/78), 92.7% for ozone (15/80) and 90.5% for NO_2 (26/117). The robustness of the data therefore falls short of the Directive requirements, and of that achieved by other pollutants. It must be appreciated, however, that technical discussions on how best to operate automated $PM_{2.5}$ monitoring networks and assess their uncertainties are currently active at a European level, although they are at a much less advanced stage than for gaseous pollutants. UK representatives are prominent in these discussions.

78. Second, we need to consider whether conclusions about changes smaller than the ±25% uncertainty required by the Directive can be drawn from UK data. Much of the measurement uncertainty is associated with differences from the reference method, which is itself more intrinsically uncertain than those used for gaseous pollutants. Data obtained using the same type of instrument and the same QA/QC procedures (such as FDMS data from individual sites in the AURN) are expected to be comparable with each other such that variations are significantly less than 25%. Variations will be less when longer term averages are taken, removing random variations. However, relevant practical issues in the operation of such relatively complicated instruments are still being discovered and evaluated, and it is difficult to put a precise figure on the relative uncertainties.

79. This aspect is directly relevant to checking compliance with the exposure reduction target in the 2008 Air Quality Directive, based on assessing the national $PM_{2.5}$ average exposure indicator (AEI) over periods ten years apart. For the United Kingdom, this is expected to mean complying with a 15% reduction target. If there is any significant change in the monitoring instrumentation during the ten-year period, the measured change in the AEI is likely to have a large relative uncertainty, even if attempts are made to correct for the effects of the instrument change. If the same FDMS instruments are used throughout the period, the operational issues may still mean difficulties in quantifying the change in the AEI with sufficient accuracy. Of course, all measurements taken to determine compliance with a limit value or target value have an associated measurement uncertainty, so there is nothing new in the fact that uncertainties can obscure a clear-cut result; however, the nature of the exposure reduction target and the difficulties of $PM_{2.5}$ measurement conspire to mean that the available data may not be fit for purpose.

80. A further aspect to consider is whether the measurements are robust enough to improve our understanding of the sources of primary $PM_{2.5}$ and $PM_{2.5}$ precursors, together with the chemical and other processes involved in $PM_{2.5}$ formation and evolution, or in other words whether we can use PM measurements effectively to evaluate $PM_{2.5}$ models and emissions inventories. As discussed in Chapter 5, the uncertainties in $PM_{2.5}$ measurement data make them far from ideal for this purpose. This situation can be seen as the result of a combination of factors, namely that the $PM_{2.5}$ metric is defined operationally (making it difficult to model *a priori*), the relatively large uncertainties that arise in the practical measurement of the metric (as described in this chapter), and the inherent complexities in the formation and evolution of airborne particles.

2.5.4 What about measurements of chemical components of $PM_{2.5}$?

81. Measurements of specific components of $PM_{2.5}$ used within this report can have lower uncertainties than the mass concentration itself, especially if they are non-volatile, as they are independent of water content. However, specific instruments such as the MARGA at Auchencorth Moss have had ongoing operational problems making the data less reliable. Moreover, care must be taken when comparing method-dependent quantities such as black carbon, elemental carbon and organic carbon. In some cases, specific components of PM_{10} have been used in this report where $PM_{2.5}$ data are not available, and the inclusion of the coarse size fraction needs to be taken into consideration.

2.6 Recommendations

82. **Measurements of PM2.5 in the UK depend heavily on the FDMS instrument, which has a relatively short track record in monitoring networks. AQEG recommends that issues including long-term reliability, dryer performance and the handling of semi-volatile components are further investigated with the aim of better understanding the measurement results and of improving data capture and measurement uncertainty.**

83. **At present the measurement of PM2.5 remains a challenge, with current measurements falling below the requirements of the Air Quality Directive. AQEG recommends a focused working group is assembled to address the achievement of Directive requirements using current methods.**

Annex 1 – $PM_{2.5}$ monitoring sites in the UK

Table A1.1: $PM_{2.5}$ monitoring sites in the UK Automatic Urban and Rural Network (AURN) 2010.

Site name	Site type	Start date	Instrument type
Aberdeen	Urban background	28/05/2009	FDMS
Acocks Green	Urban background	18/03/2011	FDMS
Auchencorth Moss	Rural background	01/01/2006	FDMS
Auchencorth Moss	Rural background	2006	Partisol
Belfast Centre	Urban background	07/11/2008	FDMS
Birmingham Tyburn	Urban background	23/01/2009	FDMS
Birmingham Tyburn Roadside	Urban traffic	12/02/2009	FDMS
Blackpool Marton	Urban background	28/01/2009	FDMS
Bournemouth	Urban background	01/01/2009	Partisol
Brighton Preston Park	Urban background	30/05/2008	Partisol
Bristol St Pauls	Urban background	08/10/2008	FDMS
Bury Roadside	Urban traffic	07/05/2009	FDMS
Camden Kerbside	Urban traffic	19/02/2009	FDMS
Cardiff Centre	Urban background	09/10/2008	FDMS
Carlisle Roadside	Urban traffic	17/03/2009	FDMS
Chatham Roadside	Urban traffic	02/07/2010	FDMS
Chepstow A48	Urban traffic	09/02/2010	FDMS
Chesterfield	Urban background	02/02/2009	FDMS
Chesterfield Roadside	Urban traffic	01/07/2009	FDMS
Coventry Memorial Park	Urban background	15/01/2009	FDMS
Derry	Urban background	21/02/2008	FDMS
Eastbourne	Urban background	01/07/2009	FDMS
Edinburgh St Leonards	Urban background	12/11/2008	FDMS
Glasgow Centre	Urban background	06/02/2009	FDMS
Glasgow Kerbside	Urban traffic	29/05/2009	FDMS
Grangemouth	Urban industrial	15/01/2009	FDMS
Haringey Roadside	Urban traffic	18/02/2009	FDMS
Harwell	Rural background	14/08/2009	FDMS
Harwell	Rural background	07/09/2000	Partisol
Hull Freetown	Urban background	06/10/2008	FDMS
Inverness Roadside	Urban traffic	06/12/2006	Partisol
Leamington Spa	Urban background	02/02/2009	FDMS
Leeds Centre	Urban background	16/01/2009	FDMS
Leeds Headingley	Urban traffic	02/04/2009	FDMS
Leicester Centre	Urban background	08/10/2008	FDMS
Liverpool Speke	Urban background	13/11/2008	FDMS

London Bexley	Suburban background	21/10/2008	FDMS
London Bloomsbury	Urban background	14/01/2009	FDMS
London Eltham	Suburban background	05/05/2008	FDMS
London Harlington	Urban industrial	29/01/2009	FDMS
London Harrow Stanmore	Urban background	16/12/2008	FDMS
London Marylebone Road	Urban traffic	20/03/2009	FDMS
London Marylebone Road	Urban traffic	07/09/2000	Partisol
London North Kensington	Urban background	17/12/2008	FDMS
London North Kensington	Urban background	07/09/2000	Partisol
London Teddington	Urban background	15/01/2009	FDMS
London Westminster	Urban background	25/12/2008	Partisol
Manchester Piccadilly	Urban background	23/01/2009	FDMS
Middlesbrough	Urban background	01/03/2009	FDMS
Newcastle Centre	Urban background	07/10/2008	FDMS
Newport	Urban background	23/01/2009	FDMS
Northampton	Urban background	05/09/2008	Partisol
Norwich Lakenfields	Urban background	12/112009	FDMS
Nottingham Centre	Urban background	21/01/2009	FDMS
Oxford St Ebbes	Urban background	24/02/2009	FDMS
Plymouth Centre	Urban background	22/10/2009	FDMS
Port Talbot Margam	Urban industrial	23/04/2008	FDMS
Portsmouth	Urban background	28/01/2009	FDMS
Preston	Urban background	30/01/2009	FDMS
Reading New Town	Urban background	17/10/2008	FDMS
Rochester Stoke	Rural background	15/07/2009	FDMS
Salford Eccles	Urban industrial	22/01/2009	FDMS
Sandy Roadside	Urban traffic	27/01/2009	FDMS
Sheffield Centre	Urban background	21/01/2009	FDMS
Southampton Centre	Urban background	18/11/2008	FDMS
Southend-on-Sea	Urban background	03/02/2009	FDMS
Stanford-le-Hope	Urban traffic	01/04/2009	FDMS
Stockton-on-Tees Eaglescliffe	Urban traffic	06/09/2008	BAM
Stoke-on-Trent	Urban background	27/11/2008	FDMS
Storrington Roadside	Urban traffic	01/08/2009	FDMS
Sunderland Silksworth	Urban background	22/01/2009	FDMS
Swansea Roadside	Urban traffic	26/09/2006	FDMS
Warrington	Urban background	09/02/2009	FDMS
Wigan Centre	Urban background	26/02/2009	FDMS
Wirral Tranmere	Urban background	30/01/2009	FDMS
Wrexham Roadside	Urban traffic	09/12/2009	Partisol
York Bootham	Urban background	15/01/2009	FDMS

Chapter 3

Concentrations and composition of $PM_{2.5}$

3.1 Introduction

1. A national $PM_{2.5}$ monitoring network was established in the UK in 2009 to meet EU Ambient Air Quality Directive (2008/50/EC) requirements. Before then few measurements of $PM_{2.5}$ concentrations were made. There is still little information on $PM_{2.5}$ composition. This chapter summarises the published data on $PM_{2.5}$ concentrations and composition, and presents new analyses of existing $PM_{2.5}$ measurements. It also draws on the recent review of $PM_{2.5}$ in the UK carried out by Laxen *et al.* (2010).

3.2 $PM_{2.5}$ concentrations across the UK: Temporal variations and trends

2. Annex 1 provides a list of sites measuring $PM_{2.5}$ within the Automatic Urban and Rural Network (AURN). Of the operational sites in the Network, 47 are classified as urban background (including sites classified officially as urban background, urban centre, suburban and airport[1]), 18 as traffic sites, four as industrial and three as rural. Of these sites, 66 operate FDMS analysers, six have Partisol only and one a BAM, while three sites with FDMS analysers had Partisols running in parallel (see Section 2.3 for information on these measurement methods). The current AURN includes 46 sites in England (excluding London), 11 sites in London, seven sites in Scotland, six sites in Wales and two sites in Northern Ireland.[2] A number of other sites with reference equivalent monitors outside of the AURN are operated by local authorities in London, and there is one site in Lisburn, Northern Ireland, for which data are readily available. Additional sites across the UK are operated by other local authorities, industries, universities and research institutes; however, information on this monitoring is not readily available and data from these sites may not be subject to the same rigorous data quality procedures as those in the national networks which meet the requirements of the Air Quality Directive.

3. $PM_{2.5}$ concentrations for 2010 have been examined by time of day and by season. For the analyses in this report only, data have been removed for two days, 6 and 7 November, as the concentrations were clearly influenced by Bonfire night celebrations at most sites across the UK. To retain these would confound the more general diurnal and seasonal patterns that are relevant to an understanding of the general behaviour of $PM_{2.5}$ in UK air.

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[1] There is one site, Harlington, officially classified as 'airport', however it is around 1 km from Heathrow Airport, and as such, $PM_{2.5}$ concentrations will be affected by the airport to a very limited extent. It is thus better to treat this site as an urban background site for $PM_{2.5}$.

[2] The locations of the sites and site photos are available at: http://aurn.defra.gov.uk.

3.2.1 Diurnal variations of $PM_{2.5}$ at urban background sites

4. The diurnal cycle of $PM_{2.5}$ during 2010 is summarised in Figure 3.1a for four areas of the UK. Concentrations have been averaged by hour of the day using local time, i.e. they take account of the change from winter to summer time. The plots show average concentrations for the hour beginning the measurement period, i.e. the value shown for 23:00 is the average over the period 23:00 to 24:00. The concentration scale is the same on all the urban background plots. The delineation of the four areas is shown in Figure 3.1b. The diurnal cycle is fairly limited in scale, spanning just a few μg m^{-3}. The central UK, southern UK and London sites have a very similar pattern, with the lowest concentrations occurring during the afternoon, between 13:00 and 17:00. They also show a morning peak, around 08:00-09:00, and a late evening peak, around 21:00. The concentrations at the northern UK sites are lower overall than those in the other three areas. There is also no afternoon dip in concentrations at the northern UK sites; the lowest concentrations thus occur during the early morning period, around 04:00-06:00. This observation is consistent with the lesser role played by secondary nitrates in the north of the UK.

5. Figure 3.2 shows distinct differences in the diurnal patterns for winter and summer at southern UK sites in 2010, although the lowest concentrations still occur during the afternoon in both seasons. The winter concentrations show more substantial morning and late evening peaks than do the summer values, which may be related to greater domestic heating requirements at these times of day. These patterns are essentially the same as those reported for 2009 by Laxen *et al.* (2010), who also analysed the diurnal patterns for nitrate, as well as those for the volatile component of $PM_{2.5}$, as defined by the FDMS analysers. They concluded that the afternoon dip was probably due to the loss of the semi-volatile nitrate particles during the warmer afternoon period. The morning peak was probably related to road traffic and domestic emissions, with the late evening peak probably related to domestic sources, both from heating and cooking. The link with heating can also be seen in the results for black carbon in Figure 3.23. Laxen *et al*. (2010) also considered that the evening peak may in part be due to reduced dispersion arising from the more stable atmospheric conditions during the night, together with a contribution from volatile particulate matter (PM) (i.e. nitrate and organic compounds) condensing on ambient particles at lower night-time temperatures. The average diurnal $PM_{2.5}$ ranges are nevertheless relatively small, around 5 μg m^{-3} in winter and 2 μg m^{-3} in summer, relative to the seasonal mean concentrations of around 17 μg m^{-3} in winter and 11 μg m^{-3} in summer, suggesting that local sources are not dominant.

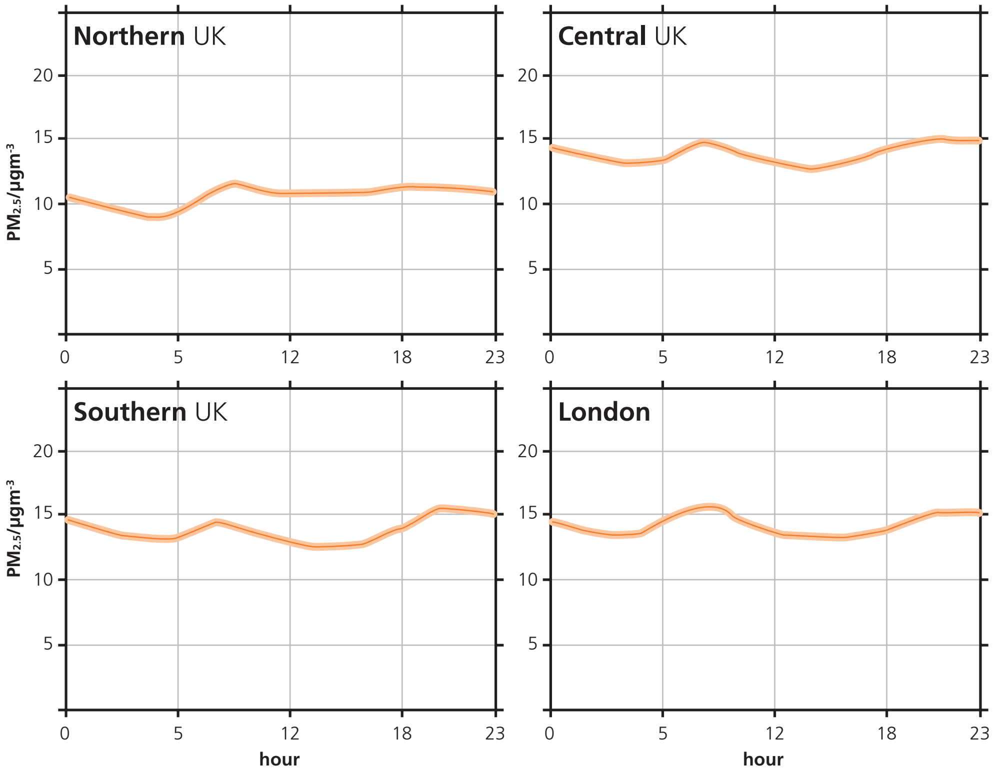

Figure 3.1a: Variation of $PM_{2.5}$ concentrations (µg m^{-3}) at urban background sites by hour of the day in 2010 at sites in northern UK (n=6), central UK (n=17), southern UK (n=10) and London (n=8). The shading represents the 95% confidence interval of the mean.

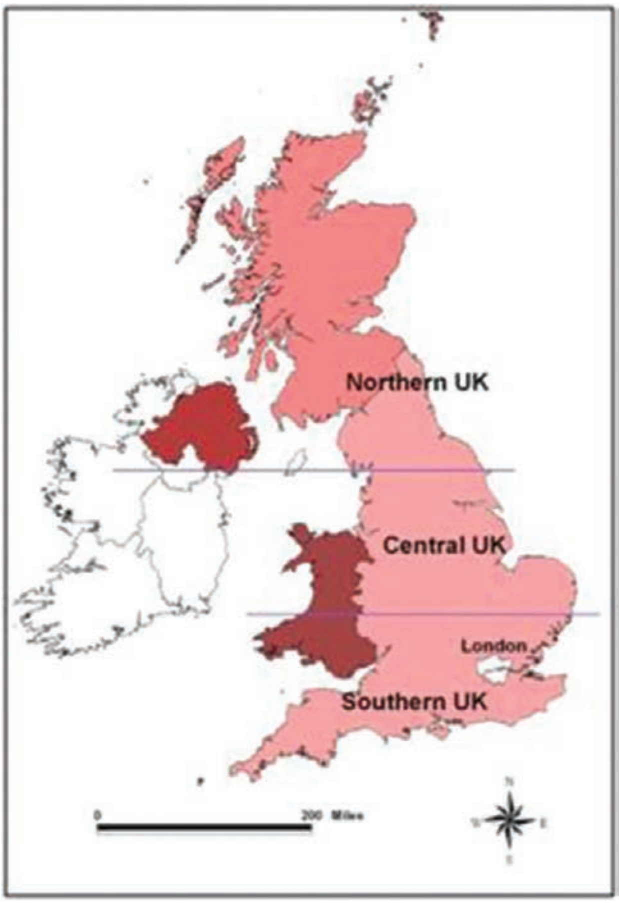

Figure 3.1b: Areas of the UK used in analysis of $PM_{2.5}$ monitoring data.

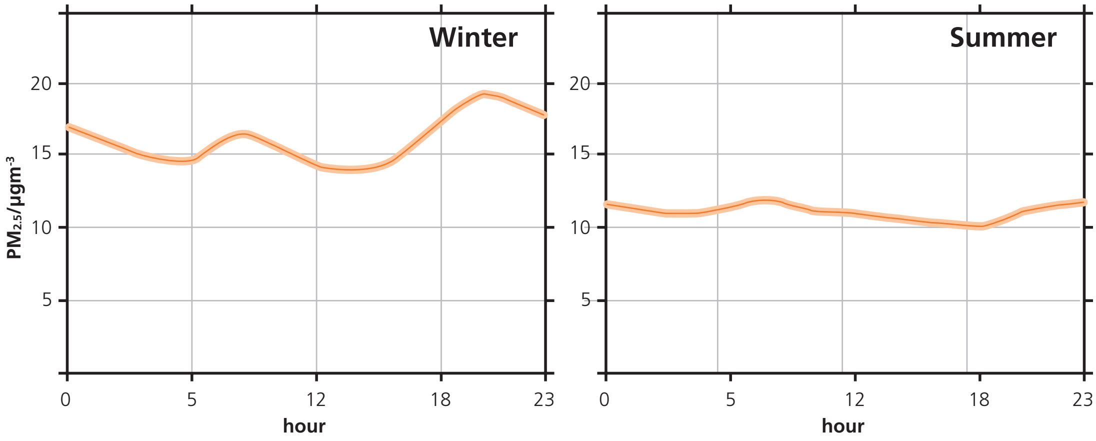

Figure 3.2: Variation of $PM_{2.5}$ concentrations (µg m^{-3}) at urban background sites by hour of the day in 2010 at southern UK sites (n=10) in winter and summer. The shading represents the 95% confidence interval of the mean.

3.2.2 Diurnal variations of $PM_{2.5}$ at roadside and industrial sites

6. The diurnal patterns for roadside and industrial sites during 2010 are shown in Figure 3.3. The diurnal range is slightly larger at roadside sites than at urban background sites, while the variation at industrial sites is broadly similar to that at urban background sites (*cf*. Figure 3.1a). However, at roadside sites the morning increase is greater and the afternoon dip is less prominent than at the urban background sites, with concentrations remaining above the early morning (03:00-05:00) minimum (*cf*. Figure 3.3 roadside and Figure 3.1a). While the morning peak is consistent with emissions during the morning rush hour, there is no clear peak during the evening rush hour (16:00-18:00), although concentrations during this period are somewhat higher than those seen in the pattern at urban background sites, suggesting an influence of the higher traffic flows at this time that is being masked by changing background concentrations, i.e. the traffic increment during the rush hour is superimposed on concentrations that are increasing at this time due to sources contributing to the late evening peak, including the condensation of semi-volatile species. A smaller evening traffic-related rush hour peak in $PM_{2.5}$ is to be expected, owing, in part, to fewer lorries on the road at this time of day, and to the greater atmospheric turbulence at this time of day compared to the morning rush hour. These effects are also seen in the nitrogen oxides (NO_x) diurnal pattern in Figure 3.9 later in this chapter.

7. The range of diurnal concentrations is much lower at industrial sites. The morning and evening peaks are still evident, suggesting that the background pattern is playing a dominant role at these sites with only a minimal contribution from industrial activities.

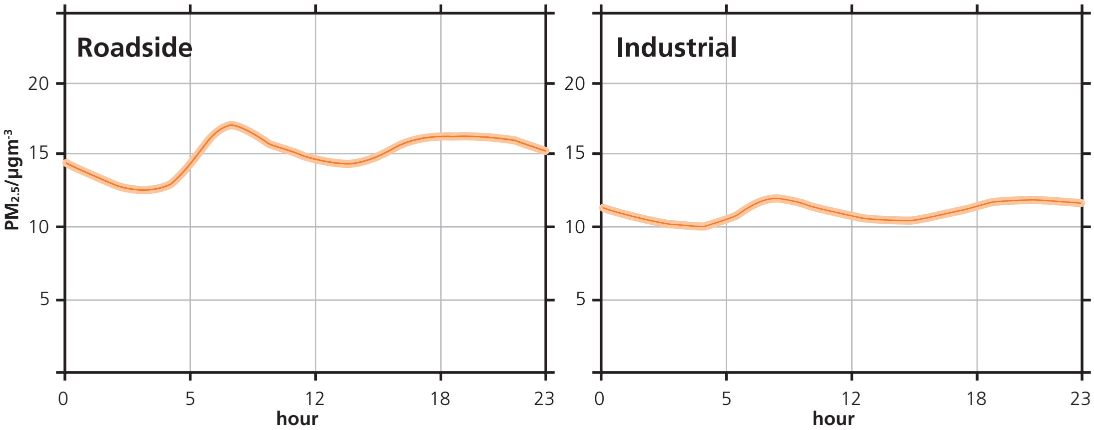

Figure 3.3: Variation of $PM_{2.5}$ concentrations (µg m^{-3}) by hour of the day at roadside (n=9) and industrial sites (n=4) in 2010. The shading represents the 95% confidence interval of the mean.

3.2.3 Diurnal variations at a site in Lisburn, Northern Ireland

8. Laxen *et al*. (2010) noted that the site in Lisburn, Northern Ireland, was anomalous, showing much higher concentrations in 2009 that expected. This anomaly was retained in 2010, with a much greater diurnal variation in $PM_{2.5}$ concentrations (Figure 3.4). The range over the day is around five times greater than at other urban background sites (*cf*. Figure 3.1). This is primarily due to high overnight concentrations at this site, which peak at a similar time to the peaks seen at other background sites (*cf*. Figure 3.2). It is suspected that these high concentrations are due to domestic heating, which is still supplied in part by solid fuel in Northern Ireland. This is supported by the observation that the evening peak is much larger during the winter than the summer (not shown). It is similar to the pattern for black carbon concentrations at Strabane (Figure 3.23), which has also been ascribed to domestic heating. The night-time peak will also relate to the more stable atmospheric conditions at night, which will enhance the impact of local emissions at this time. **Clearly domestic solid and/or liquid fuel used for domestic heating can be a significant source of $PM_{2.5}$, with black carbon being a major constituent. This source makes its most significant contribution during the evening.**

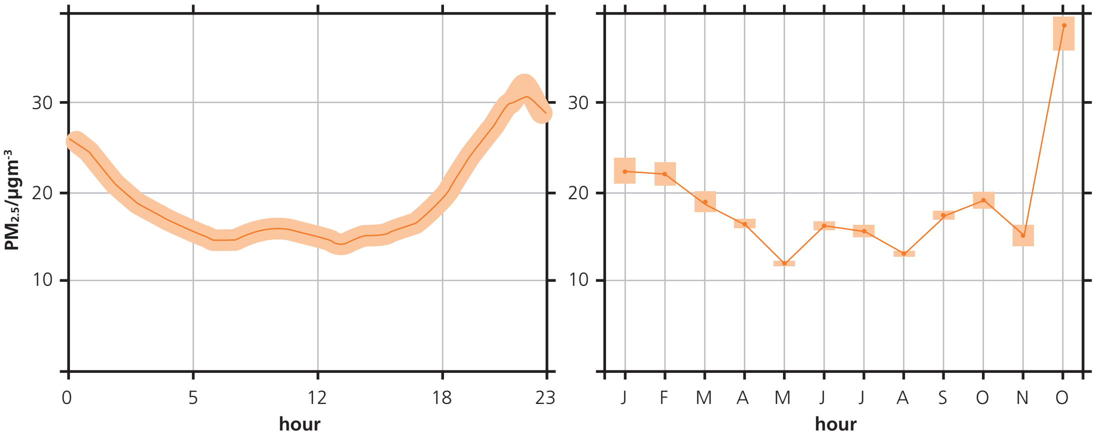

Figure 3.4: Variation of $PM_{2.5}$ concentrations (µg m^{-3}) by hour of the day and month of the year at the Lisburn site in Northern Ireland in 2010. The shading represents the 95% confidence interval of the mean. Note the different scale to the other figures.

3.2.4 Seasonal variations in PM$_{2.5}$ at urban background sites

9. The pattern of PM$_{2.5}$ concentrations by month of the year is summarised in Figure 3.5 for urban background sites in four geographic areas of the UK. The pattern during 2010 was broadly similar at all sites (and at roadside and industrial sites, not shown), with the concentrations declining steadily from January through to a minimum in July/August, before rising again to December. This is broadly similar to the pattern seen in 2009, although the highest concentrations in 2009 were in January not December (as was also the case in London in 2010) (Laxen *et al*., 2010). The patterns seen relate to greater emissions of both primary PM and secondary PM precursors during the winter, due to the higher heating load, as well as to the reduced dispersion of local sources during the winter period. It will also relate, in part, to the loss of semi-volatile PM during summer months, which will be less prevalent during winter months. The range of monthly means is substantial, from 6 to 21 µg m^{-3} in northern UK, from 8 to 22 µg m^{-3} in central UK, from 9 to 20 µg m^{-3} in southern UK and from 9 to 22 µg m^{-3} in London. The particularly high monthly mean for December 2010 in the central and northern parts of the UK coincided with the coldest December for a number of years, particularly in Scotland, which will have contributed to additional heating loads and associated PM emissions. **It is clear that wintertime concentrations will make the greatest contribution to the annual mean; it may thus be more effective to target measures at those sources contributing to the elevated wintertime concentrations.**

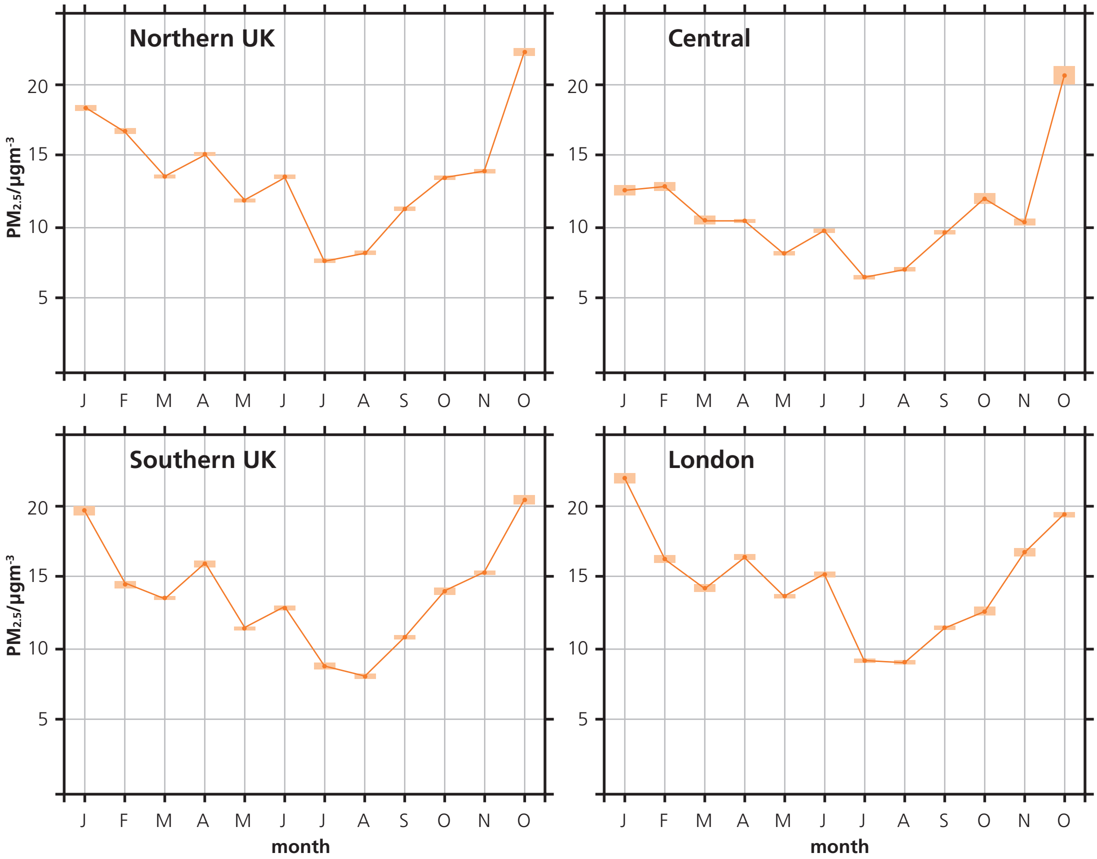

Figure 3.5: Variation of PM$_{2.5}$ concentrations (µg m^{-3}) at urban background sites by month of the year in 2010 at sites in northern UK (n=6), central UK (n=17), southern UK (n=10) and London (n=8). The shading represents the 95% confidence interval of the mean.

3.3 Trends in $PM_{2.5}$ concentrations

10. No monitoring sites have been identified with long data runs (> 5 years) using reference equivalent instruments for $PM_{2.5}$. There are, therefore, no reliable trend data available for $PM_{2.5}$.

11. An indication of trends is provided by the results of $PM_{2.5}$ monitoring carried out between 1999 and 2011 at sites in southern England using TEOM instruments (see Section 2.3.2, Chapter 2). These instruments will not have recorded the volatile component of the $PM_{2.5}$, thus there must be some uncertainty as to the trends observed (Figure 3.6). The London Marylebone Road data were not ratified during the early part of the period and have therefore been removed. There is limited evidence of a downward trend at the rural sites (the Mann–Kendall non-parametric test of significance for a trend at the 95% confidence level has been applied, which showed no significant trend at Harwell and a -0.15 µg m^{-3} yr^{-1} trend at Rochester Stoke), limited evidence of a downward trend at the urban background sites (no significant trend at London Bloomsbury and a -0.27 µg m^{-3} yr^{-1} trend at Bexley Thamesmead) and limited evidence of a downward trend at the roadside sites (no significant trend at London Marylebone Road (over a shorter six-year period) and a -0.48 µg m^{-3} yr^{-1} trend at Ealing Acton Town Hall).

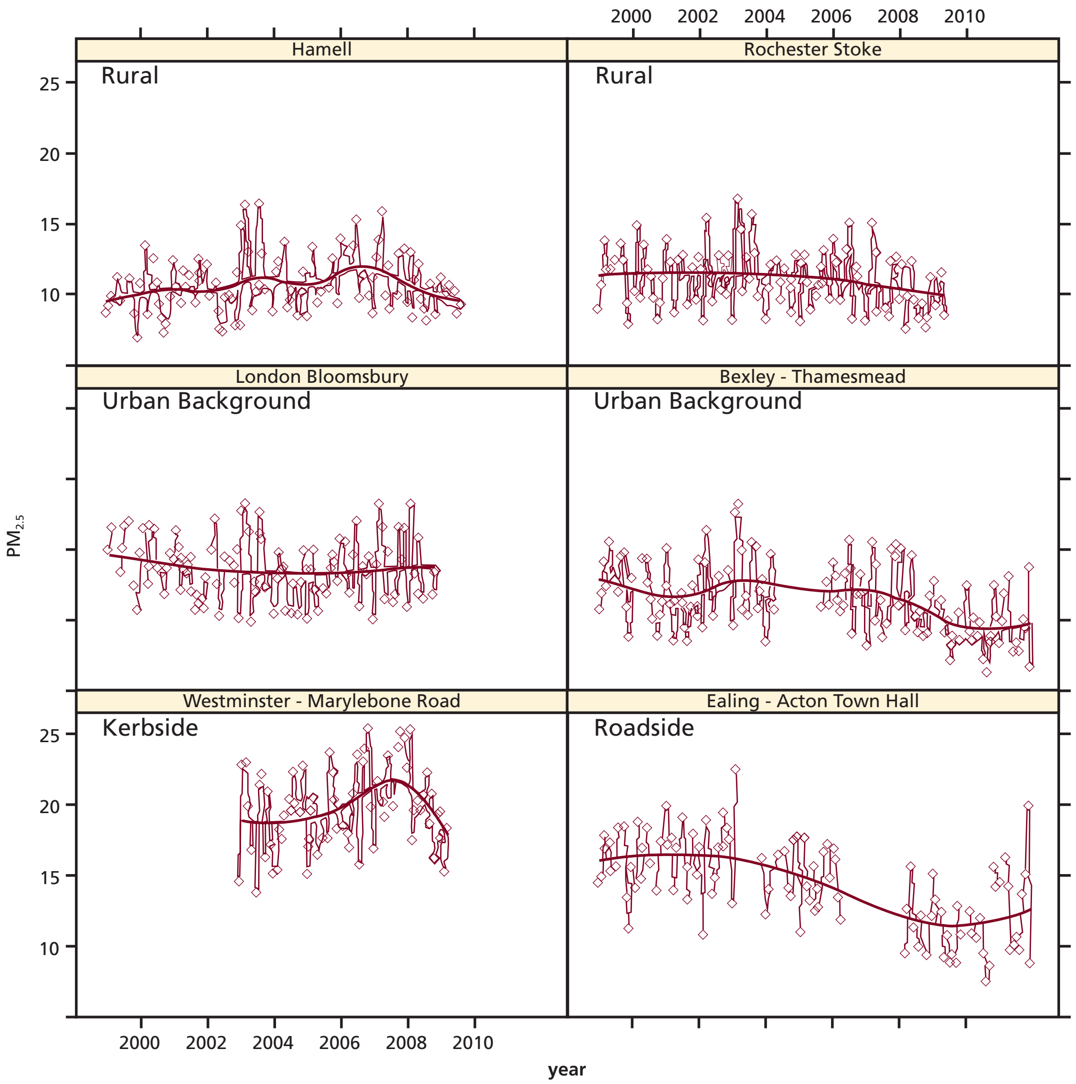

Figure 3.6: $PM_{2.5}$ concentrations (TEOM µg m^{-3} unadjusted) at rural, urban background and roadside/kerbside sites in southern England. A smoothed trendline has been fitted with the shading representing the 95% confidence interval.

12. Results are also available for two sites using FDMS monitors, although only covering a period of five years (Figure 3.7). There is no significant trend at either site over this short period (95% confidence level in a Mann–Kendall trend analysis). **The limited evidence available, including that for sulphate and nitrate in Figure 3.20, is suggestive, but no more, of a slight overall downward trend in $PM_{2.5}$ over the last decade.**

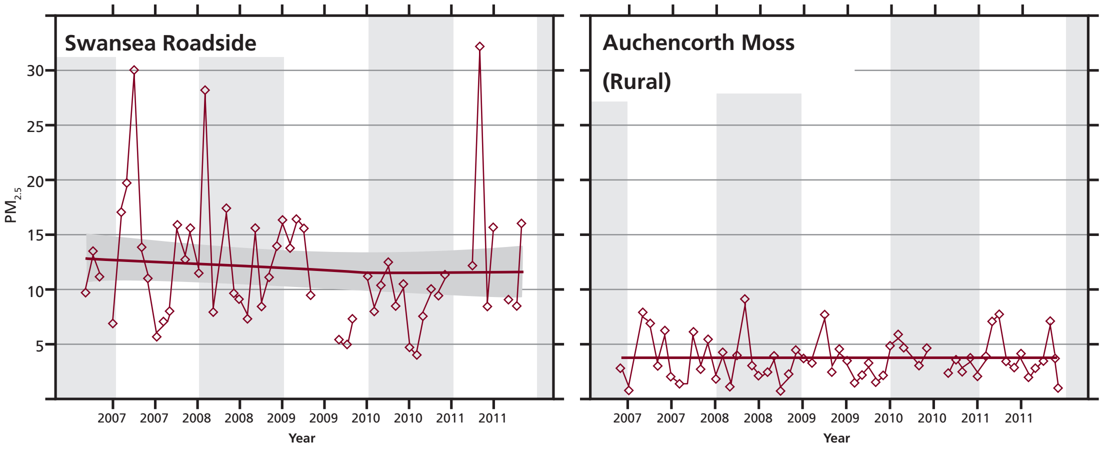

Figure 3.7: $PM_{2.5}$ concentrations (FDMS, µg m^{-3}), 2006-2011, at Swansea roadside site in Wales and Auchencorth Moss rural site in Scotland. A smoothed trendline has been fitted with the shading representing the 95% confidence interval.

3.4 Relationship of $PM_{2.5}$ with other pollutants

3.4.1 Relationship of $PM_{2.5}$ with PM_{10}

13. Laxen *et al*. (2010) examined the ratios of $PM_{2.5}$ to PM_{10} in 2009 and identified an overall decline in the ratios with distance from Dover in the south-east corner of England. The data have been examined again for 2010 and show a similar pattern, even though there were fewer sites with valid data (and a different set of sites), 16 in 2010, compared to 19 in 2009 (Figure 3.8). The ratios have been calculated as the ratio of the average concentration of $PM_{2.5}$ to the average concentration of PM_{10} for those hours when data were available for both measures. They were considered valid if the ratio was based on more than 75% of the hours in the year. For both years the ratio declines with increasing distance from the south-east of England. This is consistent with the more significant contribution of secondary PM in the south-east, with this secondary PM being more significant in the $PM_{2.5}$ fraction.

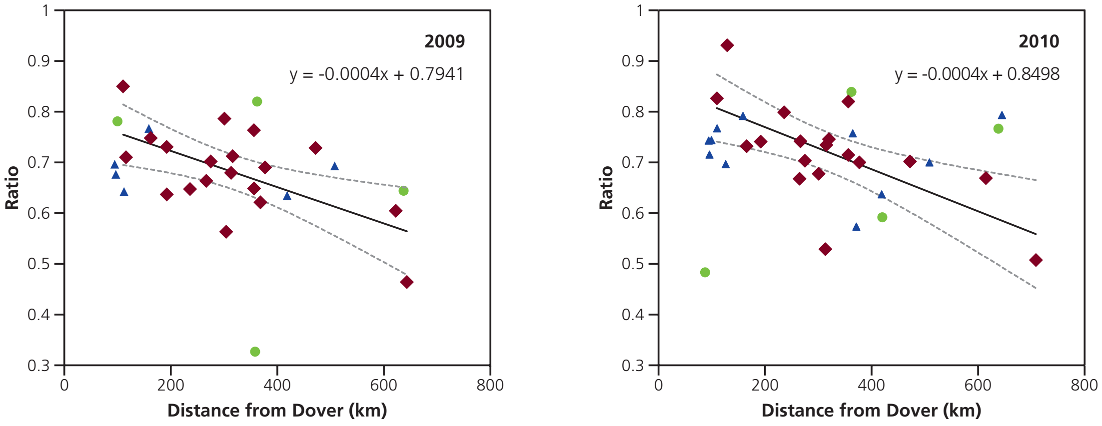

Figure 3.8: Ratio of annual mean $PM_{2.5}$ concentration to annual mean PM_{10} concentration at urban background (red diamonds), roadside (blue triangles) and industrial (green dots) sites in 2009 and 2010. The best-fit line is fitted to the urban background sites. The dashed lines are the 95% confidence limits on the best-fit line.

14. Ratios for roadside sites are also shown and reveal no strong pattern in relation to the local background, as represented by the best-fit line, although it is noted that more sites have values below the line than above. The latter observation is consistent with an analysis of data from sites across Europe, which showed slightly lower overall ratios at roadside sites (de Leeuw and Horálek, 2009). The evidence from the ratios suggests a slightly greater prominence of $PM_{2.5-10}$ at roadside sites than in the background air.

15. The ratios for industrial sites are quite variable, and reflect the variable contributions of $PM_{2.5}$ and $PM_{2.5-10}$ at these sites depending on the particles being emitted. For instance, the lowest $PM_{2.5}$:PM_{10} ratio in 2009 is for the site at Port Talbot in South Wales, which is located near a major steelworks. The ratio of 0.33 implies that the $PM_{2.5-10}$ fraction is elevated to a much greater extent than the $PM_{2.5}$ fraction at this monitoring site. PM at Port Talbot is discussed more fully in Hayes and Chatterton (2009).

16. Stevenson *et al*. (2009) have reported $PM_{2.5}$:PM_{10} ratios for sites in Scotland for 2007 based on measurements made with Partisol samplers. The data were corrected to take account of problems found with the filters being used at that time. The ratios at one suburban site and two rural sites were 0.71, 0.62 and 0.67 respectively, while those for two roadside sites were 0.64 and 0.67. These ratios were calculated from rounded annual mean data, which increases the uncertainty associated with the values. For example, the ratio for the Inverness roadside site, with annual means of 14 µg m^{-3} and 9 µg m^{-3} for PM_{10} and $PM_{2.5}$ respectively, is given as 0.64, but could be anywhere in the range 0.58 to 0.70 depending on what the unrounded concentrations are. The average $PM_{2.5}$:PM_{10} ratio measured using Partisol samplers in 2007 was 0.66, which is higher than the values of around 0.55-0.63 that would nominally apply at these sites on the basis of the relationships for 2009 and 2010 shown in Figure 3.8. The reason for this discrepancy is unclear, but may relate to the different monitoring methods used, i.e. Partisol as opposed to FDMS.

3.4.2 Relationship of $PM_{2.5}$ with PM_{10}, NO_x and NO_2

17. The diurnal pattern for $PM_{2.5}$ has been discussed above in isolation. The pattern in relation to PM_{10}, nitrogen oxides (NO_x) and nitrogen dioxide (NO_2) is examined in this section. Figure 3.9 shows the pattern for all four pollutants during 2010 at eight urban background sites across the UK where data capture was > 90% for all four pollutants. The $PM_{2.5}$ pattern is similar to that for PM_{10}, with the latter concentrations being around 5 $\mu g\ m^{-3}$ higher, although it is noticeable that the lowest $PM_{2.5}$ concentrations occur at around 15.00, while those for PM_{10} are around 05.00. The minimum for NO_x and NO_2 levels is also around 04.00-05.00. Both $PM_{2.5}$ and PM_{10} show much smaller diurnal variation than is the case for NO_x and NO_2. This is consistent with a more limited role for local emissions in the case of $PM_{2.5}$ and PM_{10}, and, conversely, a more important role for regional emissions of $PM_{2.5}$ and PM_{10}.

18. NO_x patterns will be dominated by motor vehicle emissions; this is consistent with the strong peak in concentrations during the morning rush hour (around 08.00-09.00) and to a lesser extent during the evening rush hour (around 17.00). There is evidence of a contribution of the morning rush hour to $PM_{2.5}$ concentrations, but not the evening rush hour.

19. It is also evident in Figure 3.9 that $PM_{2.5}$ and PM_{10} concentrations increase during the late evening to a peak around 20.00-21.00, at a time when NO_x and NO_2 concentrations are decreasing. Fuller *et al*. (2011) have suggested that domestic biomass combustion may result in elevated PM concentrations in the late evening and weekends based on their work using tracers for wood smoke (levoglucosan). The late evening peak may thus reflect a contribution from domestic sources, including both heating and cooking (Laxen *et al*., 2010), although evidence on the diurnal cycle of emissions related to domestic heating from gas and coal does not support a late evening peak from this source (Jenkin *et al*., 2000). The late evening peak will to some extent reflect the more stable atmospheric conditions at this time of the day, but this cannot be the main reason, otherwise NO_x emissions would not be decreasing over this period. The late evening peak may also reflect a contribution from volatile PM condensing on ambient particles, which is also evident in higher night-time nitrate concentrations (Laxen *et al*., 2010).

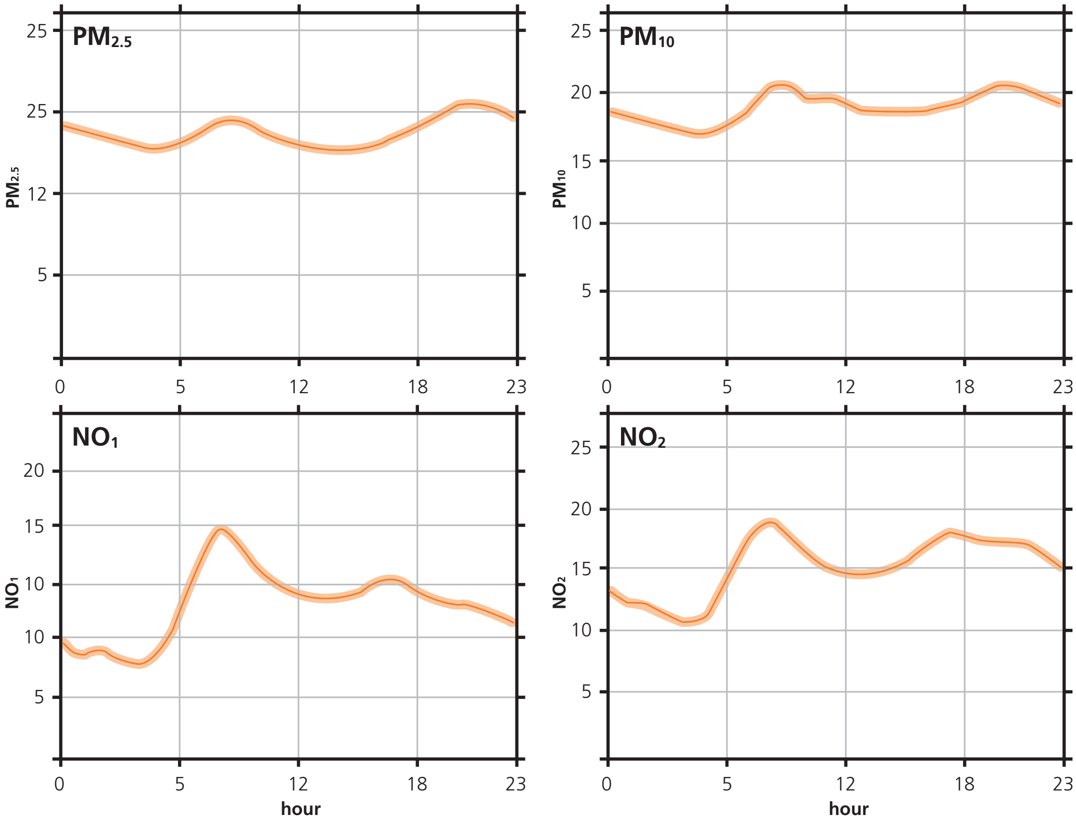

Figure 3.9: Variation of $PM_{2.5}$, PM_{10}, NO_x and NO_2 concentrations ($\mu g\ m^{-3}$) by hour of the day at eight urban background sites across the UK in 2010. The shading represents the 95% confidence interval of the mean. Note the different scales.

3.5 Spatial patterns

3.5.1 Spatial homogeneity of $PM_{2.5}$ hourly mean concentrations

20. Laxen *et al*. (2010) reported a high level of spatial homogeneity of hourly mean $PM_{2.5}$ concentrations across sites in southern England, from Oxford through to Southend. They derived correlation coefficients for paired data sets from 11 sites and plotted the results as a function of distance between the sites (see Figure 3.10). Hourly mean concentrations for sites within 20 km of each other are highly correlated (correlation coefficient > 0.8). The correlation then declines with distance, but is still high at 100 km separation (correlation coefficient ~0.7). **The high level of spatial homogeneity is consistent with $PM_{2.5}$ being dominated by regional sources, including secondary PM, with local sources being less important, but will also reflect the strong seasonal pattern linked to greater winter emissions and more stable atmospheric conditions.**

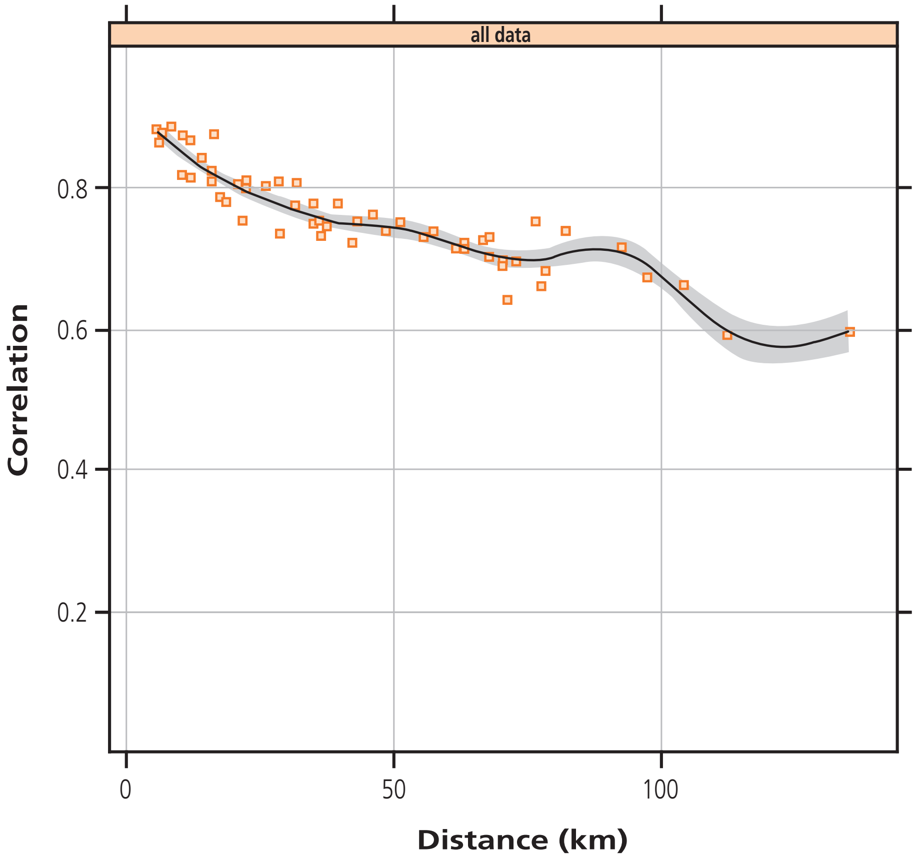

Figure 3.10: Correlation coefficients of hourly mean $PM_{2.5}$ concentrations ($\mu g\ m^{-3}$) at 11 urban background sites in the Thames Valley area of southern England as a function of distance between the sites (Laxen *et al*., 2010). The shading represents 95% confidence interval.

3.5.2 Differences in annual mean $PM_{2.5}$ concentrations by site type

21. Laxen *et al*. (2010) in their summary of 2009 annual mean $PM_{2.5}$ concentrations reported that urban background concentrations in major urban areas were around 3-6 $\mu g\ m^{-3}$ above the rural background,[3] while concentrations alongside busy roads were around 1-2 $\mu g\ m^{-3}$ above the urban background, rising to 7-8 $\mu g\ m^{-3}$ above the urban background at the kerbside (within 1 m of the kerb) of busy roads. Thus in the south of England, where the rural background is around 10-11 $\mu g\ m^{-3}$, the urban background concentrations are around 13-17 $\mu g\ m^{-3}$. This is the pattern illustrated in the transect of modelled background concentrations across London in Figure 5.6 in Chapter 5. The kerbside concentrations would then be up to 20-25 $\mu g\ m^{-3}$. Clearly the rural background is a dominant contributor to $PM_{2.5}$ concentrations at urban background sites, but as Laxen *et al*. (2010) observed, only two rural sites provided data in 2009 (Auchencorth Moss and Harwell). The same was true for 2010. Two sites are not considered sufficient to define the spatial distribution of rural background concentrations across the UK. Laxen *et al*. (2010) recommended that seven additional $PM_{2.5}$ monitors should be set up at rural sites as a minimum and that these could usefully be located at existing ozone monitoring sites. AQEG agrees that there are too few rural monitors to properly define the important rural background contribution to $PM_{2.5}$ across the UK. Additional sites will help

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[3] The term ‘rural background’ is treated as being synonymous with ‘regional background’. Rural monitoring sites must be located away from local sources.

verify modelled regional background concentrations and confirm the modelled spatial pattern of declining rural concentrations from the south-east of England to the north-west of Scotland. They will also allow the urban enhancement to be determined more precisely. These new sites will need to be sufficiently far from urban areas to define the true rural background uninfluenced by the urban area, but not too far, as they would then not represent the regional background applicable across the urban area. The latter will be a particularly important consideration where there is a strong gradient in concentrations, such as that suggested in models on moving from the south coast of England to the Midlands. In these situations it may well be appropriate to define the urban enhancement as the difference between the urban background concentration and the rural background averaged across two or more rural sites located on different sides of the urban area. **It is recommended that an expansion of the rural $PM_{2.5}$ monitoring network to allow the rural background to be properly defined is given urgent consideration.**

3.6 Relationship with wind direction and air mass trajectory

3.6.1 Relationship of hourly mean $PM_{2.5}$ concentrations with wind direction

22. The Openair software package (Carslaw and Ropkins, 2011) using the R language (R Development Core Team, 2011) was used by Laxen *et al*. (2010) to examine the relationship of $PM_{2.5}$ concentrations with wind direction and wind speed (in polar plots) for urban background sites in 2009. They found a broadly consistent pattern across the UK, with a strong easterly predominance to the higher $PM_{2.5}$ concentrations, with a tendency for the highest concentrations to occur with higher wind speeds ~10 m s^{-1}. This analysis has been repeated here for 2010 data and the results show a similar association of the highest concentrations with easterly and south-easterly winds (Figure 3.11), with the highest concentrations often being associated with higher wind speeds. The findings reinforce the view that urban background $PM_{2.5}$ concentrations are dominated by regional rather than local sources, and that PM from sources in continental Europe, probably as secondary PM, significantly affects concentrations in the UK.

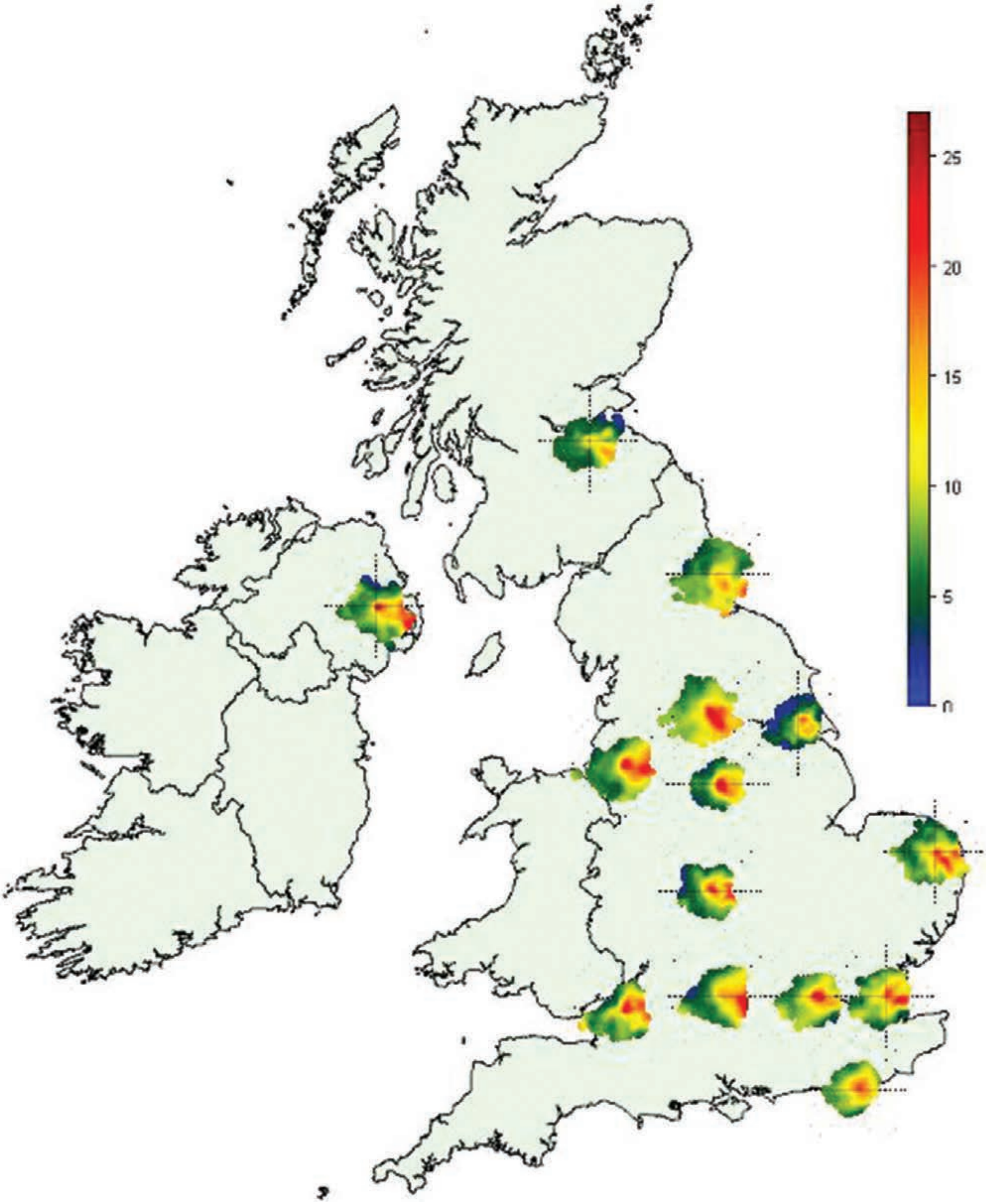

Figure 3.11: Polar plots of $PM_{2.5}$ concentrations at urban background sites in 2010, as a function of wind direction and wind speed. The concentrations are shown on the colour scale in µg m^{-3}.

3.6.2 Relationship of hourly mean $PM_{2.5}$ concentrations with air mass trajectory

23. Back trajectories provide useful information on the origin of an air mass and have been used to understand better the origins of $PM_{2.5}$ concentrations in the UK. An analysis has been carried out using HYSPLIT 96-hour back trajectories calculated for every three hours derived from NCEP/NCAR Reanalysis data (Draxler and Hess, 1997). The whole of each back trajectory, i.e. one every three hours, has been assigned the hourly mean $PM_{2.5}$ concentration for the arrival time at the arrival site. The same concentration is therefore associated with all the 96 hours preceding the arrival time, giving 96 latitude/longitude locations along the trajectory with the arrival time concentration. For a large number of trajectories that cover widely different geographic regions, this technique provides an indication of the source origin of the pollutant being analysed. There are of course uncertainties in these calculations, for example in the accuracy of the back trajectory calculations themselves. It must, however, be borne in mind that any elevated concentrations at the arrival site will be assigned to all points along the trajectory, even though the source may have only contributed at some intermediate point along the trajectory. The analysis of a large number of trajectories can, nevertheless, provide a good indication of the geographic locations most strongly associated with elevated concentrations of $PM_{2.5}$.

24. As an example, Figure 3.12a shows the time series of daily mean $PM_{2.5}$ concentrations at the Bexley Slade Green site in East London for 2009. It is apparent from this figure that there are clear periods when the $PM_{2.5}$ concentrations are elevated, particularly in the first half of the year. The bottom plot, Figure 3.12b, shows the 96-hour back trajectories month by month at the Bexley site. The low concentrations in June-August tend to be associated with trajectories from the Atlantic and the north and the absence of trajectories from continental Europe. Almost all the high concentration periods are associated with air mass trajectories from the east, although in some cases the pattern is complex. For example, in March 2009 there was a period of 4-5 days when anticyclonic conditions dominated to the east of the UK which set up circulatory air masses from continental Europe. Such conditions would ensure that precursor emissions would have accumulated as air masses passed over areas of high precursor emission source strength, and this would have been combined with sufficient time for secondary aerosol to be produced.

25. The trajectory analysis has been extended to seven sites across the UK, as shown in Figure 3.13 for 2009 (the sites are broadly ordered from north to south). For clarity, the trajectory point concentrations have been smoothed to indicate approximate source origins, similar to the work of Seibert *et al*. (1994) and Stohl (1996). The purpose of Figure 3.13 is to highlight the approximate spatial origins that contribute the highest $PM_{2.5}$ concentrations measured at the UK sites. There is consistency across the different sites in that the highest concentrations of $PM_{2.5}$ are dominated by air masses from the east and south-east. The higher background concentrations seen for the urban background Edinburgh site in comparison with the rural Auchencorth Moss site will be due to local urban sources elevating the overall concentrations measured in Edinburgh, irrespective of the trajectory direction. However, it is clear, for 2009 at least, that the contribution from mainland Europe to high $PM_{2.5}$ concentrations at these northern UK sites is less than for sites further

south. Further analysis of more sites covering a greater spatial area would yield more information on the regional differences. Note that similar patterns were observed when removing the $PM_{2.5}$ associated with local NO_x concentrations (not shown), which highlights that the patterns in Figure 3.13 are most strongly associated with non-local sources.

26. The analysis of concentrations by wind direction and wind speed, as well as the analysis of concentrations associated with different air mass trajectories, **demonstrates the importance of sources within continental Europe in contributing to high $PM_{2.5}$ concentrations at urban background sites in the UK.**

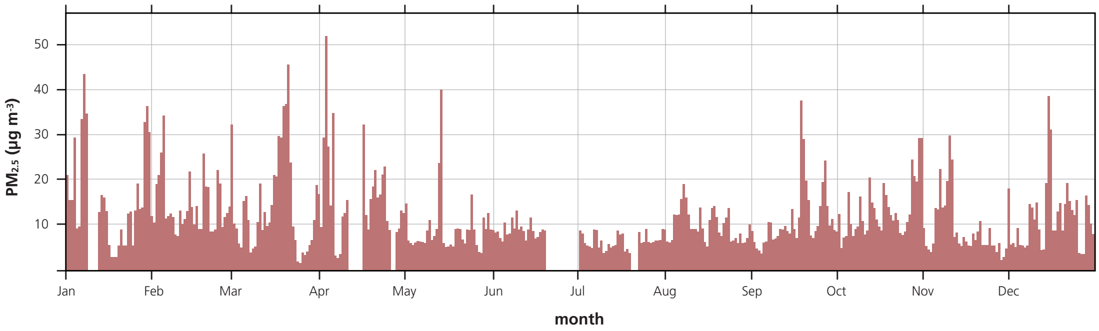

Figure 3.12a: Daily mean $PM_{2.5}$ concentration at the London Bexley Slade Green site for 2009.

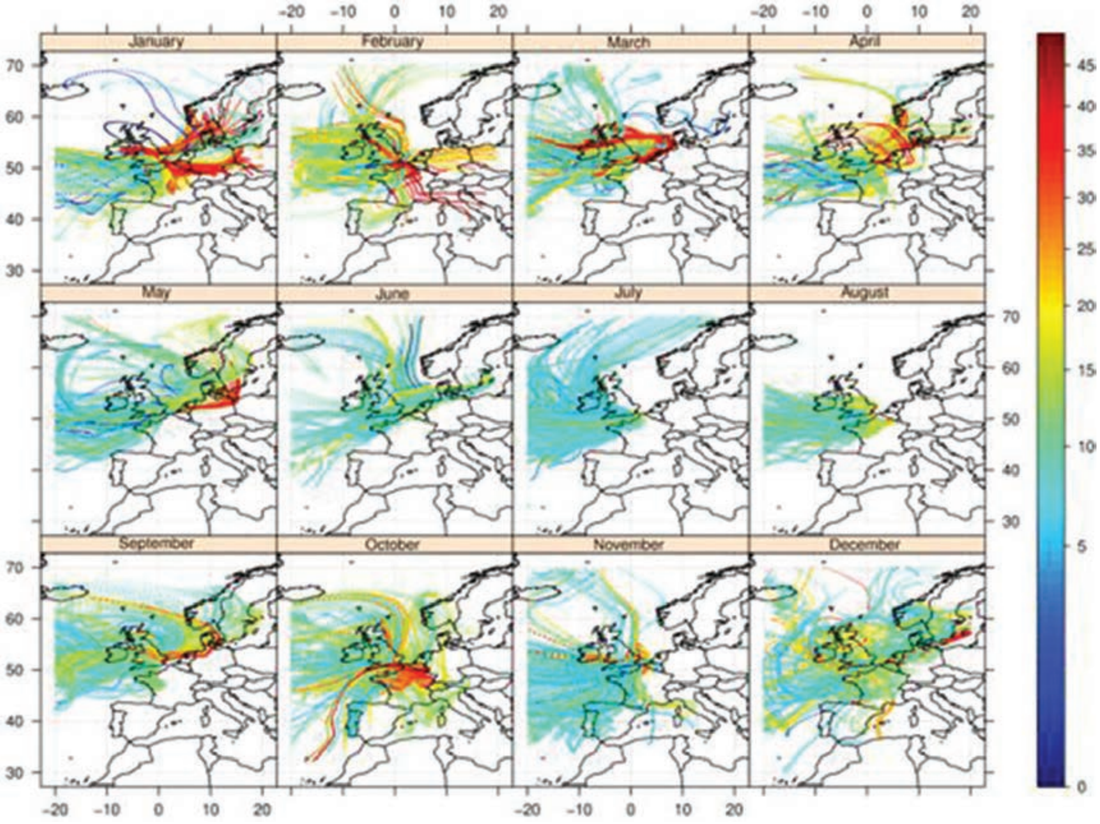

Figure 3.12b: 96-hour back trajectories for the London Bexley Slade Green site by month. Each trajectory is coloured according to the $PM_{2.5}$ concentration (µg m^{-3}) at the arrival time.

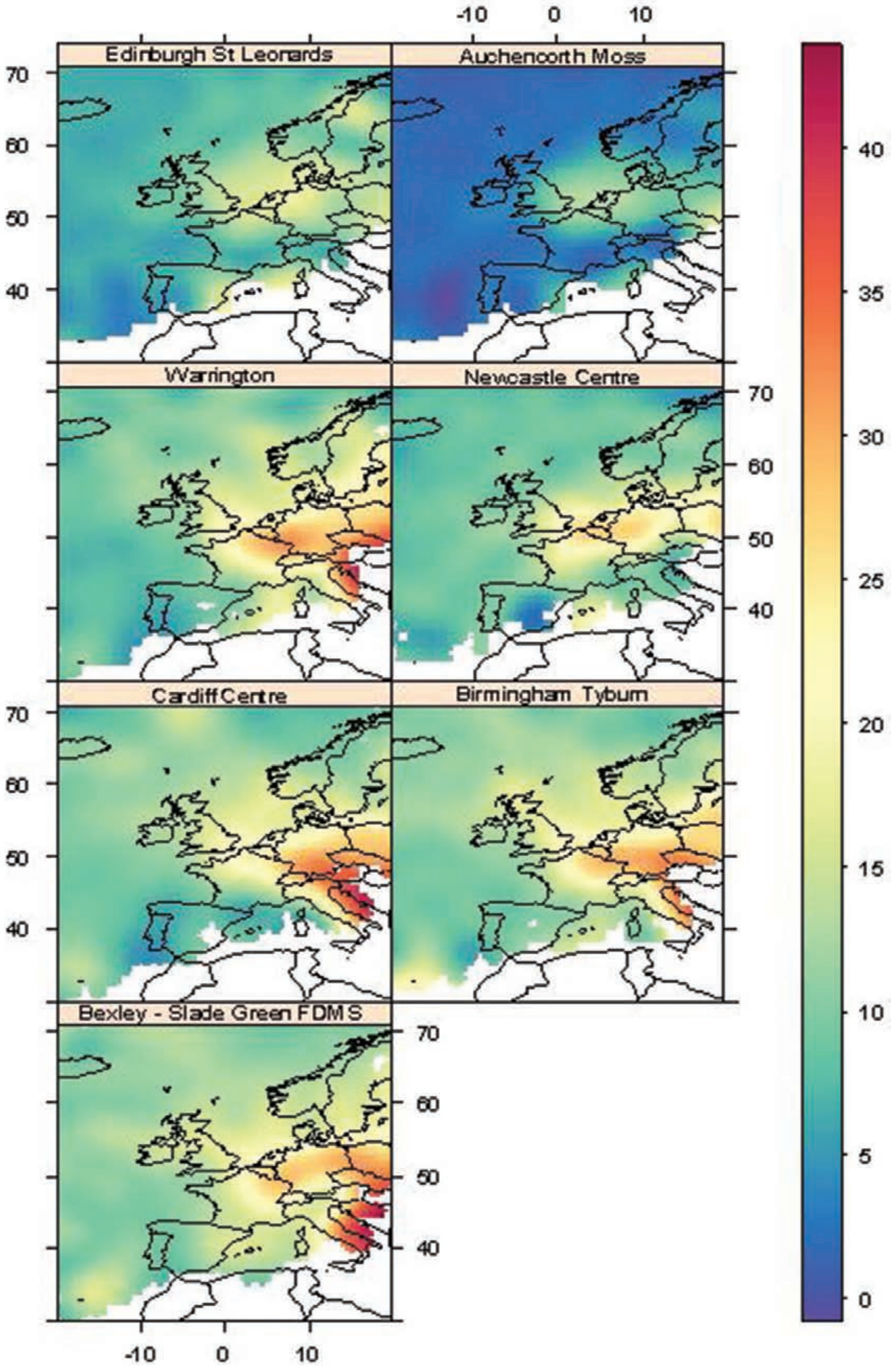

Figure 3.13: Back trajectory analysis for seven sites in 2009 for $PM_{2.5}$. The colour scale shows the concentration of $PM_{2.5}$ in µg m^{-3} associated with air mass trajectories averaged over one year. Note that the concentration does not indicate the actual $PM_{2.5}$ concentration for different locations. All sites are urban background apart from Auchencorth Moss, which is rural.

3.7 $PM_{2.5}$ episodes

3.7.1 Winter episodes

27. Episodes during the autumn and winter months are well known in the UK, occurring when a high pressure system is dominant and stagnant atmospheric conditions prevail, with little vertical mixing and low wind speeds. These conditions can allow local emissions to build up over several days. If conditions are particularly cold then local emissions from a heating plant for example will also be much higher. Such conditions arose during December 2010, when extreme (for the UK) cold persisted for a number of days across much of the country.

28. During the seven day period 19-25 December 2010, temperatures were below freezing throughout the day and wind speeds were low in Derry in Northern Ireland and Glasgow in Scotland, especially on 22 December (dropping to -12°C at night). Both temperatures and wind speed increased on 26 December. There were high PM concentrations in both locations, although they were particularly high in Derry (Figure 3.14). The main part of the PM episode was due to $PM_{2.5}$, with little contribution from the coarse $PM_{2.5-10}$ fraction. Also shown in Figure 3.14 are the NO_x and sulphur dioxide (SO_2) concentrations, which followed a similar pattern to the PM, although SO_2 was more dominant in Derry and NO_x in Glasgow. The peak concentrations in Derry occurred during the evening (higher concentrations occurred between around 13:00 and 24:00, peaking between 16:00 and 22:00), while in Glasgow the peaks were broader and occurred earlier, during the afternoon and early evening (higher concentrations occurred between around 09:00 and 22:00, peaking between 17:00 and 18:00). The linkage with SO_2 in Derry is consistent with the burning of solid and/or liquid fuels in domestic premises. The timing of the peaks suggests the use of these fuels during the evening, but not during the early morning. In Glasgow, it is likely that road traffic played a more important role, as seen in the greater NO_x concentrations. The average concentration of $PM_{2.5}$ over the seven days of the episode 19 to 25 December 2010 was 96.9 $\mu g\ m^{-3}$ at Derry and 40.6 $\mu g\ m^{-3}$ at Glasgow Centre. At Derry, this episode contributed 1.9 $\mu g\ m^{-3}$ to the annual mean, amounting to 9.6% of the annual mean of 19.3 $\mu g\ m^{-3}$; at Glasgow Centre, this episode contributed 0.8 $\mu g\ m^{-3}$ to the annual mean, amounting to 6.3% of the annual mean of 12.4 $\mu g\ m^{-3}$. **$PM_{2.5}$ episodes related to stagnant winter conditions, which allow a build-up of local emissions, can last several days and represent a not insignificant contribution to annual mean concentrations.**

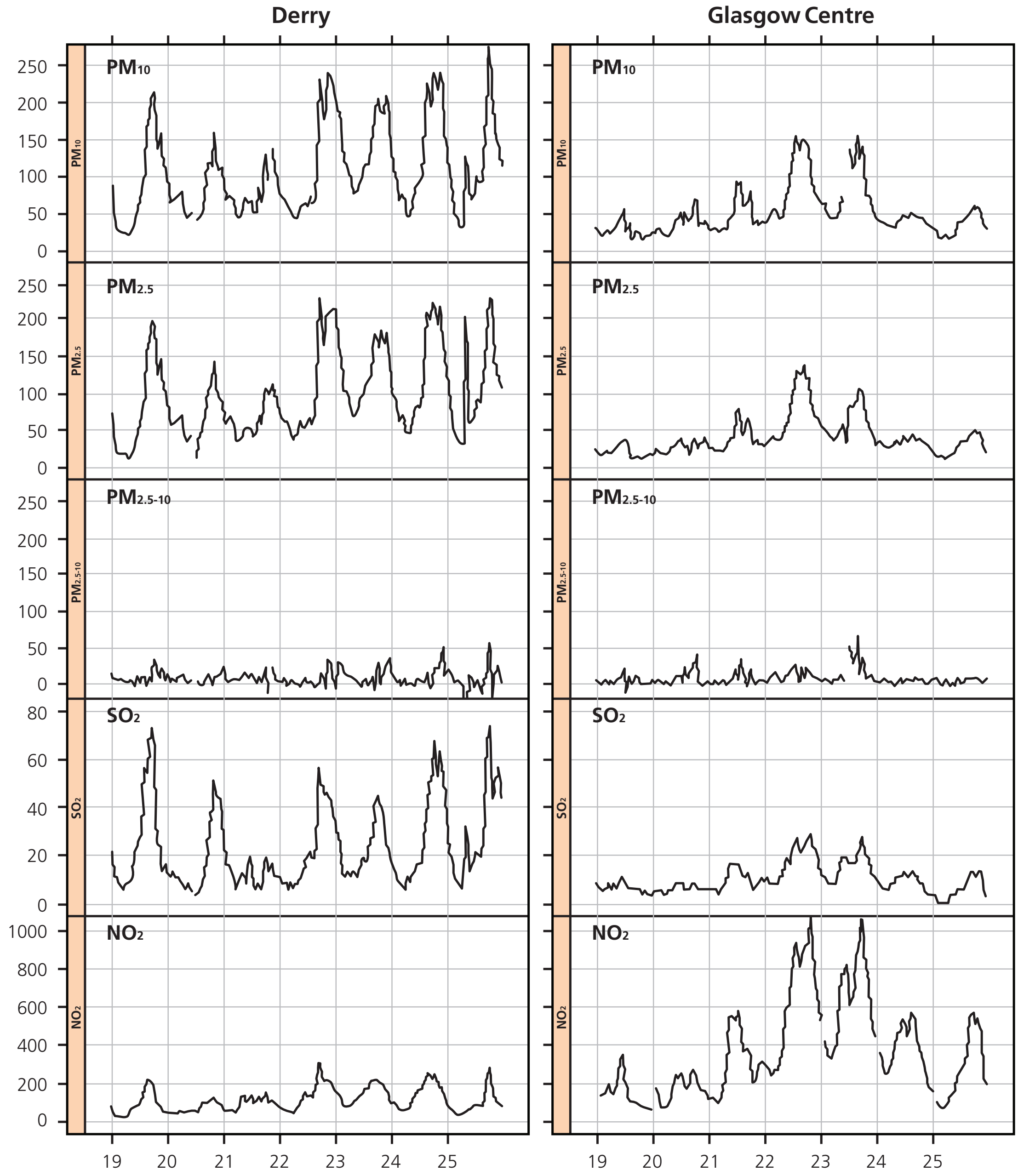

Figure 3.14: PM_{10}, $PM_{2.5}$, $PM_{2.5-10}$, sulphur dioxide and nitrogen oxides concentrations over the period 19-26 December 2010 at Derry, Northern Ireland, and Glasgow Centre, Scotland (µg m^{-3}).

3.7.2 Transport from continental Europe

29. Significant episodes also arise during periods when air masses arrive from continental Europe. As with winter episodes, these can last several days. A significant episode occurred during April 2011 affecting sites across the UK, as shown in Figure 3.15 for the London North Kensington site (the PM results for London Bloomsbury were almost identical). The episode built up over several days and gave rise to high PM_{10} concentrations that exceeded the 24-hour limit value and led to alerts for poor air quality. It is clear from Figure 3.15 that the episode was entirely due to $PM_{2.5}$, with no noticeable change in the coarse $PM_{2.5-10}$ fraction. The nitrate concentrations during this episode match the PM pattern, and assuming that the nitrate is present as ammonium nitrate (NH_4NO_3), then the vast majority of the PM during this episode will have been

secondary ammonium nitrate. It is also of note that there was a strong diurnal pattern, with the highest concentrations in the early morning (00.00-08.00) and the lowest during the early afternoon (14.00-16.00). The pattern is consistent with volatilisation of the nitrate particles during the warm afternoon and condensation of nitrate particles during the cooler early morning period. The modelled build-up of this episode across northern Europe is shown in Annex 2 (Figures A2.1.1 and A2.1.2). This episode is typical of spring episodes in the UK, and is consistent with the high nitrate concentrations at this time of year (see Figure 3.21). Further details of the April episode, including trajectory plots, are available at: http://uk-air.defra.gov.uk/library/reports.php?report_id=655. The average concentration of $PM_{2.5}$ over the 17-26 April 2011 was 43.6 µg m^{-3}; the episode contributed 1.2 µg m^{-3} to the annual mean, amounting to 7% of the annual mean of 16.3 µg m^{-3} at this monitoring site. **$PM_{2.5}$ episodes related to transport of secondary PM (mostly nitrate) from continental Europe can last several days and represent a not insignificant contribution to annual mean concentrations.**

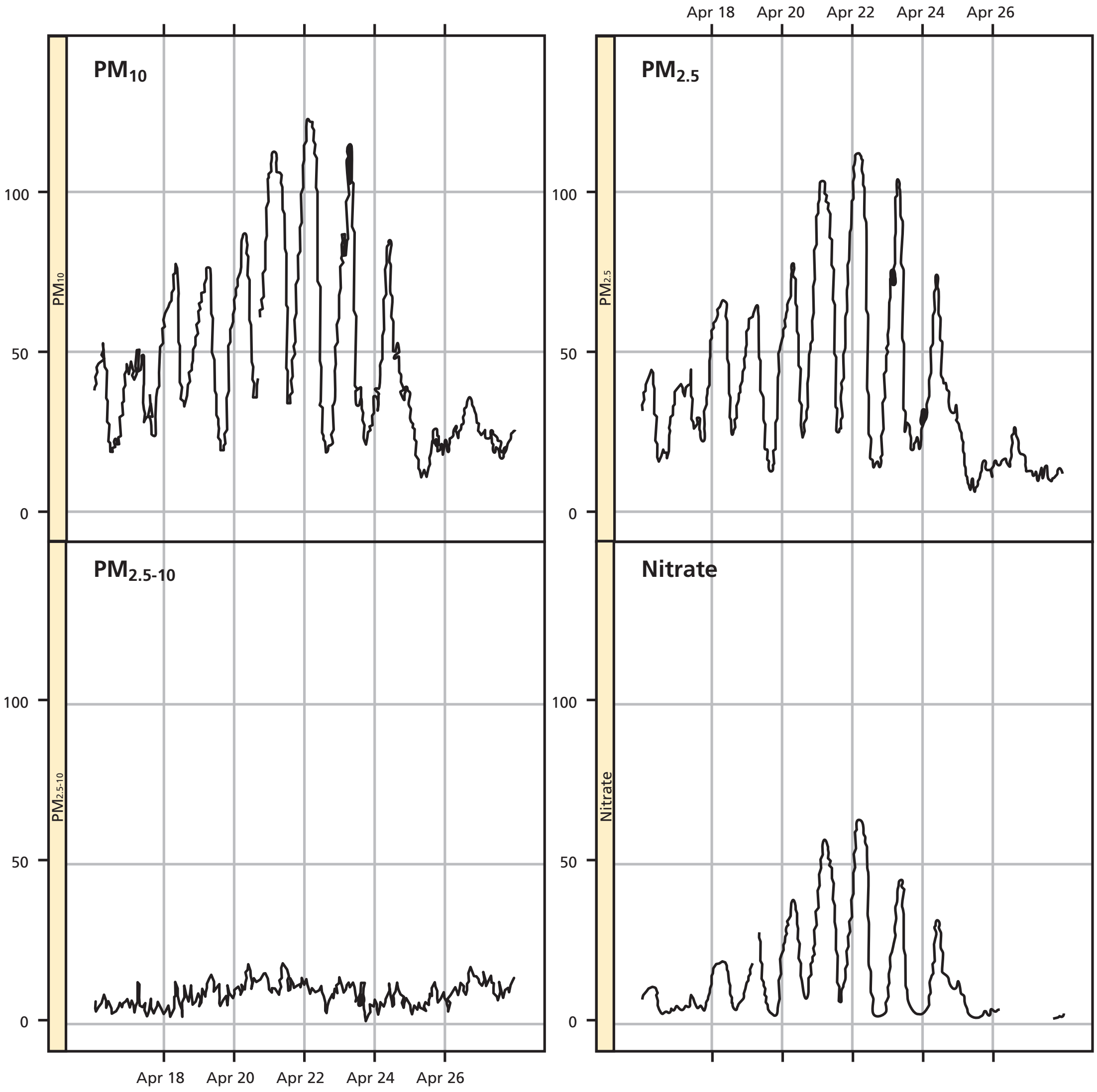

Figure 3.15: PM_{10}, $PM_{2.5}$, $PM_{2.5-10}$ and nitrate concentrations (µg m^{-3}) over 15 days in April 2011 at London North Kensington.

3.7.3 Bonfires and fireworks

30 Episodes of elevated $PM_{2.5}$ concentrations are clearly associated with emissions from bonfires and/or fireworks, as is evident in the peaks lasting for several hours that frequently occur around Bonfire night (see the example shown in Figure 3.16). The concentrations at these four London sites rose sharply on the Saturday evening, 7 November 2010, before declining more slowly. Although Bonfire night was the day before, there was only a small peak on the Friday evening. The wind speed was very low on the Saturday night but stronger on the Friday, showing the importance of local meteorological conditions in determining whether an episode will occur. Separate analysis (not shown) revealed that the peaks were almost entirely $PM_{2.5}$, with very little $PM_{2.5\text{-}10}$. Also, concentrations of NO_x rose at the same time as the $PM_{2.5}$, but there was no impact on NO_2 concentrations, which is evidence of fresh NO_x emissions. Such episodes can contribute around 0.1 µg m^{-3} to the annual mean concentration. **$PM_{2.5}$ episodes due to bonfires and fireworks are of short duration and will only have a small effect on annual mean concentrations.**

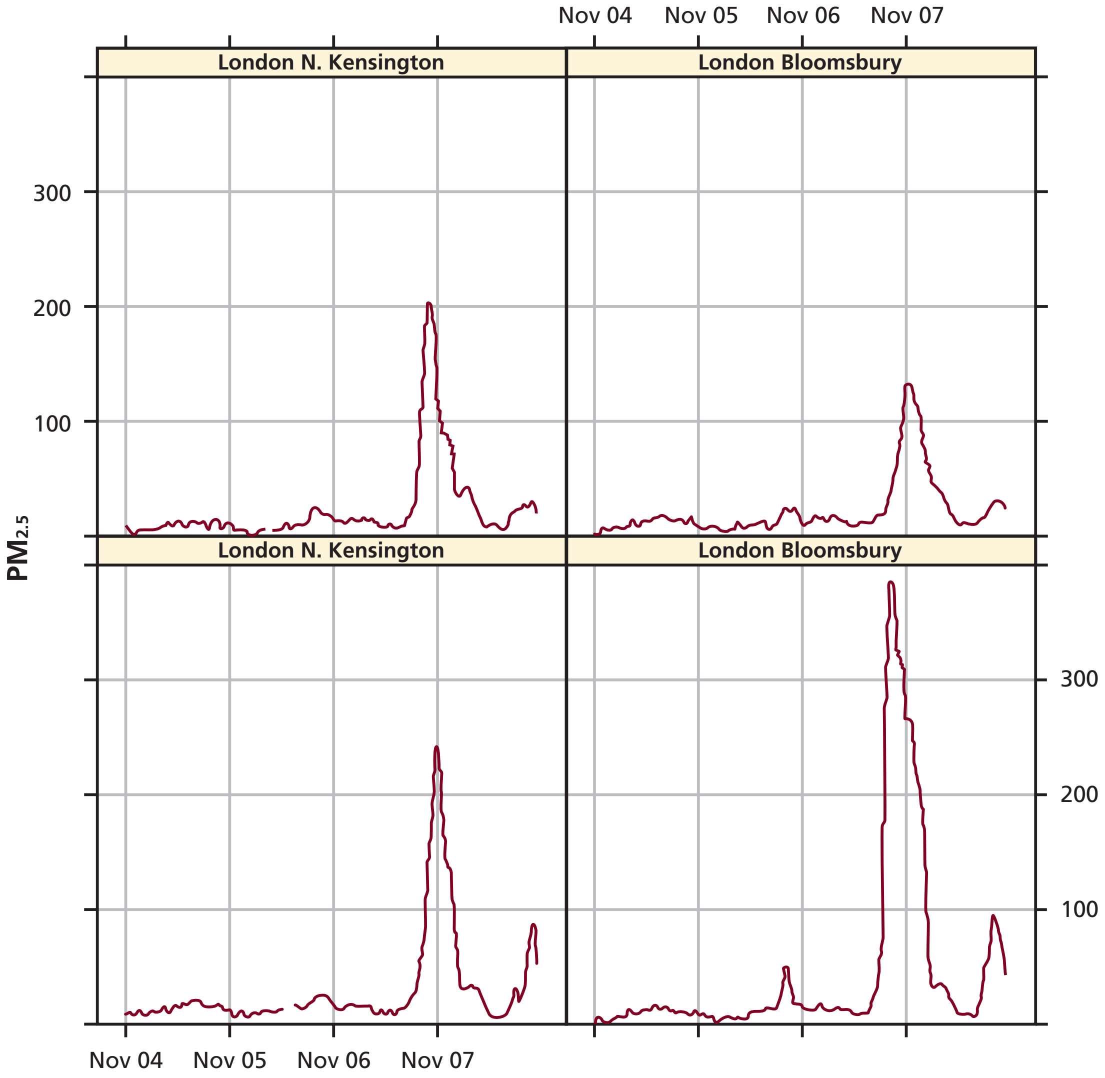

Figure 3.16: $PM_{2.5}$ concentrations (µg m^{-3}) over four days in November 2010 at four London sites. The date markers are for midnight.

3.8 $PM_{2.5}$ concentrations in relation to standards

3.8.1 EU and UK requirements for $PM_{2.5}$

31. The EU limit values and targets for $PM_{2.5}$ set out in the Ambient Air Quality Directive (2008/50/EC) are all based on annual mean concentrations (see Table 1.1 in Chapter 1). The limit value is 25 µg m^{-3} as an annual mean and it is to be met by 2015. This limit value is seen as a long-stop and is not designed to drive policy. All the evidence indicates that this concentration will not be exceeded in the UK. The highest annual mean roadside concentration in 2009 was 21 µg m^{-3} at the Marylebone Road kerbside site in London (84% data capture). In 2010 the highest concentration was at Glasgow kerbside at 23.1 µg m^{-3} (96% data capture). Although these values are below the 25 µg m^{-3} limit value for 2015, they are above the Stage 2 indicative limit value of 20 µg m^{-3} to be achieved by 2020.

32. The EU Directive exposure reduction target and exposure concentration obligation are based on the average exposure indicator (AEI). The AEI is an exposure index calculated as the average across a designated set of UK urban background sites. The indicative AEI for these sites in 2009 was 12.3 µg m^{-3} and in 2010 13.0 µg m^{-3} (these calculations were made for sites with > 75% data capture and include data collected with both FDMS and Partisol instruments). These values are very close to the boundary between a requirement for a 10% or 15% exposure reduction target. It is thus unclear at this stage what the EU target reduction for the UK will be as the AEI is based on the three-year mean (2011 results will thus be crucial in determining the AEI). A 10% target would require a reduction of around 1.3 µg m^{-3}, while a 15% target would require a reduction of around 2 µg m^{-3}, which will be more challenging.

33. Finally, there is the exposure concentration obligation (ECO) within the Directive, which sets a ceiling of 20 µg m^{-3} for the AEI, to be achieved by 2015 as a three-year mean for the same set of urban background sites used to determine the exposure reduction target. Given that the AEI is likely to be around 13 µg m^{-3}, this obligation will not be exceeded.

34. The UK Government has set an annual mean objective for $PM_{2.5}$ of 25 µg m^{-3}, which applies at all relevant exposure locations in England, Wales and Northern Ireland from 2020.[4] Given the discussion above, this is likely to be achieved throughout the UK. The UK Air Quality Strategy has also set an exposure reduction objective, which in this case is a 15% reduction between 2010 and 2020. This will either be the same as, or possibly more stringent than the EU target, which will be either 10% or 15%.

35. In Scotland the annual mean objective for $PM_{2.5}$ has been set at 12 µg m^{-3} to be achieved by 2020 at all relevant exposure locations. Given that the measured kerbside concentration in Glasgow was 23 µg m^{-3} in 2010, it is highly likely that the objective is currently being exceeded at roadside sites in major urban areas in Scotland. There is thus a risk that the Scottish objective for $PM_{2.5}$ may still be exceeded in 2020.

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[4] This was set before the EU limit value was set. The latter is the same concentration, but applies from 2015, and will effectively supersede the UK objective.

36. Given this analysis, it is expected that the exposure reduction target will be the key driver for UK policy on exposure to $PM_{2.5}$, while the PM_{10} objectives and limit values will supplement this control by driving policy on short-term (daily average) concentrations at hot spots. There may also be a role for the annual mean $PM_{2.5}$ objective in Scotland to drive policy in Scotland. However, the PM_{10} objective is likely to be more stringent for these locations and is thus more likely to drive policy.

3.8.2 Relationship between $PM_{2.5}$ and PM_{10} limit values and objectives

37. The 24-hour limit value and objective of no more than 35 days > 50 µg m^{-3} is taken to be equivalent to an annual mean PM_{10} concentration of 31.5 µg m^{-3} (Grice *et al*., 2010). Given the ratios of $PM_{2.5}$:PM_{10} identified for different parts of the UK (see Figure 3.8), it is possible to equate this limit value/objective to annual mean $PM_{2.5}$ concentrations (Table 3.1). The results in Table 3.1 show that the PM_{10} 24-hour objective/limit value is more stringent than the annual mean $PM_{2.5}$ limit value of 25 µg m^{-3}, especially in northern areas of the UK.

Table 3.1: Indicative annual mean $PM_{2.5}$ concentrations that equate to the 24-hour PM_{10} limit value/objective in different parts of the UK.

Region of UK	$PM_{2.5}$ (µg m^{-3})
Scotland	17[a]
Northern Ireland	17
northern England	21
Wales	21
south-west and central England	22
south-east England and East Anglia	24

[a] In Scotland, this analysis only applies to the limit value, as a different objective applies.

38. In Scotland the PM_{10} annual mean objective of 18 µg m^{-3} is more stringent than the 24-hour mean PM_{10} objective of no more than seven days > 50 µg m^{-3}. Given the average $PM_{2.5}$:PM_{10} ratio of around 0.55-0.6 identified for urban background sites in Scotland, the annual mean PM_{10} objective is equivalent to a $PM_{2.5}$ concentration of 10-11 µg m^{-3}. On this basis, the PM_{10} objective will be more stringent than the $PM_{2.5}$ objective of 12 µg m^{-3}.

3.9 Composition

3.9.1 Overall composition of $PM_{2.5}$

39. There have been few measurements of the overall composition of $PM_{2.5}$ in the UK. Yin and Harrison (2008) collected 24-hour samples of $PM_{2.5}$ from three sites in and around Birmingham between 2004 and 2006, sampling daily at a central urban background site (12 months), a roadside site (six months, mainly summer) and a rural site (six months, mainly winter). Samples were taken sequentially. A pragmatic mass closure model was used to assign compounds to the measured constituents. This mass closure model is a way of accounting for the measured mass concentration of airborne particles by summing scaled values of the concentrations of major chemical components in such a way as to allow for those components that are not directly measured (Harrison *et al*., 2003). The overall results for the central urban background site are shown in Figure 3.17a. Three components account for a large proportion of the total mass: nitrate, sulphate and organics. Iron-rich dusts are attributed to non-exhaust traffic emissions, calcium salts are attributed to construction/demolition dust and wind-blown soil, and sodium chloride to sea salt (although this should also include resuspended de-icing salt). Elemental carbon relates to primary combustion. Organic carbon (organics), both from combustion and natural sources, may be either primary or secondary.

40. Yin and Harrison (2008) also reported the $PM_{2.5}$ composition on high pollution episode days (i.e. days with daily mean $PM_{10} > 50\ \mu g\ m^{-3}$). They reported a substantial increase in nitrate, which accounts for just under half the $PM_{2.5}$ on episode days (Figure 3.17b). The authors note that this emphasises the importance of developing a better understanding of the sources of nitrate in airborne PM. Putaud *et al*. (2010) also report higher nitrate contributions at higher $PM_{2.5}$ concentrations based on measurements carried out elsewhere in Europe.

41. Measurements of chemical composition are important for source apportionment and **it is recommended that further measurements should be made of chemical composition in a variety of locations, principally rural, urban background and roadside, over different parts of the UK, to allow source apportionment to be conducted.**

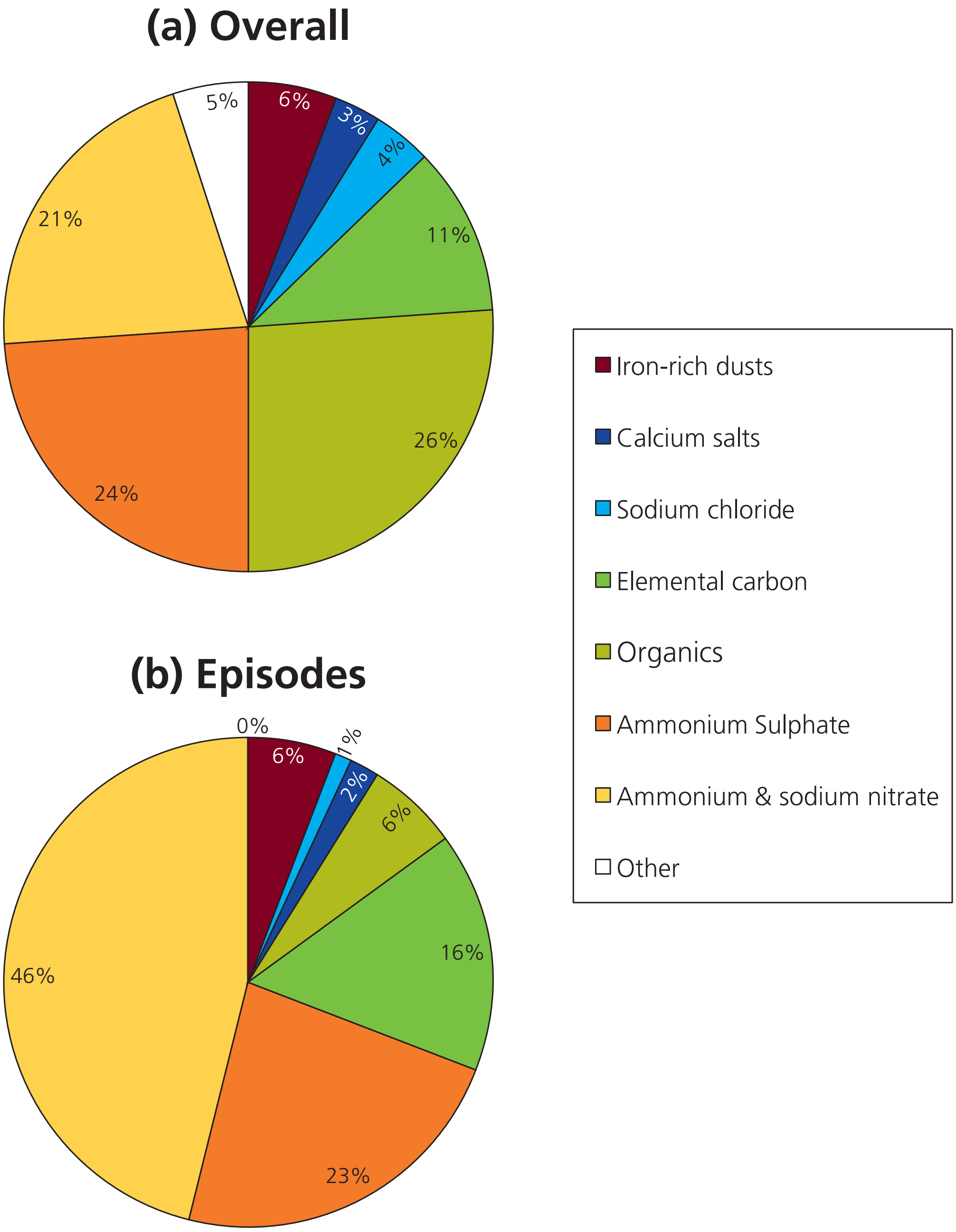

Figure 3.17: Composition of $PM_{2.5}$ on all days (overall) and episode days ($PM_{10} > 50$ µg m^{-3}) at a central urban background site in Birmingham (Yin and Harrison, 2008).

3.9.2 Individual constituents of $PM_{2.5}$

42. The Ambient Air Quality Directive (2008/50/EC) calls for measurement of the chemical composition of $PM_{2.5}$ at rural sites, covering the following minimum list of chemical species: sulphate (SO_4^{2-}), sodium (Na^+), ammonium (NH_4^+), calcium (Ca^{2+}), elemental carbon (EC), nitrate (NO_3^-), potassium (K^+), chloride (Cl^-), magnesium (Mg^{2+}) and organic carbon (OC). These data are helpful in understanding the constituents of $PM_{2.5}$, however, in order to allow further calculations of the overall composition of $PM_{2.5}$ using the mass closure model, it will be necessary to include measurement of iron (Fe). **It is therefore recommended that the measurement of iron (Fe) is included as part of the chemical composition monitoring programme.**

43. The UK has initiated a monitoring programme to meet the Directive requirements in respect of PM composition. MARGA instruments were installed at Auchencorth Moss (located to the south of Edinburgh) in 2006 and at Harwell (located to the south of Oxford) in 2009. These instruments specifically measure the species listed above in the $PM_{2.5}$ and PM_{10} fractions on an hourly basis (but not Fe). The data have been examined carefully by AQEG, but concerns about their quality make them unsuitable for analysis. These concerns include concentrations being higher in the $PM_{2.5}$ fraction than the PM_{10} fraction and a lack of ionic balance. **It is therefore recommended that the suitability of these instruments for meeting reporting obligations under the Directive is reviewed.**

44. Monitoring of total ambient nitrate, sulphate and ammonium concentrations has been undertaken over a number of years at sites across the UK (see Chapter 2). Although these measurements are not specifically for the $PM_{2.5}$ size fraction, the results are still useful for an analysis of seasonal patterns and trends.

3.9.3 Seasonal pattern of nitrate and sulphate

45. The UK Acid Gases and Aerosols Monitoring Network (AGANet) has been in operation since 1999, with 12 original sites expanded to 30 sites in 2006. This Network records monthly mean concentrations. The seasonal pattern across all sites and all years is shown in Figure 3.18. The shaded area represents the uncertainty in the mean value for each month at the 95% confidence level, it does not represent the overall measurement of uncertainty. There is clear evidence of a nitrate peak in the early spring (~3 µg m^{-3}), in particular in March and April, before a rapid drop to relatively constant concentrations for the rest of the year (~1.5 µg m^{-3}). The sulphate concentrations are also highest in March and April (~1.4 µg m^{-3}), but show only a slow decline over the summer, with the lowest concentrations occurring in the winter months (0.8-1.0 µg m^{-3}).

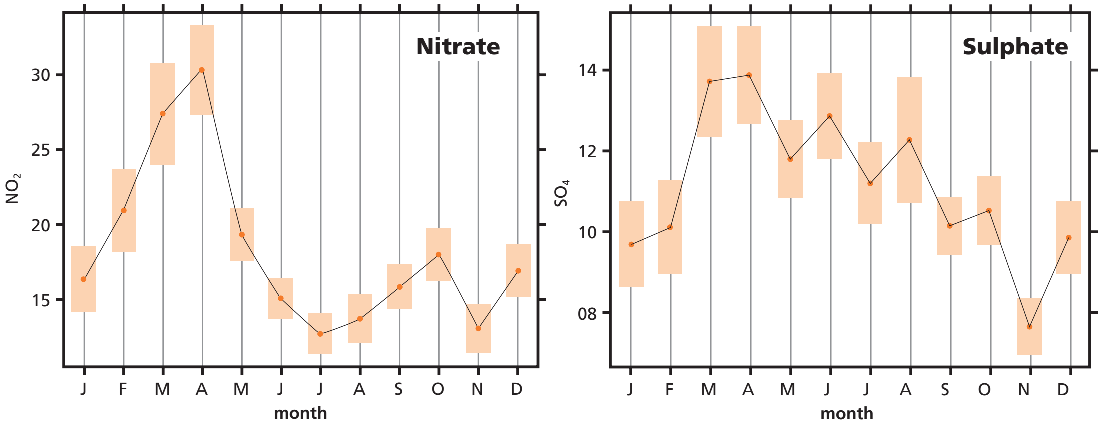

Figure 3.18: Variation of nitrate and sulphate concentrations (µg m^{-3}) by month of the year (data from 30 AGANet sites, 1999-2009). The shading represents the 95% confidence interval of the mean. Note different scales.

46. The chemical equivalence of nitrate and sulphate from AGANet with ammonium from the National Ammonia Monitoring Network (NAMN) has been tested by examining the ionic balance. The 1:1 equivalence between ammonium and the sum of "nitrate + 2 x sulphate" seen in Figure 3.19 confirms the neutrality of the particles and that nitrate and sulphate are present mainly as ammonium nitrate (NH_4NO_3) and ammonium sulphate ($(NH_4)_2SO_4$) respectively. The units are in nmol m^{-3} to allow equivalence to be demonstrated.

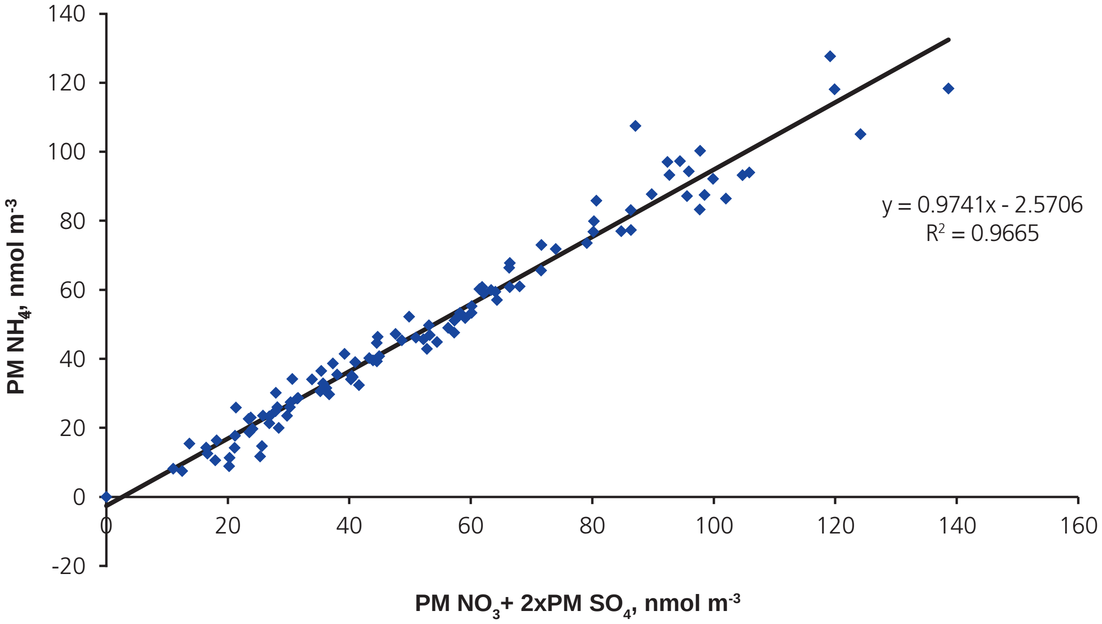

Figure 3.19: Ammonium concentrations versus nitrate plus two times sulphate concentrations in nmol m^{-3} (data from 30 AGANet sites, 1999-2009).

3.9.4 Trends in nitrate, sulphate, ammonium, black smoke and black carbon

Nitrate

47. Measurements of nitrate began at acid precipitation network sites in 1990 and the 1990-2000 measurements at Eskdalemuir show a -20% to -30% decrease over this period (Lovblad *et al*., 2004) in line with the observations for EMEP sites in Norway and Denmark. Nitrate measurements switched to the Delta denuder method in 2001 and RoTAP (2012) reports the spatial distribution of the annual mean PM nitrate concentrations using these data. No information was provided in RoTAP (2012) for the presence of any trends in nitrate, which may reflect the large annual variability in concentrations.

48. The pattern of nitrate concentrations measured between September 1999 and December 2009 across the 12 long-term sites in the AGANet programme is shown in Figure 3.20. Concentrations increase from 2000 to 2003, then decrease to 2009, leading to little overall change over this period (Mann–Kendall trend analysis at 95% confidence level shows a slight downward trend of -0.04 µg m^{-3} yr^{-1}). There is a notable peak in the spring of 2003 (February-April), although nitrate concentrations are typically high at this time of the year (Figure 3.21).

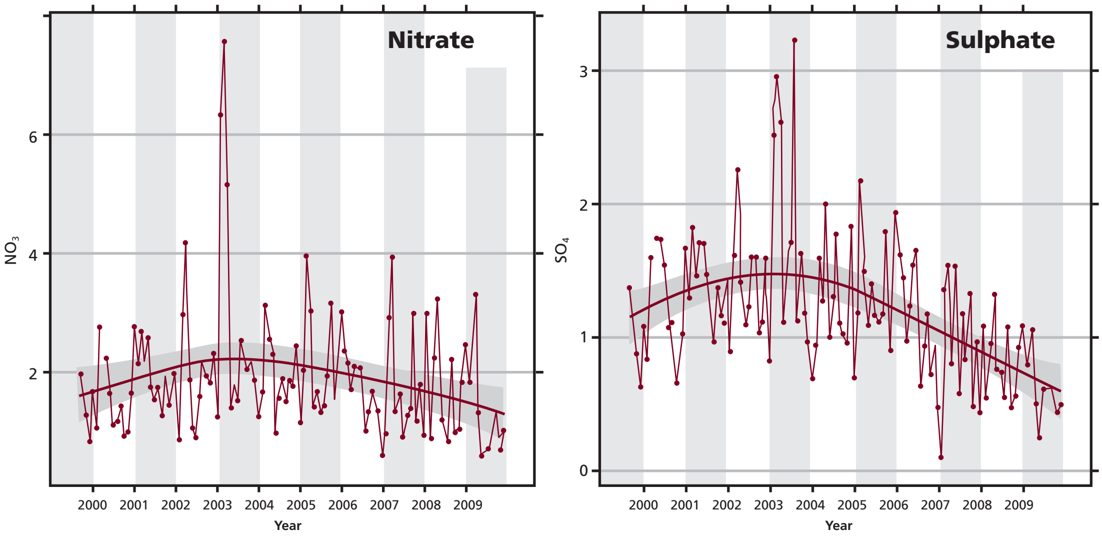

Figure 3.20: Nitrate and sulphate concentrations (µg m^{-3}) at rural sites, 1999-2009 (data from 12 AGANet sites fitted with a smoothed trendline). The shading represents the 95% confidence interval. Note different scales.

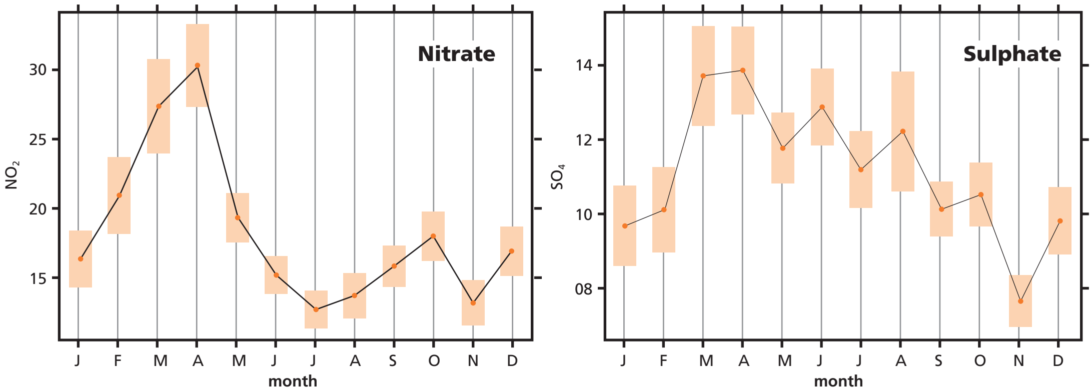

Figure 3.21: Nitrate and sulphate concentrations (µg m^{-3}) at rural sites, 1999-2009 (data from 12 AGANet sites by month of the year). The shading represents the 95% confidence interval. Note different scales.

Sulphate

49. PM sulphate concentrations have been monitored at the Eskdalemuir EMEP site for over 30 years. Over the period 1977-2002, sulphate concentrations decreased by a factor of two, whilst at the same time SO_2 concentrations decreased by a factor of seven. The fraction of airborne sulphur present as sulphate has thus increased from 0.3 to 0.65. By the end of this time series, sulphate had become the major vector of atmospheric sulphur because of its much longer atmospheric residence time compared with SO_2. Changes in sulphate have not responded linearly to changes in SO_2 emissions over the 1977-2002 period. The simultaneous trends in precipitation sulphate at Eskdalemuir have followed closely those in PM sulphate, preserving a relatively constant rain-out/wash-out ratio. This would argue against there having been any major change in the size distribution and neutralisation properties of PM sulphate.

50. The non-linear relationship found between the concentrations of sulphate and SO_2 in the Eskdalemuir time series has been seen at other long-running EMEP stations in the Netherlands, Germany and Sweden (Lovblad *et al.*, 2004). In part, it reflects the different trends in SO_2 emissions at height and those near to the ground. If emission reductions have been faster for ground-level sources compared with emissions at height, then there would be a faster decrease in SO_2 concentrations compared with sulphate. Equally well, the increasing ratio of sulphate to total airborne sulphur may reflect a long-term increase in the oxidising capacity of the European atmosphere. Because of the different atmospheric lifetimes, PM sulphate responds to changes in behaviour over a significantly wider area than SO_2.

51. More recently, Jones and Harrison (2011) have surveyed trends in sulphate over the 2001-2008 period at a number of locations across Europe, including the UK. Trends in PM sulphate over this recent period were found to be small, in agreement with the view reported in RoTAP (2012) that there were no clear trends. Values of 12-month running mean sulphate varied from year to year because of some high values in monthly concentrations which occurred in some recent years but not in others. The values of apparent trends are thus heavily influenced by the choice of time period. Nevertheless, over the entire 1977-2008 time period, sulphate at Eskdalemuir has shown a trend of 3.6% per year, which is significantly smaller than the trend in SO_2 emissions. Jones and Harrison (2011) estimated that substantial further reductions in SO_2 emissions of around 50% would be required to achieve an appreciable reduction of about -1 $\mu g\ m^{-3}$ in sulphate and hence in $PM_{2.5}$ or PM_{10} for south-east England. These emission reductions would need to apply to all sources contributing to sulphate concentrations in the UK, which in practice would include sources throughout Western Europe.

52. The pattern of sulphate concentrations measured across the 12 long-term rural sites in the AGANet programme between September 1999 and December 2009 is shown in Figure 3.20. Concentrations increase from 2000 to 2003, then decrease to 2009, leading to a small overall decrease over this ten-year period (Mann–Kendall trend analysis at 95% confidence level shows an overall downward trend of -0.07 $\mu g\ m^{-3}\ yr^{-1}$). As with nitrate, the highest concentrations are in March and April, but the higher concentrations extend through the summer months of May to August (Figure 3.21).

Ammonium

53. Ammonium measurements at Eskdalemuir from 1990-2001 show a -20% to -30% decline, which is similar to that shown by nitrate (Lovblad *et al.*, 2004). This decrease is significantly greater than that reported for UK NH_3 emissions over the same period. This can be explained by the complex interaction of SO_2 and NO_x with NH_3, whereby ammonium levels are controlled more strongly by the availability of strong acids such as sulphuric (H_2SO_4), nitric (HNO_3) and hydrochloric (HCl) acids, than by the availability of NH_3 which is assumed to be in excess. The conclusion is that, in the long term, ammonium behaviour has been such as to create an aerosol which has retained a rather constant neutrality despite year-on-year variations and long-term trends in NH_3 emissions.

54. PM ammonium measurements switched to the Delta denuder method with nitrate in 2001. Again, no information on ammonium trends from the Delta network was presented in RoTAP (2012) reflecting the large annual variability and the lack of any strong trends.

Black smoke and black carbon

55. $PM_{2.5}$ black carbon measurements are currently taken at 21 sites across the UK. The UK Black Carbon Network is based on aethalometer measurements and provides hourly mean data. It was established in late 2008 and replaces the black smoke monitoring that was previously carried out (the UK Black Smoke Network). The annual mean concentrations in 2009 and 2010 are set out in Table 3.2. They are mostly in the range 1-3 μg m^{-3}, with the exception of the Marylebone Road kerbside site in London, which has much higher concentrations (9-10 μg m^{-3}). **Traffic emissions clearly make a significant contribution to black carbon concentrations.**

Table 3.2: Black carbon annual average concentrations 2009 and 2010.

Site	Mean concentration μg m^{-3}	
	2009	2010
Bath 6	2.5	2.2
Belfast Centre	2.1	1.9
Birmingham Tyburn	2.0	1.5
Cardiff 12	1.6	1.5
Dudley Central	1.7	1.9
Dunmurry 3	1.3	1.7
Edinburgh St Leonards	1.3	1.2
Folkestone	1.0	0.8
Glasgow Centre	2.9	2.7
Halifax 17	1.5	1.3
Harwell[a]	–	0.5
London Marylebone Road	10.0	8.8
London North Kensington	1.9	1.5
Manchester Piccadilly	2.1	2.0
Norwich Lakenfields[b]	–	1.0
Nottingham Centre	1.9	1.8
South Kirkby 1	2.2	2.0
Stoke Centre	2.0	2.1
Strabane 2	1.6	2.0
Sunderland 8	1.1	0.9
Woolwich 9	1.1	0.9

a Installed September 2009.

b Installed October 2009.

56. Longer term trends in black carbon concentrations can be gauged by combining the recent aethalometer data with results from the earlier Black Smoke Network. The black smoke data can be converted to black carbon equivalents at least as an approximation, even though there are significant differences in the measurement methods, including black smoke not being selectively sampled as the $PM_{2.5}$ fraction (Quincey *et al.*, 2011). Black carbon concentrations and trends derived in this way are shown in Figure 3.22.

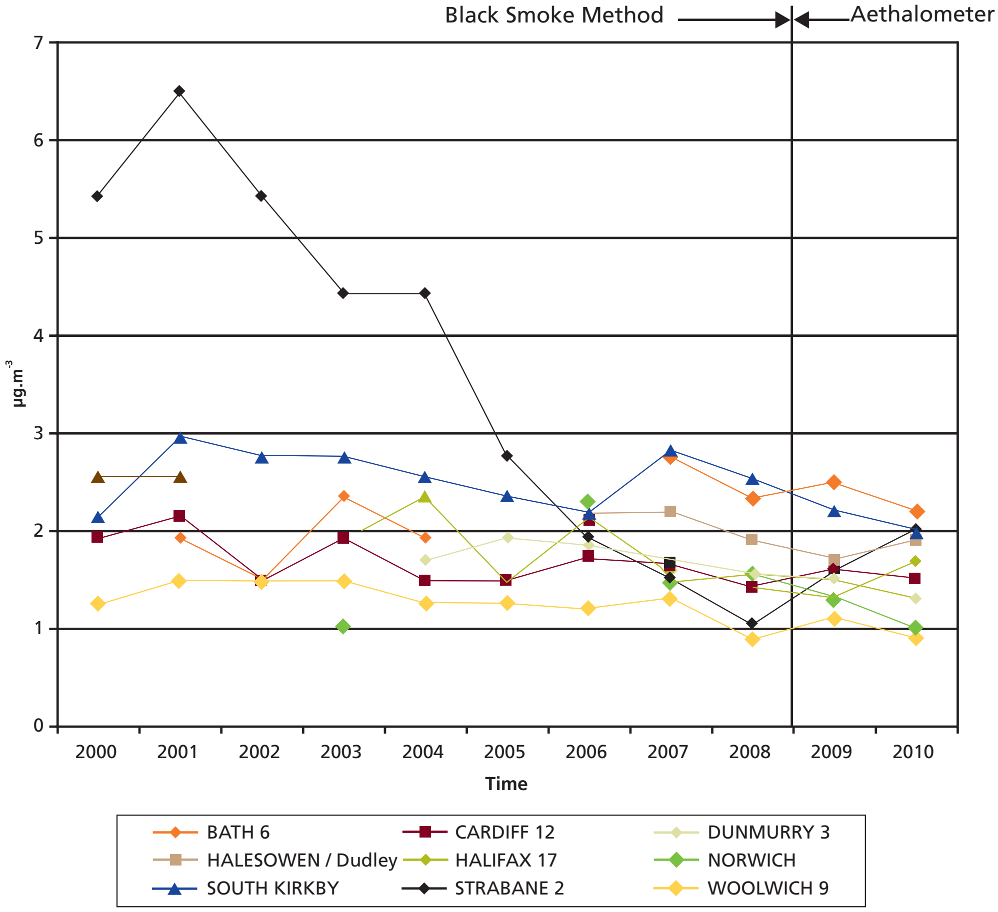

Figure 3.22: Trends in black carbon and converted black smoke concentrations 2000 to 2010.

57. Black smoke concentrations at Strabane 2 were initially much higher than at the other urban sites, but declined steadily until 2006, when they became comparable to those at the other sites. Oil-fired central heating was introduced in 2004 into the estate of houses that surrounds the monitoring site on three sides generally replacing coal burning, and this will have contributed to the decline. Apart from Strabane 2 there are no significant trends at the other urban sites across the UK.

58. Data from the aethalometer instruments are reported hourly, so that variations through the day can be observed. Diurnal variations averaged over 2010 are shown for four sites chosen to illustrate the different temporal patterns that arise from different sources (Figure 3.23). The shaded area represents the uncertainty in the mean value for each hour at the 95% confidence level. It does not represent the overall measurement uncertainty. As noted above, the London Marylebone Road kerbside concentrations are much higher and persist during the day; there are no morning and evening rush hour peaks. The influence of domestic heating on black carbon at the Strabane site is very evident, with an evening peak of a few µg m^{-3}. **There is thus evidence that the use of solid and/or liquid fuel for domestic heating can contribute to higher black carbon concentrations, with this being most significant during the evening.**

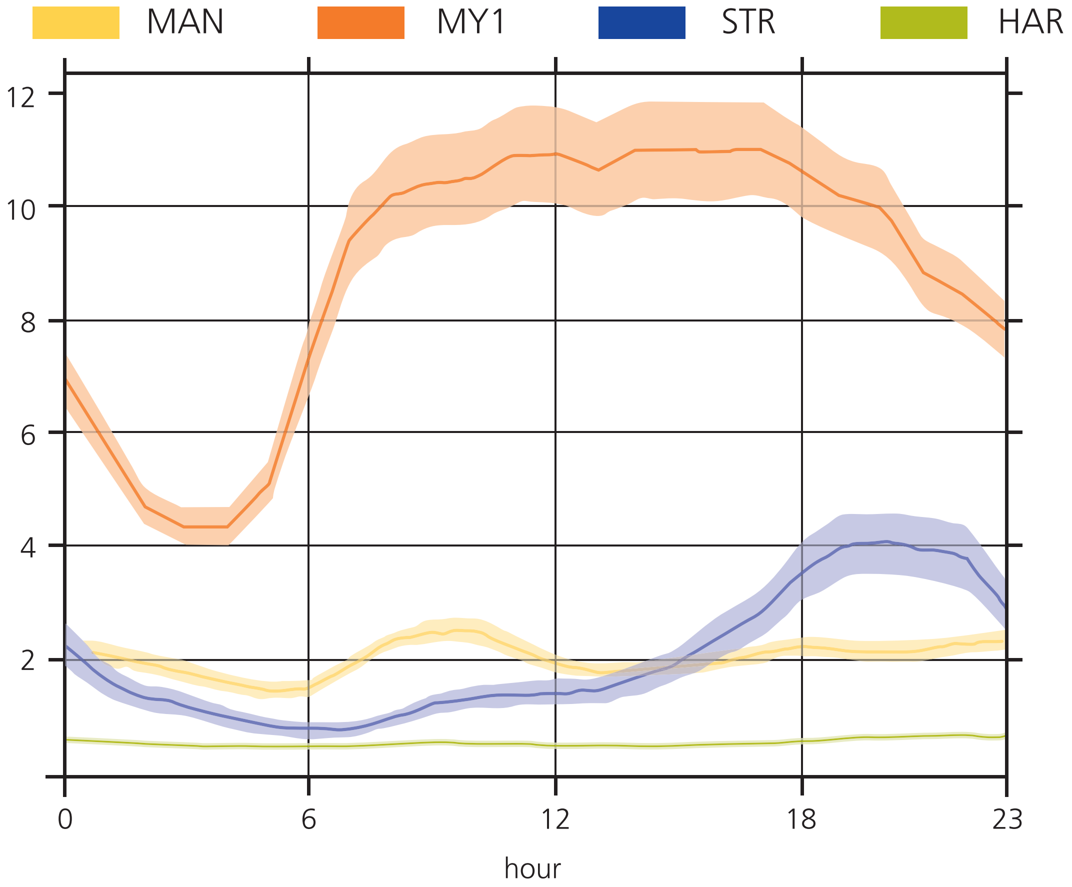

Figure 3.23: Black carbon diurnal variation in 2010 (µg m^{-3}) at London Marylebone Road (MY1), Manchester Piccadilly (MAN), Harwell (HAR) and Strabane 2 (STR) (Northern Ireland). The shading represents the 95% confidence interval of the mean.

3.10 Summary and recommendations

3.10.1 Key points from measurements

(a) There are limited measurements of the composition of $PM_{2.5}$ in different types of location and in different areas of the UK. This restricts the ability to understand sources of $PM_{2.5}$.

(b) Until recent years there have been few measurements of $PM_{2.5}$ concentrations using reference equivalent instruments. Data are now becoming available for a comprehensive network across the UK which should help understanding of $PM_{2.5}$.

(c) Regional (rural) background concentrations are particularly important, even in urban areas. In urban areas in central and southern UK at least 60-80% of the urban background $PM_{2.5}$ will on average be derived from the regional background.

(d) The regional background concentrations are dominated by secondary $PM_{2.5}$, primarily as ammonium nitrate and ammonium sulphate, but also as organic particles. In central and southern UK around 60% of the urban background $PM_{2.5}$ will be secondary particles.

(e) High $PM_{2.5}$ concentrations are frequently associated with air transported into the UK from continental Europe.

(f) Wintertime $PM_{2.5}$ concentrations are much higher and will make the greatest contribution to the annual mean. It may thus be more effective to target measures to those sources contributing to the elevated wintertime concentrations.

(g) Winter episodes can give rise to high $PM_{2.5}$ concentrations over a few days. These are due to a build-up of local emissions under stagnant weather conditions and are especially prominent in areas with continued domestic solid and liquid fuel burning.

(h) There is evidence that PM_{10} episodes associated with air arriving from continental Europe, especially during the spring, are composed of fine particles ($PM_{2.5}$) and not coarse particles ($PM_{2.5-10}$), with nitrate playing a particularly important role. This nitrate appears to be largely associated with ammonium, derived from ammonia emissions.

(i) Black carbon is a major component of the $PM_{2.5}$ associated with road traffic emissions and domestic (oil and solid fuel) combustion.

(j) Primary emissions from road traffic, including the non-exhaust component, make a significant contribution to the urban background increment of $PM_{2.5}$. They also contribute to regional secondary PM through the oxidation of emissions of nitrogen oxides.

(k) Road traffic can make substantial contributions to $PM_{2.5}$ concentrations at the kerbside (within 1 m of the kerb), but at the roadside (a few metres from the kerb) the contributions are relatively limited.

(l) There is evidence to suggest that domestic and commercial sources make a contribution to concentrations during the evening period, which may be due to solid fuel combustion and to particles released during cooking, but this needs further investigation.

(m) Sulphate particles are still important despite the large reductions in sulphur dioxide emissions.

(n) Based on the limited evidence available, primary particles from industrial sources do not appear to make a major contribution to urban background concentrations.

3.10.2 Recommendations

(a) AQEG recommends that resources should be made available to ensure that the results from the comprehensive monitoring network now in place are fully analysed, to extract as much understanding as possible about the sources contributing to $PM_{2.5}$ in different parts of the UK.

(b) AQEG recommends that measurement of iron (Fe) should be included as part of the chemical composition monitoring programme to improve source apportionment, since Fe is a marker for non-exhaust vehicle emissions.

(c) AQEG recommends that the MARGA instruments currently used for the chemical composition monitoring programme are reviewed to ensure they meet Directive requirements.

(d) AQEG recommends that additional chemical composition measurements are made in a variety of locations, principally rural, urban background and roadside, over different parts of the UK, to allow source apportionment to be carried out.

(e) AQEG recommends the expansion of the rural $PM_{2.5}$ monitoring network to allow the rural background to be properly defined. This should be given urgent consideration.

(f) AQEG recommends that further work is carried out to characterise the organic component of particles, in particular to improve understanding of secondary organic particles.

Chapter 4

$PM_{2.5}$ emissions and receptor modelling

4.1 Introduction

1. $PM_{2.5}$ is present in the atmosphere as a result of direct emissions from a range of sources (primary $PM_{2.5}$) and as a result of the chemical and physical transformation of various precursor gases from a range of sources (secondary $PM_{2.5}$). The relationship between emissions and atmospheric concentrations is therefore complex and a change in emissions does not necessarily lead to the same relative change in $PM_{2.5}$ concentrations and exposure.

2. This chapter discusses emissions of $PM_{2.5}$ and its precursor gases from various sources and gives projections to 2020. The uncertainties associated with emissions inventories are also described. Receptor modelling is an approach to the source apportionment of particles in the atmosphere which uses particle composition to estimate source contributions to airborne concentrations.

4.2 Emissions and sources of primary $PM_{2.5}$

4.2.1 Quantifying the emissions of all primary $PM_{2.5}$ components and their spatial distribution

3. Direct emissions of $PM_{2.5}$ in the UK are estimated by the National Atmospheric Emissions Inventory (NAEI).[1] A time series of the annual rates of emission by source sector is reported to the United Nations Economic Commission for Europe (UNECE) Convention on Long-Range Transboundary Air Pollution (CLRTAP). A consistent time series of UK emissions is updated annually by the NAEI; the latest version covers the years from 1980-2009 (the 2009 NAEI). The emissions are reported to comply with CLRTAP by source sector as defined under the Nomenclature for Reporting (NFR) format.[2]

4. Emissions are estimated for anthropogenic sources from combustion and non-combustion processes. The methodology for estimating emissions is described in the UK's Informative Inventory Reports (for example, in Passant *et al.* (2011)) and was described in detail in AQEG (2005). The methodology generally involves combining sector-specific emission factors and activity data. The activity data come from UK statistics on energy consumption, industrial output or transport. Emission factors are taken from emission inventory guidebooks, literature sources or national datasets, such as the compilation of emission factors for road vehicles published by the Department for Transport (DfT) (Boulter *et al.*, 2009). Exhaust emission factors for road vehicles are affected by type and size of vehicle, its age and what emission standard it complied with when manufactured and sold new, what fuel it runs on and the way the vehicle is driven. Vehicle emission factors are provided as a set of equations relating emission factors for each detailed vehicle type to average speed and are derived from measurements of emissions from vehicles driven over different 'real world' drive cycles. For some industrial point sources, emissions and activity data

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[1] See http://naei.defra.gov.uk/index.php.

[2] See http://cdr.eionet.europa.eu/gb/un/cols3f2jg/envtvpebw.

provided by specific operators may be used. Emission-estimating methodologies, emission factors and activity data are updated occasionally as further evidence emerges that helps to improve our understanding of emissions and the factors determining them, but a consistent inventory time series is always produced by back-calculating emissions from previous years.

5. Emissions from fugitive dust sources are particularly difficult to estimate, but occur as a result of many industrial and material handling processes. These include iron and steel production and working, cement production, mining and quarrying, construction and demolition, storage, handling and moving of mineral products, and a range of agricultural processes.

6. Non-exhaust emissions of $PM_{2.5}$ occur from road traffic, including tyre and brake wear, and road abrasion. Emissions are estimated for all these processes, but are highly uncertain. They are also unregulated sources, so emissions increase with increasing traffic levels.

7. Resuspension of dust from road surfaces is not included as a source of $PM_{2.5}$ in the inventory as it does not require reporting under CLRTAP. Studies have shown that this source may make a significant contribution to atmospheric concentrations of $PM_{2.5}$ in urban areas (AQEG, 2005; SNIFFER, 2010), but it is extremely difficult to quantify using traditional inventory approaches. The contribution of resuspension of road dust to $PM_{2.5}$ concentrations has usually been estimated by modelling and source apportionment methods rather than through emission inventories (e.g. by Grice *et al.*, 2010, and Abbott, 2008). For heavily-trafficked roads, it may be difficult to differentiate the contribution of road dust resuspension from the contributions of other non-exhaust traffic sources, such as tyre and brake wear emissions, but in more rural areas it may be necessary to treat the resuspension of roadside dust in the wake of moving vehicles explicitly as an additional source of airborne particulate matter (PM) in models. The contribution of this source will depend on the silt loading of the road surface and meteorological factors such as wind and precipitation.

8. Primary emissions of $PM_{2.5}$ from natural sources such as wind-blown dust, sea spray and biological material are not included in the inventory. Emissions from accidental or natural fires in forests or crops are estimated by the NAEI, but are not included in reported national emission totals.

9. In almost all cases, emission factors are expressed as mass emissions of total suspended particulate matter (TSP) per unit of activity (e.g. fuel consumed, distance travelled, tonnes output, etc.) or, at best, in terms of mass of PM_{10} emitted per unit of activity, and then fuel- and/or sector-specific $PM_{2.5}$ size fractions are applied to estimate $PM_{2.5}$ emissions. The $PM_{2.5}$ size fractions represent the mass fraction of TSP or PM_{10} emitted as $PM_{2.5}$ and are generally taken from EMEP/CORINAIR emissions inventory guidebooks (EMEP, 2009), USEPA sources (AP-42)[3], industry experts or other literature sources.

10. Where applicable, emission factors take into account control measures for the abatement of particulate matter emissions. For stationary sources, these include regulations on industrial and combustion processes and dust control measures covered under EU directives and national legislation as well as local

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[3] See http://www.epa.gov/oms/ap42.htm. *AP-42: Compilation of Air Pollutant Emission Factors (USEPA).*

measures. These measures are not primarily aimed at reducing $PM_{2.5}$ but will effectively do so. The Integrated Pollution Prevention and Control (IPPC) Directive (2008/1/EC) essentially requires operators of industrial installations to control dust emissions from plant and installations covered under the Directive, with operators demonstrating that they use best available techniques to prevent or reduce pollution. A range of installations falls under the Directive from energy production, metals and minerals production and processing, chemical production and waste management, to smaller operations in, for example, paper production and poultry farming. Similarly, the Large Combustion Plants Directive (2001/80/EC) and Waste Incineration Directive (2000/76/EC) set emission limits for dust as well as for PM precursor gases. These Directives have been brought together in various forms of national legislation to control emissions from industrial processes in England, Wales, Scotland and Northern Ireland, with regulations enforced by the Environment Agency (England and Wales), Scottish Environment Protection Agency and Environment Agency Northern Ireland. Local authorities have responsibilities for regulation and control of air pollution under the Clean Air Acts covering the prohibition of smoke from chimneys, control of dust, smoke and fumes from furnaces, and the designation of smoke control areas.

11. Fugitive dust emissions are generally controlled by national legislation related to statutory nuisance and are regulated for industrial and waste management sites and pig and poultry farms. Local authorities control dust emissions from construction sites via the planning process.

12. AQEG (2005) described a number of abatement options for mitigating PM emissions from stationary sources, categorised as process change measures, process management and end-of-pipe abatement. Process change involves modification to raw materials, process technologies and operations, and the use of cleaner fuels. Process management involves improvement to operations such as cleaning up dust spillages, preventing dust escaping to ambient air and introducing more efficient combustion. Practices involving surface wetting are used to control PM emissions from the resuspension of dust from road surfaces in and around quarries and construction sites. End-of-pipe controls are widely used to reduce dust in waste streams through the use of electrostatic precipitators, fabric filters, scrubbers and cyclones.

13. Exhaust emissions of PM from mobile sources with diesel engines are regulated by a series of European vehicle emission directives, complemented by directives on fuel quality and the regulation of emissions from non-road mobile machinery, railway locomotives and vessels on inland waterways. For road vehicles, emission factors take into account vehicles equipped with diesel particulate filters, either on new vehicles to meet vehicle emission directives or as retrofits. These measures have resulted in a significant reduction in PM emissions (> 95%). Other methods for reducing PM emissions from vehicle exhausts include diesel oxidation catalysts, which are also used on diesel vehicles to help reduce carbon monoxide (CO) and hydrocarbon emissions, and a variety of fuel additives. The use of sulphur-free diesel, biofuels and alternative fuels such as compressed natural gas also help to reduce PM emissions.

14. The London Low Emission Zone (LEZ) was specifically introduced as a policy to reduce PM emissions from traffic in London. Since 2008, the LEZ requires heavy goods vehicles (HGVs) and buses in much of Greater London to meet a minimum of Euro III standards for PM; the requirement was strengthened to Euro IV in January 2012. The LEZ scheme will also be extended to large vans and minibuses which will be required to meet a minimum of Euro III standards for PM from January 2012. Transport for London (TfL) is also introducing hybrid and hydrogen fuel cell vehicles to its bus fleet which will help to reduce PM exhaust emissions.

15. Mitigation of non-exhaust emissions from vehicles is far more difficult. TfL is carrying out a trial of new power washing and dust suppressant technology as a means of reducing PM emissions from road dust resuspension. The roads in two locations will be jet-washed to remove existing particles, then sprayed with a biodegradable solution to stick particles to the road.

16. Further details on legislation and abatement measures for controlling PM emissions are given in AQEG (2005) and a recent SNIFFER report (SNIFFER, 2010). Although introduced to control total PM mass emissions, all of these measures are assumed to reduce emissions of the $PM_{2.5}$ fraction in inventories.

17. Emissions of $PM_{2.5}$ in the UK projected forward to 2020 are estimated by making assumptions about future levels of activities and changes in emission factors (Wagner, 2010). For stationary sources, consideration is given to the implementation of emissions legislation, new technologies and fuel switching in combustion (e.g. in power stations, domestic heating and in industry), as well as to the latest UK energy projections for industrial, commercial, domestic, agricultural and power generating industries. For mobile sources, the penetration of new vehicles meeting tighter emission regulations (up to Euro VI for light duty vehicles and Euro VI for heavy duty vehicles) is taken into account, together with figures from DfT on future traffic projections and other assumptions affecting the fleet in the future. The projections also account for the uptake of biofuels reaching 10% of transport fuels by energy content by 2020 in accordance with the conditional target in the EU Biofuels Directive (2003/30/EC). Consumption of low-strength blends of bioethanol and biodiesel lead to a reduction in exhaust emissions of PM (AQEG, 2011). New regulations on PM emissions from non-road mobile machinery are also taken into account.

18. Figure 4.1 shows the trends in primary $PM_{2.5}$ emissions from sources in the UK between 1990 and 2020. The figures are taken from the latest version of the NAEI covering the years up to 2009 (Passant *et al.*, 2011) and projections up to 2020 based on the Department of Energy and Climate Change's (DECC's) UEP38 energy projections and DfT's AF09 traffic projections. The figures are also presented in Table 4.1.

19. Total UK emissions of $PM_{2.5}$ in 2009 amounted to 70 ktonnes. The inventory covers around 165 individual sources with many of these making similar contributions to the UK totals. These sources have been combined into key groups in Figure 4.1. When grouped in this way, the single largest source of $PM_{2.5}$ emissions in 2009 was road transport exhausts (18%) followed by residential combustion (14%) and non-exhaust emissions from tyre and brake wear, and road abrasion (11%). This indicates that the combined contribution of road transport sources was 29%.

20. According to the inventories, total $PM_{2.5}$ emissions have fallen by 55% since 1990. This has largely been due to a reduction in emissions from the power generation sector caused by the switch from coal to natural gas and nuclear power electricity generation, as well as improvement in the performance of particulate abatement plants at coal-fired power stations.

21. Exhaust emissions of $PM_{2.5}$ from road vehicles have fallen by 57% over this period, due to the penetration into the fleet of diesel vehicles meeting tighter standards on PM emissions and the use of cleaner fuels offsetting the growth in traffic during this period, and also to the switch to diesel in the car fleet. Non-exhaust emissions from traffic have increased by 20% over the same period as traffic has increased with no accompanying controls on these emissions; they are now responsible for 38% of all traffic emissions of $PM_{2.5}$ in 2009 whereas in 1990 their contribution was just 18%. Figure 4.2 shows a more detailed breakdown in emissions from road transport by vehicle type over the 1990-2020 period. Diesel cars were responsible for the largest share in exhaust emissions (41%) in 2009. Most of the decline in exhaust emissions since 1990 has come about through reductions in PM emissions from HGVs.

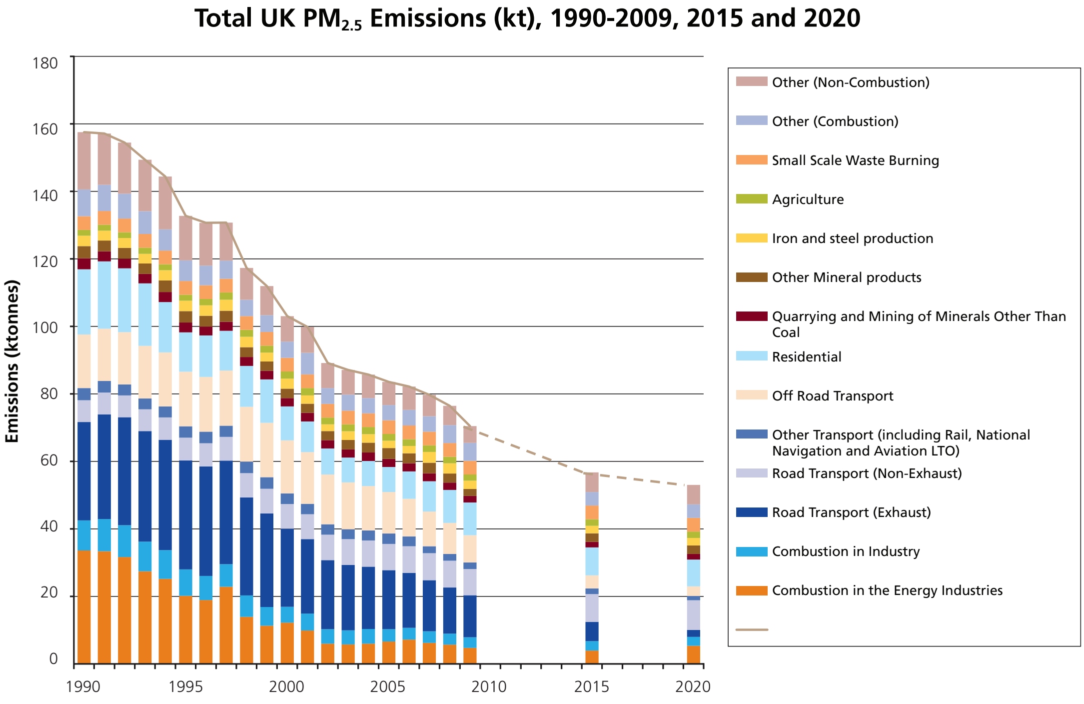

Figure 4.1: UK emissions of primary $PM_{2.5}$ from different sources from 1990-2009 and projected to 2020 according to the NAEI (Passant *et al.*, 2011). The projections are based on assumptions about future levels of activities and changes in emission factors according to current legislation (Wagner, 2010).

Table 4.1: UK emissions of primary $PM_{2.5}$ from different sources from 1990-2009 and projected to 2020 according to the NAEI (Passant *et al.*, 2011). The projections are based on assumptions about future levels of activities and changes in emission factors according to current legislation (Wagner, 2010).

	UK $PM_{2.5}$ emissions (ktonnes)						
Emission source	**1990**	**1995**	**2000**	**2005**	**2009**	**2015**	**2020**
combustion in the energy industries	33.6	20.2	12.2	6.6	4.8	3.9	5.4
combustion in industry	8.9	7.8	4.7	3.7	3.1	2.8	2.6
road transport (exhaust)	29.2	32.3	23.1	17.4	12.4	5.7	2.0
road transport (non-exhaust)	6.4	6.7	7.3	7.8	7.8	8.2	8.8
other transport (including rail, national navigation and aviation landing and take-off)	3.6	3.4	3.2	3.1	2.0	1.6	1.3
off-road transport	15.9	16.2	15.7	12.3	8.0	3.9	2.9
residential	19.3	11.7	10.0	7.4	9.8	8.3	7.9
quarrying and mining of minerals other than coal	3.3	2.9	2.5	2.4	1.9	1.7	1.7
other mineral products	3.6	3.4	2.8	3.2	2.1	2.5	2.5
iron and steel production	3.1	3.1	3.0	2.2	2.5	2.2	2.2
agriculture	1.7	1.8	2.1	2.0	1.9	1.9	1.9
small-scale waste burning	4.1	4.1	4.1	4.1	4.1	4.1	4.1
other (combustion)	7.9	6.1	4.8	4.6	5.3	4.0	4.0
other (non-combustion)	17.0	13.2	7.6	6.8	5.0	5.8	5.8
TOTAL	**157.6**	**132.8**	**103.1**	**83.6**	**70.5**	**56.8**	**53.0**

22. As stated earlier, inventories for $PM_{2.5}$ are generally calculated by applying $PM_{2.5}$ mass fractions to sector-specific emission factors for PM_{10} or TSP. To demonstrate this, Figure 4.3 shows the $PM_{2.5}$:PM_{10} ratio in emissions for a number of key sectors in 2009. These have been back-calculated from detailed inventories for both PM_{10} and $PM_{2.5}$ using ratios for each individual sub-sector, so they are in effect weighted averages of ratios for each key sector. The figure demonstrates how emissions from combustion processes are generally associated with high values of $PM_{2.5}$:PM_{10} ratio (e.g. 0.95 for vehicle exhausts), while PM emissions from more mechanical, non-combustion sources, such as mining, quarrying and agriculture, are associated with smaller $PM_{2.5}$:PM_{10} ratios indicating that a higher proportion of the emitted PM mass is in the coarse mode. The ratios for tyre wear, brake wear and road abrasion are 0.70, 0.40 and 0.54 respectively, giving a combined average of 0.55.

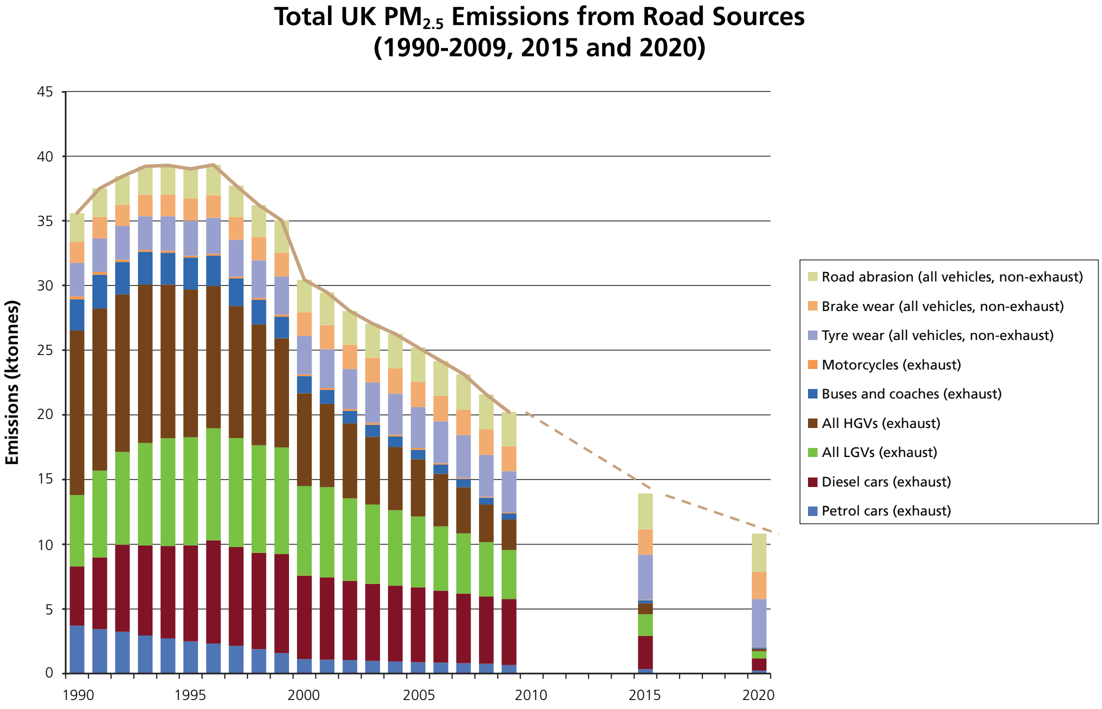

Figure 4.2: UK $PM_{2.5}$ emissions from road sources (ktonnes).

23. The reduction in UK emissions of $PM_{2.5}$ (Figure 4.1 and Table 4.1) can be compared with trends observed over the rest of Europe based on inventories submitted under CLRTAP by other EU member states. Figure 4.4 shows total EU-27 emissions of $PM_{2.5}$ from 1990 to 2008. According to these figures, residential combustion is the largest source of $PM_{2.5}$ emissions, responsible for 35% of total EU-27 emissions in 2008 compared with a contribution of 13% from this sector in the UK. This probably indicates the importance of solid fuel combustion for domestic heating in many other countries. Caution should be applied when comparing trends in emissions from sources in the UK with trends in other countries because of variability in the quality and completeness of inventories of $PM_{2.5}$ reported by different countries. Improvements have been made in the UK inventory that apply across the time series, but this cannot be assumed for all other countries.

24. National inventories provide an overall trend in emissions over time and indicate the contribution made by difference sources. Air pollution models require information on the spatial variability in source emissions. This is illustrated for the UK in Figure 4.5, which shows the distribution of total $PM_{2.5}$ emissions in 2009 on a 1 km x 1 km grid, as provided by the NAEI.[4] The methodology used for mapping emissions from different sources is provided by Bush *et al.* (2010). The map shows the dominance of major urban centres and road networks. The emissions shown around the UK coast are from shipping. The emissions are taken from implementation of the spatially-resolved inventory of emissions from shipping in 2007 developed by Entec (Entec, 2010), rescaled to 2009 and covering an area 12 nautical miles from the coast. These are not the same as the shipping emissions included in Figure 4.1 and Table 4.1 as 'national navigation'. The figures reported there refer to the definition of national shipping emissions specified by CLRTAP for national inventory reporting. Here, national shipping emissions are defined as emissions from coastal shipping between UK ports regardless of the distance the vessel sails from the coast and excludes emissions from international shipping movements.

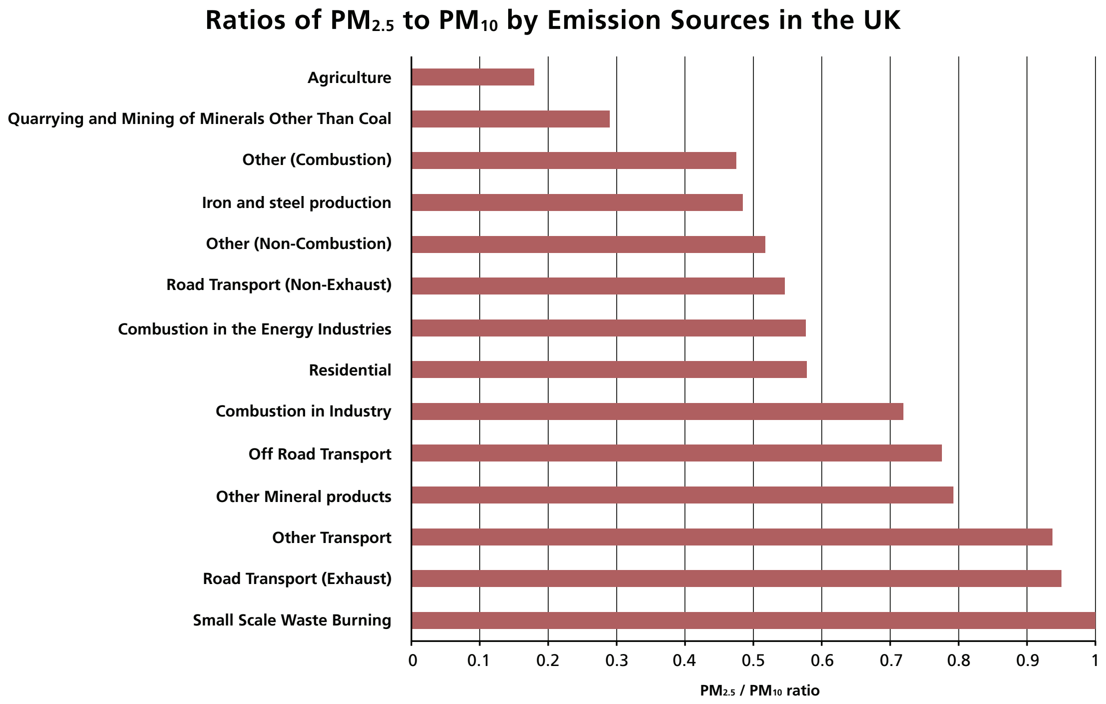

Figure 4.3: $PM_{2.5}$:PM_{10} ratio in direct emissions of PM from main source sectors in the NAEI in 2009.

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[4] See http://naei.defra.gov.uk/mapping/mapping_2009.php.

25. Figures 4.1 and 4.2 showed the latest UK emission projections for $PM_{2.5}$ to 2020. Future emissions of $PM_{2.5}$ are predicted to fall by nearly 17 ktonnes by 2020, a decrease of 25% relative to 2009 levels. Most of this decrease (10 ktonnes) is due to a reduction in exhaust emissions from road transport due to the continued fleet penetration of vehicles meeting tighter emission standards. Emissions from off-road transport are expected to fall by 5 ktonnes, the next largest contributor to overall UK emission reductions. Figure 4.2 illustrates how much more important the non-exhaust components of traffic emissions will become by 2020. Unless measures are taken to reduce these emissions, and taking into account the predicted decrease in exhaust emissions, the contribution made by non-exhaust traffic emissions (tyre and brake wear, and road abrasion) will increase from 38% of all road transport emissions in 2009 to 81% in 2020. This is based on current assumptions about the fraction of PM emitted from non-exhaust traffic sources as $PM_{2.5}$, but there is doubt, as discussed later in this section, as to whether any of the tyre wear PM mass is emitted in the $PM_{2.5}$ fraction. If this is the case, then the contribution from the remaining non-exhaust $PM_{2.5}$ emissions (brake wear and road abrasion) to total traffic $PM_{2.5}$ emissions will be 27% in 2009 rising to 71% in 2020. **This clearly emphasises the need to introduce measures to control emissions from these non-exhaust traffic sources.**

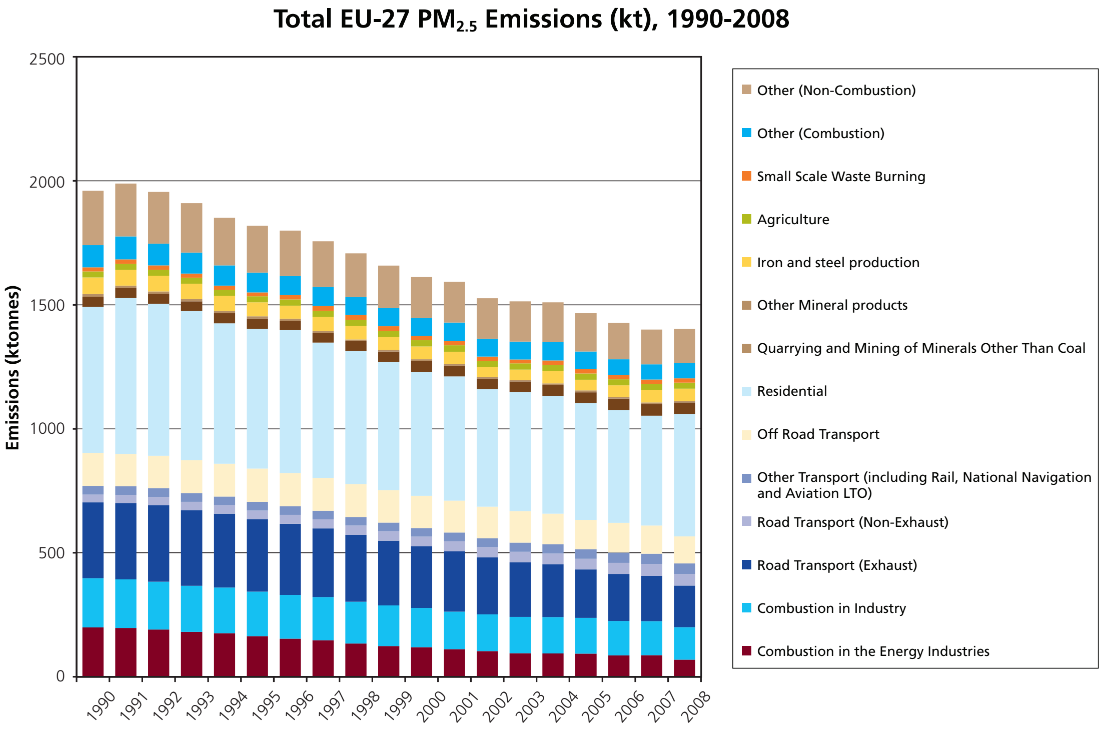

Figure 4.4: Total EU-27 $PM_{2.5}$ emissions (ktonnes), 1990-2008.

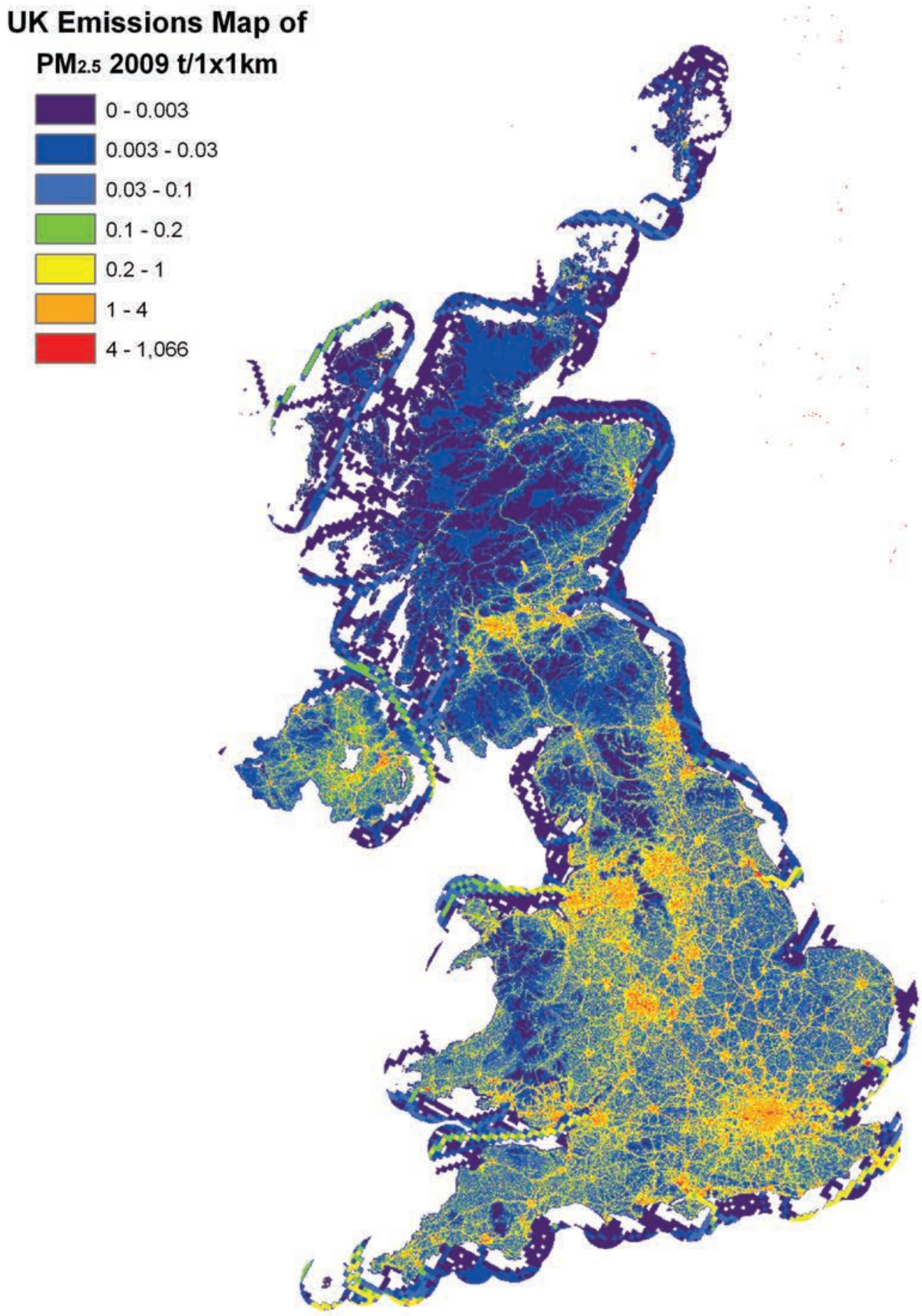

Figure 4.5: Spatial distribution of $PM_{2.5}$ emissions in the UK in 2009.

4.2.2 Inventory uncertainties and gaps

26. The uncertainties in emission inventory estimates stem from the uncertainties in emission factors, in the levels of activity for each source sector and in the size distribution of the particles emitted from each source. At the national level, the NAEI quantifies uncertainties in annual rates of UK emissions of PM

using a statistical Monte Carlo simulation approach consistent with the Tier 2 method in Good Practice Guidance for CLRTAP emission inventory reporting, details of which are given in Passant (2003) and Passant *et al.* (2011). The approach requires consideration of the available data on emission factors and levels of activity, combined with expert judgement to estimate the uncertainty parameters applicable to each source sector.

27. The estimated uncertainty in total UK $PM_{2.5}$ emissions is estimated to be between -20% and +30%. However, this estimate of uncertainty at the UK level, when compared with inventory uncertainties for other pollutants (Passant *et al.*, 2011), masks the much higher uncertainties in emissions from individual sectors and in emissions at specific locations and times. These are difficult to quantify, but were addressed in Annex D of the report *Evaluating the Performance of Air Quality Models* (Defra, 2010)[5] building on the work of Bush *et al.* (2008).

28. Emission estimates for the combustion of fuels are generally considered more reliable than those from industrial and agricultural processes and other non-combustion sources such as quarrying, construction, tyre and brake wear, and road abrasion. Many of these sources are diffuse or fugitive in nature, e.g. emissions from coke ovens, metal processing, mining, quarrying and construction. Emissions from these sources are variable in time and location around a specific plant or operation and are difficult to measure and it is likely that no entirely satisfactory measurements have ever been made. Even emissions from combustion processes can be subject to high uncertainty, especially in cases where PM emissions are very low and difficult to measure (e.g. from gas combustion or emissions from vehicles with a diesel particulate filter) or where the combustion process is not controlled or the fuel is of variable quality. This may be especially true for combustion of solid fuels including biomass. Inventories partly rely on emission factors and particulate size distributions based on measurements or information from other countries (e.g. the US) and the relevance of these data to UK emission sources can be questioned. Vehicle exhaust emissions of PM are dependent on many factors, including the driving cycle, engine technology and state of maintenance of the vehicle, and inventories are only able to use nationally-averaged information on these parameters.

29. Emissions of $PM_{2.5}$ from non-exhaust traffic sources, such as tyre and brake wear and road abrasion, are particularly uncertain. The $PM_{2.5}$:PM_{10} mass fraction for tyre wear of 0.7 used in the NAEI has been brought into question by recent evidence suggesting that very little PM emitted from tyre wear occurs in the $PM_{2.5}$ size fraction. The NAEI uses $PM_{2.5}$:TSP and PM_{10}:TSP mass fractions for tyre wear (and brake wear) taken from the EMEP Emissions Inventory Guidebook.[6] They are used in conjunction with TSP emission rates for tyre wear given by the same source. The Guidebook itself takes the information from an earlier review of measurements by the UNECE Task Force on Emissions Inventories.[7] However, the evidence given in this review for all non-exhaust traffic sources covers a very large range. Recent studies reported in the literature suggest that for normal all-weather tyres, the particles are primarily in two size ranges,

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[5] See http://uk-air.defra.gov.uk/reports/cat05/1006241607_100608_MIP_Final_Version.pdf.

[6] See Table 3-4 in: http://www.eea.europa.eu/publications/emep-eea-emission-inventory-guidebook-2009/part-b-sectoral-guidance-chapters/1-energy/1-a-combustion/1-a-3-b-vi-road-tyre-and-brake-wear.pdf.

[7] See http://vergina.eng.auth.gr/mech0/lat/PM10/.

either nanoparticles generated transiently at high temperatures which represent very little mass, or coarse particles, generally greater than 10 µm, from normal attrition processes.[8] These studies suggest very little mass of PM from tyre wear in the $PM_{2.5}$ size range. There is clearly a need for this conflict between available $PM_{2.5}$ size fractions for national inventory reporting and the more recent evidence to be resolved by those responsible for inventory guidebooks and emission factor compilations. **AQEG recommends this area is urgently addressed for inventory compilers and modellers and that further research is undertaken to improve available $PM_{2.5}$ emission factors for all non-exhaust traffic sources.**

30. The national inventory of $PM_{2.5}$ emissions is associated with higher levels of certainty than is associated with emissions at specific locations because it is largely derived from national statistics on, for example, total consumption of coal or diesel. The NAEI maps national emissions on a 1 km x 1 km grid for different sectors, but the spatial variability in emissions from many sources cannot be known with as much certainty because its estimation relies on proxy statistics such as household, employment and population census data to map emissions from area sources (e.g. domestic and industrial process emissions). On the other hand, emissions from some major combustion point sources such as power stations can be assigned with reasonably high levels of accuracy because the source location is broadly known and operators provide specific emissions data for their operations on the site either from measurements or calculated from known levels of activity at the site.

31. Emissions of $PM_{2.5}$ from road transport can be spatially disaggregated with reasonably high levels of accuracy using traffic flow information on individual links of the road network. Even here though, assumptions have to be made about the detailed composition of the fleet (e.g. the age composition and mix of petrol and diesel cars) as well as about the way people drive, all of which can be variable and increase the uncertainties in emissions at specific sections of the network.

32. Overall, the uncertainties in the spatial distribution of emissions broadly depend on the relative importance of point source emissions, which may be known reasonably accurately, and the line sources (e.g. road, rail) and area sources, such as domestic combustion and many fugitive sources, which are known with much less accuracy. In providing the 1 km x 1 km maps of UK emissions, the NAEI has considered the quality of the maps in terms of the contribution of point and area sources to mapped emission totals for each pollutant. These are shown in Table 4.2.

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[8] Workshop organised by RIVM and TNO for the Dutch Ministry for Infrastructure and the Environment: *The policy relevance of wear emissions from road transport, now and in the future.* Amsterdam, 22 June 2011.

Table 4.2: Contribution of point sources to UK emission totals in the NAEI (2006) (Bush *et al.*, 2008).

Pollutant	Point sources (%)	Area sources
CO	24%	76%
NH_3	2%	98%
NMVOCs	20%	80%
NO_x	32%	68%
PM_{10}	20%	80%
SO_2	78%	22%

33. Equivalent figures for $PM_{2.5}$ have not been estimated, but one might expect the contribution from point sources to be slightly higher than for PM_{10} because these mainly arise from combustion sources associated with higher $PM_{2.5}$ fractions than most area sources. This effectively means that the spatial distribution of PM_{10}, and most likely $PM_{2.5}$, emissions cannot be known as accurately as that of sulphur dioxide (SO_2) emissions because a much smaller proportion of emissions of $PM_{2.5}$ come from point sources. Considering emissions at a finer degree of resolution will lead to even higher levels of uncertainties. For example, the movement of traffic and the emissions near a specific road junction may be quite different to emissions occurring a few metres away on the same road link. Emissions in different parts of a major industrial plant where many different operations take place (e.g. an iron and steel works) can be highly variable but on a 1 km x 1 km grid may be considered nominally as a single point source.

34. Sources where the spatial distribution of PM emissions are particularly uncertain are domestic combustion, off-road machinery, shipping, construction, agriculture and other fugitive releases of dust.

35. Although it is not possible to quantify the uncertainties in the spatial distribution of emissions in terms of confidence levels, the NAEI has developed a fairly sophisticated approach to provide an overall data quality confidence rating for each pollutant map (Bush *et al.*, 2008). This is aimed at ranking the confidence rating for mapping emissions for different pollutants based on the quality ratings of the various 'grids' used to spatially resolve the data. The quality ranking of PM mapped emissions is relatively poor compared with the ranking for SO_2 and nitrogen oxides (NO_x) but higher than for ammonia (NH_3). This is because of the relatively high contribution to emissions of PM from diffuse sources.

36. Another consideration is the temporal variability in emissions. Many combustion sources follow a relatively regular pattern of activity by time of day and day of week or month (e.g. emissions from road traffic, power stations and domestic and industrial combustion), while others are far more sporadic in nature in terms of temporal and spatial variability, such as emissions from off-road machinery and construction, which can be transient in nature, starting and ending at any time throughout a year. Emissions from other fugitive dust sources can also be highly irregular and dependent on unpredictable changes in operating and weather conditions, e.g. emissions from agricultural processes. Other intermittent sources include natural and accidental occurrences, including forest and grass fires, bonfires and building fires.

37. Further consideration of all these aspects of emission inventory uncertainties can be found in Annex D of the report *Evaluating the Performance of Air Quality Models* (Defra, 2010) which gives some detail of the uncertainties in the spatial and temporal variability in emissions in the context of modelling uncertainties.

38. The NAEI only estimates emissions from sources which need to be included in national inventory reporting under various international commitments (e.g. CLRTAP) and/or where at least some information is available to make a reasonable estimate. Gaps in the inventory largely occur where there is insufficient source activity information available to make an estimate of emissions. In recent years, the NAEI has closed many of the gaps in the inventory for anthropogenic and some natural sources, but acknowledges the very high levels of uncertainties associated with some of their estimates, e.g. for bonfires, small-scale burning of waste, natural fires, etc. However, a number of gaps still remain in specific areas or for some additional processes in sectors which are already covered in the inventory. These include emissions from:

- certain arable farming processes and harvesting;
- domestic cooking and barbecues;
- building demolition processes;
- certain quarrying processes such as blasting and filling of used quarries;
- certain fugitive emissions in the metals industry (e.g. smelting); and
- use of munitions by military operations and for quarrying.

39. Without constructing an inventory, it is impossible to judge the magnitude of these emissions, but the sources are ranked above in an anticipated decreasing order of importance to emissions on a national scale. However, in some locations and at certain times, these sources could make a significant contribution to local emissions, e.g. from building demolition.

4.3 Quantifying the emissions of $PM_{2.5}$ precursor gases, their conversion to particles and their spatial distribution

40. Emissions of $PM_{2.5}$ precursor gases from anthropogenic sources in Europe are also estimated by inventories and reported by countries to CLRTAP. The NAEI provides a time series for UK emissions of the precursors NO_x, SO_2, non-methane volatile organic compounds (NMVOCs) and NH_3 from 1980-2009 and projections to 2020. These four pollutants are those covered under the National Emission Ceilings (NEC) Directive which sets national emission ceilings for each of these pollutants for EU member states to be met by 2010. Emissions are estimated in the same way as for $PM_{2.5}$ using sector-specific emission factors and activity data.

41. Emissions of these pollutants occur to varying degrees from stationary and mobile combustion, industrial processes and agricultural sources. Many of the European regulations and national legislation that control direct emissions of PM also control emissions of these precursors, although the abatement options are different for each pollutant. The Large Combustion Plants Directive and IPPC Directive apply to NO_x and SO_2, while SO_2 emissions are also influenced by the Sulphur in Liquid Fuels Directive (1999/32/EC). Vehicle emission directives limit emissions of NO_x and NMVOCs from vehicle exhausts, though there is evidence to suggest that these directives have not been effective in reducing "real world" NO_x emissions from modern diesel vehicles manufactured to meet Euro III-V standards (Carslaw *et al.*, 2011). The Fuel Quality Directive (2009/30/EC) limits the volatility and sulphur content of transport fuels. The Solvent Emissions Directive (1999/13/EC) limits emissions of NMVOCs due to the use of organic solvents in certain activities and installations. Emissions from shipping are controlled under the International Convention for the Prevention of Pollution from Ships (MARPOL), which sets limits on the sulphur content of marine fuels and NO_x emissions from new engines. More stringent standards are now controlling emissions from new aircraft engines. Further information on legislation and abatement options for these pollutants can be found in previous AQEG reports[9] and SNIFFER (2010).

42. Figure 4.6 shows the UK emissions of NO_x, SO_2, NMVOCs and NH_3 from 1990-2020. The figures are taken from the latest version of the NAEI, covering the years up to 2009 (Passant *et al.*, 2011), and projections up to 2020 based on DECC's UEP38 energy projections. Figure 4.6 also shows how precursor emissions in the UK have fallen by varying amounts over the period from 1990-2009, partly due to the varying contributions made by different sectors to each pollutant. Emissions of NO_x have fallen by 59% since 1990 due mainly to reductions from road transport and combustion for power generation. Estimations are on the basis of the current vehicle emission factors used in the NAEI which have been brought into question. The NAEI is currently switching to a new set of emission factors that are more in line with up-to-date evidence on the efficiency of recent and current Euro standards for diesel vehicles. When implementation is completed, this is likely to lead to a reduction in the estimated rate of decline in UK NO_x emissions over recent years. NMVOC emissions have fallen by 70% since 1990, mainly due to reductions from road transport. SO_2 emissions have fallen by 89% since 1990, almost entirely due to reductions in combustion emissions from the power generating industry. Emissions of NH_3 are dominated by agricultural sources and have only declined by 21% since 1990.

43. As well as showing different trends over time because of differences in source contributions, the $PM_{2.5}$ precursor emissions also exhibit different spatial patterns, as shown in Figure 4.7, for example, where NO_x emissions are dominant in major urban areas, and NH_3 emissions occur predominantly in more rural areas of England. The contribution of different UK precursor emissions to ambient $PM_{2.5}$ therefore varies spatially as well as having varied over time due to the different trends in emissions of each precursor gas.

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[9] See http://www.defra.gov.uk/environment/quality/air/air-quality/committees/aqeg/publish/.

44. Due to abatement of emissions from stationary and mobile combustion sources, largely brought about by legislation and EU directives, UK emissions of both NO_x and SO_2 are predicted to continue falling, by around 35-40% by 2020 relative to 2009 levels. Much smaller reductions are predicted in UK emissions of NMVOCs (8%) and NH_3 (< 1%). Again, the projections for NO_x use the existing vehicle emission factors and, when the new emission factors are used, a smaller reduction in NO_x emissions for 2020 is expected.

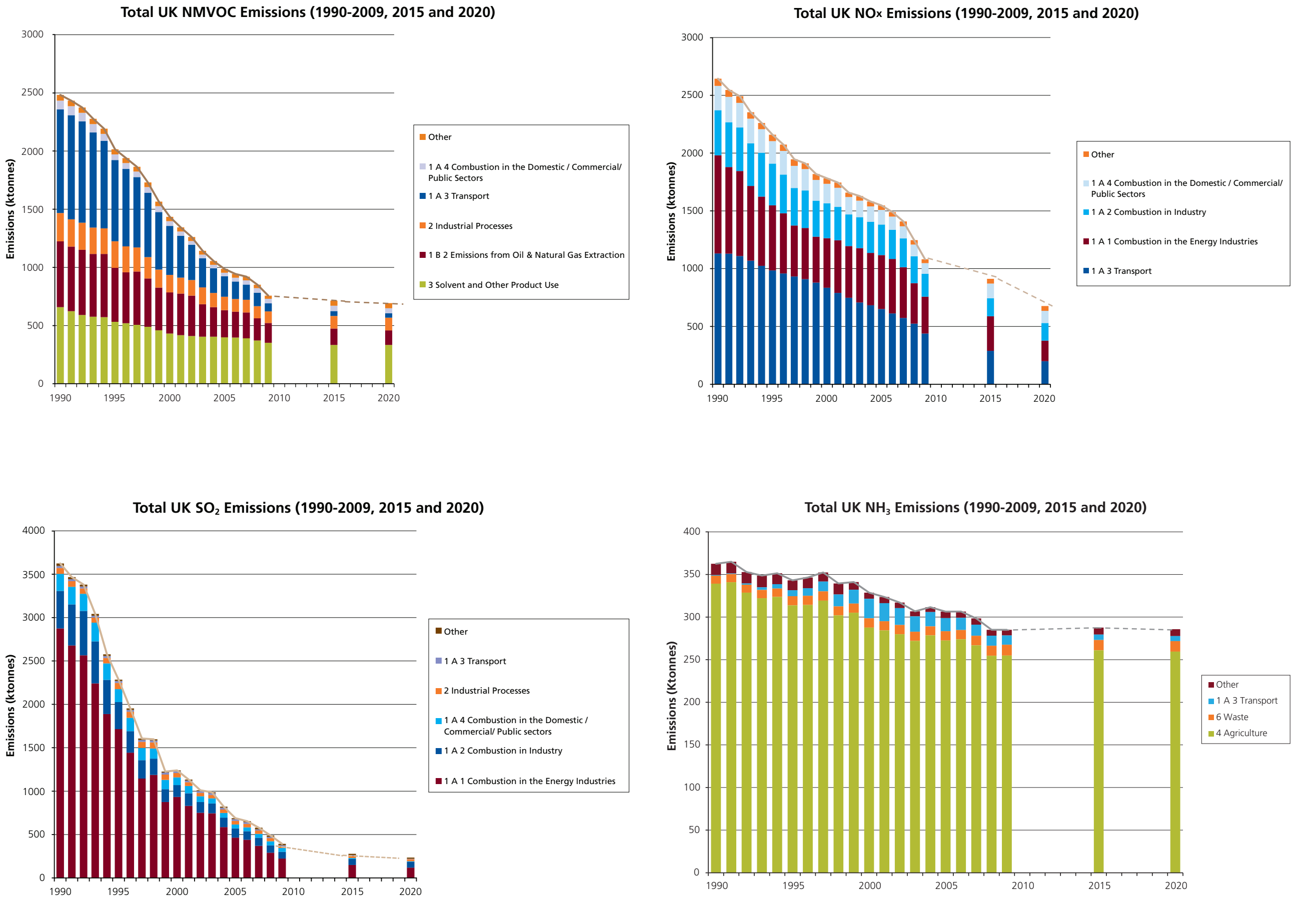

Figure 4.6: UK emissions of $PM_{2.5}$ precursor gases: NO_x, SO_2, NMVOCs and NH_3 (1990-2020).

45. Road transport is a relatively small source of NH_3 emissions compared to agriculture, but its contribution in urban areas, where it could make a larger contribution to local ammonium nitrate formation, will be higher if traffic emissions are allowed to rise. Traffic emissions of NH_3 are predominately from petrol cars and, according to the emissions inventory, are on the decline due to the fleet penetration of modern cars with improved catalytic converters and lower emission factors. However, the situation could change in the future if Euro V and VI diesel vehicles with Selective Catalytic Reduction (SCR) systems for controlling NO_x emissions fail and lead to NH_3 slippage from the catalyst system. SCR works by intentionally adding NH_3 to the exhaust stream through the injection of urea. There is no evidence yet of NH_3 slippage from modern diesel vehicles, and the control systems are designed to prevent this from happening, but real world emissions performance of in-service diesel vehicles with SCR will need to be monitored to ensure that this is the case and that there are no increases in NH_3 emissions from road transport in urban areas as these vehicles penetrate the fleet.

46. Emissions of precursor emissions from sources in Europe make an important contribution to secondary inorganic and organic components of $PM_{2.5}$ in the UK. Table 4.3 shows the emissions of NO_x, SO_2, NMVOCs and NH_3 from the EU-27 countries between 2005 and 2020. These are taken from the baseline emissions scenario from IIASA's GAINS model used for the Negotiations on the Revision of the Gothenburg Protocol under CLRTAP (Amann *et al*, 2011).

Table 4.3: EU-27 emissions of $PM_{2.5}$ precursor gases: NO_x, SO_2, NMVOCs and NH_3.

ktonnes	2005	2010	2015	2020	% decrease from 2010 to 2020
SO_2	8055	3911	3090	2735	30%
NO_x	11158	8524	7175	5553	35%
NH_3	3855	3753	3709	3667	2%
NMVOCs	9161	7379	6492	5989	19%

47. According to the figures in Table 4.3, the changes in EU-27 precursor emissions between 2005 and 2010 are similar to those for the UK. The predicted changes in emissions between 2010 and 2020 for EU-27 shown in Table 4.3 are also similar to those predicted for the UK (Figure 4.6) for NO_x, SO_2 and NH_3, although rather larger reductions are predicted for NMVOC emissions in EU-27 than in the UK.

48. Shipping activities around European waters also make a significant contribution to PM precursor emissions, especially to NO_x and SO_2. Table 4.4 shows total emissions from shipping in the North Sea and North-East Atlantic sea territories; these figures are also provided by IIASA and used in the UKIAM (see Chapter 5). The figures illustrate how NO_x and NMVOC emissions from shipping are predicted to grow as emissions from other sources decline. Emissions of SO_2 are expected to fall slightly, due mainly to the reduction in the sulphur content of marine fuels. Considering only the North Sea region, which is designated a Sulphur Emissions Control Area (SECA), the reductions in SO_2 emissions are expected to be much greater, i.e. around 88% between 2010 and 2020. Without further abatement, emissions from shipping will become a dominant source of $PM_{2.5}$ precursor emissions in Europe.

Table 4.4: Emissions of $PM_{2.5}$ precursor gases from shipping in European waters: NO_x, SO_2 and NMVOCs.

ktonnes	2005	2010	2015	2020	% decrease from 2010 to 2020
SO_2	1060	1060	735	832	3%
NO_x	1510	1510	1792	1929	-16%
NMVOCs	57	57	83	101	-47%

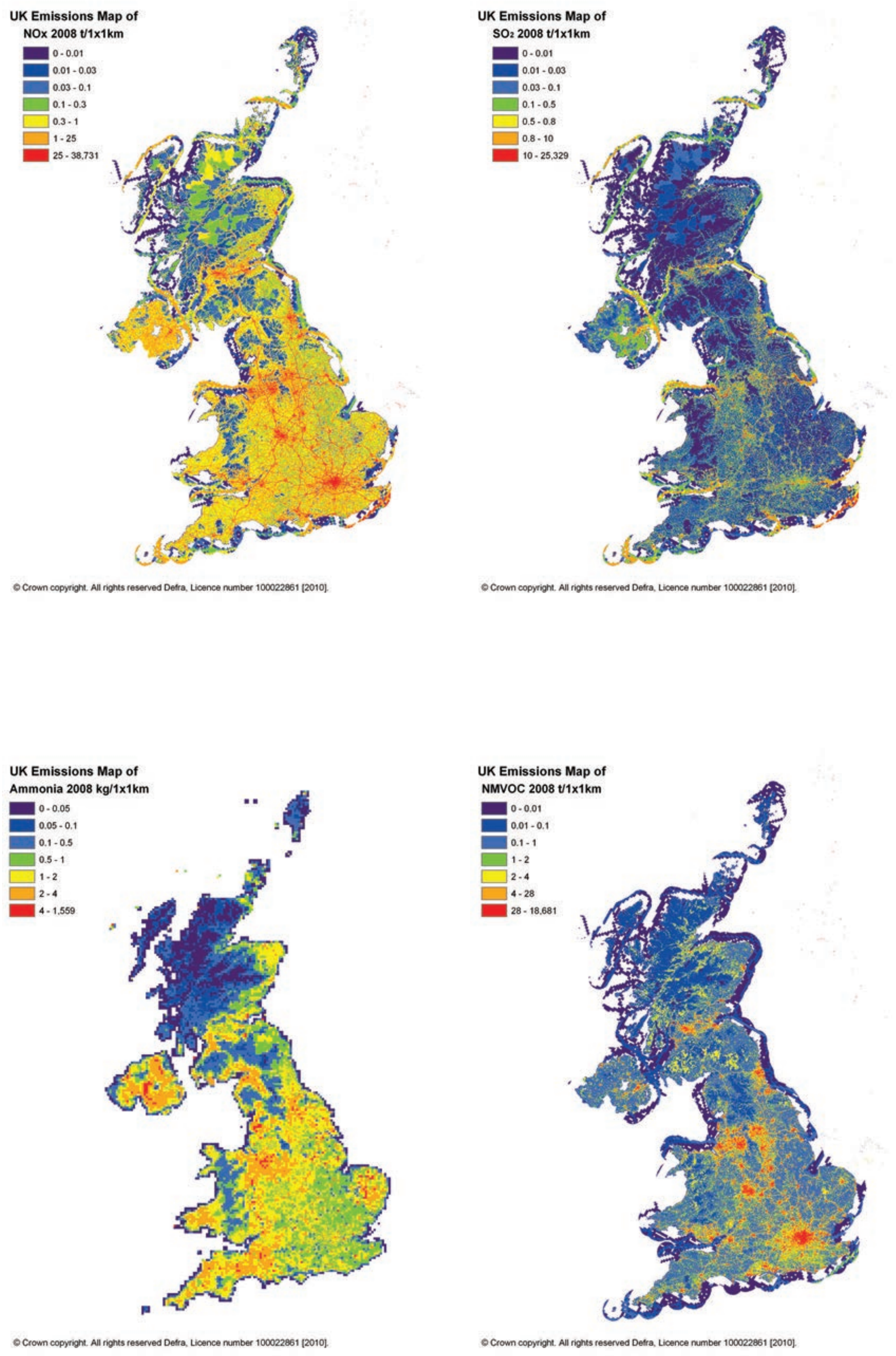

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Figure 4.7: Spatial distribution of $PM_{2.5}$ precursor gases (NO_x, SO_2, NH_3 and NMVOCs) in 2008.

4.3.1 Primary versus secondary PM

49. Not all of the particulate matter found in the atmosphere has been directly emitted into the atmosphere by primary sources. There are significant sources of both primary PM and secondary PM, the latter being formed in the atmosphere by chemical reactions involving primary emitted precursor species. Each secondary PM component would thus have its own primary PM precursor or precursors.

50. PM sulphate, for example, is an important component of secondary PM. It is formed by homogeneous gas phase oxidation of SO_2 by hydroxyl (OH) radicals and by cloud phase oxidation of SO_2 by hydrogen peroxide and ozone. These chemical reactions lead to the formation of particles of sulphuric acid which may take up ammonia from the atmosphere, leading to partial and ultimately complete neutralisation through the formation of ammonium sulphate. Particulate sulphate is a mixture of sulphuric acid and ammonium sulphate dissolved in the water associated with the atmospheric aerosol. Particulate sulphate is thus a secondary PM component with SO_2 and NH_3 as its primary pollutant precursors. Because of the exceedingly low volatility of sulphuric acid and ammonium sulphate, particulate sulphate is stable in the atmosphere and, once formed irreversibly, will not decompose back to ammonia and sulphuric acid vapours under normal atmospheric conditions.

51. There is an important class of secondary PM components whose atmospheric formation is reversible. The most important example of which is ammonium nitrate, formed by the chemical reaction of gaseous ammonia with gaseous nitric acid on pre-existing particles. Ammonium nitrate formation is thus associated with an increase in the PM mass rather than an increase in the PM number density. Ammonium nitrate is thermally unstable and may revert to gaseous ammonia and nitric acid with a time constant of minutes to hours depending on atmospheric conditions.

52. The atmospheric oxidation of certain volatile organic compounds (VOCs) can lead to the formation of low volatility, multi-functional organic compounds. If the volatilities of these oxidation products are sufficiently low, they can absorb onto pre-existing particles, passing into the particulate phase and increasing the PM mass but not the PM number density. Since the absorption is reversible, this component of organic PM may pass back into the atmosphere with a time constant of minutes to hours, again depending on atmospheric conditions. Once back in the atmosphere, these semi-volatile organic compounds may be further oxidised to oxidation products of even lower volatility, which may again absorb onto pre-existing particles, further increasing the PM mass, or they may be oxidised through to CO and water, depending on their chemical structures.

53. A wide range of VOCs are able to contribute to the formation of secondary organic aerosol. Laboratory studies show that precursors can include both anthropogenic and natural, biogenic compounds. Studies of airborne particles using carbon-14 as a tracer of contemporary (as opposed to fossil) carbon (Heal *et al.*, 2011) suggest that biogenic precursors play a substantial role (Section 4.6.3). Naturally-emitted VOCs from vegetation, termed biogenic VOCs, are an important contributor to the formation of secondary organic particles. Current knowledge of emissions within the UK is inadequate and AQEG recommends development of a natural speciated inventory for biogenic VOC.

4.4 A critical assessment of emission inventories for modelling of $PM_{2.5}$ concentrations

54. Modelling concentrations of $PM_{2.5}$ from emissions data is complicated by the fact that it requires inventories for a range of pollutants, including direct emissions of $PM_{2.5}$ itself as well as its precursor gases SO_2, NO_x, NH_3 and NMVOCs. These pollutants are emitted in varying amounts from different sources and exhibit different spatial and temporal behaviour. With contributions from four different precursor gases and direct emissions to concentrations of ambient $PM_{2.5}$, there are therefore more emission sources to include in the inventories used in modelling $PM_{2.5}$ concentrations than are required to model other pollutant concentrations. Many of these, especially non-combustion and diffuse sources, are very difficult to quantify. Many of the major sources of $PM_{2.5}$ in the atmosphere, both primary and secondary, are also difficult to regulate and control. Because of the wide variety of pollutants and sources that contribute to direct $PM_{2.5}$ emissions and to its formation in the atmosphere, the uncertainties in the emission inventories for each of these pollutants and sources are compounded in the models used to estimate concentrations.

55. Modellers turn to emission inventories as the primary source of emissions data. For anthropogenic emissions these are developed mainly by national inventory agencies. There is a well-established mechanism for reporting national emission inventories driven by the requirements of international bodies, such as the UN and EU, under various protocols. The emphasis is on providing inventories using common methodologies so that inventories provided by different countries are comparable and are also consistent with other national statistics, for example on energy consumption. This leads to a method of accounting for emissions which is ideal for policy-makers, who can identify which are the major sources and assess the costs and benefits of alternative control strategies. This approach works particularly well for greenhouse gases where the long-lived nature of these emitted gases means they can be treated almost as a commodity that can be traded; this is evident in the concept of "emission trading schemes". Using common inventory approaches that define what sources are and are not included in national inventories is also ideal for tracking progress against national emission reduction targets. For this, most national inventories are fit for purpose. They may also be adequate for air quality modelling of primary pollutants.

56. However, national inventories may fall short of what is required by models for $PM_{2.5}$ concentrations. Simply knowing the annual rate of emissions for a given pollutant and source sector is not sufficient, nor is it sufficient to consider only anthropogenic sources. The spatial and temporal variation in emissions is important and this is far less well-understood than the annual rate of emissions at a national level which is usually derived from national statistical datasets. The question is how do emissions vary with time of day and day of the week and season, where exactly do they occur and what are the influences of meteorological factors? Whilst some of these aspects can be assessed, e.g. for combustion sources, many cannot, especially for fugitive sources of dust and many agricultural processes.

57. National emissions inventories such as the NAEI must follow prescribed reporting guidelines defining what sources are and are not included, and what methods and emission factors should be used to calculate emissions. Most effort will therefore be expended in developing inventories that meet these requirements. The significance of this as far as $PM_{2.5}$ is concerned is that many of the sources that make a significant contribution to ambient concentrations of $PM_{2.5}$ are not included in national inventories, e.g. road dust resuspension, wind-blown dust and biogenic sources. There are no established methods for quantifying emissions from these sources and traditional inventory methods based on source-specific emission factors and activity datasets cannot be used. Inventories for biogenic sources are not developed on a regular basis as they are not required for national inventory reporting to the UNECE and Intergovernmental Panel on Climate Change (IPCC). Although techniques for estimating biogenic emissions from forests and grasslands are given in the EMEP/EEA air pollutant emission inventory guidebook (EMEP, 2009), these are not used to provide biogenic emission inventories for individual countries by respective inventory agencies. Air quality models normally use methods based on meteorologically-driven emission potentials to estimate the temporal and spatial variability in biogenic emissions. Emission estimates are uncertain, especially for individually speciated VOCs (isoprene and terpenes), and these techniques are not frequently used to provide an overall estimate of national NMVOC emissions from biogenic sources to compare with anthropogenic sources on a regular basis.

58. Although national inventories for most anthropogenic sources may be considered more reliable then inventories for natural sources, especially when they involve only an annual emission rate, even these can be of variable quality, consistency and completeness. Emission inventories reported by different countries can also be of variable quality and this will be more pertinent to models of $PM_{2.5}$ than it might be for nitrogen dioxide (NO_2) for example, because of the strong influence of precursor emissions of PM transported over a longer distance from different countries. There is a time lag of over a year between when emissions are reported and the inventory year they refer to and one question that can be asked is whether inventories for different countries used in models even refer to the same inventory year.

59. The quality of inventories of ammonia emissions may become of increasing concern in future years when it is considered how little NH_3 emissions are expected to change over time across Europe when compared with emissions for other $PM_{2.5}$ precursors, SO_2, NO_x and NMVOCs, as highlighted in Section 4.3. The question then becomes how well and how consistently inventories for NH_3 emissions are produced in the UK and other European countries; this inevitably focuses attention on the key sources from agriculture. It is particularly difficult to quantify agricultural emissions of NH_3. A similar argument may apply to the consistency and quality of inventories of SO_2 and NO_x from shipping, which will become more dominant as a source of $PM_{2.5}$ as emissions of these pollutants from other sources diminish. Shipping emissions are not captured well in national inventories and there will be an increased need to ensure consistent emissions datasets are made available for modellers covering sea territories across Europe.

60. At a local level, direct emissions of $PM_{2.5}$ from non-exhaust traffic sources will dominate exhaust emissions overall, assuming control measures such as diesel particulate filters are effective. There needs to be a consolidated effort to reduce the uncertainty in methods for quantifying emissions from tyre and brake wear and other non-exhaust processes for use in national and local inventories.

61. Inventories have not traditionally provided much, if any, detail on the component parts of $PM_{2.5}$. This situation is improving with the availability of some information on the fractions of organic and elemental carbon in emissions from combustion sources, but there is much more that needs to be done to improve understanding of the chemical composition of particulate matter emissions from different sources.

62. Section 4.2 listed several sources which are not included in the NAEI. For modelling $PM_{2.5}$, it is necessary to look beyond this and consider areas where primary $PM_{2.5}$ emissions and emissions of its precursors are most uncertain and further work is needed to improve methods for quantifying them in a manner suitable for air quality models. In the following list we highlight key sources (in order of importance), selected because of their contribution to total primary $PM_{2.5}$ emissions in the inventory and/or their levels of uncertainty and because of their potential influence on $PM_{2.5}$ concentrations locally or at certain times; we also identify specific areas of uncertainty for further work:

    - non-exhaust vehicle emissions including tyre and brake wear, road abrasion and road dust resuspension;
    - fugitive dust emissions from construction, demolition, quarrying, mineral handling and industrial and agricultural processes and methods for quantifying them nationally and locally;
    - $PM_{2.5}$ emissions from domestic and commercial cooking;
    - small-scale waste burning and bonfires;
    - wood burning and the effectiveness of control measures;
    - biogenic emissions of NMVOCs, for which a definitive inventory or estimation method is required;
    - emissions of NH_3 from agriculture, their temporal variability and methods for control;
    - emissions of SO_2 and NO_x from shipping, in particular their spatial distribution around ports and harbours, their temporal variability and future emissions;
    - exhaust emissions from off-road machinery used in construction and industry; and
    - exhaust emissions from diesel vehicles under real world driving conditions and the factors and technologies affecting them.

63. This list can be used to guide future areas of research so that modellers have access to information that goes beyond what is provided by traditional inventories.

4.5 Receptor modelling to estimate the source apportionment of $PM_{2.5}$

64. Receptor modelling refers to the use of monitoring data collected in the atmosphere (as opposed to the modelling of stack emissions) to infer the sources responsible for the measured concentrations of a pollutant. In many situations it can yield quantitative as well as qualitative estimates. Two generic methods are used most commonly for receptor modelling of airborne concentrations. Both require the collection of temporally-resolved, chemically-speciated data on the composition of airborne particles, often supplemented, in the case of the multivariate statistical method, by meteorological and gas phase pollutant data. The two types of method are:

(a) Chemical mass balance (CMB). This method requires *a priori* knowledge of the composition of all sources contributing to the airborne pollution, but not their emission rates. The measured air quality is assumed to be a linear sum of the contributions of the known sources, which are summed over each different sampling period to give the best match to the concentrations of the many chemical species measured in the atmosphere. In many studies, organic "molecular markers" which may be only minor constituents of emissions are measured, as these help to discriminate between similar sources (e.g. petrol and diesel engines). This method has been applied to airborne particles sampled in the West Midlands (Yin *et al.*, 2010).

(b) Multivariate statistical methods. A suite of methods is based upon factor analysis, of which Positive Matrix Factorisation (PMF) has been developed specifically for the purpose of source apportionment of air quality data, and is the most commonly applied. Earlier studies used Principal Component Analysis, but PMF has the advantages of being constrained not to give negative solutions, and allowing the weighting of input variables according to analytical uncertainty. The method requires no *a priori* knowledge of source composition, but such data are valuable in discriminating between similar sources. The method requires a substantial number of separate air samples (at least 50) which are analysed for a wide range of chemical constituents. Constituents which come from the same source have the same temporal variation and if unique to that source are perfectly correlated. Typically, however, a given chemical constituent will have multiple sources and the programme is able to view correlations in a multidimensional space and can generate chemical profiles of "factors" with a unique temporal profile characteristic of a source. Past knowledge of source chemical profiles is used to assign factors to sources; typically up to ten different sources can be assigned factors. The method works best with a large dataset in which the number of samples far exceeds the number of analytical variables, and gives a clearer distinction of sources if sampling times are short, so that overlap of multiple point source contributions to a given sample is minimised. Inclusion of meteorological measurements and gas phase pollutant data in the model will also assist in identifying the location of sources. The combined dataset of size-resolved and chemically-speciated particle concentrations, together with meteorological data and gaseous pollutant concentrations, will be a very powerful probe into the sources.

65. Receptor modelling in Europe has used a number of methods and lacks overall co-ordination (Viana *et al.*, 2008). Compositional data for PM_{10} and $PM_{2.5}$ are available from a sizeable number of European sites (Putaud *et al.*, 2010), but there have been rather few substantial studies in Europe, largely because of the lack of suitable measurement datasets. One of the best recent studies (Mooibroek *et al.*, 2011) applied the multivariate PMF method to $PM_{2.5}$ data from the Netherlands, generating a seven factor solution. The sources identified were nitrate-rich secondary aerosol, sulphate-rich secondary aerosol, traffic and resuspended road dust, industrial (metal) activities/incineration, sea spray, crustal material and residual oil combustion. The necessary comprehensive chemical composition datasets for UK sites are very limited and the only substantial study is Yin *et al.* (2010) which applied the chemical mass balance (CMB) model to specially collected datasets from one urban and one rural site in the West Midlands.

66. The main advantage of the CMB model is that unlike multivariate models, no deductions are needed to establish the identity of sources. The model is able to quantify unassigned mass and therefore gives a clear indication, not readily available from the multivariate models, of whether sources are missing. One of the main weaknesses of the CMB modelling approach is the need for locally relevant source profiles, which are frequently not available from recent measurements in Western Europe. Consequently, source chemical profiles from North America are used and these may not be wholly representative of UK sources, hence contributing to error. Another main weakness is that CMB can only account for those sources which are included and, whilst as indicated above it will quantify unassigned mass, it will give no clues as to the origins of that mass. In addition, CMB does not readily account for secondary pollutants or for the chemical modification of primary pollutants between source and receptor.

67. The main advantage of multivariate statistical models is that they are able to take account of secondary pollutants or chemical change between source and receptor and require no *a priori* knowledge of the contributing sources or their source profiles. On the other hand, there are disadvantages following from an inability to distinguish sources of similar composition or sources whose concentrations vary in a similar manner. It is notable from the literature that many of the source signatures generated by multivariate methods are extremely difficult to assign unequivocally to a given source type. This leads to uncertain assignments and the problems which flow from that.

4.5.1 Markers of primary sources

68. There are few sources for which a single chemical tracer can be used as a marker. Frequently sources can only be identified and quantified by use of a combination of chemical components. Commonly used elemental tracers are silicon or aluminium (soil and crustal dust), sodium (sea salt), barium (vehicular

brake wear) and nickel and vanadium (fuel oil combustion). Considerable care is required in their use as other sources may contribute in some localities.

69. One of the few sources which is typically quantified from a single component is biomass burning, which in the UK would typically refer to wood burning and bonfires, although occasionally woodland and forest fires would also contribute. The carbohydrate compound levoglucosan is typically used as a single marker of biomass burning as this is by far its major atmospheric source. Consequently, there is little risk of contributions from other sources but there remains the problem of converting the mass of levoglucosan into a mass of wood smoke particles. While many measurements exist of the ratio of wood smoke particles to levoglucosan mass, the ratio is highly variable depending on combustion conditions. Consequently, when using levoglucosan as an atmospheric tracer, there are large uncertainties in the subsequent conversion to a wood smoke mass. Other tracers of wood smoke include fine particle potassium (after correction for a contribution from wind-blown soil and sea salt), but a similar problem remains, namely that the wood smoke to fine potassium mass ratio is highly dependent upon combustion conditions and there is no unique factor for the conversion as it relates to the atmosphere. It is also possible to use an aethalometer to estimate wood smoke mass but the method (Sandradewi *et al.*, 2008) was developed in a Swiss valley where there are only two sources of carbonaceous particles, road traffic and wood smoke. In situations such as the UK where there may well be other sources of carbonaceous particles, the two component model on which the calculation is based is unreliable; as yet there is no agreed way of using the aethalometer to calculate wood smoke mass in the UK. Perhaps the most reliable way of estimating wood smoke mass is from the analysis of radiocarbon (^{14}C). Radiocarbon is associated with contemporary sources of carbon and not with fossil sources. Consequently, if contemporary elemental carbon is found in the atmosphere, it most likely arises from the combustion of biomass. Consequently, it is a fairly reliable tracer of wood smoke but there again remains a question over conversion of the elemental carbon mass to the mass of wood smoke particles, once again this is heavily dependent upon combustion conditions.

70. One of the other problem areas in source attribution relates to cooking aerosol. Early work from the United States used cholesterol as a marker of meat cooking and this was used by Yin *et al.* (2010) in their UK study, but the airborne concentrations were extremely low and no mass concentration was assigned to particles from meat cooking. However, Allan *et al.* (2010) used a variant on the multivariate statistical receptor modelling techniques to identify a contribution from cooking particles in the atmosphere of London. They applied PMF to mass spectral information obtained from non-refractory atmospheric particles using an aerosol mass spectrometer (AMS). The AMS volatilises particles before measuring their mass spectrum, and PMF is able to decompose the overall mass spectrum into the individual mass spectra of specific contributory particle types. Allan *et al.* (2010) found a particle type whose mass spectrum did not fit that of the conventional sources (road traffic and coal burning) but was similar to that of particles generated from hot corn oil. As a result, they assigned 34% of the primary organic particles in their sample to cooking, but this finding has yet to be replicated by other techniques.

4.5.2 Quantifying the secondary inorganic contribution

71. It is relatively straightforward to identify the contribution of secondary inorganic particles to the $PM_{2.5}$ mass in the atmosphere. Measurements of the sum of sulphate and nitrate expressed in chemical equivalents are typically very similar to the concentration of ammonium expressed in chemical equivalents, suggesting that within the fine particles these components are chemically combined as ammonium sulphate and ammonium nitrate, and the combined sum represents the secondary inorganic contribution to the $PM_{2.5}$ mass. Occasionally, there may also be a contribution from ammonium chloride formed from the reaction of hydrogen chloride, typically emitted from coal burning and incineration, with ammonia. However, ammonium chloride is semi-volatile (Pio and Harrison, 1987) and current emissions of hydrogen chloride are frequently too low to sustain an atmospheric concentration sufficient to lead to the formation of ammonium chloride particles.

4.5.3 Estimation of the secondary organic aerosol contribution

72. Differentiation of primary and secondary organic matter in particles is challenging. The most frequently used method is the elemental carbon tracer method which assumes that primary organic matter exists in combination with elemental carbon and that if the ratio between primary organic carbon (OC) and elemental carbon (EC) is known, then any organic carbon in excess of this ratio is attributable to secondary organic matter. This is a relatively well accepted concept but estimation of the ratio of OC to EC in primary emissions is difficult. Typically, this is estimated by plotting OC versus EC and identifying a minimum ratio in the data as in Figure 4.8. This ratio is assumed to be representative of time periods when no secondary organic carbon was present and the extent to which individual data points are above the minimum line is used to estimate their secondary organic carbon content. This method tends to fail in rural areas where secondary organic carbon is dominant and the minimum ratio inevitably includes some secondary organic matter. The presence of wood smoke, which is a primary material with a high OC:EC ratio, can also cause difficulties in disaggregating the contributions. Recent work by Pio *et al.* (2011) examining data from different locations has indicated that the graphical method of determining the primary OC:EC ratio frequently overestimates this ratio and consequently many of the data representing primary and secondary organic matter in the atmosphere may be in error. A number of assumptions have to be made to extract estimates of primary and secondary organic matter from radiocarbon measurements but this method has the important attribute of being able to distinguish between organic material derived from fossil fuel sources and that from biogenic sources.

73. A more recent method of estimating secondary organic particles is through the application of PMF to data from AMS instruments, as described in Section 4.5.1 for cooking particles. Typically, the disaggregation of AMS data using the PMF programme will identify one or two components enriched in ions indicative of oxidised carbon species, i.e. secondary organic matter. These are by convention referred to as OOA1 and OOA2, where OOA refers to oxidised organic aerosol. Some studies have shown that one of these components correlates relatively highly with sulphate and is of low volatility, while the other correlates much more closely with nitrate and is of appreciably higher volatility. The former is typically more oxidised than the latter.

4.5.4 Aerosol dynamics

74. A number of important constituents of $PM_{2.5}$ are semi-volatile, i.e. they exist simultaneously in the condensed and vapour phases and are able to transfer between the two. The most important semi-volatile inorganic components are ammonium nitrate and ammonium chloride. Both constituents will tend to equilibrate between the condensed phase and vapours as in the reactions below:

$$NH_3(g) + HNO_3(g) \rightleftharpoons NH_4NO_3\ (s\ or\ aq) \qquad (1)$$

$$NH_3(g) + HCl(g) \rightleftharpoons NH_4Cl\ (s\ or\ aq) \qquad (2)$$

These equilibria are sensitive to changes in the airborne concentrations of ammonia, nitric acid and hydrochloric acid vapours. In the vicinity of a source of ammonia, the chemical reactions can operate quite rapidly to re-establish equilibrium in the event of a change in the atmospheric concentration of any of the species. The implication is that nitrate concentrations may vary on a spatial scale of hundreds of metres if local ammonia concentrations vary due to source characteristics on the same spatial scale. However, a study in central England (Marner and Harrison, 2004) reported far less local variability in nitrate than in ammonia.

75. The partition between particles and vapour depends primarily upon the atmospheric temperature and relative humidity, which determine whether the particles are solid or present as deliquescent aqueous solutions. Generally, lower temperature and higher humidities favour incorporation into particles, whereas high temperatures and low humidities favour the vapours. A further complication is that the particle phase is typically made up of a mixture of substances which affects the thermodynamic relationship between the two phases. However, the thermodynamic properties of the condensed phase are reasonably well understood and programmes such as ISORROPIA II (Fountoukis and Nenes, 2007) are available to predict partitioning between the phases.

76. The other main semi-volatile component of $PM_{2.5}$ is organic matter, particularly secondary organic compounds. The partitioning of these compounds between the phases is far less well understood than for the inorganic components. It was for a long time assumed that the partitioning was based upon vapour equilibrating with a solution of the compound in organic liquids of low volatility present in the particles and that the partitioning could be described by the octanol–air partition coefficient. This concept was used for many years for polycyclic aromatic hydrocarbons (PAHs) but it was subsequently recognised that, in addition to the absorption process, polycyclic aromatic hydrocarbons are also likely to be subject to adsorption onto substrates such as elemental carbon. It was found that by including adsorption processes, numerical models could better describe the partition of PAHs between vapour and particles (Dachs and Eisenreich, 2000). Robinson *et al.* (2007) have argued that as vehicle-emitted particles advect away from their source, the adsorbed organic compounds vaporise and are oxidised to less volatile compounds which condense into secondary organic aerosol (SOA).

77. Early efforts towards understanding secondary organic aerosol formation were based on the assumption that each SOA precursor formed a SOA surrogate species by atmospheric oxidation. When the concentrations of the SOA surrogates reached saturation in the gas phase, then any additional material formed was transferred to the particulate phase and equilibrium was restored (Pandis *et al.*, 1992). Odum *et al.* (1996) built upon the absorptive partitioning approach of Pankow (1994) by assuming that each SOA precursor formed several SOA surrogates, typically two products. A major improvement to this approach, referred to as the Volatility Basis Set (VBS), was proposed by Donahue *et al.* (2006). This assigns compounds to volatility categories which partition into the particles according to empirically-derived factors. These approaches based on absorptive partitioning are the basis for the methods of SOA modelling that have been implemented in the CMAQ and CAMx models in the USA. When Utembe *et al.* (2005) tried to use absorptive partitioning to describe the incorporation of secondary organic matter into airborne particles, they found that they needed to increase the partition coefficients by a factor of several hundred in order to simulate the measured mass of organic matter. This has led to a recognition that most secondary organic compounds are appreciably oxidised and are therefore rather polar molecules which partition far more effectively into aqueous droplets than organic liquids. This is leading to the development of models of the partitioning into the aqueous phase of particles, but even that is likely to prove an inadequate descriptor of the partition process as there is now accumulating evidence for chemical reactions of secondary organic compounds within the aqueous phase, hence displacing the equilibrium further in favour of the condensed (particle) phase.

78. Another important process affecting semi-volatile materials is connected with the fact that the vapour pressure above a highly curved surface exceeds that above a less curved surface (the so-called Kelvin effect). The implication is that semi-volatile materials have a tendency to evaporate from smaller particles and condense into larger particles, hence affecting the PM size distribution. However, this process is not generally sufficiently rapid or important enough to influence the distribution of material into the coarse particle fraction. One process, however, which is important in shifting material from the fine to the coarse particle mode involves chemical reaction. In particular, nitric acid vapour, either arising directly from the oxidation of nitrogen dioxide or from the dissociation of ammonium nitrate (reaction (1) above), can react with the surface of coarse particles, as exemplified in equations (3) and (4) below for sodium chloride and calcium carbonate respectively. As a result, one acid displaces another and nitrate is incorporated into coarse particles with the displacement of hydrogen chloride or carbon dioxide respectively into the gas phase.

$$NaCl + HNO_3 \rightarrow NaNO_3 + HCl \qquad (3)$$

$$CaCO_3 + 2HNO_3 \rightarrow Ca(NO_3)_2 + H_2O + CO_2 \qquad (4)$$

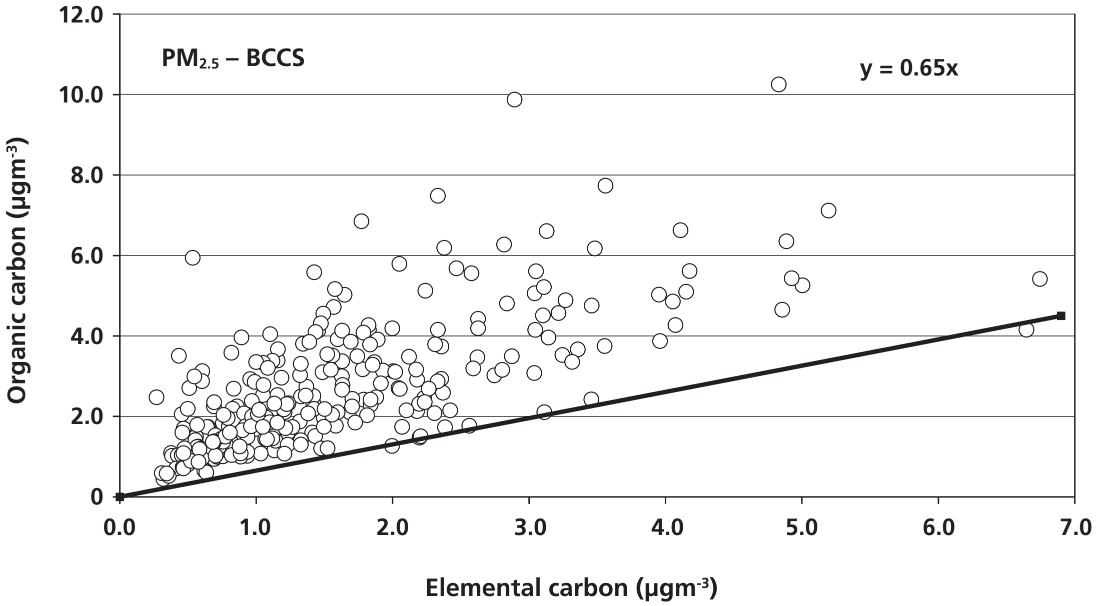


Figure 4.8: Relationship of organic carbon to elemental carbon in the $PM_{2.5}$ fraction at the Birmingham City Centre site (BCCS) (urban centre) showing the minimum ratio line.

4.6 Receptor modelling sources of $PM_{2.5}$ in the UK

79. Two generic methods of estimating the contributions of different sources to concentrations of particulate matter in the atmosphere are available as follows:

(a) Dispersion modelling and chemistry–transport models both start with spatially-disaggregated emissions inventories, from which concentrations of unreactive primary pollutants can be estimated by dispersion modelling. Modelling different sources or source types individually will give an estimate of the contribution of that source to airborne concentrations. Where distances of more than a few kilometres from source are involved, models of atmospheric transport in either a Lagrangian or Eulerian framework are more appropriate than simple dispersion models. For secondary pollutants, or pollutants that undergo chemical reactions in the atmosphere, it is necessary to use chemistry–transport models which combine dispersion and advection of pollutants with chemistry and deposition schemes, allowing an estimate of concentration as a function of location and altitude.

(b) Receptor modelling methods use measured atmospheric concentrations of chemically-speciated particles to infer the sources responsible for their emission or the pathways of formation of secondary pollutants. There are essentially two main types of receptor models, those based on multivariate statistical methods and those using a chemical mass balance approach (described in more detail in Section 4.5 above).

80. The Pollution Climate Mapping (PCM) model used extensively in the UK to inform policy is a hybrid of the two approaches. It uses measured airborne concentration data as the basis for estimating concentrations and source contributions for certain types of particles, and also dispersion modelling to estimate the contributions from primary sources. It is described in detail in Chapter 5.

4.6.1 Receptor modelling of particulate matter in the UK

81. Early approaches to source apportionment of particles in the UK atmosphere (e.g. Clarke *et al.*, 1984) used major component chemical composition to "reconstruct" the measured mass of particles, but this left a significant fraction of mass unassigned. This approach was developed further by Harrison *et al.* (2003) based upon the simplified premise that the mass of airborne particles could be accounted for by the following chemical components/sources:

- ammonium sulphate derived from the oxidation of sulphur dioxide and neutralisation by ammonia. Earlier work had shown very low levels of acid sulphate in the UK and consequently it is a fair assumption that the sulphate was wholly neutralised as ammonium sulphate;
- ammonium nitrate derived from the neutralisation by ammonia of nitric acid, itself formed from the oxidation of nitrogen dioxide. The compound is formed by gas-to-particle conversion and exists mainly in the fine particle fraction;
- sodium nitrate derived mainly from the reaction of sea salt with nitric acid vapour leading to formation of nitrate in the sea salt particles which are predominantly in the coarse size range;
- sodium chloride derived from sea salt;
- soil minerals represented by gypsum ($CaSO_4.2H_2O$);
- road dust, mainly coarse particles, generated by traffic for which iron is a valuable tracer;
- elemental carbon derived from combustion sources. In UK cities the vast majority arises from diesel vehicle emissions;
- organic compounds, both primary and secondary in nature. The primary component is derived from a wide variety of primary sources, and the secondary component from many different VOC precursors; and
- bound water. Under the conditions of weighing the air filters (specified by EN12341 as 45-55% relative humidity and 20 ± 2°C), the hygroscopic particles retain a significant amount of strongly bound water which is not taken account of directly in the chemical analysis.

82. Airborne particles are sampled onto a filter which is weighed before and after sampling to determine the mass of particles. It is subsequently analysed for sulphate, nitrate, chloride, calcium, iron, elemental carbon and organic carbon, whose masses are converted to chemical compounds or source-related constituents using the numerical factors in Table 4.5. Some of the numerical factors (for example, the one that converts sulphate to ammonium sulphate) are determined directly from molecular weights, whilst others, such as the factor converting iron to a mass of road dust, are based upon regression analyses, the aim being ultimately to account through the model for entire "mass closure" such that the reconstructed particle mass equals the gravimetrically-determined mass. By applying this method to particles from adjacent roadside and urban

background sites, it was shown that the mass of particles making up the roadside increment (i.e. the difference between the roadside concentration and the urban background) was comprised almost wholly of elemental carbon (54.8%), organic carbon (27.4%) and road dust (18.3%) (Harrison *et al.*, 2004).

Table 4.5: Adjustment factors used in mass closure (Harrison *et al.*, 2003).

Analyte	Conversion to	Numerical factor
sulphate	$(NH_4)_2SO_4$ *	1.38
	hydrate	1.29
nitrate (fine)	NH_4NO_3	1.29
	hydrate	1.29
nitrate (coarse)	$NaNO_3$	1.37
	hydrate	1.29
chloride	NaCl	1.65
calcium	$CaSO_4.2H_2O$	4.30
iron	soil/road dust	5.50 (roadside) 9.00 (background) 3.50 (roadside increment)
elemental carbon	elemental carbon	1.00
organic carbon	organic compounds	1.30 (roadside) 1.40 (background) 1.20 (roadside increment)

* After subtraction of sulphate derived from gypsum ($CaSO_4.2H_2O$).

83. This method was subsequently applied by Yin and Harrison (2008) to samples of $PM_{1.0}$, $PM_{2.5}$ and PM_{10} from roadside, urban background and rural sites in the West Midlands. The method was shown to account well for the gravimetrically-measured mass of particles without invoking the presence of bound water, which the authors attributed to the lower humidity in the weighing room compared to the previous study. The results for $PM_{2.5}$ at the urban background Birmingham City Centre site on all days and on days when PM_{10} exceeded 50 µg m^{-3} (episode days) appear in Figure 3.17 in Chapter 3. A number of points can be drawn from this average account of particle mass:

- secondary sulphates and nitrates make up a very large proportion of average $PM_{2.5}$ mass;
- nitrate tends to dominate mass on high pollution days, defined as when PM_{10} exceeds 50 µg m^{-3}; and
- there are substantial contributions from organic compounds and iron-rich road dusts which are likely to include contributions from a range of sources.

84. In a further paper, Harrison and Yin (2008) analysed the data for organic and elemental carbon from their mass closure study. They calculated separate concentrations of primary and secondary organic carbon based upon the "elemental carbon tracer method" of Castro *et al.* (1999). This method

is predicated on the assumption that emissions of elemental carbon from combustion sources are always accompanied by a constant proportion of organic carbon, and that the ratio of OC to EC in those primary emissions is equal to the minimum ratio observed in atmospheric measurements. An interesting finding was that secondary organic carbon showed a marked seasonal variation, shown in Figure 4.9, which closely paralleled that of nitrate but not sulphate in $PM_{2.5}$. This is strongly suggestive of the semi-volatile nature of secondary organic matter, broadly paralleling the semi-volatility of ammonium nitrate, and hence leading to higher concentrations in the cooler parts of the year and substantial evaporation in the summer months. The observed peak in April, which has been observed in March or April data for nitrate in many years, is thought to arise from a combination of the prevalence of advection of continental air masses in the spring combined with low average atmospheric temperatures.

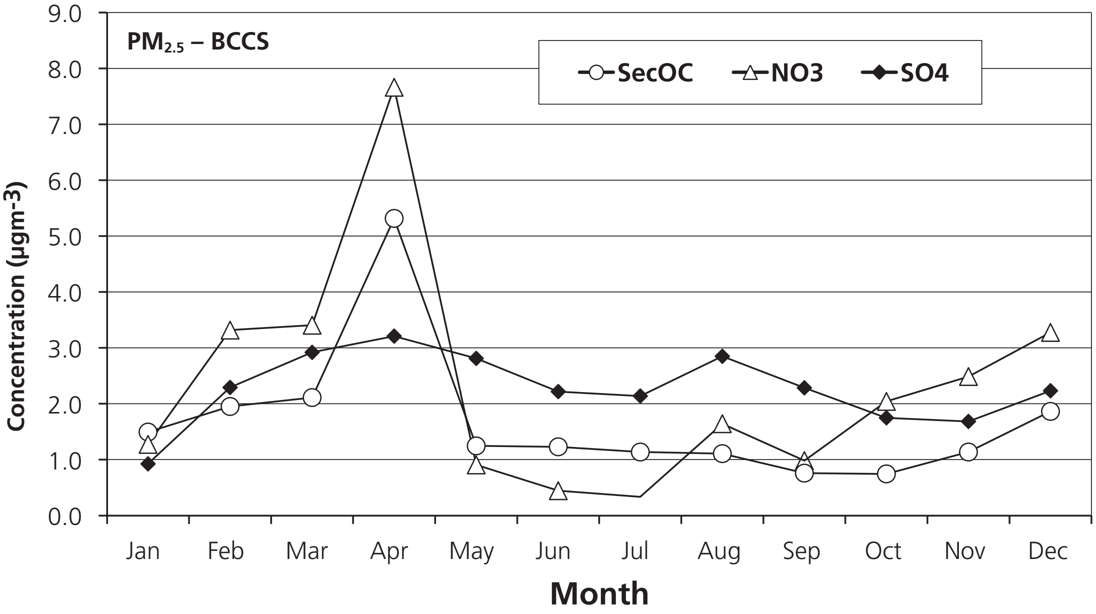


Figure 4.9: Monthly mean concentrations of secondary OC, nitrate and sulphate in $PM_{2.5}$ at the Birmingham City Centre site (BCSS) (urban centre) (Yin *et al.*, 2010).

85. The examination of differences between roadside, urban background and rural sites also led to the following conclusions:

(a) There is a substantial regional background of organic carbon consisting of long-lived primary compounds and secondary species. This tends to dominate the overall concentration of organic carbon.

(b) Superimposed upon the regional background described by rural measurements is an urban increment of mainly elemental carbon with a composition consistent with that of road traffic emissions, but not with wood burning emissions.

(c) Roadside samples contain an additional EC-rich contribution due to vehicle emissions. In this traffic-generated increment, elemental carbon typically accounts for about 70% of total carbon.

86. In order to obtain greater insight into the sources responsible for organic compounds in the atmosphere, Yin *et al.* (2010) carried out a chemical mass balance (CMB) modelling study of the organic matter combined with major component chemical composition information to allow a more sophisticated reconstruction of organic matter mass. In order to employ a CMB model, they analysed a large number of organic molecular marker compounds within the particulate matter, including 13 n-alkanes, nine hopanes, 13 PAHs, 14 organic acids and two sterols. These were in addition to major chemical components and a range of trace element species (Harrison and Yin, 2010). This allowed disaggregation of the organic carbon (Yin *et al.*, 2010) into the following source components:

- vegetative detritus, i.e. fragments from leaves and other components of plants
- wood smoke
- particles from natural gas combustion
- particles from coal combustion
- suspended dust and soil
- particles from diesel engines
- particles from gasoline engines
- particles from smoking engines.

87. The chemical profiles of the sources used in the CMB model are derived from North American studies. Smoking engines are made up of poorly-tuned diesel engines (black smokers) and older petrol engines burning significant oil (white smokers). These are thought to parallel most closely engine emissions from off-road machinery such as tractors, diggers, etc., and two-stroke engines in the UK.

88. The CMB method is able to apportion those components for which source chemical profiles are input. It is not possible to approach secondary organic carbon directly as there is no unique profile, but the method assigns mass to "other organic carbon", i.e. from sources for which profiles have not been input. In the case of the samples from urban background and rural sites in the West Midlands, the "other organic carbon" represented a substantial proportion of the total carbonaceous mass and was found to correlate highly ($R^2 = 0.92$ for the rural site) with secondary organic carbon estimated using the elemental carbon tracer method (Yin *et al.*, 2010). Once again, in this dataset the secondary organic carbon showed a close relationship to nitrate concentrations.

89. Measurements were also made of other major ionic components of the particles allowing estimation of concentrations of ammonium sulphate, ammonium nitrate and sea salt. The results for an urban background site in Birmingham (EROS) and a rural site (CPSS) located approximately 20 km west of Birmingham appear in Figure 4.10.

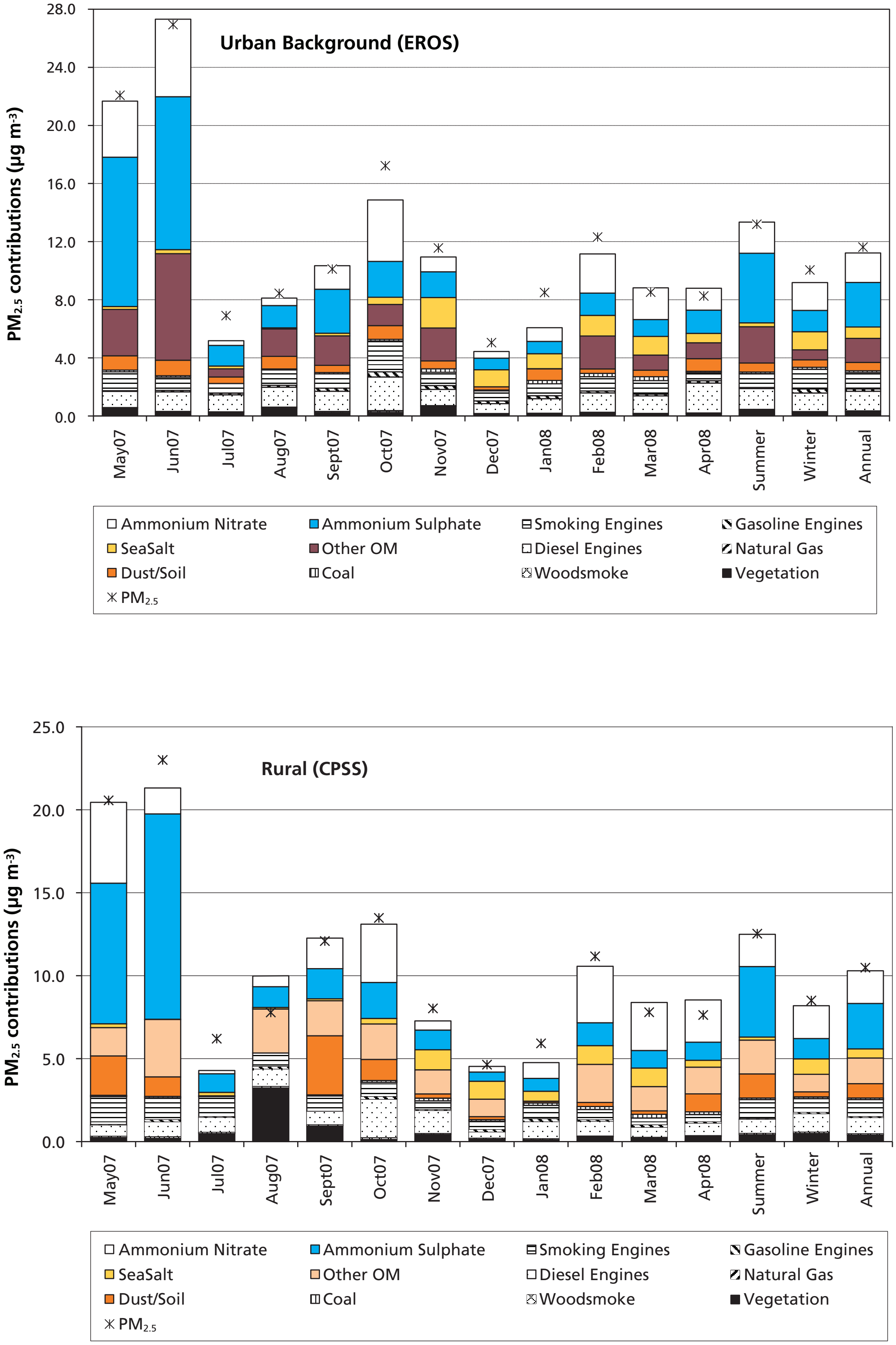


Figure 4.10: Source contribution estimates for PM$_{2.5}$ from the CMB model (Yin *et al.*, 2010).

4.6.2 Comparison of receptor modelling results with output from the PCM model

90. Both receptor modelling methods and the PCM model inevitably have weaknesses and uncertainties associated with their outputs. The chemical mass balance approach to source apportionment is limited to quantifying those sources for which source chemical profiles are available as inputs and consequently this may miss many minor sources. Additionally, the source chemical profile information is derived in the main from US studies which may not be wholly applicable to the UK situation. One example is that of road vehicle emissions, for which Yin *et al.* (2010) highlight differences in the vehicle parc between the fleet at the time of sampling and the vehicles used in the key North American study which characterised the source emissions profiles. This inevitably adds uncertainties to the assignments. In the case of PCM, those components estimated by dispersion modelling are only as good as the source emissions inventories, which for some sources are subject to very large uncertainties arising from the difficulties in collecting suitable data.

91. Comparison of the two approaches to source apportionment is made especially difficult by the fact that the source categories in the two models do not map directly onto one another. However, by making certain assumptions, it is possible to compare generic categories. The other key reservation in comparing the two modelling approaches is that data are not available for the same time periods. The Yin *et al.* (2010) study involved aerosol sampling over a 12-month period from May 2007 to April 2008. Daily $PM_{2.5}$ samples were collected for five days (Monday to Friday) at the beginning of each month using two co-located samplers at each site. Consequently, the results, although covering a 12-month period, represent the analysis of only 60 weekday samples. On the other hand, results from the PCM represent the analysis of annual means for the year 2009. A comparison of the outputs of the two approaches appears in Table 4.6 and Figure 4.11. In order to make this comparison, source categories disaggregated by the PCM have had to be combined in order to map onto the sources identified by the chemical mass balance receptor model, and in some cases categories identified by the receptor model have had to be combined in order to match the PCM outputs. The assumptions made are listed in the notes to Table 4.6.

92. Viewing Table 4.6 and Figure 4.11, the most obvious difference is in the secondary inorganic fraction and this can be explained by the use of different sampling periods. The traffic and off-road/smoking engine categories are broadly similar for the two models, especially when viewing the sum of the two categories, given that the CMB model probably does not adequately distinguish off-road emissions from malfunctioning on-road vehicles. By far the largest divergence between the models is in the category of industry/commercial/domestic emissions (14% of total emissions in the PCM and 2% in the CMB). This category (see note to Table 4.6) in the case of the PCM comprises the sum of industry, commercial and domestic categories and half of the long-range transported primary particulate matter, while for the CMB model it is the sum of natural gas, coal and wood combustion aerosol. Since a substantial proportion of the industrial, commercial and domestic categories in the PCM model comprises particles from the combustion of natural gas and coal, there is a very real divergence. It appears that the NAEI uses a very high emission factor for emissions from natural gas combustion. However, the PCM also includes

inorganic particles from industries such as quarrying which are not accounted for in the source profiles input to the CMB and which are therefore a significant omission from the latter model. One of the other major differences is in the secondary organic fraction, which in the case of the Yin *et al.* (2010) model is derived by difference from the primary sources and is in close agreement with that estimated by the elemental carbon tracer method; in the case of the PCM, however, it is calculated by an off-line model which may not accurately describe the very complex physico-chemical processes involved in secondary organic aerosol formation, in particular the partitioning of secondary organic species between the gas and condensed phases. However, the use of different averaging periods may also be important, as for secondary inorganic particles.

Table 4.6: Comparison of $PM_{2.5}$ source apportionment by receptor modelling (CMB) and PCM model.

Category	**PCM**		**CMB (Yin *et al.*, 2010)**	
	Mass (μg m^{-3})	**%**	**Mass (μg m^{-3})**	**%**
sea salt	0.66	4.7	0.78	6.7
secondary – inorganic[a] – organic	 4.31 0.85	 30.7 6.0	 5.10 1.66	 43.9 14.3
traffic (exhaust, brake and tyre wear)	2.26[b]	16.1	1.51[c]	13.0
soil and dust	1.90[d]	13.5	0.85[e]	7.3
off-road/smoking engines	0.93[f]	6.6	1.13[g]	9.7
industry/commercial/ domestic	1.93[h]	13.7	0.21[i]	1.8
other/residual[j]	1.22	8.7	0.39	3.4
Total	**14.06**	**100**	**11.63**	**100**

Notes:

a. Comprises ammonium nitrate, fine sodium nitrate and ammonium sulphate.
b. Includes traffic exhaust, brake and tyre wear and half long-range transported primary PM.
c. Comprises diesel and gasoline emissions including non-exhaust fine particles.
d. Comprises urban and rural dust categories.
e. Comprises dust/soil and vegetative detritus categories.
f. Off-road vehicle emissions.
g. Smoking engine category.
h. Sum of industry, commercial and domestic categories and half long-range transported primary PM.
i. Sum of natural gas, coal and wood combustion aerosol.
j. Unaccounted for by model.

Note: Long-range transported primary PM in the PCM model output is assumed to be 50% from road traffic and 50% from industry/ commercial/domestic emissions.

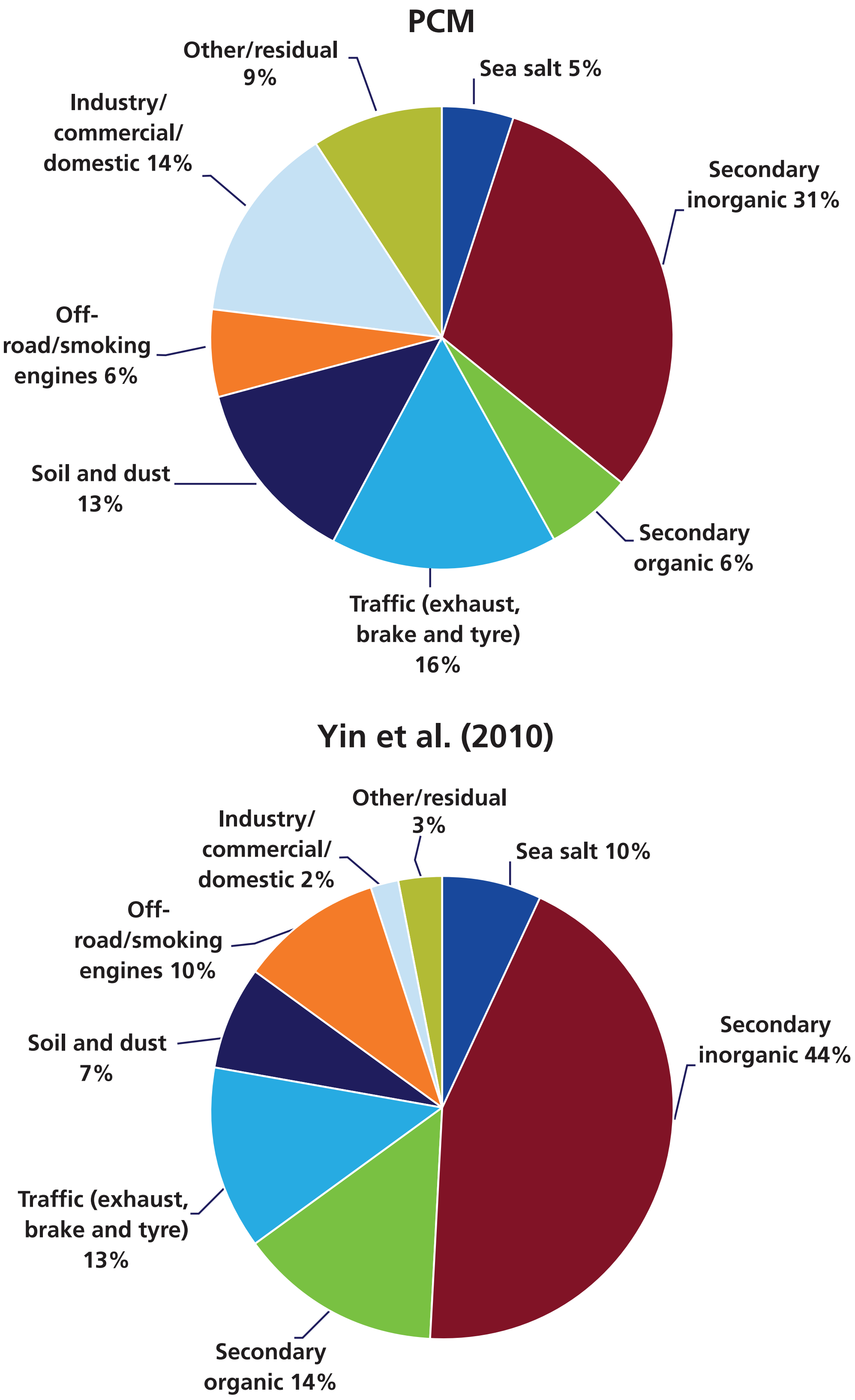


Figure 4.11: Comparison of PCM model outputs for 2009 (top) with CMB model output for 2007-2008 (bottom) (Yin *et al.*, 2010) for source apportionment of $PM_{2.5}$ in Birmingham.

93. While there are substantial similarities between the output of the PCM model and the CMB results, there are also significant differences which warrant examination. The most important is the industry/commercial/domestic category which requires close study to resolve the discrepancies. While the sources contributing to this category are not identical for PCM and CMB, they should nevertheless not diverge by such a large factor. The other major area of discrepancy is with secondary organic aerosol, which is unlikely to be explained by the different sampling periods. As indicated earlier in this chapter, predictive models for secondary organic aerosol are still at a relatively early stage of development, and given the agreement between the CMB model and elemental carbon tracer method in estimating secondary organic aerosol by receptor modelling, it seems most likely that the numerical model used to predict secondary organic aerosol for use in PCM is underestimating the SOA mass.

94. The results of the PCM and CMB models in Figure 4.11 provide food for thought in relation to abatement strategies. The very large contribution of secondary inorganic particles suggests that large improvements in air quality could be achieved through abatement of the precursor gases sulphur dioxide and NO_x. However, a study of the relationship of measured sulphate concentrations at European sites to their precursor sulphur dioxide (Jones and Harrison, 2011) suggests that due to the non-linearity of the relationship, substantial reductions in sulphur dioxide will be needed to achieve relatively small gains in relation to atmospheric sulphate. Specifically, Jones and Harrison (2011) predicted that a reduction in sulphate concentrations of 1 $\mu g\ m^{-3}$ at Harwell and London North Kensington would require a reduction in sulphur dioxide emissions from sources affecting the two UK sites of 55% and 49% respectively. Measured data for nitrate are far less adequate than those for sulphate and hence establishing relationships between nitrate aerosol and either emissions or concentrations of NO_x is more difficult than for sulphur dioxide. Numerical models rely upon substantial parameterisations in order to describe the atmospheric formation of nitrate aerosol and its subsequent behaviour and hence much still needs to be done to generate reliable predictions of how abatement of NO_x would benefit concentrations of nitrate in air. Traffic exhaust emissions of $PM_{2.5}$ are likely to continue to decrease as a result of new Euro standards requiring diesel particle filters on new vehicles. However, there are at present no regulations affecting non-exhaust particles from road traffic, which currently account for around 50% of the traffic contribution to PM_{10}, although they contribute substantially less to $PM_{2.5}$. Other source categories which require substantially more information before abatement policies can be formulated are wood burning and cooking. Current knowledge of the magnitude of their contribution to airborne concentrations is wholly inadequate and hence the possible benefits of abatement policies are unpredictable. Another component of particulate matter making a significant contribution to total $PM_{2.5}$ concentrations is secondary organic aerosol (SOA).

4.6.3 Use of carbon-14 as a tracer of contemporary carbon

95. A further, complementary way of evaluating particulate carbon sources is by analysis of the radiocarbon (^{14}C) content of airborne particulate matter, which yields insights into the proportion of the carbonaceous material derived from fossil and contemporary carbon sources. Heal *et al.* (2011) applied radiocarbon analysis to a total of 26 samples of $PM_{2.5}$ collected at the EROS urban

background site in Birmingham. They used a thermal separation of organic carbon from elemental carbon and were able to determine the radiocarbon content of each. By making a number of assumptions, they were able to disaggregate the carbonaceous component of the $PM_{2.5}$ into the following components:

- EC biomass, representing elemental carbon from the burning of wood and other contemporary fuels.
- EC fossil, representing elemental carbon from the combustion of fossil fuels predominantly in diesel engines but including, for example, industrial oil and coal combustion.
- OC fossil, representing organic compounds derived from fossil fuel sources and hence including emissions from road vehicles, but also of solvent-derived compounds from industry and secondary particles derived from them.
- OC biomass, representing organic carbon from the combustion of wood and other biomass fuels.
- OC biogenic, representing primary organic carbon contained, for example, in vegetative detritus, but also secondary organic carbon deriving from biogenic precursors.

96. The average composition of the samples analysed by Heal *et al.* (2011) appears in Figure 4.12 where it is compared with data from Zurich, Switzerland, and Göteborg, Sweden. In Table 4.7, the masses of organic carbon reported for the Birmingham sites have been converted to approximate masses of organic matter, so as to give a breakdown of the carbonaceous aerosol based upon the average concentration (over 26 samples) of total carbon of 5.00 $\mu g\ m^{-3}$ in the $PM_{2.5}$ fraction. The rather low percentage attributable to the burning of wood and other biomass tends to confirm the low contributions seen in the results of Yin *et al.* (2010), but perhaps the most striking finding is the high percentage attributable to biogenic organic carbon. Given the relatively modest contribution of vegetative detritus shown by Yin *et al.* (2010) and seen in Figure 4.10, this is most probably largely secondary organic carbon, and it appears that secondary organic matter (OM) from biogenic precursors makes a much larger contribution to the overall total OM than secondary organic carbon from fossil fuel precursors.

97. The work by Heal *et al.* (2011) to distinguish contemporary from fossil carbon suggests that a large proportion of secondary organic carbon is biogenic in origin (Table 4.7) and hence unlikely to decrease significantly in concentration in the foreseeable future as it is unlikely to be subject to control measures.

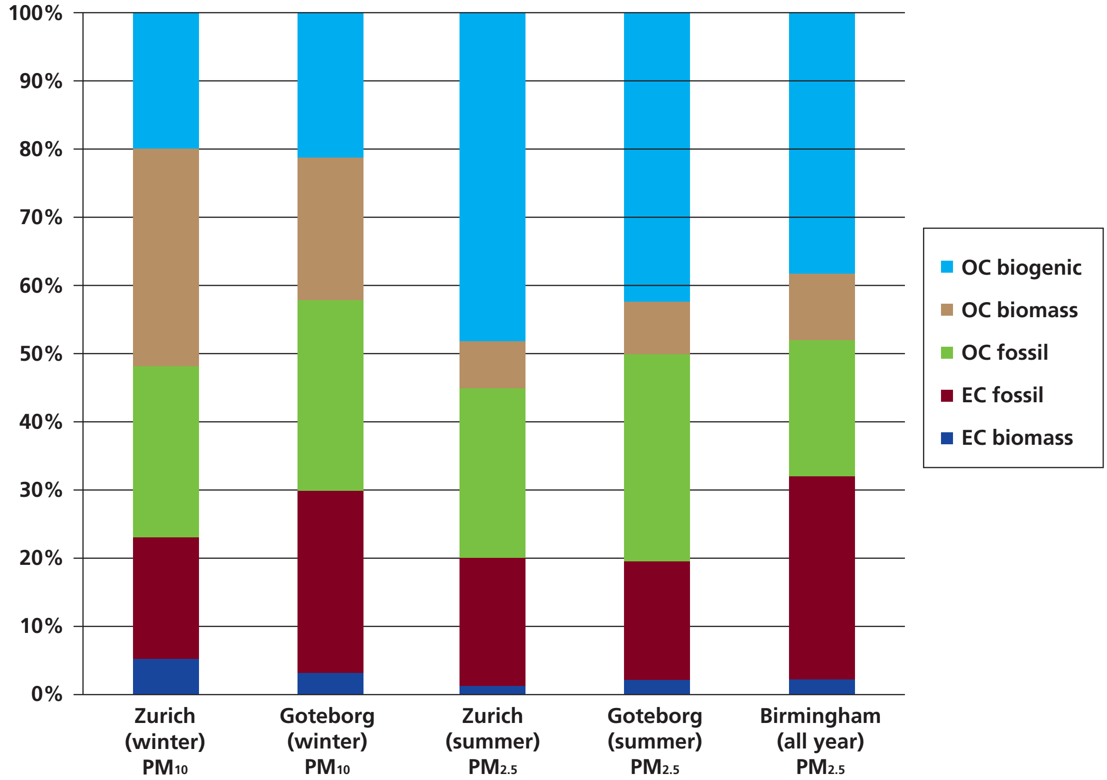


Figure 4.12: Mean five-source apportionment of Total Carbon in Birmingham (Heal *et al.*, 2011) compared with similar work from Zurich (Szidat *et al.*, 2006) and Göteburg (Szidat *et al.*, 2009). $OC_{biomass}$ is POC from combustion of biofuels/biomass, OC_{fossil} is both fossil-derived POC and any SOC from fossil-derived VOC, and $OC_{biogenic}$ is SOC formed from BVOC oxidation together with any other contemporary OC material not explicitly accounted for elsewhere, for example spores, vegetative detritus, tyre rubber, etc.

Table 4.7: Conversion of mass of organic carbon (OC) to organic matter (OM) in samples collected by Heal *et al.* (2011) in Birmingham in 2007-2008.

Component	%	Mass C (µg m^{-3})	OM: OC factor	Mass OM (µg m^{-3})	%
fossil EC	27	1.35	1.0	1.35	18
fossil OC[a]	20	1.00		1.54	
– primary		0.47	1.25	0.59	8
– secondary		0.53	1.80	0.95	13
biomass EC	2	0.10	1.0	0.10	1
biomass OC	10	0.50	2.0	1.00	13
biogenic OC[b]	41	2.05		3.57	
– primary		0.20	1.2	0.24	3
– secondary		1.85	1.80	3.33	44
TOTAL	**100**	**5.00**		**7.56**	**100**

Notes:

a Split of fossil OC into primary and secondary is based upon primary OC = 0.35 fossil EC.

b Based upon average ratio at urban site between vegetative detritus and "other" OC at EROS site reported by Yin *et al.* (2010) of 0.10.

4.7 Summary

98. The major sources of primary emissions of $PM_{2.5}$ are combustion in the energy industries, road transport (both exhaust and non-exhaust emissions), off-road transport, residential combustion and small-scale waste burning.

99. Total $PM_{2.5}$ emissions for the UK are predicted to decrease significantly by 2020, with an especially large contribution from reductions in road traffic exhaust.

100. The main traffic sources of $PM_{2.5}$ are exhaust emissions from diesel cars, light goods vehicles and heavy goods vehicles, together with tyre wear, brake wear and road surface abrasion. A broadly similar picture prevails across the European Union.

101. There are significant uncertainties attached to some of these emissions estimates, particularly to the emissions of $PM_{2.5}$ from non-exhaust traffic sources.

102. With reductions in exhaust emissions of PM, non-exhaust components of traffic emissions will become much more important, emphasising the need to introduce measures to control emissions from these non-exhaust traffic sources.

103. Emissions of precursor gases for secondary $PM_{2.5}$ components have also been considered. UK total emissions of NO_x have been declining since 1999 and are set to decline further by 2020. There is some uncertainty in inventories for road transport emissions for NO_x; evidence suggests that vehicle emission directives have not been effective in reducing "real world" NO_x emissions from modern diesel vehicles manufactured to meet Euro III-V standards. While future road transport emissions are expected to fall, the rate of reduction may not be as fast as previous inventory projections have indicated. UK emissions of sulphur dioxide and non-methane volatile organic compounds have also been declining and are expected to continue to do so. For ammonia, emissions have fallen only slightly since 1990 and are not predicted to fall significantly between 2010 and 2020. EU emissions of NO_x have not fallen as rapidly as in the UK but are projected to decline rapidly by 2020 and significant reductions in emissions of both sulphur dioxide and non-methane volatile organic compounds from the EU-27 are predicted. On the other hand, emissions of ammonia from the EU-27 are predicted to increase in the coming years.

104. Emissions from shipping are not well quantified. Emissions of NO_x and SO_2 from shipping in Europe are predicted to increase or only slightly fall in the next decade, although SO_2 emissions in Sulphur Emission Control Areas around the UK coast are expected to fall significantly. Without further abatement, emissions from shipping will become a more dominant source of $PM_{2.5}$ precursor emissions in Europe.

105. Receptor modelling methods depend upon measured airborne concentrations to infer the contributions of different source categories to concentrations in the atmosphere. Both chemical mass balance and multivariate statistical methods are applicable and results for the UK are available from a chemical mass balance model. The results have been compared with those of the PCM model and highlight significant differences in relation to industrial/commercial/residential emissions of primary particles and the model predictions for secondary organic aerosol particles. The receptor modelling results highlight the weaknesses in current knowledge of a number of sources, including wood smoke and cooking aerosol, and also suggest that NAEI emission factors for gas combustion may be rather high. Use of carbon-14 as a tracer allows a distinction to be drawn between carbon derived from contemporary sources, such as wood burning or emissions from vegetation, and that derived from fossil fuel sources. Analysis of carbon-14 in airborne particulate matter collected in Birmingham indicates a major contribution to secondary organic carbon from biogenic precursors.

106. Formulation of abatement strategies is made difficult by inadequacies in knowledge about the contribution of certain sources and weaknesses in understanding precursor–secondary particle relationships for the major secondary components.

107. Enhancement of emissions inventories is essential if numerical models of atmospheric $PM_{2.5}$ are to be improved. Areas of particular importance are emissions of wood smoke, cooking aerosol, abrasion particles from traffic and the $PM_{2.5}$ precursor gas ammonia. Both the emissions and atmospheric chemistry of biogenic VOCs are also in urgent need of further research.

108. A critical assessment of emission inventories and their ability to provide the data required for modelling $PM_{2.5}$ concentrations and its component parts has been carried out. Inventories have traditionally been constructed for reporting to international bodies following prescribed methods and procedures, but these can fall short of the requirements of air quality modellers. **AQEG recommends developing inventories that provide a quantification of the spatial and temporal variability in emissions of primary $PM_{2.5}$ and its precursors from all contributing sources including those not covered in national inventories or provide the means for calculating them in air quality models.** This should include spatially-gridded inventories with high resolution temporal profiles for different source sectors. This requires a better understanding and means of quantifying emissions from key sources. Several areas are identified for further research to achieve this goal, and which would help underpin the development of more complete and reliable inventories for modellers to use. The key areas are:

- non-exhaust vehicle emissions including tyre and brake wear, road abrasion and road dust resuspension;
- fugitive dust emissions from construction, demolition, quarrying, mineral handling, and industrial and agricultural processes, and methods for quantifying them nationally and locally;
- $PM_{2.5}$ emissions from domestic and commercial cooking;

- $PM_{2.5}$ emissions from small-scale waste burning and bonfires;
- $PM_{2.5}$ emissions from domestic wood burning accounting for the effectiveness of control measures;
- biogenic emissions of NMVOCs;
- emissions of NH_3 from agriculture, their temporal variability and methods for control;
- emissions of SO_2 and NO_x from shipping, in particular their spatial distribution around ports and harbours, their temporal variability and future emissions;
- exhaust emissions from off-road machinery used in construction and industry; and
- exhaust emissions from diesel vehicles under real world driving conditions and the factors and technologies affecting them.

Chapter 5

Modelling $PM_{2.5}$ and the future

5.1 Introduction

1. This chapter discusses modelling of $PM_{2.5}$ in the UK, covering what models can do and their limitations, the different model scales considered, how different components of $PM_{2.5}$ are modelled, how models are evaluated and what models can tell us about future $PM_{2.5}$ trends. A number of models are used in the UK which may differ in basic methodology, model domain size, inputs and output (i.e. level of chemical speciation, averaging times and spatial resolution). A non-exhaustive survey of the approaches used to model $PM_{2.5}$ in the UK is presented in Table 5.1. A description of these models and some examples of how they have been used is given in Annex A2. Outputs from these models are used in the discussions throughout this chapter.

2. An important application of models is the synthesis of data from emission inventories and observations. However, such modelling of $PM_{2.5}$ is challenging because of uncertainties in the measurement data (Chapter 2), limited trends data and uncertainties in the different particulate matter (PM) components (Chapter 3), coupled with uncertainties in the emission data and their projections (Chapter 4).

5.2 What is modelling? What can models do?

3. Models for predicting concentrations of $PM_{2.5}$ have a number of important roles, some of which are complementary to measurement. These roles include assessing concentrations at locations without monitors and answering questions such as how will PM levels change in the future, what are the most important emission sources to control to reach acceptable air quality and what balance should be struck between policy actions within the UK and abroad. The models encapsulate our current scientific understanding of the different physical and chemical processes which determine the generation, transport and fate of small particles in the atmosphere and therefore help understand how these different processes interact and which of them are most important in different situations.

4. $PM_{2.5}$ concentrations at a particular location are determined as a superimposition of the processes taking place at a large range of spatial scales from continental (e.g. long-range transport) to regional (e.g. secondary particulate production), as well as urban and local scales (close to sources of primary emissions). Because of this diversity of spatial ranges no single model currently represents the full range of scales, and a hierarchy of models is used for predictions of $PM_{2.5}$ in the UK. These are typically regional (e.g. European-scale), national (UK-scale) or local (e.g. urban-scale) models. These models all have particular strengths and weaknesses and are suitable for different applications.

5. At the regional scale, both Eulerian (grid-based) and Lagrangian ("particle-following") models are used. These model systems typically have output resolution of a few hundred kilometres or more and in some cases are able to assimilate measured air pollution data, both surface measurements and satellite data. They generally require meteorological fields and can incorporate complex chemical reaction schemes. Models based on these frameworks can calculate short-term concentrations, however, their use for long-term averages can, dependent on computer resources and efficiency, be limited by model run times. Examples of regional-scale models used in the UK include the Eulerian models EMEP4UK (Annex 2, A2.5) and CMAQ (A2.1-A2.3), and the Lagrangian model NAME (A2.4). Most regional-scale air quality policy model development within the EU and UNECE has utilised the RAINS/GAINS integrated assessment model which is based on source–receptor relationships derived from the EMEP model. Many studies are also conducted in Europe using other Eulerian models (e.g. Chimere and EURAD).

6. At the national scale, models include nested versions of regional numerical models complete with complex meteorological and chemical algorithms (e.g. EMEP4UK (A2.5) and CMAQ (A2.1-2.3), the trajectory model PTM (A2.6), the straight-line trajectory model FRAME (A2.7), the semi-empirical model PCM (A2.8) and UKIAM (A2.9), which combines input of source–receptor footprints from models at different scales. These models are not able to resolve concentration gradients at local scales (e.g. below 1 km), however, PCM and the urban component of UKIAM (BRUTAL) include roadside enhancement factors. PCM, UKIAM and BRUTAL are designed to calculate long-term averages only.

7. Local- or urban-scale models have very high spatial resolution and typically resolve the concentration distribution at roadside locations; they can include the impacts of local buildings, for example in algorithms, to estimate the impact of street canyons. Their overall domain size is usually limited to tens of kilometres by underlying assumptions including spatially uniform meteorology and stationarity (i.e. dispersing plumes do not evolve in time but are recalculated hour by hour). An example of a local model used in the UK is ADMS-Urban (A2.10). In principle, local-scale models can be nested in regional-scale models and this approach is likely to become more common in future.

8. As there is a wide diversity of emission sources of PM, some of which are poorly specified (e.g. fugitive emissions), some emission processes and categories are omitted from models. This is generally compensated for by adding additional concentrations to represent unknown emissions or components.

9. Whilst many of the processes determining $PM_{2.5}$ concentration are understood and can be represented reasonably well in models (e.g. the generation of inorganic aerosols, deposition processes, etc.), there remain some processes where there is incomplete understanding and/or knowledge. This limits the representation of these processes in models; examples include the generation of secondary organic aerosol, treatment of bound water and, relevant only to local models, initial dispersion from road traffic.

10. Annex A2 summarises the principal models used in the UK (listed in Table 5.1) to predict and understand $PM_{2.5}$ concentrations, and highlights different aspects of modelling $PM_{2.5}$. Annex 2 shows models are currently used for a

wide range of applications related to predicting and understanding $PM_{2.5}$. These applications include work to better quantify the non-linearities of $PM_{2.5}$ formation in response to precursor emission reductions, the prediction of the individual components that contribute to $PM_{2.5}$ mass, short-term forecasting and the longer term prediction of trends, and how predictions compare with measured values.

11. The CMAQ model outlined in A2.1 is used to provide two-day forecast predictions of PM_{10} and $PM_{2.5}$ and predict how concentrations respond to reductions in precursor emissions of sulphur dioxide (SO_2), nitrogen oxides (NO_x) and ammonia (NH_3). The CMAQ model described in A2.2 is used to predict hourly concentrations of $PM_{2.5}$ at several sites, including the rural (Harwell) and urban background (London North Kensington) sites. Whilst much of the temporal variation is captured by the model, predictions of $PM_{2.5}$ are generally 30-40% lower than observed values. Model underpredictions are also observed in other CMAQ modelling discussed in A2.3, which considers the major components that constitute $PM_{2.5}$ and shows that model predictions underestimate some of the major components of $PM_{2.5}$ in terms of absolute mass. The estimated relative contributions of each component to total $PM_{2.5}$ are, however, similar to observed values.

12. The Lagrangian NAME model described in A2.4 shows how an understanding of the emission sensitivity of $PM_{2.5}$ concentrations can be developed. Emission sensitivity is expressed as a coefficient that provides a measure of how the concentration of PM changes as a result of a known change in emission of a precursor gas. Such calculations provide useful information on how $PM_{2.5}$ concentrations are likely to respond to controls in precursor emissions and can also reveal important non-linear behavior between pollutants in secondary particle formation. Annex 2.6 shows the PTM model which has been used to model $PM_{2.5}$ and other species using detailed chemical schemes. Predictions of $PM_{2.5}$ have been compared with observations and the response of reductions to precursor emissions on $PM_{2.5}$ considered. The PTM model again captures important non-linearities in the chemical system, which are essential to understand if policies are to be developed to reduce concentrations of $PM_{2.5}$. The receptor–oriented Lagrangian model, FRAME, is described in A2.7; this model illustrates the effect of a finer grid resolution, for example with respect to ammonia emissions and ammonium nitrate formation, and is used to provide source–receptor relationships for UKIAM.

13. In A2.5 the Eulerian EMEP4UK model is used to predict fine particulate nitrate over seven years at a site in Scotland. Longer-term predictions such as these provide useful information on trends and also capture important episodes, such as occurred in the spring of 2003. Similarly, EMEP4UK and the other regional-scale models can provide surface concentration maps that help to better understand the spatial distribution of $PM_{2.5}$ in the UK and Europe.

14. It is noteworthy that the regional-scale models do not predict $PM_{2.5}$ mass directly, but estimate each component that contributes to its mass such as particulate sulphate and nitrate (see Chapter 3). The mass of $PM_{2.5}$ is then calculated from the size distribution of the different components.

15. Some of the characteristics of local-scale models are summarised in A2.8 to A2.10. All of these models are capable of predicting concentrations down to a scale of a few metres or so and are driven by inventories on a more local scale, such as the National Atmospheric Emissions Inventory (NAEI) or the London Atmospheric Emissions Inventory (LAEI). Unlike the regional models, they do not attempt to treat explicitly the formation of secondary particulate matter at a regional scale but use assumptions based on measurements or the outputs from other models as boundary conditions. For example, when considering a specific urban area, the relatively large regional component and its speciation are separately estimated and the increment due to explicitly modelled urban sources added to it. Nevertheless, as shown in A2.8 and A2.9, it is possible to disaggregate the contributions to $PM_{2.5}$ to a high level of detail. In addition, the ADMS-Urban model described in A2.10 is capable of producing both highly time- and spatially-resolved predictions of $PM_{2.5}$ mass (hourly predictions at a 1 m resolution). Furthermore, these models can provide useful information on urban transects, as shown in Figure 5.6 which reveals the importance of the large regional component of $PM_{2.5}$, the overall urban increment and the importance of individual roads.

Table 5.1: A survey of the principal models employed to address $PM_{2.5}$ in the UK.

Annex	Model	Institution	Model type	Scale
A2.1	WRF/CMAQ/AEA	AEA Technology	Eulerian grid	Regional/UK
A2.2	WRF/CMAQ/CAIR	University of Hertfordshire	Eulerian grid	Regional/UK
A2.3	WRF/CMAQ/KCL	King's College London	Eulerian grid	Regional/UK
A2.4	NAME	Met Office, Exeter	Lagrangian	Regional/UK
A2.5	EMEP4UK	University of Edinburgh	Eulerian grid	Regional/UK
A2.6	PTM	rdscientific, Newbury	Trajectory	Regional/UK
A2.7	FRAME	CEH, Edinburgh	Trajectory	UK
A2.8	PCM	AEA Technology	Semi-empirical/ Gaussian	UK and local
A2.9	BRUTAL and UKIAM	Imperial College London	Gaussian/Trajectory	UK and local (BRUTAL) Regional (UKIAM)
A2.10	ADMS-Urban	CERC, Cambridge	Gaussian plume/ Trajectory	Urban and local

5.3 What do models predict across the UK?

16. Figure 5.1 shows the annual mean background $PM_{2.5}$ concentration for 2009 (μg m^{-3}, gravimetric) estimated with the PCM model and Figure 5.2 gives an equivalent map using data from the UKIAM model for 2010 (maps for 2020 are also shown and discussed later in Section 5.6). Both models show similar spatial patterns in general with concentrations increasing from the north-west of the UK to the south-east, however, there are differences in detail of up to a few μg m^{-3}. Background concentrations in south-east England are greater by more than a factor of two than over much of Scotland and Northern Ireland. Superimposed on the general pattern are local maxima due to emissions from major urban areas and arterial roads.

17. The model calculations are consistent with rural background levels which are lowest in the north and west of the British Isles because of the greater geographical separation from the large UK and European PM sources. However, background levels do not decline to zero in either rural areas with negligible emissions or in marine air masses arriving at the North Atlantic Ocean coastline of the British Isles.

18. The models show that the contributions to rural background levels include the following:

- vehicular and stationary sources on the regional scale, including shipping;
- short- and long-range formation and transport from UK PM precursor sources;
- long-range transboundary formation and transport of primary and secondary PM;
- intercontinental-scale PM formation and transport; and
- natural background sources which are estimated in some models and which include sources such as secondary organic aerosol (SOA) from oceanic dimethyl sulphide (DMS), Saharan dusts, forest fires and volcanic eruptions.

19. Figure 5.3 shows a calculation using ADMS-Urban of annual average $PM_{2.5}$ concentrations across London for 2008, and includes an inset for concentrations in central London at higher resolution. In this study, as the ADMS-Urban model considers the rural background to be constant across the model domain and the local generation of secondary particulates is negligible, the variations in concentrations in Figure 5.3 arise solely from primary emissions in the urban area. These comprise a number of contributions including emissions from road vehicles (combustion-derived particles, brake and tyre wear particles and resuspended road dusts), and also other combustion sources. The background annual average concentration rises towards the centre of the urban area with local peaks close to roads resulting from exhaust and non-exhaust road traffic emissions. This general pattern is typical for all significant urban areas in the UK.

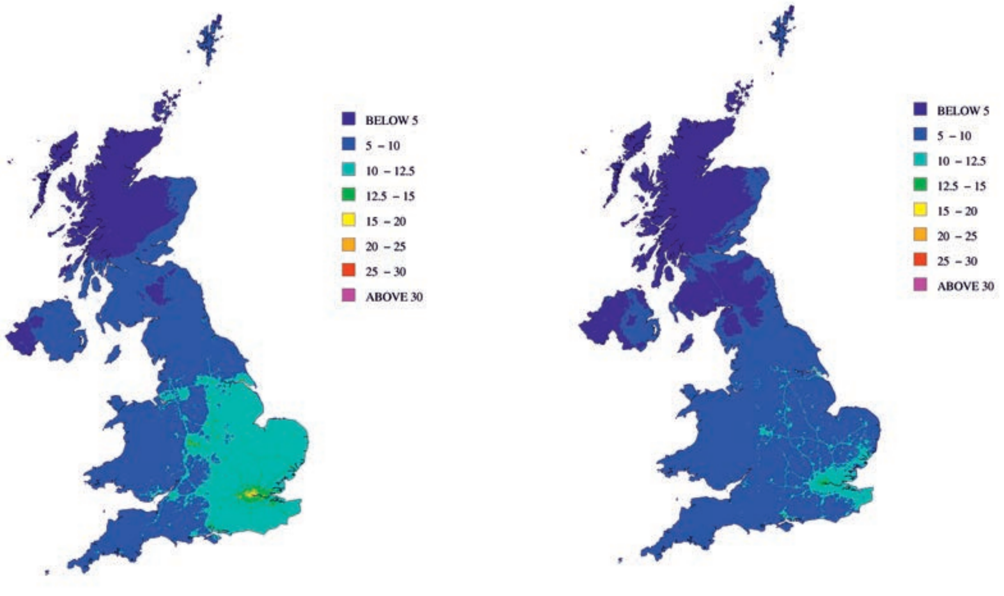


Figure 5.1: Concentrations of total annual mean $PM_{2.5}$ as calculated by the PCM model (µg m^{-3}) for 2009 (left) and 2020 (right).

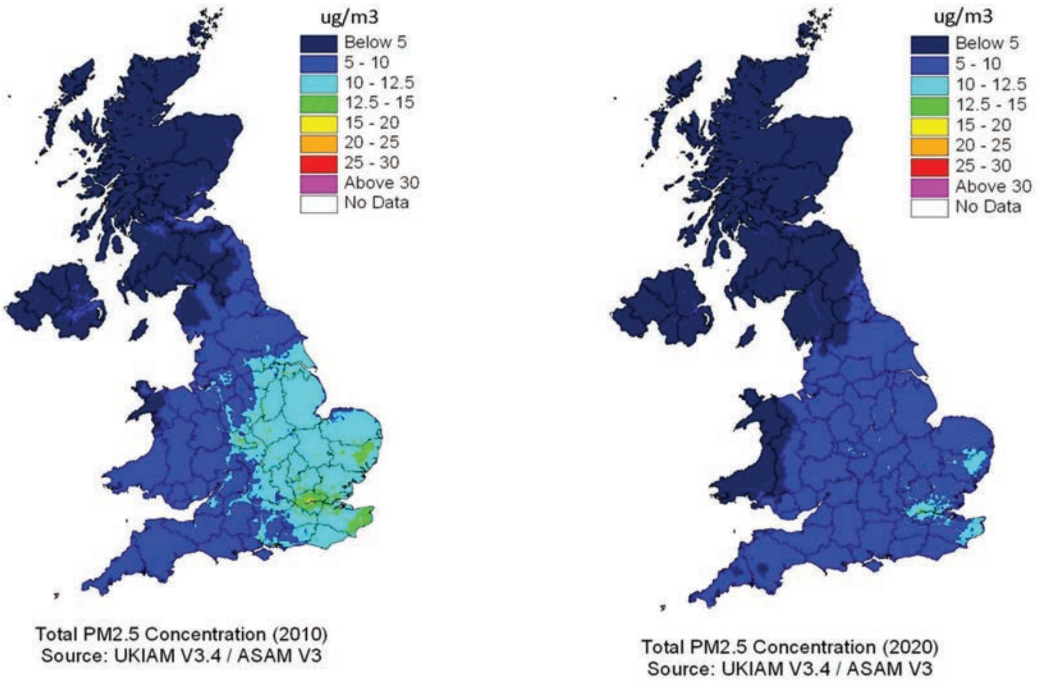


Figure 5.2: Total annual mean PM$_{2.5}$ concentrations as calculated using the UKIAM model (µg m^{-3}) for 2010 (left) and 2020 (right).

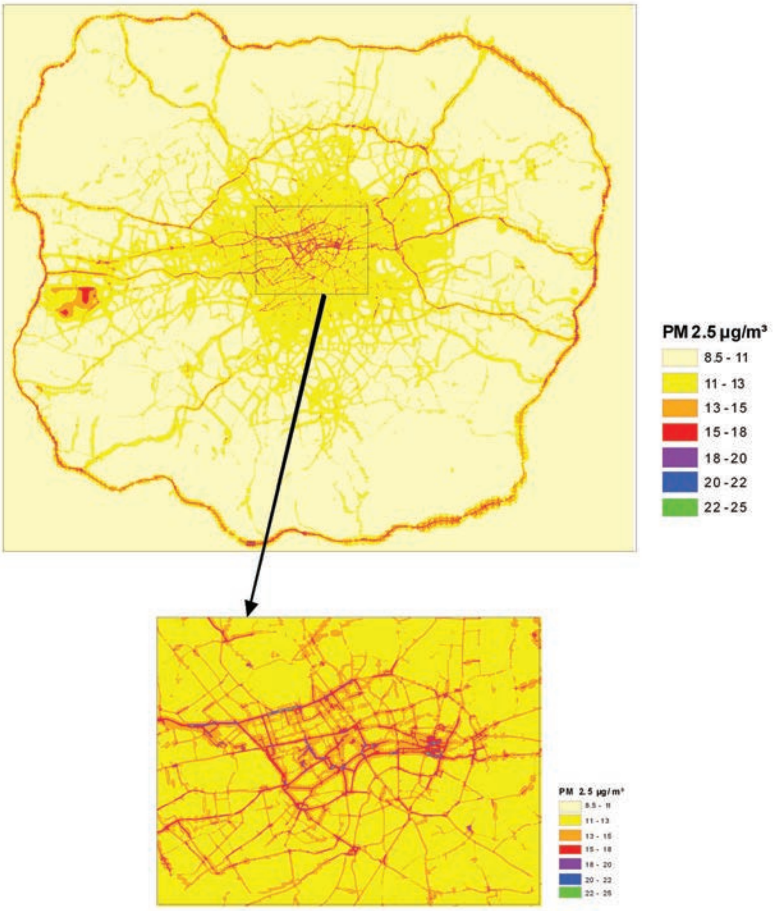


Figure 5.3: Annual average PM$_{2.5}$ concentration over Greater London for 2008 as calculated by ADMS-Urban. The inset shows central London at higher resolution.

5.3.1 $PM_{2.5}$ modelling for public information and forecasts

20. $PM_{2.5}$ was added to the UK's Daily Air Quality Index (DAQI) and public information systems in January 2012. Models are required to support the issuing of daily air quality forecasts for this pollutant. The requirement for the DAQI is to forecast a 24-hour mean concentration of $PM_{2.5}$. The range of concentrations and breakpoints for the $PM_{2.5}$ index are illustrated in Table 5.2.

Table 5.2: Daily Air Quality Index (DAQI) bands and breakpoints for $PM_{2.5}$.

Index	**1**	**2**	**3**	**4**	**5**	**6**	**7**	**8**	**9**	**10**
Band	**Low**	**Low**	**Low**	**Moderate**	**Moderate**	**Moderate**	**High**	**High**	**High**	**Very High**
µg m^{-3}	**0-11**	**12-23**	**24-34**	**35-41**	**42-46**	**47-52**	**53-58**	**59-64**	**65-69**	**70 or more**

21. In addition, the following information is required from modelling for the $PM_{2.5}$ daily forecasts in the UK:

- prediction of the headline "worst-case" pollutant level in each of the nominated zones and agglomerations;
- within each zone further determination of the differences in pollutant concentrations between rural, background and roadside locations; and
- public forecasts for at least 24 hours ahead and model runs to support a longer term outlook.

22. The operational concerns for modelling $PM_{2.5}$ for the daily air quality forecasts are similar to those for forecasting other pollutants such as PM_{10}, nitrogen dioxide (NO_2) and SO_2. In particular, the accuracy of the $PM_{2.5}$ forecast is dependent on the accuracy of the weather data and the emissions inventory data or chemical schemes which are required to configure the model. Models used for forecasting also need to be able to operate subject to the following constraints:

(a) Run-time. The model needs to be able to run on a daily basis and reliably provide the results in time for the daily air quality forecast to be issued.

(b) Sufficient temporal resolution. As a minimum the model is required to output daily mean concentrations for the following day for the forecast.

(c) Ability to cover the domain required. The model must run over the required domain and allow the forecasts for different location types to be determined. For $PM_{2.5}$ forecasting a model run for a small domain will need to include the impacts of emissions and transport over a much wider area.

(d) Sufficient output information. If a pollution episode is forecast then further details of the likely source or components of the $PM_{2.5}$ may be required in order to issue further advice to the public on possible health effects or on how to reduce the emissions which are contributing to the episode. To help in providing this further information, a chemical transport model such as CMAQ can provide the breakdown of $PM_{2.5}$ components in a speciation plot such as that illustrated in Figure 5.4.

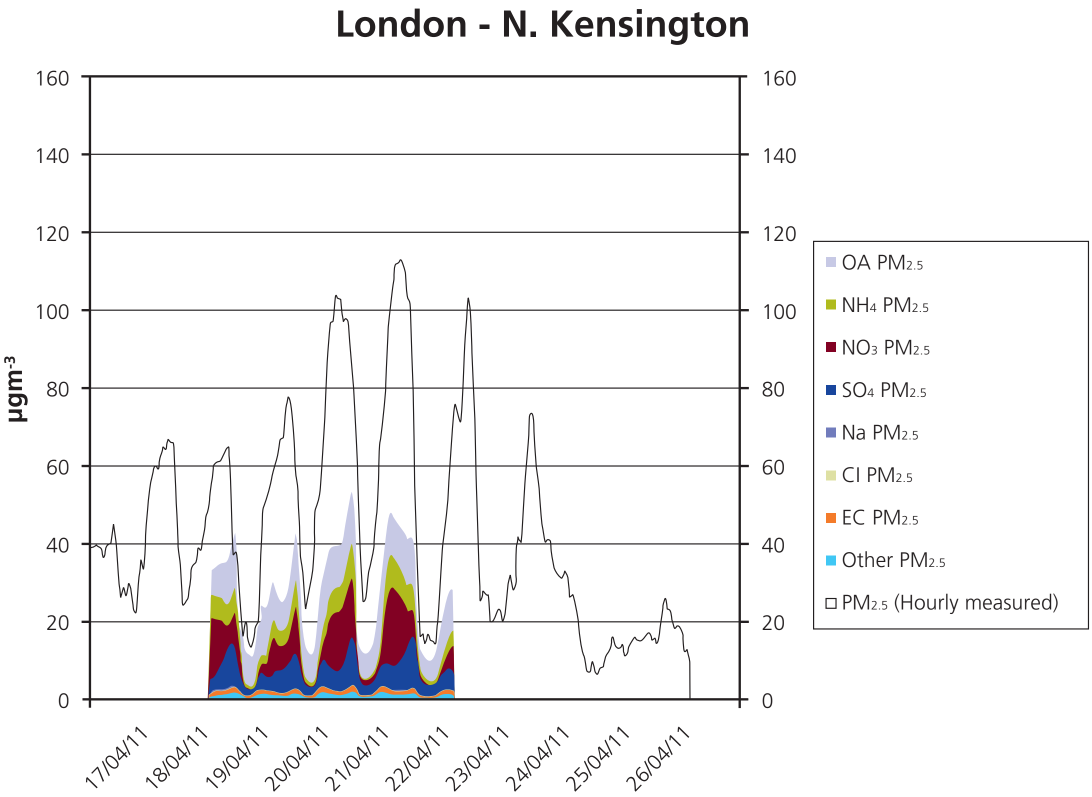


Figure 5.4: Hourly forecast concentrations of $PM_{2.5}$ components versus measured total $PM_{2.5}$ mass at London North Kensington using CMAQ, April 2011.

5.3.2 Transects in $PM_{2.5}$ across London

23. One of the principal advantages of models is their ability to predict spatial patterns and gradients in $PM_{2.5}$ concentrations. This is illustrated in Figure 5.5, where the ADMS-Urban and PCM models have been used to generate west–east annual average transects through central London from Henley-on-Thames and Reading in the west to Basildon and Southend-on-Sea in the east. Because of the significantly higher spatial resolution achieved in ADMS-Urban compared with the PCM model, that is 10 m x 10 m as opposed to 1 km x 1 km, ADMS-Urban has also been presented at 1 km x 1 km resolution. Note that the ADMS-Urban calculations are for 2008, those from PCM for 2009, and the monitored data are in all but one case for 2009. At the 1 km resolution both models show an urban increment which generally increases towards the centre of London, but which even at its maximum is smaller (by about 3-5 µg m^{-3}) than the background outside the urban area (10-12 µg m^{-3}); PCM's urban increment extends over a greater area. At the higher resolution ADMS-Urban shows a much larger local variation and a peak concentration of 20.95 µg m^{-3} in central London.

24. Some indication of the accuracy of the transects can be given by the monitored data in Figure 5.5 which for 2009 shows observations from the FDMS and Partisol instruments (see Chapter 2) which can be compared with PCM; FDMS data from the site can also be compared with ADMS-Urban for 2008. However, note the discrepancy between the co-located FDMS and Partisol instruments at London North Kensington of about 3 µg m^{-3} (the FDMS concentration is higher) which makes definitive statements and conclusions about model performance

problematical, and which is also illustrative of the general problem of evaluating $PM_{2.5}$ models because of uncertainties regarding measured data.

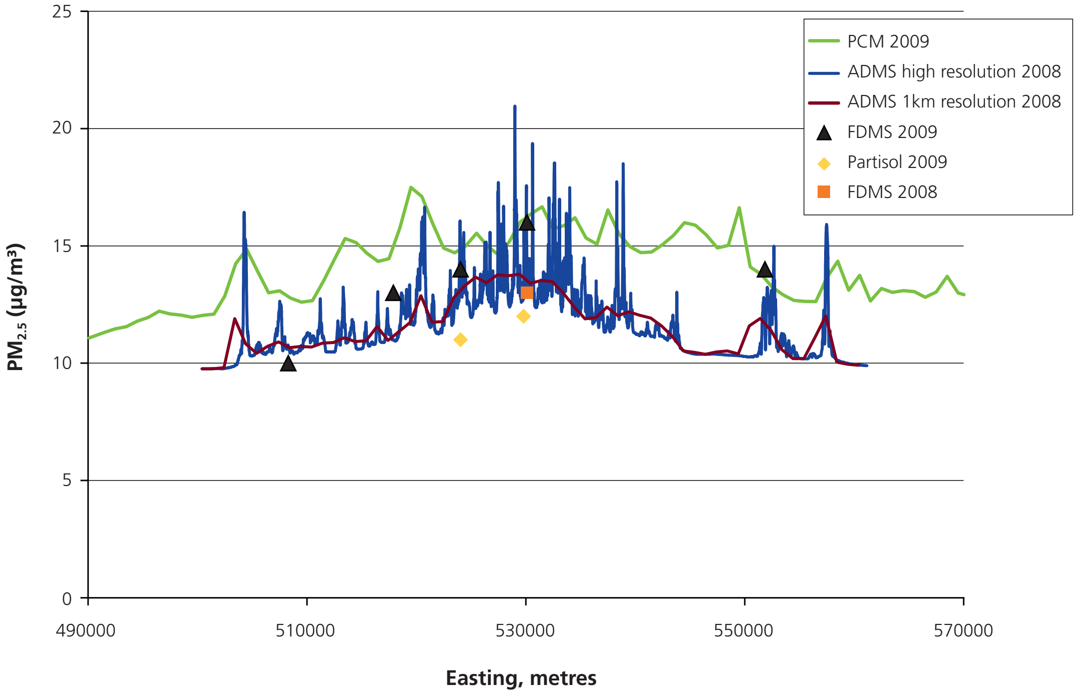


Figure 5.5: Annual mean $PM_{2.5}$ concentrations predicted using the ADMS-Urban (2008) and PCM (2009) models together with observations from FDMS and Partisol instruments (mainly 2009) though Central London. The ADMS-Urban predictions are shown at 10 m x 10 m resolution (blue line) and at 1 km x 1 km resolution (red line).

5.4 Components of $PM_{2.5}$ and source attribution

25. Total $PM_{2.5}$ includes contributions from primary sources, not all of which are represented in emission inventories, and from secondary particulates formed from precursor gases during atmospheric transport. The latter includes both secondary inorganic aerosol (SIA), in the form of nitrate, sulphate and ammonium compounds, and secondary organic aerosol (SOA). In addition, other contributions come from natural sources and water (see Chapter 2 for measurement perspective).

26. An important function of modelling is source attribution, i.e. differentiating components and estimating how different sources or groups of sources contribute to concentrations. Examples are given in Figures 5.6 and 5.10, and Tables 5.4 and 5.5. Figure 5.6 is derived from the PCM model (A2.8) and gives a breakdown of contributions to concentrations of $PM_{2.5}$ for a transect across London and south-east England (coincident with but extending further than the transect shown in Figure 5.5), and Figure 5.10 gives a more detailed breakdown of components at background monitoring sites where totals can be compared with measurements. As an indicator of exposure, Tables 5.4 and 5.5 give a breakdown of the different contributions to population-weighted mean exposures from both the PCM and UKIAM models.

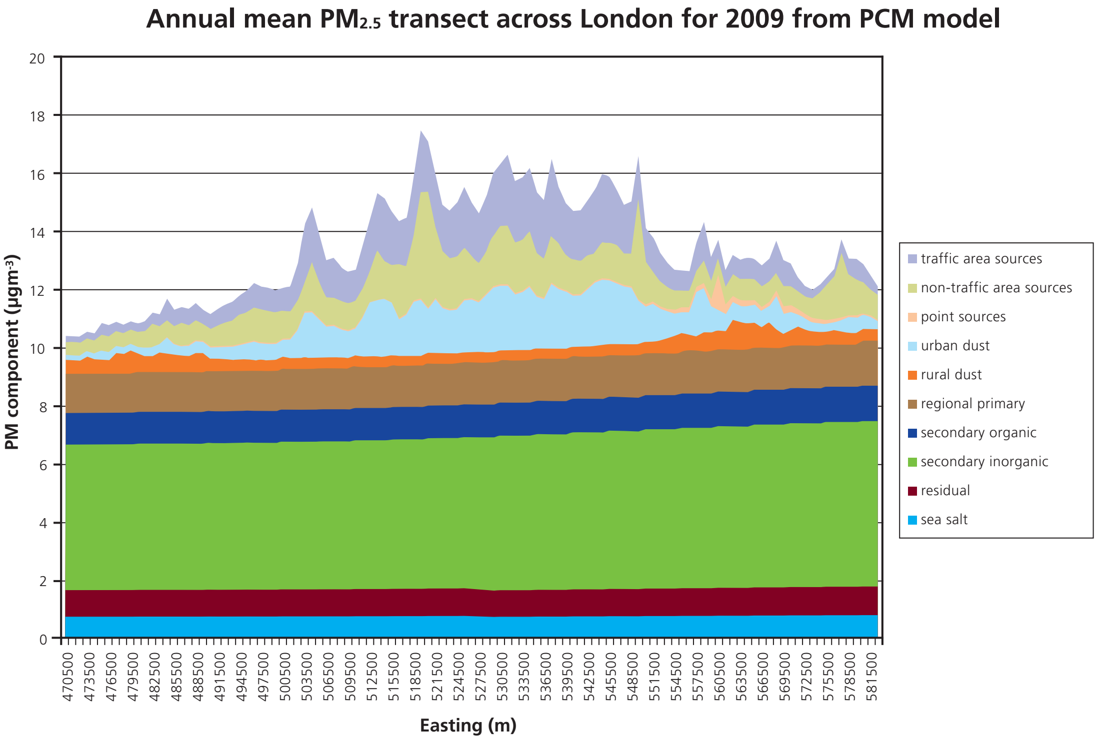


Figure 5.6: Transect through the PM$_{2.5}$ concentration distribution in London, showing a number of individual PM components from Henley-on-Thames in the west to Southend-on-Sea in the east (derived from PCM model). The transect is coincident with but extends further than that shown in Figure 5.5.

27. All of these examples show that the secondary inorganic aerosol accounts for a large proportion of total PM$_{2.5}$ (~40% averaged over the UK), with data in Table 5.5 indicating a substantial contribution to this from sources outside the UK. The longer range nature of this transport accounts for the smooth spatial variation across the UK in Figure 5.7. Superimposed on this, the contribution from primary sources shows a much greater variability with sharp peaks in central London areas where emissions are concentrated. The remaining components of secondary organic aerosol, dust, sea salt and water content, are small individually. However, their combined contribution makes up a considerable fraction of the total. Representing each of these components and achieving mass closure (see Chapter 4) poses different problems as discussed below.

5.4.1 Modelled primary concentrations

28. Chapter 4 discusses the primary emissions of PM$_{2.5}$ that can be quantified in emission inventories, and hence represented in modelling. The large uncertainties in these emissions and missing sources feed through to the models and the estimated concentrations. Although the contribution of primary PM$_{2.5}$ emissions to overall concentrations in the UK is smaller than that of the secondary aerosol, the spatial pattern is correlated with the emissions and results in higher concentrations in London and other cities. This, together with additional urban dust, accounts for PM$_{2.5}$ annual mean concentrations weighted by population density ('population-weighted mean') being around 3 to 4 μg m^{-3} higher in Inner London than in the Rest of England (see Table 5.3, derived from PCM).

Table 5.3: Population-weighted annual mean $PM_{2.5}$ concentrations (µg m^{-3}) calculated using the PCM model for different parts of the UK.

	2009	2010	2015	2020
Scotland	6.83	6.61	6.14	5.85
Wales	8.95	8.62	8.02	7.64
Northern Ireland	7.27	6.93	6.35	5.98
Inner London	15.05	14.47	13.26	12.59
Outer London	13.91	13.37	12.28	11.67
Rest of England	10.80	10.39	9.61	9.13
UK	10.70	10.29	9.51	9.04

5.4.2 Secondary inorganic aerosol

29. The secondary inorganic aerosol (SIA) in the form of sulphate (SO_4^{2-}), nitrate (NO_3^-) and ammonium (NH_4^+) particulates is formed from precursor emissions of SO_2, NO_x and NH_3. Most of the SIA is within the $PM_{2.5}$ range, and gives a contribution to population exposure several times greater than primary $PM_{2.5}$ emissions, although there are questions as to whether this component is as toxic as some of the primary material. The modelling of SIA components is complicated by the chemical interaction between pollutants, resulting in the formation of ammonium sulphate and ammonium nitrate, as well as a coarser nitrate component of SIA. The formation of ammonium nitrate particulate matter is reversible, with models frequently assuming an equilibrium between gaseous and particulate states depending on ambient NH_3 and nitric acid (HNO_3) concentrations. This system is extremely difficult to model given the highly variable emissions of NH_3 spatially and temporally, and hence the very patchy and intermittent pattern of NH_3 concentrations. These NH_3 emissions arise predominantly in rural areas from agricultural activities, but there are also some urban sources, in particular from some vehicle exhausts (see Chapter 4).

30. The chemical interactions between pollutants result in a complex response to the reduction of pollutant emissions, for example a change in NO_x or SO_2 emissions can affect NH_4^+ concentrations as well as NO_3^- and SO_4^{2-}, depending on the mix of pollutants. This results in a non-linear relationship, whereby percentage changes in NO_3^-, SO_4^{2-} and NH_4^+ are not directly proportional to percentage changes in NO_x, SO_2 and NH_3 emissions respectively. However, source–receptor relationships, derived from more complex models by estimating the change in SIA concentration at receptor points in response to small reductions of one pollutant at a time from each emitting source, are often used as a linear approximation in simpler modelling approaches to analyse different emission scenarios. This is the approach used in integrated assessment models such as GAINS and UKIAM, avoiding the need to run a complex model such as EMEP or CMAQ for each new scenario, but introducing increasing uncertainties

with larger deviations in emissions from the original baseline scenario used to derive the source–receptor relationships (that is the response of concentrations at a receptor point to unit changes in emissions from a specified source).

31. As an alternative, some models such as PCM use an empirical approach to SIA concentrations, interpolating between measurements; for example, see Figure 5.7 for $PM_{2.5}$ maps of SO_4^{2-}, NO_3^- and NH_4^+ derived from the measurement network in 2009 and scaled for the $PM_{2.5}$ fractions. This approach is subject to interannual variations in measurements influenced by different meteorology in different years, and still leaves the problem of making forward projections. By comparison, Figure 5.8 shows corresponding $PM_{2.5}$ maps for the same components calculated using the integrated assessment model UKIAM (A2.9). This model utilises source–receptor relationships from a combination of models, trying to best reflect the strengths of the EMEP model at the European scale and the FRAME model at the UK scale. Comparison studies based on straight use of the FRAME model result in population-weighted mean concentrations of SIA around 20% lower than when using the EMEP model.

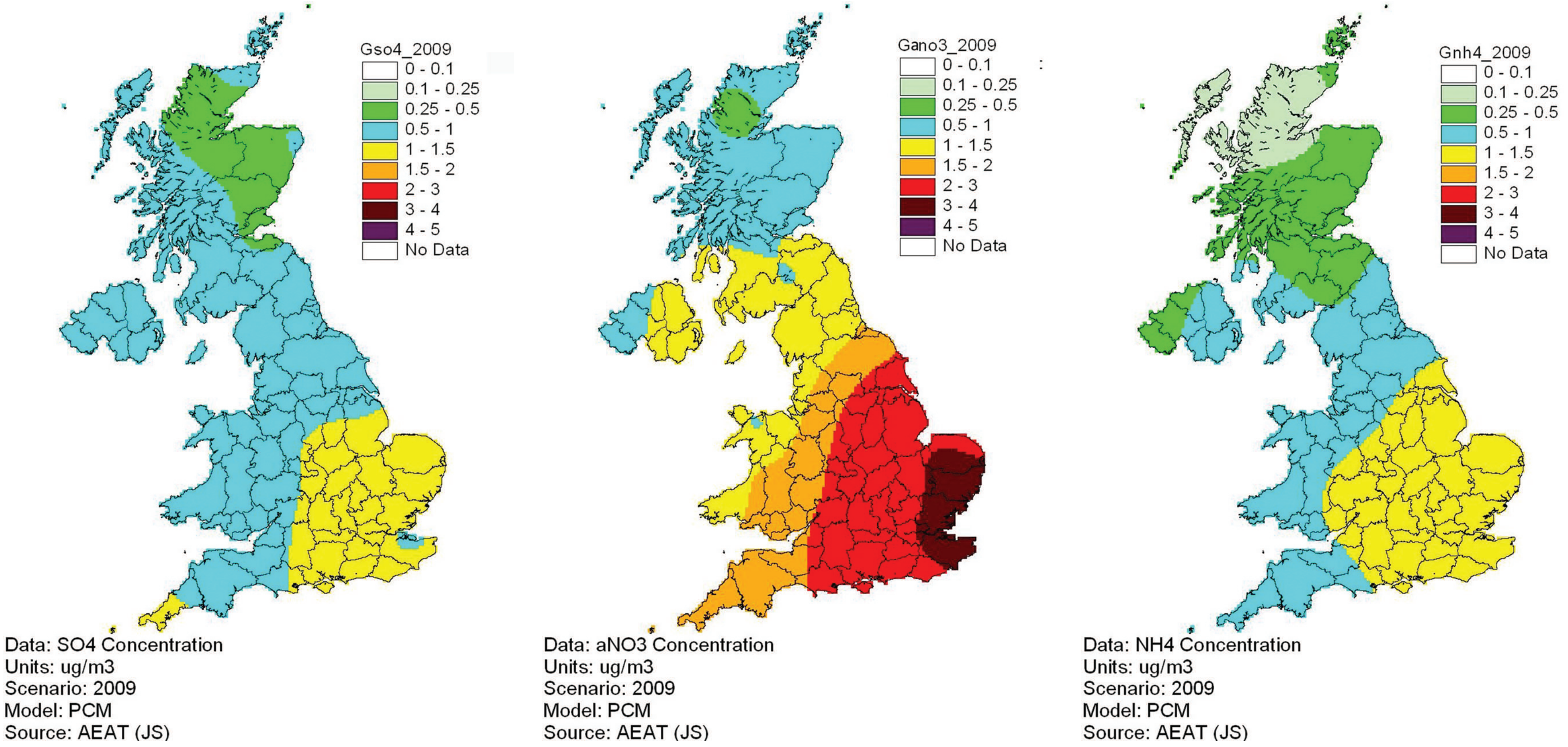
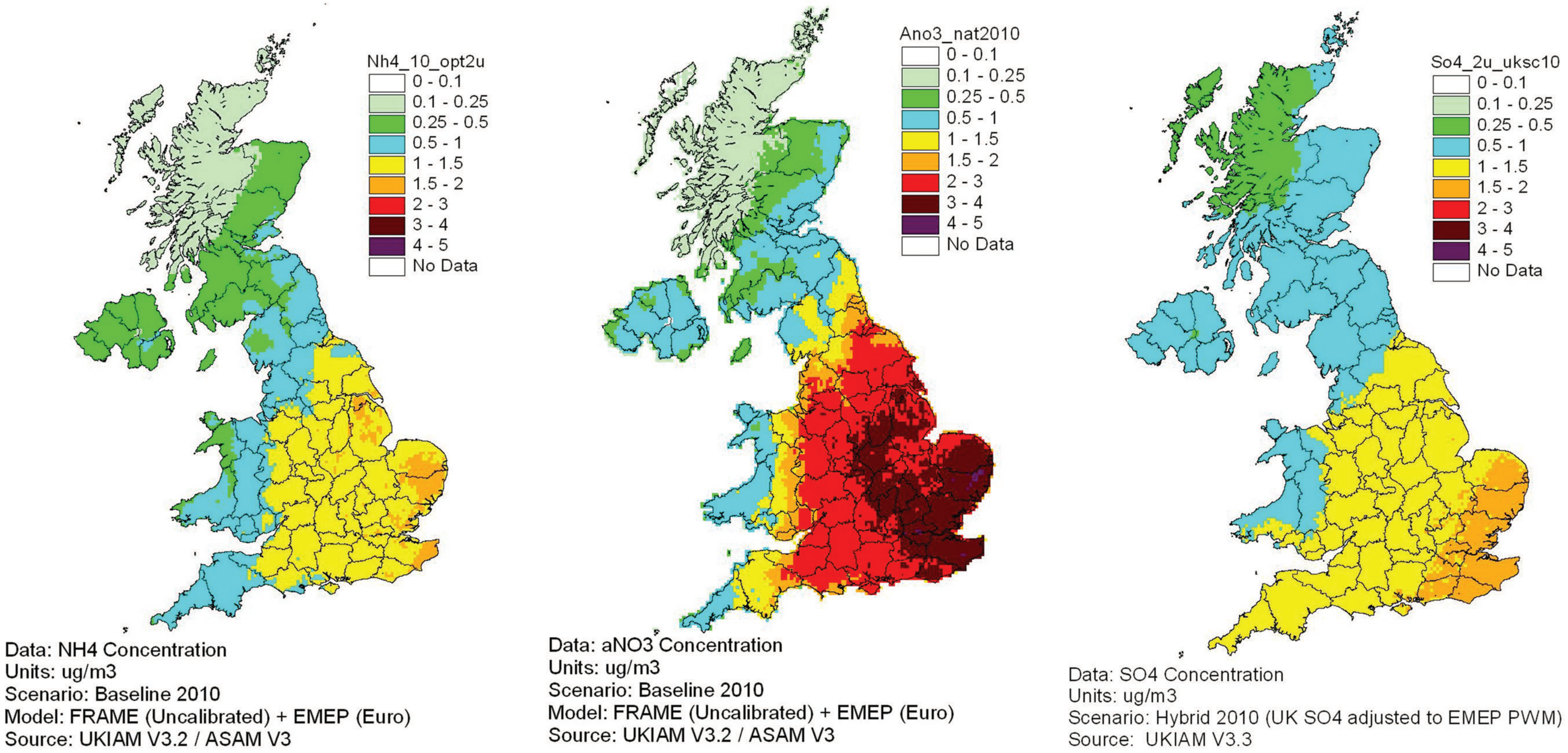


Figure 5.7: Maps of SIA components derived for use in PCM based on interpolation between measurements (2009).



Data: NH4 Concentration
Units: ug/m3
Scenario: Baseline 2010
Model: FRAME (Uncalibrated) + EMEP (Euro)
Source: UKIAM V3.2 / ASAM V3

Data: aNO3 Concentration
Units: ug/m3
Scenario: Baseline 2010
Model: FRAME (Uncalibrated) + EMEP (Euro)
Source: UKIAM V3.2 / ASAM V3

Data: SO4 Concentration
Units: ug/m3
Scenario: Hybrid 2010 (UK SO4 adjusted to EMEP PWM)
Source: UKIAM V3.3

Figure 5.8: UKIAM maps of NH_4^+, fine NO_3^- and SO_4^{2-} contributions to $PM_{2.5}$ in 2010 derived from combinations of the EMEP and FRAME models.

32. Comparison of the two sets of maps in Figure 5.7 and 5.8 shows quite good general agreement although there are some spatial differences, with UKIAM giving slightly higher concentrations in the south-east, especially for SO_4^{2-}. The spatial distribution of NO_3^- with UKIAM is much patchier, influenced by the variability of ammonia emissions in both rural and urban areas; this is not apparent from the smoother interpolation between sparse measurements in the maps from PCM. But both sets of maps show the same general pattern of higher concentrations in the south-east influenced by transboundary contributions from Europe and shipping in the North Sea, decreasing across the UK to very low concentrations in Scotland. NO_3^- is the biggest component of SIA, and will become even more dominant in future with decreasing SO_2 emissions, including those expected from shipping under the MARPOL Convention.

33. Secondary organic aerosol (SOA) is another component with a large biogenic contribution, which raises many uncertainties both in precursor emissions and chemical processes. SOA is derived from the oxidation of a wide range of organic precursor compounds, including both anthropogenic volatile organic compounds (VOCs) and biogenic compounds. Many of the precursors are large molecules subject to complex reaction pathways that in most cases are incompletely characterised. The initial oxidation products are also subject to oxidation leading to a further set of products. As outlined in Chapter 4, many components of SOA are semi-volatile and hence actively partition between vapour and particle phases in a manner which is hard to predict. Consequently, it is a major challenge for a model to simulate the oxidation of hundreds of potential precursor compounds and the subsequent partitioning of the oxidation products into SOA.

34. Because of these problems, and because of limited options to reduce the small anthropogenic part of the SOA, it has not been addressed in integrated assessment modelling towards setting national emission ceilings in the GAINS model. The estimate included in the maps of total $PM_{2.5}$ from the PCM modelling for 2009 (Figure 5.1), and also in the modelling with UKIAM (Figure 5.2), is based on the HARM/ELMO model (Whyatt *et al.*, 2007). More recent modelling with the NAME model[1] gives a broadly similar maximum contribution but a more uniform spatial distribution, resulting in population-weighted mean concentrations of SOA nearly 20% higher. Figure 5.9 provides a comparison of maps from the two models.

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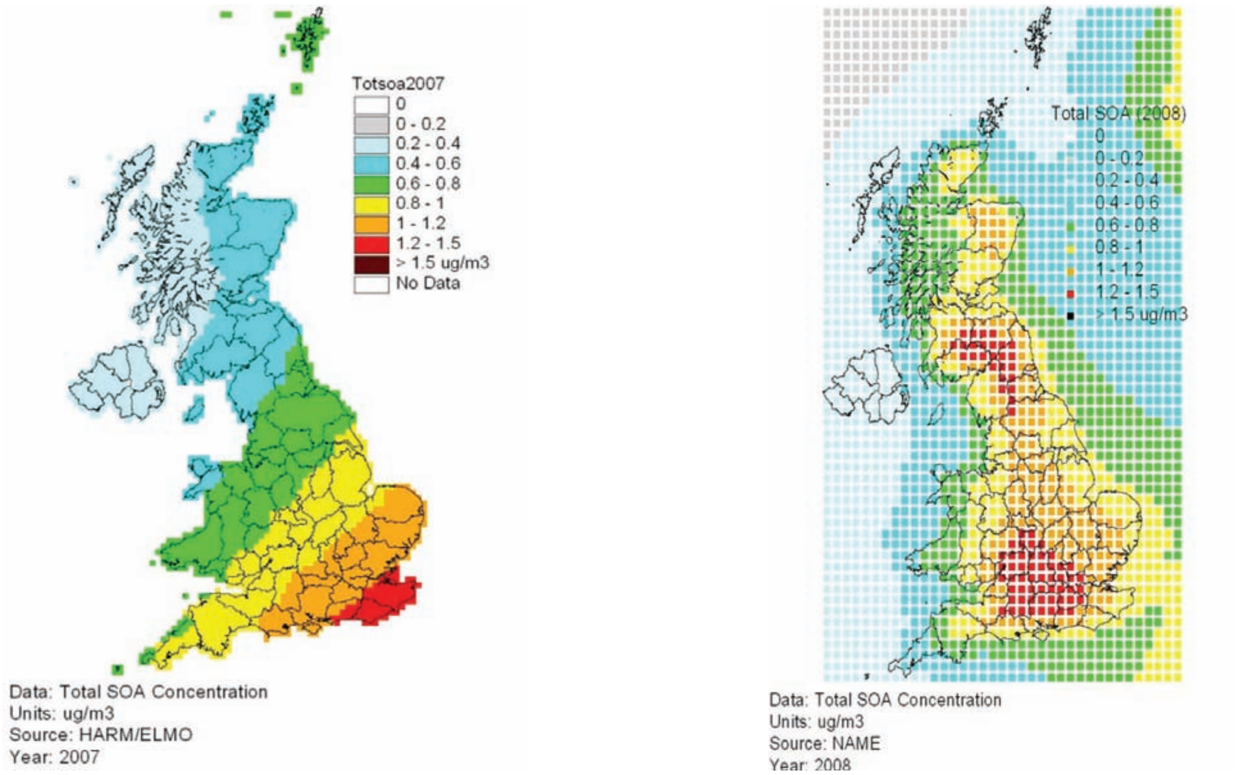
[1] Redington, A.L. Derwent, R.G. Modelling secondary organic aerosol in the United Kingdom. Atmospheric Environment 64 (2013) 349-357. Also described in a Met Office report to Defra, *NAME modelling to provide emission sensitivity coefficients for SOA for the PCM model 2008*, dated 12 July 2011.



Data: Total SOA Concentration
Units: ug/m3
Source: HARM/ELMO
Year: 2007

Data: Total SOA Concentration
Units: ug/m3
Source: NAME
Year: 2008

Figure 5.9: Comparison of total SOA concentrations from HARM/ELMO model (left) and the NAME model (right).

5.4.3 Semi-volatile components

35. A number of the major components of $PM_{2.5}$ are semi-volatile. This term implies that they actively partition between vapour and the condensed phase of the aerosol and, in doing so, can significantly influence the measured mass of $PM_{2.5}$. There are at least three main mechanisms by which this partitioning occurs:

(a) Some chemical compounds have vapour pressures which are high enough so that an appreciable proportion of their mass is present as vapour, but low enough that not all of their mass vaporises from particles; consequently some remains to be weighed as $PM_{2.5}$. Such compounds typically adsorb to the surface of other particles, an example being higher molecular weight hydrocarbons present in engine exhaust.

(b) Water-soluble compounds of intermediate vapour pressure will tend to partition into the aqueous component of the particles. Their equilibrium with the particles is determined by Henry's Law but may also be influenced by chemical reactions within the aqueous phase which serve to reduce the dissolved component concentration. Many components of secondary organic aerosol are highly oxygenated organic compounds which partition in this way.

(c) Some compounds such as ammonium nitrate are able to dissociate into vapour phase components (nitric acid and ammonia in the case of ammonium nitrate) establishing a partitioning between the vapour phase components and the original compound within the solid or liquid particle. Ammonium nitrate and ammonium chloride are prime examples of compounds behaving in this way.

36. The behaviour of semi-volatile constituents is a major problem both for the measurement and modelling of $PM_{2.5}$. In the case of measurement, the degree of partitioning of semi-volatile compounds into the measured particles is determined by factors such as atmospheric temperature and relative humidity. Consequently, if these change during the sampling interval (as they typically do from day to night), sampling artefacts can occur through the evaporation or condensation of such materials from/on the air filter used in sampling. Additionally, the reduced pressure used to draw air through a sampling filter can encourage the vaporisation of semi-volatile components. The difficulties for modelling start with the prediction of the formation of secondary semi-volatile components and continue with the problem of describing their partition into the particles. This is affected by many factors, most notably temperature, relative humidity and the existing composition of the particles, which affect the thermodynamic activities of the soluble components and the uptake into organic films for the hydrophobic components. A further difficulty for modellers is caused by the fact that air sampling methods for $PM_{2.5}$ are not artefact free and therefore measure concentrations that may not reflect well the true airborne suspended particle mass.

37. Since semi-volatile organic matter and ammonium salts comprise a substantial part of $PM_{2.5}$ mass, these issues have major implications for both measurement and modelling of concentrations.

5.4.4 Other components

38. In addition to primary $PM_{2.5}$ from sources represented in the emission inventory and secondary inorganic aerosol, there is a large contribution from other components, many of which are more uncertain and include natural or land use related contributions not subject to control. These include rural dust from wind-suspended soil particles varying with soil characteristics, and urban dust including material resuspended by traffic. Sea salt is another component of natural origin, the influence of which decreases with distance from the coast.

39. Finally, particle bound water makes an additional contribution to particle mass. It might seem that this is another natural component, but it has been argued in legislation concerning PM_{10} that it is partly associated with man-made SIA contributions. However, estimating any reduction in particle bound water in response to reductions in SO_2, NO_x and NH_3 emissions is extremely uncertain, involving both direct and indirect effects on cloud processes. Hence, in Table 5.5 for example, where water content in UKIAM is based on modelling provided by EMEP, water content is kept constant in future projections (which may be pessimistic). By contrast the PCM model associates the water entirely with the SIA components and scales it accordingly.

5.5 Model evaluation for $PM_{2.5}$

40. Evaluating models that predict $PM_{2.5}$ is complex due to the multiple components that make up $PM_{2.5}$ mass. At one level it is possible to compare absolute mass predictions directly with $PM_{2.5}$ measurements, as illustrated in Figure 5.10. The increased number of sites measuring $PM_{2.5}$ in recent years will aid model evaluation in this respect. However, while useful, such a comparison is limited because it will not be known *why* model predictions depart from measured values, which is a critical issue for effective model evaluation. For this reason,

almost all model evaluation work that considers $PM_{2.5}$ separately considers the major components that make up $PM_{2.5}$ mass. Verification of source attribution as in Figure 5.10 requires corresponding measurements of chemical composition which are not available for many of the components.

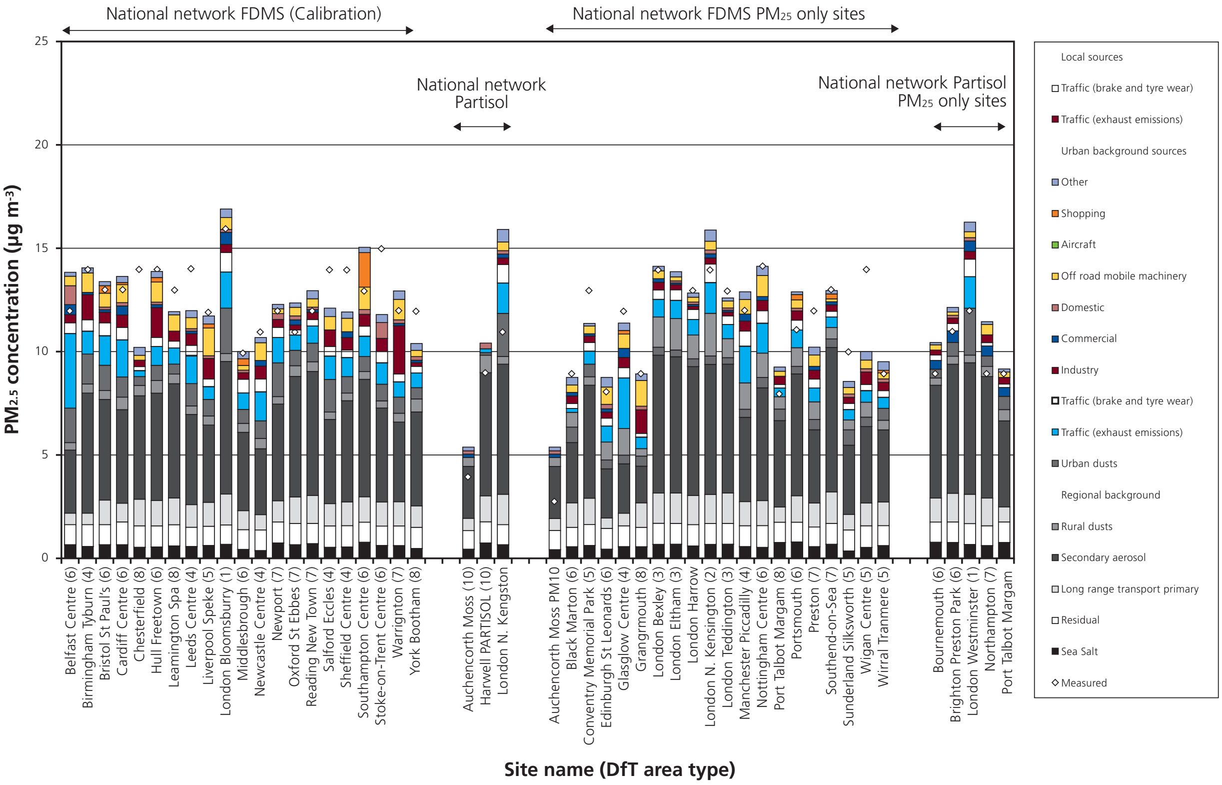


Figure 5.10: Source apportionment for background sites in 2009 from PCM model.

41. In common with other species, the model evaluation of $PM_{2.5}$ can be frustrated by a lack of information or accuracy concerning emission inventories, the chemical and physical processes involved and the availability of reliable measurements with which to compare predictions. However, in the case of $PM_{2.5}$ these issues are in some situations a considerable limitation affecting the reliable evaluation of models. For example, at the local scale there is lack of knowledge concerning road vehicle tyre and brake wear, the amount of material resuspended from the ground and the contribution made by biomass. Similarly, there is also a lack of adequate information concerning NH_3 emission inventories for both rural and urban sources (including the temporal variation of agricultural emissions) and the influence that they have on the assessment of model performance for particulate nitrate and ammonium and the representativeness of measurements for comparison.

42. Modelling and detailed analysis can help identify some model system deficiencies. For example, Appel *et al.* (2008) considered the evaluation of $PM_{2.5}$ made by CMAQ version 4.5. They noted that large overprediction of particulate nitrate and ammonium in the autumn was likely the result of a large overestimation of seasonal ammonia emissions. Furthermore, the carbonaceous aerosol concentrations were substantially underpredicted during the late spring and summer months, which they considered to be due in part to the omission

of some secondary organic aerosol formation pathways from the model. This underprediction can arise for a number of reasons including: incomplete knowledge of precursor VOCs; inadequacies in the description of VOC oxidation processes; and poor treatment of vapour partition processes. Most probably, all three factors play a role.

43. Of the models considered in this report, there are several important points to note with respect to model evaluation. For models which aim to model chemical and physical processes explicitly, for example CMAQ, NAME and EMEP, there is a tendency to underestimate total $PM_{2.5}$ mass, sometimes by substantial amounts. The CMAQ model described in A2.2, for example, underpredicts $PM_{2.5}$ mass at a London background location by 30-40%, consistent with the underprediction noted in A2.3. However, a consideration of specific components shown in A2.3 reveals mixed model performance. For example, fine particulate nitrate is underpredicted by about a factor of two, whereas the performance for coarse particulate nitrate was considerably worse. The general underprediction compared with measurements seems not to have a single, dominant cause but is the result of underestimates in many key $PM_{2.5}$ components.

44. It is worth stressing that while there remain many challenges involved in evaluating models that predict $PM_{2.5}$, there is active ongoing research in this area. Model evaluation initiatives such as AQMEII, which bring together many models (from the USA and Europe) and large datasets with which to evaluate them, should help lead to an improved understanding of $PM_{2.5}$ model evaluation (Galmarini and Rao, 2011).

5.6 Prediction of future trends

45. Of particular importance is the change in $PM_{2.5}$ concentrations over the next decade. This section brings together preliminary modelling projections already undertaken, and indicates some of the main uncertainties and needs for further work.

46. Figures 5.1 and 5.2 compare future concentrations calculated for 2020 derived from the PCM and UKIAM models, together with corresponding maps for recent years (2009 and 2010 respectively). The maps from the two models look broadly similar, with both still showing higher concentrations in 2020 in the south-east and around London where higher SIA concentrations are superimposed on higher primary emissions. But there is a bigger decrease in concentration estimates in the UKIAM model over the time span illustrated than in the estimated concentrations in the PCM model.

47. Tables 5.4 and 5.5 provide a breakdown of population-weighted means for different source components for each model and indicate that overall there is a greater predicted percentage change in $PM_{2.5}$ (21%) according to the UKIAM scenario analysis compared to the PCM estimates (12% change). A large part of this difference is in the SIA concentrations. Whereas the UKIAM scenarios used emissions from other countries outside the UK in 2020 (from a recent study with the GAINS model based on energy projections from the PRIMES model (PRIMES, 2010) and assumed implementation of currently agreed legislation up to 2020 to limit emissions), PCM used earlier estimates with higher emissions reported to EMEP. In addition, the UKIAM scenario allowed for the MARPOL Convention leading to reductions of the order of 85% in SO_2 emissions from

the North Sea (although this is more than offset by increases in NO_x from the growth in shipping). This emphasises the dependence of trends in $PM_{2.5}$ on future projections of emissions outside the UK, and hence on the revision of national emission ceilings under CLRTAP and the EU's Air Quality Directive. Another uncertainty in both models arises from the linear extrapolation of the response of SIA concentrations to changes in emissions (see Section 5.4).

48. Trends in primary components are more consistent between the two models, but UKIAM estimates lower concentrations than the PCM model, and both may underestimate where emission inventories are incomplete.

49. For both models there is still a substantial contribution from other components which is highly uncertain. The UKIAM model used the same treatment of urban and rural dusts and sea salt developed for the PCM model, so these are effectively the same; and both adopt SOA modelling undertaken independently and assumed to be unchanged over time. The UKIAM model uses modelled water content from the EMEP model but does not allow for any change in this component in conjunction with soluble SIA components. Further work is needed on the contribution of all these additional components.

50. In conclusion, there are significant differences between the preliminary projections to 2020 from the two models, both in source apportionment and trends, and in assumptions about future emissions. These need further investigation, ideally with extension to other models, taking note of the uncertainties and gaps in knowledge indicated in this report concerning, *inter alia*, emission inventories and projections. When considering the multiple components of $PM_{2.5}$, each of which presents different problems to quantify, model validation is not possible in the absence of new speciated measurements to give a detailed breakdown of overall $PM_{2.5}$ concentrations.

Table 5.4: Population-weighted mean contributions to annual mean $PM_{2.5}$ in the UK in 2009 and projections to 2010 and 2020 from the PCM model ($\mu g\ m^{-3}$). The % reductions between 2010 and 2020 are also shown.

	2009	2010	2020	Reduction 2010 to 2020
sea salt	0.67	0.67	0.67	0.0%
residual	1.00	1.00	1.00	0.0%
secondary inorganic aerosol	4.05	3.94	3.34	15.2%
secondary organic aerosol	0.86	0.86	0.86	0.0%
regional primary	1.14	0.90	0.80	12.1%
rural dust	0.51	0.51	0.51	0.0%
urban dust	0.62	0.62	0.62	0.0%
point sources	0.07	0.06	0.06	0.3%
non-traffic area sources	1.02	0.99	0.78	20.5%
traffic area sources	0.75	0.73	0.38	47.3%
Total	**10.70**	**10.29**	**9.04**	**12.2%**

Table 5.5: Population-weighted mean contributions to annual mean $PM_{2.5}$ in Great Britain in 2010 and projections to 2020 from the UKIAM model (µg m^{-3}). The % reductions between 2010 and 2020 are also shown.

Component		2010	2020
Primary $PM_{2.5}$		**1.23**	**0.82 (33%)**
SIA ($SO_4^{2-} + NO_3^- + NH_4^+$) as $PM_{2.5}$			
– from UK emissions		2.30	1.61
– from shipping (within 200 nautical miles)[1]		0.80	0.61
– other, including imported from Europe		1.65	0.95
	Total	**4.75**	**3.17 (33%)**
Other components			
– soil and other dust particles[2]		1.01	same
– sea salt[2]		0.66	as
– secondary organic aerosol (SOA)[3]		0.65	2010
– water (based on EMEP model)		1.37	
	Total	**3.69**	**3.69 (0%)**
TOTAL		**9.67**	**7.63 (21%)**

[1] Shipping emissions from AMEC/ENTEC excludes reductions under MARPOL in 2010 but reductions under MARPOL are in effect by 2020.
[2] UKIAM makes use of results from the PCM model for these components.
[3] Based on the HARM/ELMO model (Whyatt *et al*., 2007).

5.7 Conclusions and recommendations

51. Models have important roles to play in understanding $PM_{2.5}$. These include assessing concentrations at locations without monitors and answering questions such as how will PM levels change in the future, what are the most important emission sources to control to reach acceptable air quality and what balance should be struck between policy actions within the UK and abroad. However, **modelling of $PM_{2.5}$ remains a substantial challenge** because of uncertainties in the measurement data, uncertainties/lack of understanding of some aspects of the dynamic, physical and chemical processes which need to be described within the models, and uncertainties in the emission data and their projections.

52. A wide range of PM models covering all scales from the urban to the regional are used to predict UK air quality. The models are based on a range of modelling systems (e.g. Eulerian, Lagrangian and Gaussian plume). Models are useful for aggregating the different contributions to PM, for example to rural background PM from: vehicular and stationary sources; short- and long-range formation and transport from the UK PM precursor sources; long-range transboundary formation and transport of primary and secondary PM; and intercontinental-scale PM formation and transport.

53. Modelling results have illustrated how primary $PM_{2.5}$ concentrations show localised peaks in urban areas owing to local sources, superimposed on a regional background. The sources which cause these peaks are potentially subject to abatement and the dispersion of these sources are generally well represented by models, except when close to roads with complex street geometries. An important limiting factor in estimating concentrations and human exposure is likely to be uncertainty in the emissions, including missing sources.

54. The largest contribution to $PM_{2.5}$ concentrations overall is secondary inorganic aerosol (SIA). Secondary inorganic aerosol contributions are more smoothly varying, resulting from advection on a range of scales up to continental and illustrated by higher average concentrations in the south-east graduating to much lower values over Scotland. Nitrate is the largest component of SIA over the UK, and also the most spatially variable in space and time, depending as it does on the variability of ammonia emissions and concentrations. More detailed research is required to investigate the effect of temporal variations in emissions, especially of ammonia, and explain the seasonal variation and the higher nitrate levels observed in winter. Sulphate now makes a smaller contribution to $PM_{2.5}$ concentrations than nitrate owing to major reductions in sulphur emissions in the UK and in other countries and from shipping.

55. The ratio of urban increment to regional background points to future directions for $PM_{2.5}$ control. Control strategies should be considered for the regional background where secondary inorganic aerosol is by far the largest component according to models. It is also worth noting that given the exposure reduction targets outlined in Chapter 1, the removal of the whole of the urban increment would be required to satisfy them if nothing is done to address the regional background.

56. Source apportionment from modelling shows how further reductions in SIA depend on the control of emissions of SO_2, NO_x and NH_3 in other countries, and from shipping more generally, as well as in the UK. Scenario analysis shows dependence on future emission ceilings in the EU-27 countries and also the modelled reduction of sulphate resulting from the MARPOL agreement of the International Maritime Organization (IMO), counteracted by enhanced nitrate due to increasing shipping emissions of NO_x. Modelling indicates a complex non-linear response of SIA concentrations to reductions in precursor emissions due to chemical interactions between pollutants, in particular the high dependence on the availability of NH_3 and the reversible and temperature-dependent formation of ammonium nitrate. This needs to be borne in mind when considering the effectiveness of further SO_2 and NO_x reductions, whilst emissions of NH_3 have remained more constant.

57. Modelling of the smaller secondary organic aerosol (SOA) component is far more uncertain and speculative than for SIA, both in terms of precursor emissions (see Chapter 4) and chemical processes, and further work is required in this area. However, it is more difficult to control SOA and its precursors, of which biogenic emissions are a large component. It is worth noting that the oxidants for biogenic VOC precursors, namely hydroxyl ions (OH^-), ozone (O_3) and NO_3^-, are all controlled by atmospheric chemistry, and will respond to further reductions in carbon monoxide (CO), SO_2, NO_x and VOC emissions. It is

therefore not clear whether SOA levels will remain constant in the future if man-made emissions change significantly. This issue should be the subject of further research.

58. The semi-volatile components of organic aerosols and ammonium salts comprise a substantial fraction of $PM_{2.5}$ and present a substantial modelling and measurement issue. Other components, such as sea salt, rural and urban dusts, and water content, must be accounted for in order to explain total $PM_{2.5}$ concentrations and achieve mass closure. These still make a substantial contribution to overall concentrations and exposure for the finer $PM_{2.5}$ fraction, albeit not as large a contribution as for PM_{10}. Further work is required to investigate these other contributions and how they may be represented in modelling, including, for example, the response of the water content associated with the $PM_{2.5}$ fraction to reductions in pollutant emissions.

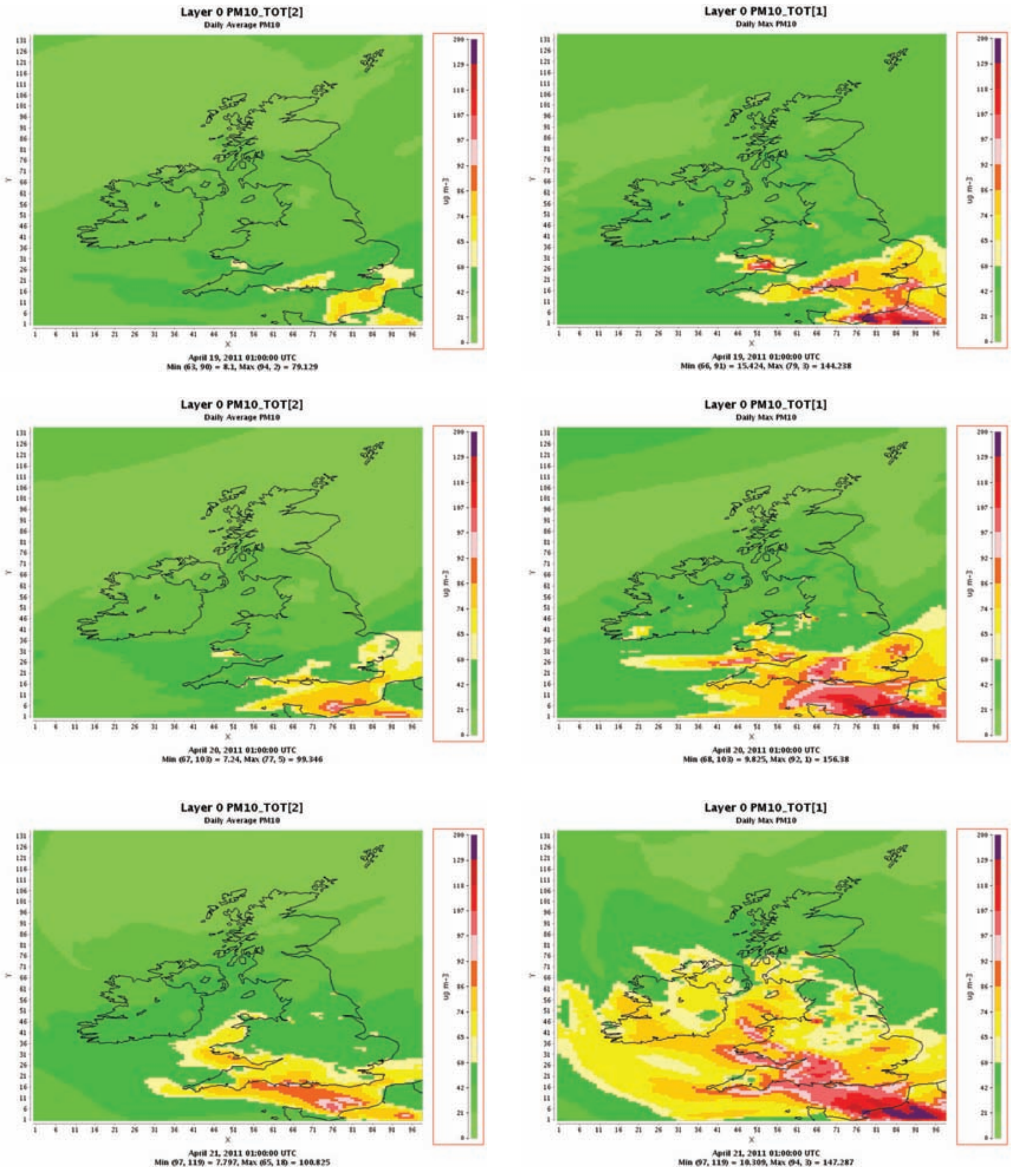
59. In common with other species, the model evaluation of $PM_{2.5}$ can be frustrated by lack of information or accuracy concerning emissions inventories, the chemical and physical processes involved and the availability of reliable measurements. **There is a need for more extensive and consistent evaluation of $PM_{2.5}$ models in the UK**, considering for example, similar time periods and the speciated components of $PM_{2.5}$. Such an evaluation should also consider the temporal and spatial characteristics of the key components of $PM_{2.5}$. Furthermore, the evaluation would provide a more robust assessment of model performance beyond meeting the Air Quality Directive requirements (see Chapter 1) for model performance. Verification of models, particularly source attribution, remains challenging largely because of the lack of availability of chemically-speciated measurements. There is also a need to develop methodologies for quantifying uncertainties in modelled values.

Annex 2: PM modelling in the UK

A2.1: Applications of CMAQ to PM-related projects at AEA

1. CMAQ is one of the tools used to produce the UK daily air quality forecast on behalf of Defra. 48-Hour forecasts for PM_{10} and $PM_{2.5}$ are produced using CMAQ at 10 km resolution. Figure A2.1.1 gives examples of the forecasts over a period of elevated particulate matter (PM) at the end of April 2011. The classification of PM air quality is based on a 24-hour average. The yellow areas of the daily average plots in Figure A2.1.1 identify areas where moderate air quality was predicted (see http://uk-air.defra.gov.uk/air-pollution/daqi for the air pollution health bandings used in the daily forecasts; see also Table 5.2 in Chapter 5). CMAQ tends to underestimate PM_{10}, particularly when dust and resuspension are contributing factors. The maximum hourly plots demonstrate areas where PM was elevated but not sufficiently so to be classed as moderate on the 24-hour average. Further analysis of the PM components could be used to identify the major contributors.

Daily Average PM_{10} **Maximum Hourly PM_{10}**



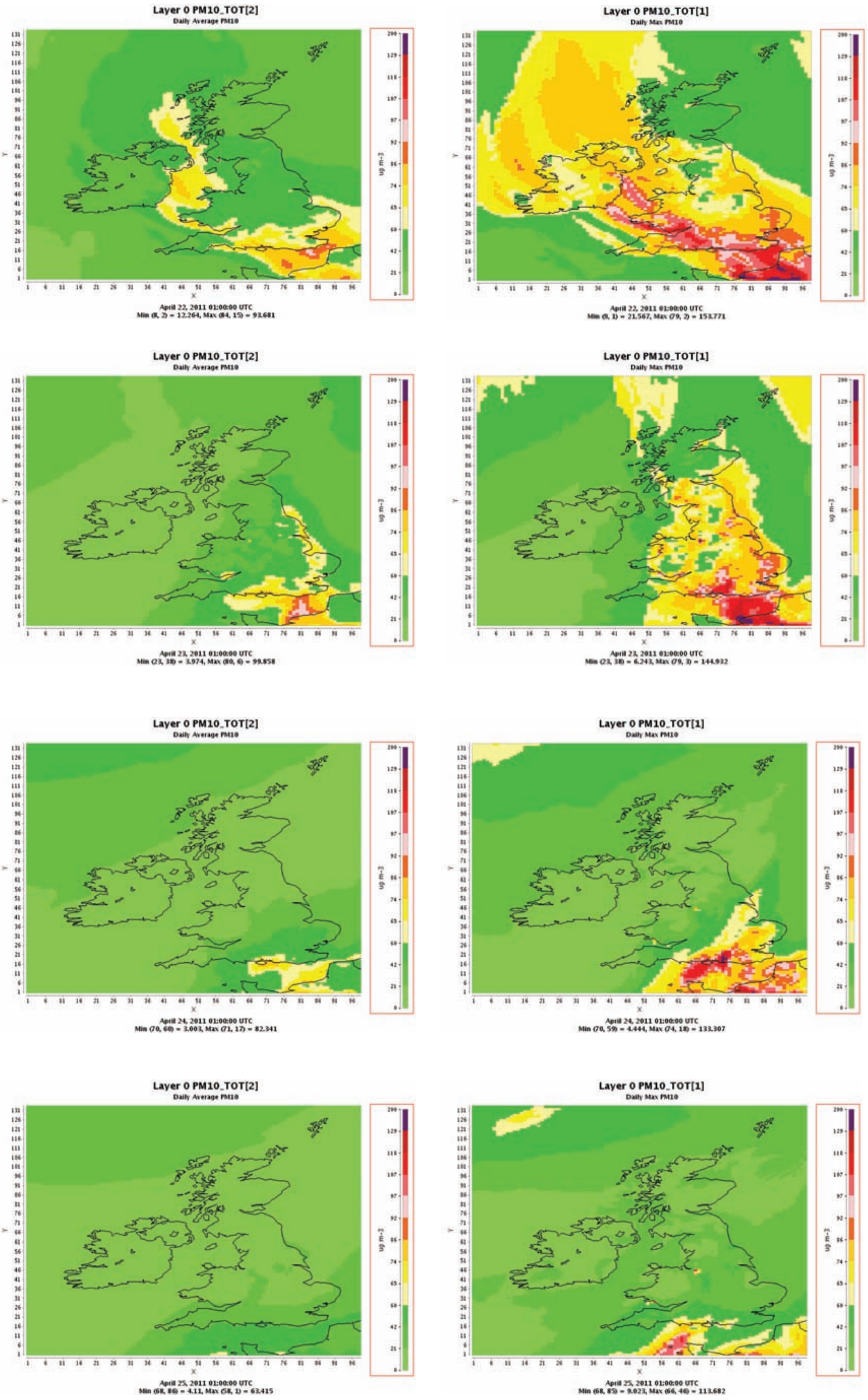


Figure A2.1.1: Daily average and hourly maxima for PM_{10} from 19-25 April 2011 from the UK daily air quality forecast.

2. Figure A2.1.1 shows the moderate levels of PM building up and subsiding over a series of days. This is demonstrated in Figure A2.1.2 which gives an extract from the model evaluation of 16 Automatic Urban and Rural Network (AURN) urban background sites from around the UK for the period 12-26 April 2011. The evaluation is based on hourly values and during this period model performance was within acceptable limits as defined by the Model Evaluation Protocol (Derwent *et al.*, 2009a). Table A2.1.1 summarises the model performance for a selection of rural, urban background and urban AURN sites.

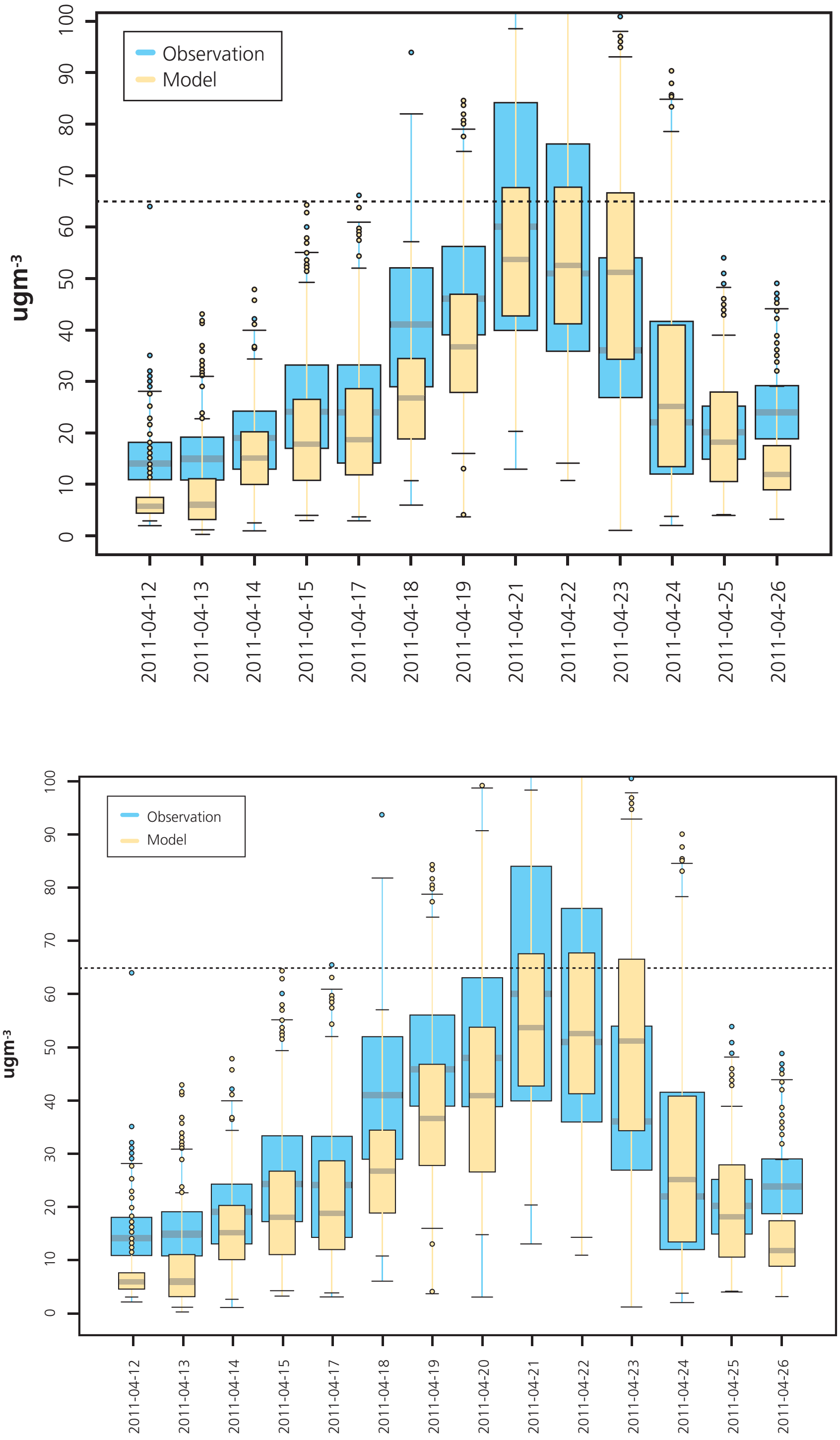


Figure A2.1.2: Evaluation of CMAQ forecast with hourly PM_{10} provisional data from 16 AURN urban background sites, 12-26 April 2011.

Table A2.1.1: Evaluation of CMAQ forecast with hourly PM_{10} provisional AURN data, 12-26 April 2011.

	Rural and remote	Urban background	Urban
Number of sites	4	16	12
normal mean bias (%)	8	-14	-24
normal mean error (%)	44	37	41
% of pairs within a factor of two	68	73	68
Forecast the hourly PM_{10} exceeding 65 µg m^{-3}			
proportion correct	0.96	0.91	0.97
odds ratio skill score	0.98	0.90	0.64

3. The WRF-CMAQ air quality model has been used to investigate the sensitivity of PM to a reduction in precursor (sulphur dioxide (SO_2), nitrogen oxides (NO_x) and ammonia (NH_3)) emissions. The simulations are based on 2006 using four months – January, April, July and October – as representatives of winter, spring, summer and autumn respectively, allowing evaluation over a range of different conditions. The response is not easy to predict due to the non-linearity of the relationship between the change in emissions and PM components.

4. The 12 km resolution WRF-CMAQ model run of the UK has been used. It uses the ECMWF (European Centre for Medium-Range Weather Forecasts) ensemble model as the boundary conditions for the Weather Research and Forecasting model (WRF), and emissions from EMEP and the National Atmospheric Emissions Inventory (NAEI); biogenic emissions are calculated using the weather conditions from WRF and the Biogenic Potential Inventory (Dore *et al.*, 2003). CMAQ is operated using the Carbon Bond 05 gas-phase chemistry mechanism, with additional aqueous and aerosol processing. Aerosol concentrations (hourly values in each grid point) and wet and dry deposition are output for 18 organic species, three natural organic species, nitrate (NO_3^-), sulphate (SO_4^{2-}), chloride (Cl^-), ammonium (NH_4^+), sodium (Na^+), soil, elemental carbon (EC), and additional fine and coarse mode PM.

5. The response to emissions reductions in particulate matter were in line with those reported for the PTM (A2.6). The reduction in SO_2 emissions has the largest overall effect on PM, the largest individual effect being on sulphate. This is a non-linear response which also varies with season and location. The response of SO_4^{2-} and NH_4^+ show a seasonal response which is lower in winter than summer. Reducing NO_x emissions has the smallest effect. There is an overall increase in sulphate for January, April and October as reported for the PTM, with no effect in summer. The effects on both fine and coarse NO_3^- show a less than linear response, with a large spatial variation. Again, reducing NH_3 emissions shows a response very similar to the PTM studies. It results in a reduction in NH_4^+ and fine NO_3^- by similar amounts, with a smaller reduction in SO_4^{2-}. This is the only scenario where no PM component increases.

6. The non-linearity of the model response to emission reduction is the result of complex interactions. It highlights the importance of introducing the emissions into the model using realistic temporal profiles.

A2.2: WRF/CMAQ applications at the Centre for Atmospheric and Instrumentation Research (CAIR), University of Hertfordshire

7. CMAQ is not currently being used as a policy tool in the UK but is being considered for regulatory applications as part of the Comparison of Simple and Advanced Regional Models (CREMO) funded by the Environment Agency. Defra is commissioning work to assess the potential of CMAQ to meet its policy needs. The intention of this work will be to develop an operational version of the model for UK policy applications. This and the following section provide examples of applications for the years 2003, 2005 and 2006, which formed part of the AQMEII, MEGAPOLI (FP7), Defra model inter-comparison and CREMO projects. Further details on the model set-up and applications can be found in Yu *et al.* (2008) and Chemel *et al.* (2010).

8. The focus of research has been on $PM_{2.5}$ and modelled results are compared with the observations from Harwell, London North Kensington and London Bloomsbury. Overall, CMAQ underestimates $PM_{2.5}$ concentration at the selected sites but reproduces the temporal variations. There are important considerations when comparing modelled and measured data for the results presented here. First, the spatial grid resolution is 18 km x 18 km and is not optimum for simulating pollutants that are, at least partly, generated on smaller, local scales. This set-up has been used as a pragmatic approach to develop a regional configuration to model hourly concentrations over multiple years. Second, previous results (not shown here) have indicated sensitivity of $PM_{2.5}$ concentrations to boundary conditions, for example, in the comparison conducted with boundary conditions from GEMS and from GEOS-Chem (global air pollution model). Third, the treatment of aerosols is part of ongoing model developmental work and significant changes will be introduced in the next version of CMAQ. The results shown in Figure A2.2.1 are annual $PM_{2.5}$ modelled results for 2003 using CMAQ version 4.6 and annual $PM_{2.5}$ modelled results for 2006 using CMAQ version 4.7.1. For 2003 the grid spacing was 15 km. The 2006 run conducted at 18 km grid spacing was part of the AQMEII model inter-comparison for a domain which covered all of Europe.

9. The daily average $PM_{2.5}$ concentrations were calculated for a rural background station Harwell (HAR) for 2003 and 2006, and for urban background stations London North Kensington (LNK) for 2006 and London Bloomsbury (LBB) for 2003. Modelled $PM_{2.5}$ ground (first level) results are compared with measurements from the selected stations for the year 2006 and 2003 for the appropriate stations in Figure A2.2.1. This figure shows that overall CMAQ values reproduce the temporal variations for all three stations but show about a 30-40% underestimation especially for the urban stations. Further analysis is required to understand the model response during peak occurrences, where it correctly captures the timing but not necessarily the magnitude of the event. This will include examination of the local and regional nature of $PM_{2.5}$ and its precursors, as well as the governing meteorological processes (simulated with WRF).

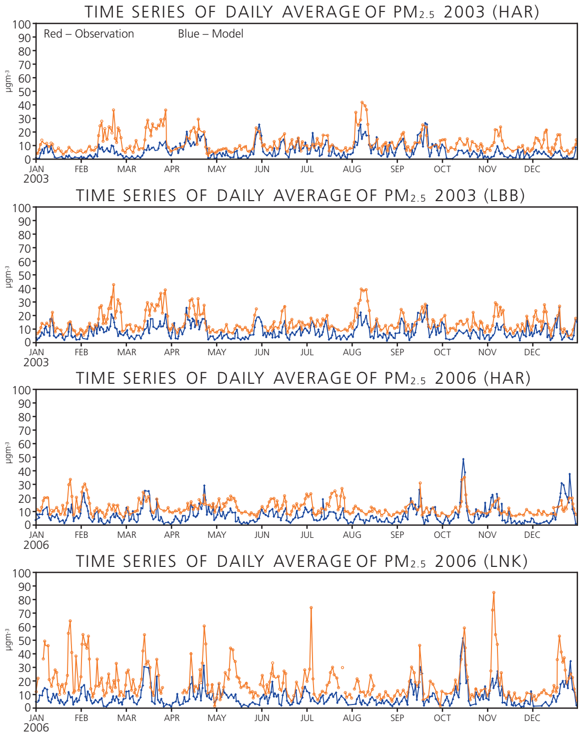


Figure A2.2.1: Time series of 24-hour means of $PM_{2.5}$ concentrations for 2003 and 2006 from CMAQ and measurements from Harwell (HAR), London North Kensington (LNK) and London Bloomsbury (LBB) stations. Red is observation and blue is model results.

10. The underestimation of modelled results is observed for both stations in the 2006 run. However, the Harwell results shown in Table A2.2.1 for 2005 (January and July) using the same model configuration, including meteorological fields and grid resolution, but with year-specific emissions, indicate closer agreement with measurements as indicated by the factor of 2 statistical metric (FACT2). A full year run for 2005 is being planned and will lead to more insight into the model performance. Specifically, it is recommended that sensitivity of $PM_{2.5}$ concentration to boundary conditions and the long-term year-to-year variations over multiple years be investigated to provide confidence in the performance of models such as CMAQ to address policy issues. Scatter plots are shown for 2006 (Figure A2.2.2) and for January and July 2005 (Figure A2.2.3).

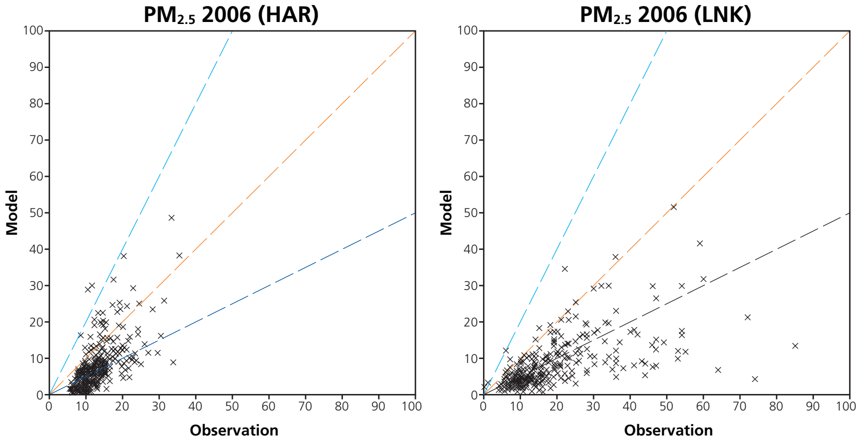


Figure A2.2.2: Scatter plots of 24-hour means of $PM_{2.5}$ concentrations for Harwell (HAR) and London North Kensington (LNK) for 2006. The red dashed line represents 1:1 line, the purple dashed line represents 2:1 line and the blue dashed line represents 1:2 line.

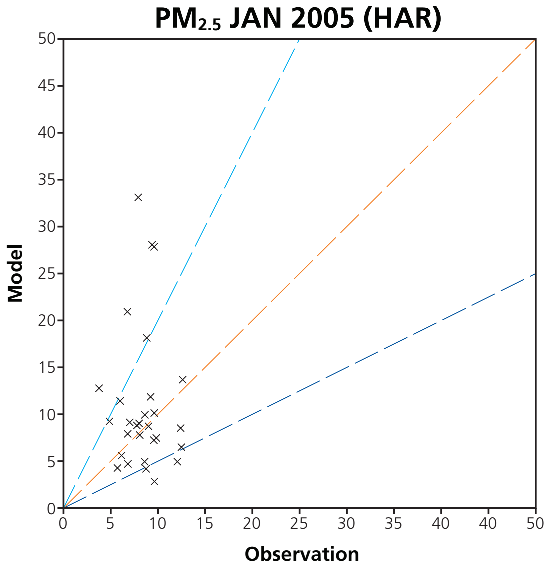


Figure A2.2.3: Scatter plots of 24-hour means of $PM_{2.5}$ concentrations for Harwell for January and July 2005. The red dashed line represents 1:1 line, the purple dashed line represents 2:1 line and the blue dashed line represents 1:2 line.

Table A2.2.1: Statistical model performance measures for 2006 and 2005 (January and July) $PM_{2.5}$ concentrations at Harwell (HAR) and London North Kensington (LNK) sites.

	FACT2 (%)	RMSE	BIAS
HAR (2006)	45	7.0	-5.0
LNK (2006)	33	14.5	-10.3
HAR (January 2005)	69	8.2	2.6
HAR (July 2005)	58	4.6	-4.0

A2.3: WRF/CMAQ applications at King's College London

Analysis of CMAQ PM predictions for 2008

Overview

11. It is important not only to look at the total modelled and measured concentration of PM but to assess the performance of the model for each component, as this is a well established way of finding weaknesses in the modelling approach be they associated with model chemistry, dispersion or emissions. In this example we have followed this approach and present predictions of total $PM_{2.5}$ as well as the performance of the model components, nitrate (NO_3^-), sulphate (SO_4^{2-}), elemental carbon (EC), ammonium (NH_4^+) organic carbon (OC), primary organic aerosol (POA), secondary organic aerosol (SOA), chloride (Cl^-), sodium (Na^+), particle bound water and "other" particles (principally metals and minerals). The evaluation of the model includes components that exist mainly in the coarse (PM_{10}-$PM_{2.5}$) mode but have a proportion in the fine mode.

12. The evaluation has followed the availability of measurements of $PM_{2.5}$ and PM_{10} species in 2008 and, as such, some comparisons were for hourly $PM_{2.5}$, some

were for daily $PM_{2.5}$ nitrate and for daily PM_{10} sea salt and sulphate, and some were for daily PM_{10} EC/OC (for the last five months of 2008).

13. In general, the model underpredicts hourly $PM_{2.5}$ measurements when using estimates of modelled $PM_{2.5}$ mass without particle bound water (Figure A2.3.1). A similar conclusion can be drawn for total PM_{10} concentrations. Despite the underprediction of PM_{10}, the model replicates the proportion of each species reasonably well, slightly overpredicting observed NO_3^- and SO_4^{2-} fractions and underpredicting others such as Cl^-, EC, SOA and OC (Figure A2.3.2). The model results for fine mode PM nitrate (Figure A2.3.3) and POC (Figure A2.3.7) are in reasonable agreement with measurements, although some of the peak concentrations were not well predicted. Some of the coarse mode particles were underpredicted and require further evaluation, especially in the case of nitrate and sea salt. EC, SO_4^{2-} (Figure A2.3.5) and SOA were also underpredicted.

14. Improving the predictive capability of the model for some components (EC) can be achieved in a straightforward way by improving emissions estimates. Improving the predictive capability for others (Cl^- and coarse mode nitrate) may prove to be more difficult because there is a combination of possible reasons for the model underprediction.

15. An examination of the chemical composition of the $PM_{2.5}$ mass in 2008 revealed that 58% was estimated to be particle bound water (PBW) (Figure A2.3.1). This is a model estimate of ambient PBW and contrasts with measurements, where PBW is mostly removed by conditioning in the field or in the laboratory and water content is typically reduced to around 10% (Harrison *et al.*, 2004, and Green *et al.*, 2009). As a consequence, including modelled PBW without correcting for the measurement conditions can undermine attempts to evaluate the model for total $PM_{2.5}$ or PM_{10} as well as for hygroscopic particles such as SO_4^{2-} and possibly NO_3^- and SOA. These results demonstrate the importance of PBW when quoting PM concentrations and it would be worth considering quoting the assumptions made alongside the concentrations from measurements and models.

Hourly predictions of $PM_{2.5}$

16. Speciated PM analysis was conducted against measurements from the AURN and London Air Quality Network (LAQN) during 2008, using CMAQ (v4.7) and the WRF meteorological driver. The WRF-CMAQ model was operated with 23 vertical layers (up to approximately 15 km above ground) and two nesting levels, downscaling from 81 km grid resolution over Europe to 9 km grid resolution over the UK. The emissions from EMEP, NAEI and the European Pollutant Emission Register (EPER) were processed into hourly 3-D gridded chemical species and used the CB05 chemical scheme which included the aqueous and aerosol (AERO5) extension.

17. In 2008 CMAQ PM_{10} and $PM_{2.5}$ predictions were assessed against measurements from AURN and LAQN, including 70 PM_{10} sites (three rural, 12 suburban and 55 urban background) and 29 $PM_{2.5}$ sites (two rural, six suburban and 21 urban background). In comparing the hourly average concentrations we have removed the model's predictions for water. The reason for doing this is that CMAQ water estimates can be high (58%), as demonstrated by the modelled estimate of particle bound water (PBW) at ambient conditions in Figure A2.3.1a.

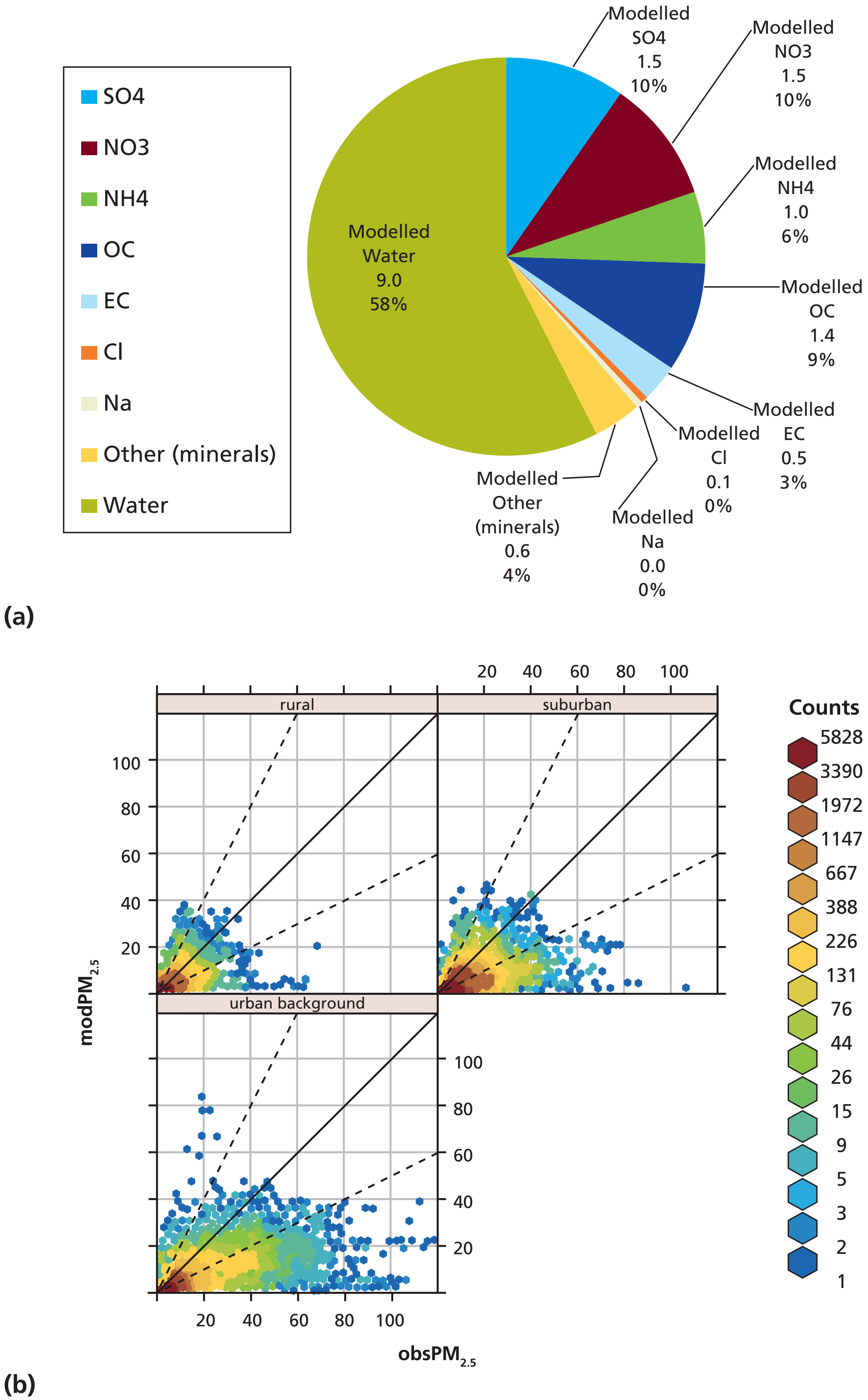
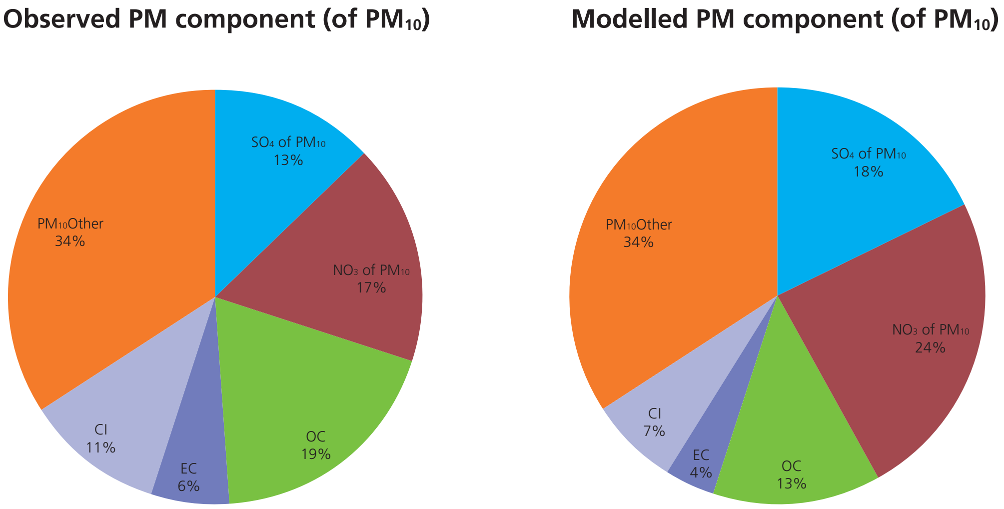


Figure A2.3.1: (a) London North Kensington PM2.5 components in 2008, including particle bound water without correction for measurement conditions; and (b) scatter plot of modelled and observed 2008 PM2.5 at two rural, six suburban and 21 urban background sites without particle bound water.

18. The consequence of including this contribution without consideration of the measurement conditions would be misleading as a more realistic estimate of PBW would be ~10% (Harrison *et al.*, 2004, and Green *et al.*, 2009). The dry results (Figure A2.3.1b) show that the model underpredicts $PM_{2.5}$ for 29 sites across the UK; the results are similar for PM_{10}.

Evaluation of CMAQ PM species

19. In the next step of the evaluation we compared the proportion of PM species in the model with the combined measurements at Harwell and London North Kensington. The PM components included nitrate (NO_3^-), sulphate (SO_4^{2-}), elemental carbon (EC), organic carbon (OC) and chloride (Cl^-), and are summarised in Figure A2.3.2. The results indicate that whilst the model underpredicts total PM_{10} concentrations, it replicates the proportion of each PM_{10} species reasonably well, slightly overpredicting observed NO_3^- and SO_4^{2-} fractions and underpredicting others such as Cl^-, EC and OC.


Observed PM component (of PM_{10})

Modelled PM component (of PM_{10})

Figure A2.3.2: Average observed and CMAQ PM_{10} components for 2008 at Harwell and London North Kensington.

$PM_{2.5}$ nitrate

20. We then looked at the daily time series of each species, beginning with fine nitrate. Modelled daily $PM_{2.5}$ NO_3^- at London North Kensington (Figure A2.3.3) showed that the CMAQ model predicted the temporal trends and magnitudes of measurements reasonably well, although it was unable to predict some of the highest peaks. For the 12-month period the average modelled and measured fine nitrate concentrations were 1.3 and 2.4 µg m^{-3} respectively. Similar results were found at Harwell which gave model and measured concentrations of 1.4 and 2.6 µg m^{-3} respectively.

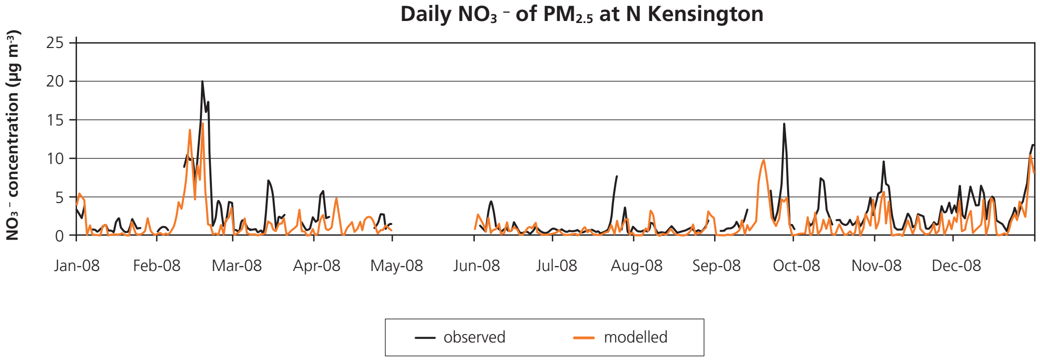


Figure A2.3.3: Comparison between observed and modelled daily nitrate (NO_3^-) of $PM_{2.5}$ at London North Kensington.

21. In contrast, CMAQ underestimated the coarse NO_3^- fraction (2.5-10 μm) by a large margin. Model versus measured concentrations were 0.19 and 2.8 μg m^{-3} respectively. The main coarse mode NO_3^- includes sodium nitrate ($NaNO_3$) and calcium nitrate ($Ca(NO_3)_2$) from the reaction of nitric acid (HNO_3) with sea salt and minerals (Hodzic *et al.*, 2006) and the overnight reaction of sodium chloride (NaCl) with dinitrogen pentoxide (N_2O_5) (AQEG, 2005).

22. Elsewhere, Zhuang *et al.* (1999), Hien *et al.* (2005) and Kelly and Wexler (2005) reported that calcium and magnesium from mineral dust (especially, calcite ($CaCO_3$) and dolomite ($MgCa(CO_3)_2$)) play an important role in coarse nitrate ($Ca(NO_3)_2$) formation. Sources of Ca^{2+} and Mg^{2+} cations include dust from soil erosion as well as emissions from urban and industrial sources (e.g. limestone quarrying, cement manufacture, concrete batching, industrial processes using limestone and dolomite, liming of soils, dust due to cultivation, construction, demolition and resuspension by traffic). Whilst these are estimated as part of the UK NAEI (AEA, 2006), it is important to further evaluate these emission sources and their role in coarse mode nitrate formation.

PM_{10} chloride

23. CMAQ was unable to capture the magnitude of Cl^- at both Harwell and London North Kensington. However, a comparison with the coastal predictions for three Norwegian monitoring sites (Birkenes, Kårvatn and Hurdal) (Figure A2.3.4) taken from the EBAS database (see http://ebas.nilu.no/) shows there to be good agreement for both Na^+ and Cl^- at these locations. The annual average modelled and measured Cl^- at the three Norwegian coastal sites was 0.25 and 0.32 μg m^{-3} respectively.

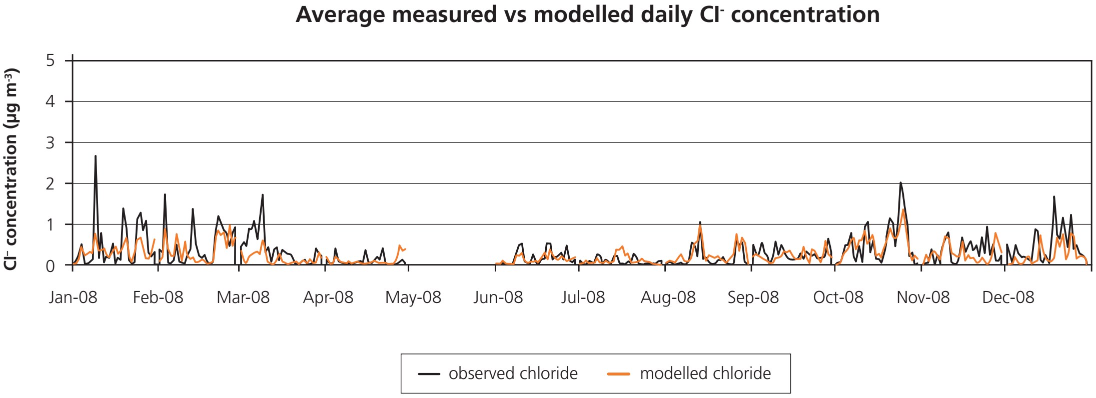


Figure A2.3.4: Comparison between observed and modelled chloride (Cl^-) at three EMEP sites in Norwegian coastal areas.

24. This would suggest that the sea salt parameterisation in the model is reasonable and that in the UK a man-made source of Cl^- is underestimated (consistent with Jones *et al.*, 2010) or that deposition is overestimated. However, it is notable that the three Norwegian sites were located at a minimum of 190 m above sea level and in very remote areas. Given that there is likely to be a vertical concentration profile of sea salt it would seem reasonable to assume that the sea salt estimates for the UK could also be too small, however this would need further investigation.

PM_{10} sulphate

25. For daily PM_{10} SO_4^{2-}, the model predicted the non-episode concentrations of the observations well at Harwell and London North Kensington. However, the model was unable to capture peak SO_4^{2-} at both sites, leading to a difference between modelled and observed annual average concentrations of approximately 1 µg m^{-3} or 49%. Figure A2.3.5 shows model versus measured daily PM_{10} SO_4^{2-} concentrations at London North Kensington, where in April a long period of high SO_4^{2-} concentrations was detected.

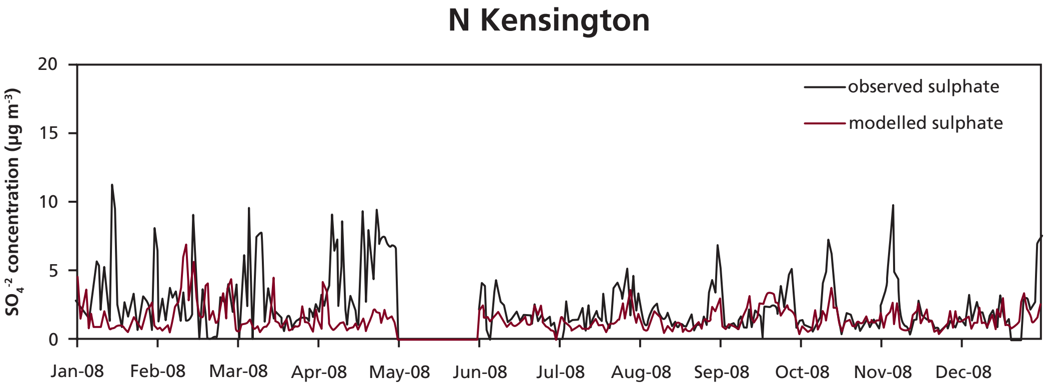


Figure A2.3.5: Time series of measures and CMAQ daily SO_4^{2-} at London North Kensington, 2008.

26. This was investigated using a trajectory model and OpenAir to define the possible source of SO_4^{2-} during the period (Carslaw, 2011). The trajectories were three-hourly and were coloured according to the measured SO_4^{2-} concentration (assumed to be constant for each hour of the day) (see Figure A2.3.6). A preliminary inspection of the trajectories and emission inventories suggests a potentially significant contribution from ships. Furthermore, comparison between TNO and EMEP emissions estimates show that for ships, SO_2 emission rates can differ by up to a factor of two. The combination of errors in model trajectory estimates, emissions sensitivity tests and further data mining should provide an important insight into these periods of high PM concentrations and the role of shipping emissions.

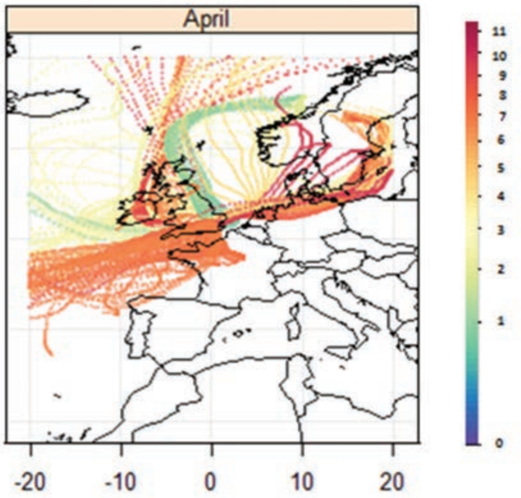


Figure A2.3.6: Trajectory of observed daily SO_4^{2-} in April 2008.

PM_{10} elemental carbon

27. The daily analysis of EC predictions for the final five months of 2008 indicates that the model underpredicts observed EC at London North Kensington in 2008, giving an average concentration of 0.44 µg m^{-3} compared with a measurement of 1.5 µg m^{-3}. There are a number of possible reasons for this, including underestimation of the contribution that EC makes to overall PM_{10} emissions. For road traffic in particular, and other sources in general, a more comprehensive calculation of the emission of EC (and primary organic carbon (POC)) should be made as part of future model runs.

Estimating POC and SOC from OC measurements

28. Prior to comparing the CMAQ predictions of POC and secondary organic carbon (SOC), it was necessary to split the measurement of OC into primary and secondary components. To do this we used the EC tracer approach described in Jones and Harrison (2006), giving average estimates of observed POC and SOC at London North Kensington of 1.9 and 1.3 µg m^{-3} respectively.

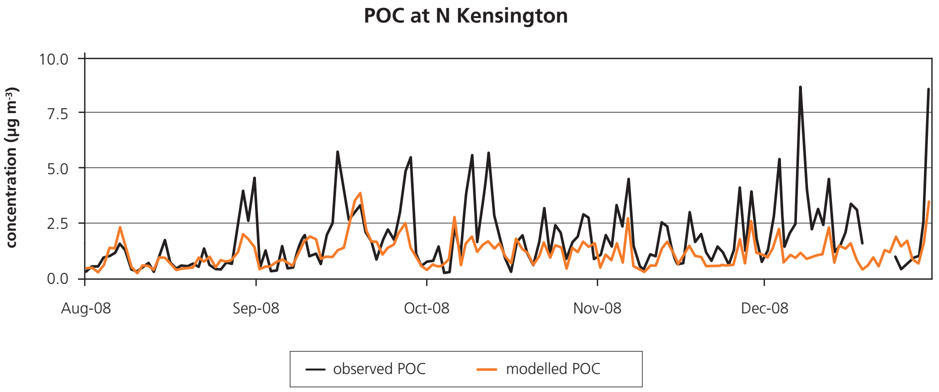


Figure A2.3.7: Comparison between observed and CMAQ POC between August and December 2008 at London North Kensington.

29. The CMAQ model was able to predict average POC concentrations reasonably well (Figure A2.3.7), although it failed to predict a number of concentration peaks. On average the model underpredicts measurements by 0.7 µg m^{-3} or 37%. However, the CMAQ model fails to predict SOC by a large margin, with the model and measured averages being 0.04 and 1.3 µg m^{-3} respectively (not shown). Poor results of this kind are reported elsewhere (Zhang and Ying, 2011) and are the focus of changes to the chemical scheme in version 5 of the CMAQ model.

A2.4: Numerical Atmospheric-dispersion Modelling Environment (NAME)

30. NAME is a three-dimensional Lagrangian dispersion model that simulates dispersion and deposition processes occurring in the atmosphere and parameterises the key chemical processes involved in formation of secondary inorganic and organic aerosols. Pollutant emissions are represented by releasing hundreds of thousands of air parcels, each able to represent the released mass of many different species, driven by three-dimensional meteorological data from the Met Office's Unified Model (UM).

31. Recent modelling work (Redington *et al.*, 2009) has studied the sensitivity of modelled sulphate and nitrate aerosol to cloud, pH and ammonia emissions. Sulphate aerosol production in the aqueous phase was found to be very sensitive to modelled cloud pH. As the cloud becomes acidic, sulphate production is greatly limited, conversely if the cloud is basic, large amounts of sulphate aerosol are produced. Aqueous phase sulphate aerosol production was also found to be sensitive to ±30% ammonia emissions due to the effect of ammonia on the modelled pH. The work highlighted the importance of ammonia in understanding complex links between the precursors and subsequent production of secondary inorganic aerosol (SIA).

32. The NAME model has been run for 2006 to produce maps of emission sensitivity coefficients (ESCs) for SIA components over the UK output as a 20 km national grid. The emission sensitivity coefficient is defined as the change in concentration of the PM component divided by the base case PM component concentration, all divided by the change in precursor emission divided by the base case precursor emission. These emission sensitivities have been incorporated into the PCM model (A2.8) and used to calculate projections of

SIA components for future years. These projections were compared with PCM scenario predictions made using the ESCs from the EMEP model. It was found that the models gave broadly consistent results, with the NAME ESCs tending to indicate a greater impact of change in emissions on concentrations than EMEP. Comparison of maps of the ESCs showed a greater spatial variation in NAME.

33. Figure A2.4.1 shows an example of annual ESCs calculated by the NAME model and demonstrates the non-linear effect on SIA components of a 30% emission reduction in NH_3 over the UK and Europe. The scale runs from -2.0 to 2.0, where a value of 1.0 indicates a linear positive response, i.e. a reduction in the primary pollutant leads to the same reduction in the particulate component. A value greater than 1.0 indicates a greater reduction in particulate component than in primary emission; conversely a sensitivity coefficient less than 1.0 but greater than 0.0 implies a reduction in particulate component less than the reduction in the primary pollutant. A negative emission sensitivity indicates that the particulate component increases as the primary pollutant decreases. In Figure A2.4.1, light orange shows sensitivity coefficients in the range -0.5-0.0, orange in the range 0.0-0.5, red in the range 0.5-1.0, purple in the range 1.0-1.5 and blue in the range 1.5-2.0. The results from this work confirmed the expected non-linear response of SIA components to emissions in primary precursors and also highlighted considerable spatial variation in the response.

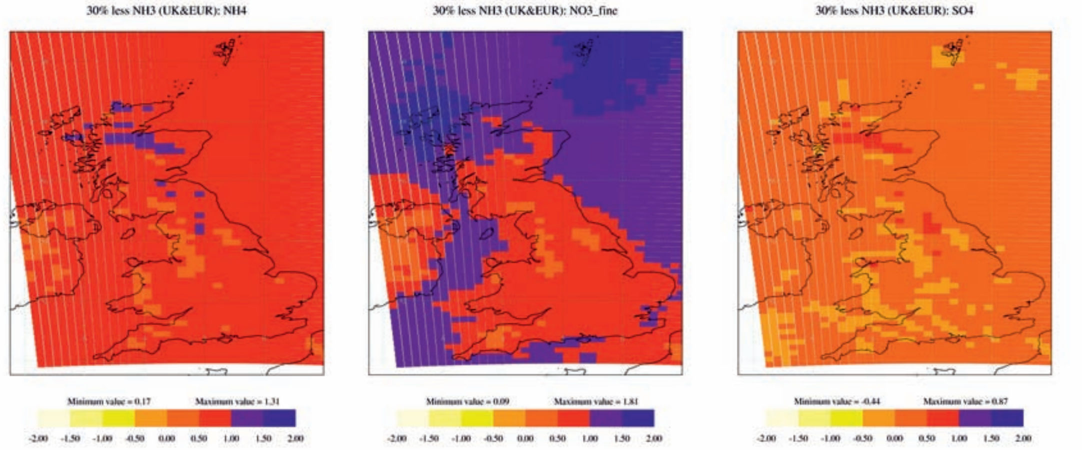


Figure A2.4.1: Annual average emission sensitivity coefficients calculated by the NAME model, demonstrating the non-linear effect on PM ammonium, sulphate and nitrate (from left to right respectively) of a 30% emission reduction in NH_3 over the UK and Europe.

34. NAME model simulations of primary PM_{10} emissions have been undertaken to establish the frequency and magnitude of potential transport of particulate matter from the US to the UK. It was found that the maximum 24-hour mean air concentration resulting from US emissions did not exceed 2.5 µg m^{-3}. The annual mean was below 0.05 µg m^{-3}. It was concluded that it was unlikely that US particulate emissions would make a significant contribution to a UK or European pollution event.

35. The NAME model has been used to attribute particulate matter by country in 2003 using EMEP definitions of emission zones. For example, the top row of Figure A2.4.2 shows the total annual average modelled PM_{10}, annual average PM_{10} originating from UK emissions, annual average PM_{10} originating from French (FR) emissions and annual average PM_{10} from emissions from western

Germany (FFR). The second row of plots shows the same set but presented as a daily average on 8 August 2003. As would be expected, on an annual basis, it is the southern and eastern parts of the UK that receive the most imported pollution, with the far south-east of the UK importing 2-4 $\mu g\ m^{-3}$ from both France and western Germany in 2003.

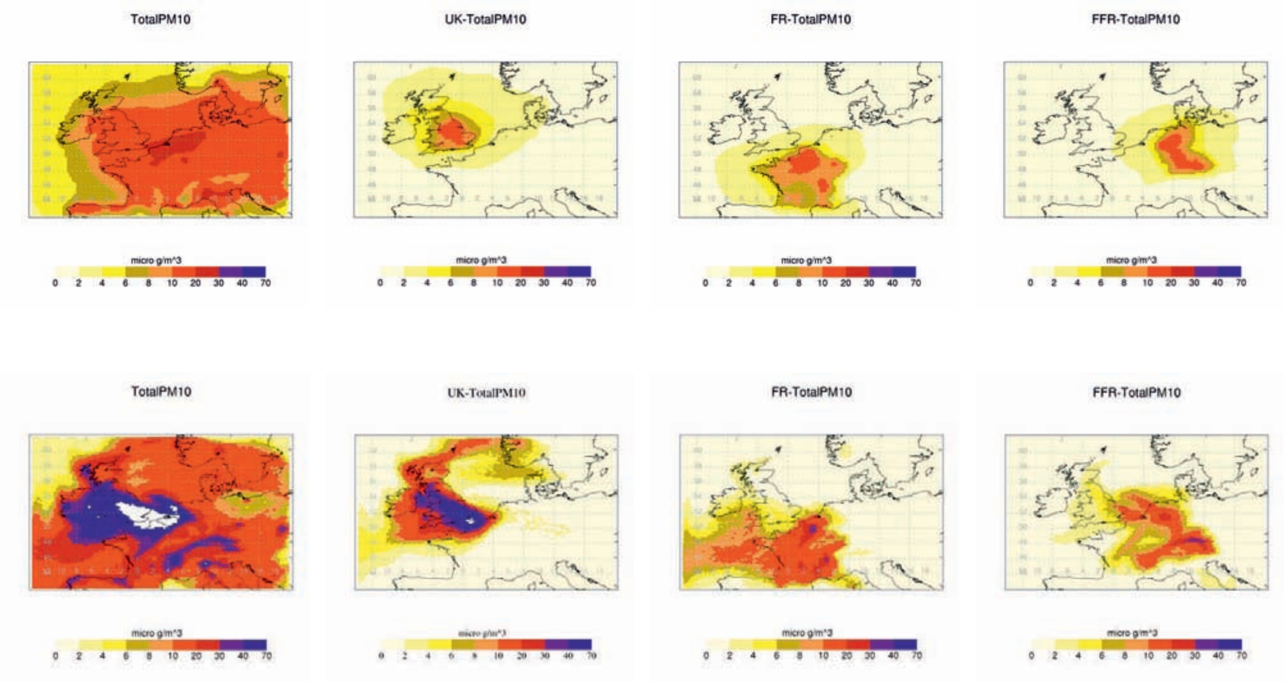


Figure A2.4.2: NAME-modelled total PM_{10} (sulphate, nitrate, ammonium, secondary organic aerosol and primary PM_{10}). Top row from left, annual average total PM_{10} concentration for 2003 resulting from: emissions from all countries within the model domain, UK emissions, French emissions (FR) and western German emissions (FFR). Bottom row from left, daily average total PM_{10} on 8 August 2003 resulting from: emissions from all countries within the model domain, UK emissions, French emissions (FR) and western German emissions (FFR). The white areas indicate concentrations greater than 70 $\mu g\ m^{-3}$.

36. The daily average plots for 8 August 2003 cover a PM episode and indicate how, on a daily basis, import of particulate matter from other European countries can significantly contribute to levels measured in the UK at widespread locations. For example on 8 August, the far south-west of the UK received 8-10 $\mu g\ m^{-3}$ from France and 2-4 $\mu g\ m^{-3}$ from western Germany on top of its UK concentrations of 20-30 $\mu g\ m^{-3}$. This work concluded that to fully understand particulate episodes, with a view toward introducing measures to reduce exceedences of air quality thresholds, it was important to understand both the composition of the PM_{10} and its country of origin.

A2.5: EMEP4UK

37. The EMEP4UK model is a nested regional chemistry transport model (CTM) driven by high-resolution meteorology and national emissions that is used to produce a detailed representation of the physical and chemical evolution of the atmosphere over Europe and, in particular, over the UK (Vieno *et al.*, 2009 and 2010). EMEP4UK is based on the EMEP (European Monitoring and Evaluation Programme) Unified Model and the horizontal resolution varies from a 50 km

x 50 km grid for the European domain to a 5 km x 5 km grid for the domain covering the UK, Ireland and the near continent. The vertical column extends from the surface (centre of the surface layer ~45 m) up to 100 hPa (~16 km). The model can also be run at the global scale with a resolution of 1° x 1°. The EMEP4UK meteorological driver is the Weather Research and Forecasting (WRF) model (see www.wrf-model.org).

38. The current EMEP Unified Model is a development of the 3-D chemical transport model, extended with photo-oxidant chemistry (Andersson-Sköld and Simpson, 1999) and the EQSAM gas/aerosol partitioning model. Secondary organic aerosol (SOA) was first introduced into the EMEP model by Andersson-Sköld and Simpson (2001), using both semi-explicit chemical schemes and parameterised versions. Simpson *et al.* (2007) presented developments and applications of these schemes and demonstrated how extremely sensitive SOA mechanisms are to both unknown physical parameters and emissions uncertainties. Recent work has explored the so-called volatility basis set (VBS) mechanisms (e.g. Donahue *et al.*, 2006 and 2009) in European SOA production (Bergström and Simpson, 2010). This recent work again highlights the uncertainties and the need for more field and laboratory observations in this important area.

39. The EMEP4UK emission input data of NO_x, NH_3, SO_2, $PM_{2.5}$, PM_{CO} (coarse particulate matter), carbon monoxide (CO) and non-methane VOCs (NMVOCs) are derived from the UK National Atmospheric Emissions Inventory (NAEI) on a 1 km x 1 km grid and mapped to the 5 km x 5 km EMEP grid. Where high resolution emissions are not available outside the UK, the EMEP 50 km x 50 km emissions are used (see EMEP at: www.emep.int and CEIP at: http://www.ceip.at/). Biogenic emissions of isoprene are calculated based on Guenther *et al.* (1993), driven by land cover for the appropriate grid. Emissions from forest fires are available as eight-day averages from the GFED (Global Fire Emissions Database) of van der Werf *et al.*(2006).

40. The removal processes also include dry deposition (Emberson *et al.*, 2001) and wet deposition (scavenging coefficients applied to the 3D rainfall).

41. As an example of PM output simulated by EMEP4UK, a multi-year calculation of surface fine (< 2.5 µm) and coarse (2.5-10 µm) PM nitrate is shown in Figure A2.5.1 for a Scottish site near Edinburgh (Bush Estate) (Vieno *et al.*, 2011, in preparation). The EMEP4UK hourly values have been averaged monthly for comparison with the monthly observations at this site from the UK Acid Gases and Aerosols Monitoring Network (AGANet). The EMEP4UK model not only predicts the seasonal variability of surface nitrate well, but is also able to reproduce the unusual elevated events in spring 2003. The sampling technique used in AGANet has a particle size cut-off at approximately PM_4, so it is expected that the observations will fall between the modelled concentrations of fine and total nitrate. Similar or better performances are found for other SIA components such as sulphate and ammonium (see Defra model inter-comparison at: http://uk-air.defra.gov.uk/library/reports?report_id=652).

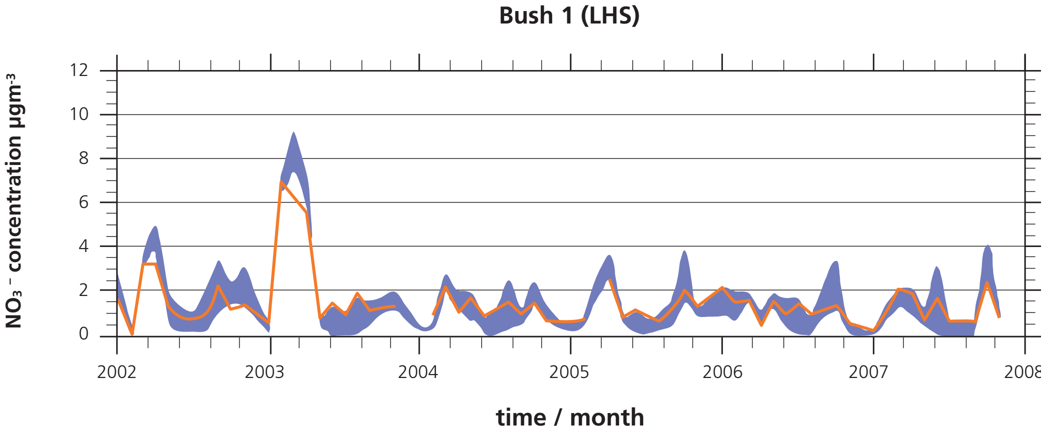


Figure A2.5.1: Monthly-averaged EMEP4UK-simulated fine nitrate (< 2.5 µm) (bottom of the blue shading) and coarse nitrate (2.5-10 µm) (width of the blue shading) for the model grid square containing the Bush site (µg m^{-3} NO_3^-). The top of the blue shading corresponds to total nitrate. The red line shows the monthly observations from AGANet (which has a sampling cut-off of approximately PM_4).

42. Figure A2.5.2 shows the EMEP4UK annual average total surface nitrate over the UK for the year 2003. A strong south-east to north-west gradient is visible, reflecting the co-location of pollutants such as ammonia and oxidised nitrogen in the south-east of the UK and the vicinity of countries such as Germany, the Netherlands and France which have high emissions of ammonia and nitrogen oxides and contribute to export of nitrate to the UK domain. Further examples of EMEP4UK applications can be found in Doherty *et al.* (2009) and Vieno *et al.* (2010).

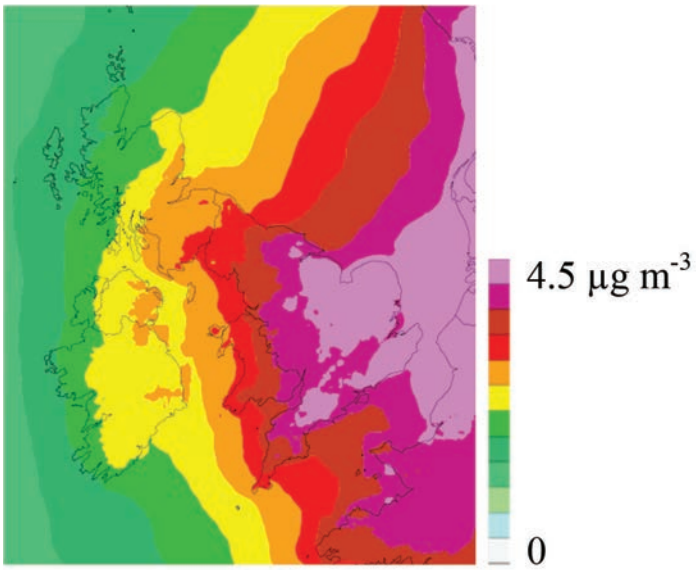


Figure A2.5.2: EMEP4UK calculated annual average surface nitrate for the year 2003 (µg m^{-3}).

A2.6: Photochemical Trajectory Model (PTM)

43. The PTM moving air parcel trajectory model has been used to estimate the mid-afternoon mass concentrations of a number of suspended particulate matter (PM) components for each day of 2006 at a rural location in Harwell, Oxfordshire, southern UK. A large number of equally probable and randomly-selected 96-hour three-dimensional air mass trajectories were used to describe the variability of the atmospheric transport paths during each day. A chemical kinetic description was given for the major PM formation processes. Further details are given in Derwent *et al.* (2009b).

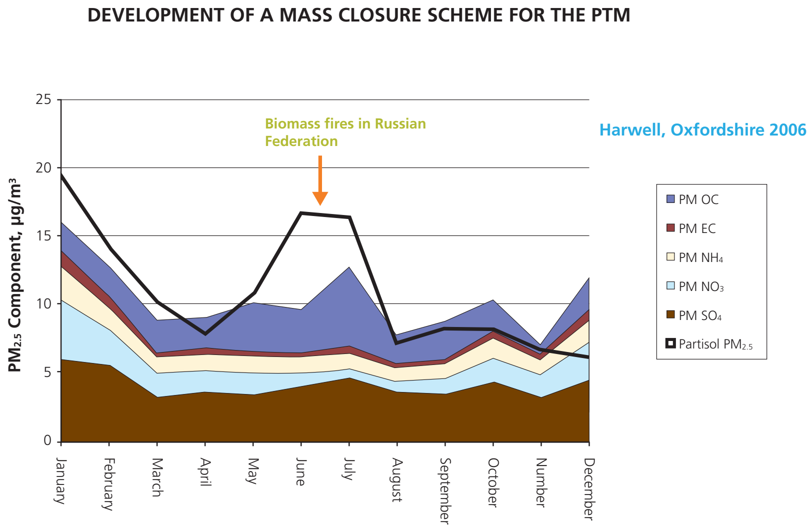


Figure A2.6.1: Mass closure for $PM_{2.5}$ as predicted by PTM for Harwell, Oxfordshire, 2006.

44. The PTM output comprised the histories of the chemical development of the 51 model species along the 30 randomly-selected 96-hour trajectories arriving at Harwell, Oxfordshire, at 15:00 (GMT) on each day of 2006. Examination of the 30 sets of results for each day and each model species revealed the presence of a significant amount of scatter about the average result for the arrival point. There was evidence that this scatter increased dramatically on more polluted days compared with cleaner days. There was apparently much more variability in the model description of air mass origins on polluted days compared with clean days. This reflected the increasing stagnation and decreasing wind speeds associated with pollution episodes. The arithmetic mean of the 30 sets of results was taken as the best estimate of the model result for that day and these estimates have also been evaluated against observations for 15:00 (GMT) (see Figure A2.6.1).

45. Model performance requirements have focused on achieving mean fractional biases in the range ±0.2 and 50% of the model results within a factor of two of the observations. On this basis, model performance against observations was found to be satisfactory for NO_x, NH_3, HNO_3, PM ammonium, PM sulphate, PM nitrate and $PM_{2.5}$. The lack of adequate observations precluded a satisfactory evaluation of model performance for EC and OM.

46. The response of $PM_{2.5}$ to 30% reductions in SO_2 emissions is necessarily the result of a number of factors and interactions involving each of the $PM_{2.5}$ components. Sulphate levels decrease but the increased availability of NH_3 leads to an increase in ammonium nitrate formation and an increase in the extent of neutralisation of sulphuric acid (H_2SO_4). As a consequence, ammonium decreases by much less than 30%, fine nitrate increases and coarse nitrate decreases. Hence, $PM_{2.5}$ responds less than linearly to reductions in SO_2 emissions, with a sensitivity coefficient of 0.21.

47. The corresponding response of $PM_{2.5}$ to 30% reductions in NO_x emissions is much less than linear. Fine nitrate levels decrease in response to NO_x emission reductions but the attendant increase in hydroxyl (OH^-) levels reduces the fine and coarse nitrate responses and also leads to an increase in sulphate. Ammonium levels fall somewhat, as a result of decreasing levels of ammonium nitrate and increasing levels of ammonium sulphates. The sensitivity coefficient of $PM_{2.5}$ to NO_x emissions was accordingly 0.13.

48. Because the chemical environment of the southern UK was found to be 'ammonia-limited', the response of $PM_{2.5}$ to 30% reductions in NH_3 emissions was not straightforward. Fine nitrate declined exactly linearly with the decline in NH_3 emissions because gaseous nitric acid formation was independent of ammonia and hence there was a linear decline in ammonium nitrate formation. This decline in ammonium nitrate formation drives an increase in coarse nitrate formation. Sulphate levels were left unchanged by reductions in ammonia emissions but significant changes were observed in the extent of neutralisation of H_2SO_4. Overall, the sensitivity of $PM_{2.5}$ to NH_3 emissions was found to be 0.30 and was the largest for the SO_2, NO_x and NH_3 PM precursors.

49. The linearity of the chemical production pathways forming secondary PM components was examined by sensitivity studies to 30% reductions in SO_2, NO_x, NH_3, VOC and CO emissions. The chemical environment revealed by these sensitivity studies appeared to be 'ammonia-limited'. Consequently, PM mass concentrations appeared to be markedly non-linear with PM precursor emissions. Policy strategies for $PM_{2.5}$ therefore need to take into account emission reductions for a wide range of primary PM components and secondary PM precursors and to focus primarily on the abatement of NH_3. This complex interlinking may help to explain why PM levels have remained constant despite falling primary PM emissions.

50. In summary, Figure A2.6.2 presents the fractional reduction in annual mean $PM_{2.5}$ concentrations at Harwell, Oxfordshire, for a given reduction in precursor emissions. That is to say, for an x% reduction in precursor emissions, the reduction in ammonia emissions would give the greatest reduction in $PM_{2.5}$ levels out of all the precursor species considered (i.e. NH_3, NO_x, SO_2, VOCs, CO, EC and OC).

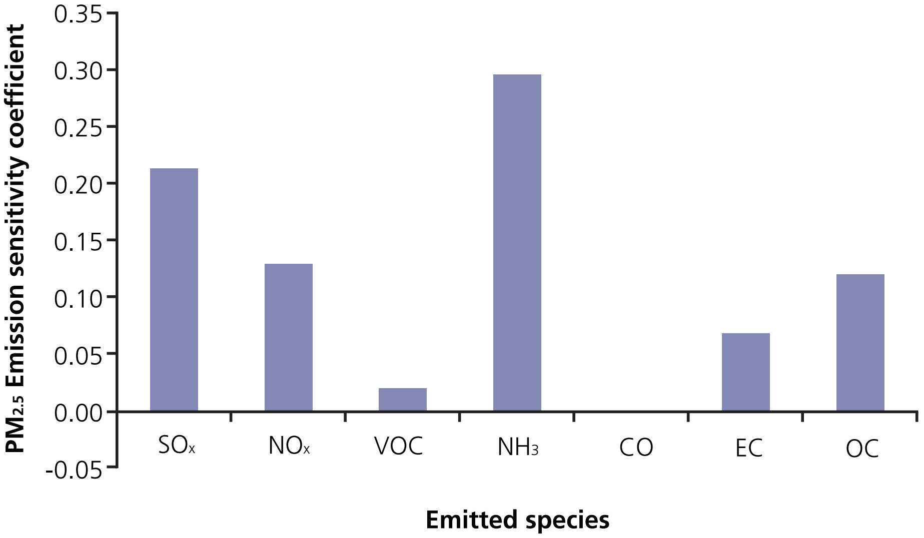


Figure A2.6.2: Fractional reduction in annual mean $PM_{2.5}$ at Harwell, Oxfordshire, for a given reduction in the emissions of each precursor species.

A2.7: FRAME

51. FRAME is a Lagrangian model using straight line trajectories with a 1° angular resolution which runs at either a 1 km or a 5 km resolution over the British Isles and 50 km resolution over Europe. The model includes 33 layers with a fine vertical grid spacing (1 m at the surface layer). Area emissions are injected into sector-dependent levels and point source emissions are treated with a plume rise routine. Vertical diffusion in the air column is calculated using K-theory eddy diffusivity. Wet deposition is calculated using a "constant drizzle" approximation driven by an annual rainfall map. Five land classes are considered and a vegetation-specific canopy resistance parameterisation is employed to calculate dry deposition. The model chemistry includes gas phase and aqueous phase reactions of oxidised sulphur and oxidised nitrogen leading to the formation of fine ammonium sulphate and ammonium nitrate aerosol as well as a large nitrate aerosol category. The modelled concentrations of secondary inorganic aerosol have been validated by comparison with measurements from the UK Acid Gases and Aerosols Monitoring Network (AGANet). Modelled nitrate aerosol across the UK and validation against measurements for the year 2008 is illustrated in Figure A2.7.1. A comprehensive validation of the modelled aerosol concentrations is given in Dore *et al.* (2007) and, for the year 2003, in the report of the Defra model inter-comparison (Carslaw *et al.*, 2011). Both the measurements and the model show a strong decreasing gradient in nitrate aerosol concentrations from the south-east to the north-west of the UK.

52. Source–receptor matrices of particulate concentrations have been generated for use in the UK Integrated Assessment Model (UKIAM) (Oxley *et al.*, 2003). This involves calculating the contribution to particulate matter from different emissions sources (SO_2, NO_x, NH_3, etc.) according to sub-SNAP sector and region (England, Scotland, Wales, Northern Ireland and London), as well as from European sources and international shipping. The UKIAM source–receptor matrices are the basis for calculating future changes in particulate concentrations driven by implementation of policies to abate targeted primary emissions.

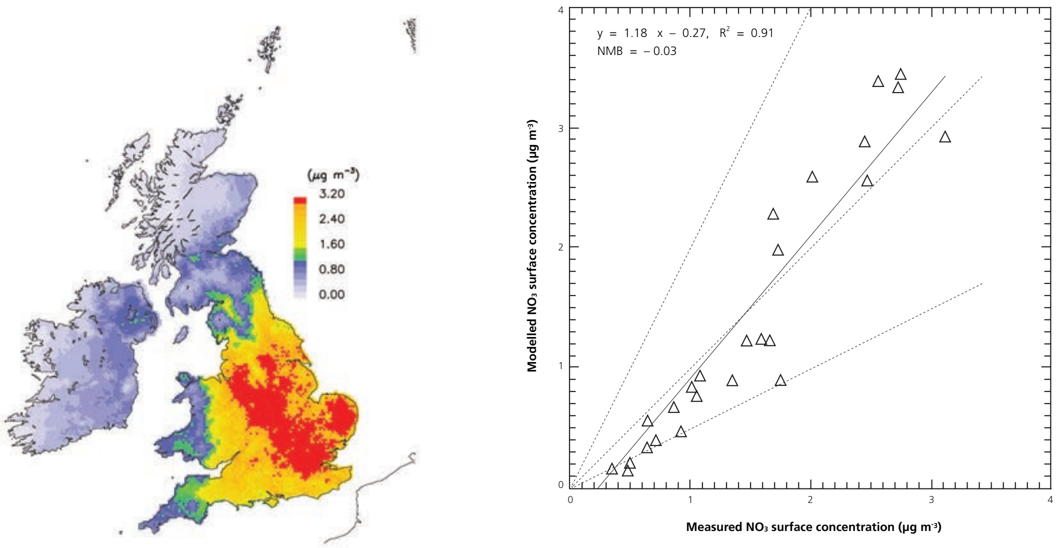


Figure A2.7.1: Left: Nitrate concentrations in air modelled with FRAME for the year 2008; Right: Comparison of modelled nitrate concentrations in air with measurements from AGANet.

53. The model has also been used to calculate concentrations of base cations (Na^+, Mg^{2+}, Ca^{2+}) in the UK using emissions from both marine and land-based sources. Figure A2.7.2 illustrates the comparison with measurements of modelled concentrations of Mg^{2+} emitted from sea salt spray. The model was found to obtain satisfactory agreement with measurements from the Acid Gases and Aerosols Monitoring Network. Also illustrated is the modelled concentration of Ca^{2+} in air. Calcium concentrations in air exhibit a strong gradient near the coast as their primary emission source is also sea salt spray. However, anthropogenic emission sources and contributions from wind-blown dust are also present in the model. Calcium concentrations were not as well correlated with measurements as magnesium. This was attributed to the large uncertainty in the contribution to land-based emissions from wind-blown dust (Werner *et al.*, 2011).

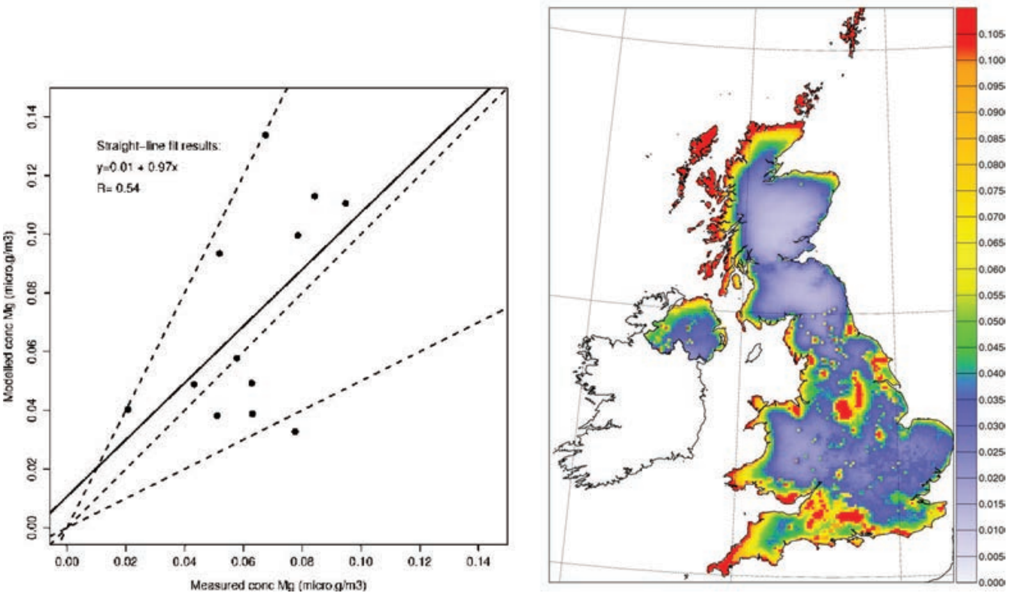


Figure A2.7.2: Left: Comparison of modelled Mg^{2+} concentrations in air with measurements from AGANet; Right: Ca^{2+} concentrations in air modelled with FRAME (all μg m^{-3}).

A2.8: PCM PM model

54. A detailed description of the Pollution Climate Mapping (PCM) models for PM in 2004 can be found in Stedman *et al.* (2007). The methods used to derive the maps for 2009 are largely the same as adopted for the 2008 maps described in Grice *et al.* (2010), except for the more direct linkages with the calibration of the models for $PM_{2.5}$.

55. The maps of annual mean background PM concentrations have been calculated by summing contributions from different sources:

- secondary inorganic aerosol (derived by interpolation and scaling of measurements of SO_4^{2-}, NO_3^- and NH_4^+ at rural sites);
- secondary organic aerosol (semi-volatile organic compounds formed by the oxidation of non-methane volatile organic compounds. Estimates derived from results from the HARM/ELMO model);
- large point sources of primary particles (modelled using ADMS and emissions estimates from the NAEI);
- small point sources of primary particles (modelled using the small points model and emissions estimates from the NAEI);
- regional primary particles (from results from the TRACK model and emissions estimates from the NAEI and EMEP);
- area sources of primary particles (modelled using a dispersion kernel and emissions estimates from the NAEI);
- regional calcium-rich dusts from resuspension of soils (modelled using a dispersion kernel and information on land use);
- urban calcium-rich dusts from resuspension of soils due to urban activity (estimated from a combination of measurements made in Birmingham and population density);
- regional iron-rich dusts from resuspension (assumed to be a constant value, estimated measurements made in the vicinity of Birmingham);
- iron-rich dusts from resuspension owing to vehicle activity (modelled using a dispersion kernel land and vehicle activity data for heavy duty vehicles);
- sea salt (derived by interpolation and scaling of measurements of chloride at rural sites); and
- residual sources (assumed to be a constant value).

56. The concentrations of many of these components have been estimated separately for the fine and coarse fraction. This enables a consistent method to be adopted for estimation of PM_{10} (the sum of the fine and coarse fractions) and $PM_{2.5}$ (fine fractions only). These component pieces are then aggregated to a single 1 km x 1 km background PM_{10} grid. An additional roadside increment is added for roadside locations.

57. The map of the annual mean $PM_{2.5}$ in 2009 at background locations is shown in Figure 5.1 (Chapter 5). This map has been calibrated using measurements from TEOM FDMS instruments (see Chapter 2) within the national network for which co-located $PM_{2.5}$ and PM_{10} measurements are available for 2009, the first year for which $PM_{2.5}$ measurements from an extensive network of sites in the UK are available. The models for PM_{10} and $PM_{2.5}$ are designed to be fully consistent. Each component is either derived from emission estimates for PM_{10} or $PM_{2.5}$ or the contributions to the fine and coarse particle size fractions are estimated separately. This enabled an additional check that the calibration parameters for the two pollutants are reasonably consistent. Measurements from national network sites without co-located PM_{10} instruments have been used as an additional verification dataset. The results from the annual mean model could then be directly compared with the annual mean limit value in order to carry out air quality assessments and policy analyses.

58. An important application of the PCM model is its ability to provide a source apportionment of the observed $PM_{2.5}$. Figure 5.10 (Chapter 5) illustrates this ability for a number of background locations in 2009. The importance of secondary PM is clearly illustrated and dominates all other PM components, particularly traffic exhaust emissions.

59. Figure A2.8.1 presents a verification plot for the PCM model estimates of the annual mean $PM_{2.5}$ concentrations. The model performance indicated is entirely satisfactory, with the vast majority of the points in the scatter plot falling within ±50% of the observations.

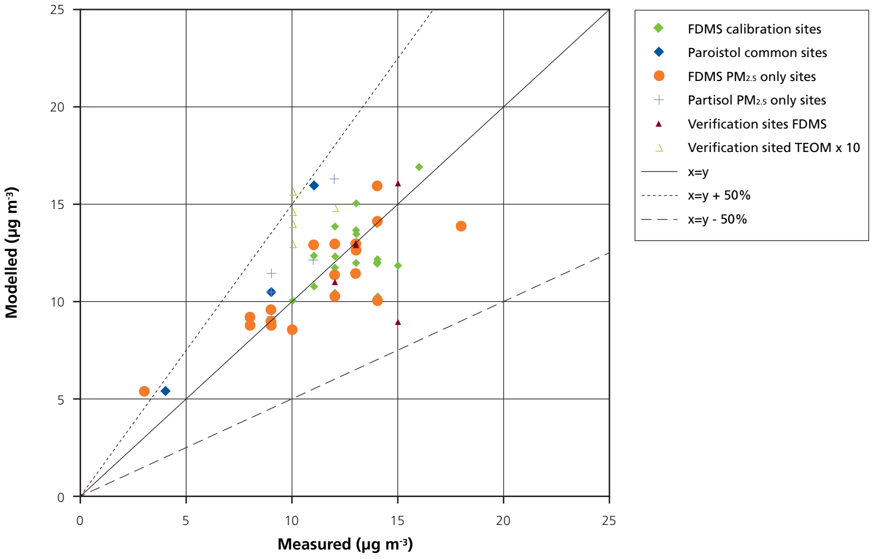


Figure A2.8.1: Verification plot for the PCM model estimates of $PM_{2.5}$ for background sites in 2009.

60. An interesting feature of the PM observations over the years has been the magnitude of the traffic and London increments, as for example shown by the differences between London Marylebone Road and London North Kensington, and between London North Kensington and Harwell, Oxfordshire. These have pointed to the large influence that long-range transport has on observed PM levels in London. The PCM model has provided a view on the contributions played by a number of PM components to the traffic and London increments, as

illustrated by the transect through London and the south-east region shown in Figure 5.6 (Chapter 5).

61. The transect confirms the view that $PM_{2.5}$ levels in London and the south-east region are dominated by the long-range transport of secondary PM, with the PM contribution from traffic exhaust emissions significantly smaller.

62. The PCM model has also been used to calculate projections of $PM_{2.5}$ concentrations from 2009 to 2020. Table 5.3 (Chapter 5) shows population-weighted annual mean $PM_{2.5}$ concentration projections. These projections have been made on the basis of expected changes in primary PM emissions and SIA precursor emissions in the UK and across Europe. Many components such as sea salt, urban and rural dusts, and SOA are assumed to be unchanged in 2020 from the concentration in 2010. The projections indicate a reduction in UK $PM_{2.5}$ concentration of 6.8% between 2010 and 2020. This can be compared with the expected exposure reduction target for urban $PM_{2.5}$ required by the EU Air Quality Directive of either 10% or 15%. The projected concentration reduction is very sensitive to the base year source apportionment between components that are expected to respond to changes in anthropogenic emissions and components that are expected to remain unchanged.

A2.9: Brutal and UKIAM

63. UKIAM, and its urban sub-model BRUTAL, is a national-scale integrated assessment model analogous to the GAINS model at the European scale, which has been developed at Imperial College in collaboration with other Defra contractors. It is designed for rapid overall assessment of future scenarios to 2020 and beyond, focused on the UK but taking into account transboundary pollution from other countries. The aim is to explore emission control strategies for achieving national emission ceilings set for the UK that are also effective in reducing human exposure to air pollution in the UK and exceedence of air quality limit values, and in improving protection of the UK's natural ecosystems. UKIAM distinguishes contributions from different sources in the UK, from surrounding sea areas and imported from other countries. The UK sources comprise individual major point sources, and a breakdown of other stationary sources into 41 other sources gridded on to a 1 km x 1 km grid. Road transport emissions are built up on a road-by-road basis across the UK road network and used with local-scale modelling to assess urban background concentrations and roadside increments. This is combined with longer range transport represented in the FRAME and EMEP models. Pre-calculated source–receptor footprints from these models are used to assess the approximate response of concentrations (and deposition) to changes in emissions from different sources, thus avoiding the need to run the more complex models directly. The framework is flexible, allowing some interchange of different model source–receptor relationships in order to explore, for example, the different estimates of imported contributions.

64. More details may be found in Oxley *et al.* (2012). There are many similarities with the PCM model, although the approach is less empirical and more deterministic. The secondary inorganic aerosol components, SO_4^{2-}, NO_3^- and NH_4^+, are based on the FRAME and EMEP models, where different combinations for UK sources and imported contributions have been explored as a component of uncertainty analysis (Oxley and ApSimon, 2011). Particulate concentrations due to primary sources are estimated using the Gaussian model, PPM, for area,

line and point sources. But the same treatment used in the PCM model has been adopted for secondary organic aerosol and other PM components not covered in the emissions inventory and thus not directly modelled. Total PM concentrations are calculated for each 1 km x 1 km grid square by adding all the different contributions for the appropriate size fraction, PM_{10} or $PM_{2.5}$. Bearing in mind the uncertainties of future projections, the treatment of roadside concentrations is aimed at an overall statistical comparison with air quality limit values across the UK, rather than accurate projections at specific locations as for example in ADMS. Roadside enhancement factors for street canyon effects are related to population density and roadside concentrations are calculated for the road with the highest emission density in each grid square. Results from UKIAM/BRUTAL were submitted for the Defra model inter-comparison exercise, showing comparable performance with other models.

Applications to modelling of $PM_{2.5}$ and source apportionment

65. Illustrative results on source apportionment of population-weighted mean concentrations are given below in Figure A2.9.1, with comparisons for the years 2000 and 2020 to complement results given in Chapter 5.

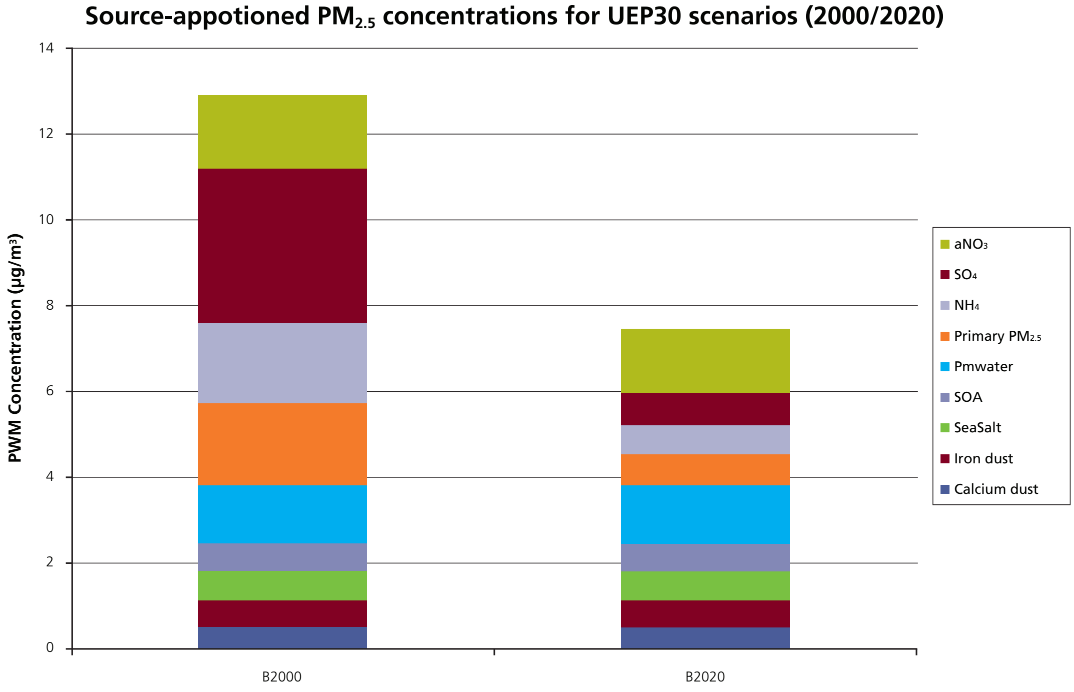


Figure A2.9.1: Breakdown of $PM_{2.5}$ concentrations by component for 2000 and 2020.

A2.10: ADMS-Urban

66. The ADMS-Urban model is described in Carruthers *et al.* (1998) and its treatment of particulates in particular is covered in AQEG's report on PM (AQEG, 2005). In essence the model calculates the concentration of PM as the sum of the calculated contribution from sources represented in an emission inventory for the domain of interest and the rural background estimated from measured data or from a regional model(s). The transport and diffusion of PM emitted from the domain of interest is calculated using the ADMS dispersion algorithms for point, line, area and grid sources nested within a

trajectory model. The ADMS algorithms include allowance for the impacts of plume rise, street canyons and traffic-produced turbulence; they also include a simplified chemistry scheme which includes generation of sulphate and nitrate particulates.

67. The following data are taken from the results of ADMS-Urban calculations for $PM_{2.5}$ undertaken as part of the model inter-comparison study (Carslaw *et al.*, 2011) for London for 2008. This study also considered other pollutant species (PM_{10}, NO_x, NO_2 and ozone) and the results of a number of other models. In this example, emissions data were either used directly from the London Atmospheric Emission Inventory for 2008 (LAEI, 2008) in the case of roads, or derived from PM_{10} using factors relating $PM_{2.5}$ to PM_{10} emissions (AQEG, 2005) (for emissions from agriculture, airports, the combustion of domestic coal, domestic gas, domestic oil, industrial coal and industrial gas, natural sources, shipping and the use of solvents).

68. In this study the background concentrations of $PM_{2.5}$ were accounted for using monitored data for the year 2008 from the sites at Rochester and Harwell depending on the wind direction. The Heathrow site was used to provide hourly sequential meteorological data for input into the model.

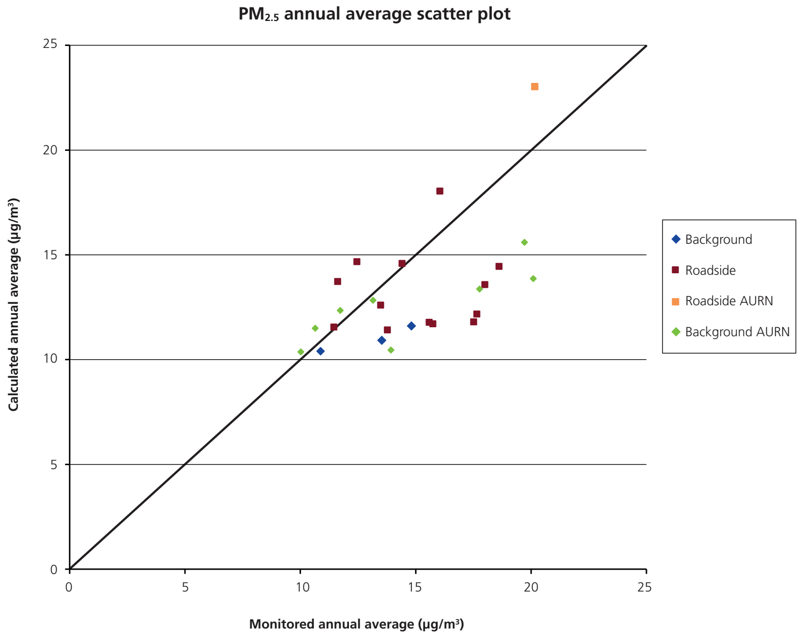


Figure A2.10.1: Scatter plot of calculated and monitored annual average concentrations of $PM_{2.5}$ for 2008.

69. A comparison of modelled and monitored annual average $PM_{2.5}$ concentrations is shown in Figure A2.10.1. The comparison shows reasonable agreement between modelled and measured data, but an overall tendency for some underprediction of the higher monitored values. Note here that the annual average background concentration is 9.4 µg m^{-3}.

70. Annual average concentrations of $PM_{2.5}$ over Greater London are shown in Figure 5.3 (Chapter 5), with the levels of the scale chosen in relation to the limit values and reduction targets stipulated in the European Air Quality Directive (2008/50/EC). Specifically, they correspond to the limit value for 2015 (25 µg m^{-3}), the indicative limit value for 2020 (20 µg m^{-3}) and levels corresponding to the different exposure reduction targets (18-22 µg m^{-3} for 20%, 13-18 µg m^{-3} for 15% and 8.5-13 µg m^{-3} for 10%). Areas and percentage areas within each of the exposure bands, and corresponding to exceedence of the limit values, are shown in Table A2.10.1. It is noted that background concentrations are mainly below 13 µg m^{-3} whilst values at a number of hot spots in central London are above 20 µg m^{-3}.

Table A2.10.1: Areas of exceedences for London for a range of $PM_{2.5}$ bandings for the calculated annual average concentration for 2008.

$PM_{2.5}$ banding (µg m^{-3})	Area (km^2)	% of total modelled area
>25	0.015	0.0005%
>20	0.504	0.0158%
>22	0.125	0.0039%
18-22	2.277	0.071%
13-18	125.71	3.933%
8.5-13	3068.4	95.993%
<8.5	0	0.0000%

Chapter 6

Conclusions and future directions

1. $PM_{2.5}$ is an important issue in the UK. It is currently recognised that exposure to particulate matter (PM) can give rise to significant health effects and to date there is no evidence of a safe level of exposure. Further, there is no current consensus on the relative contributions of different chemical components of PM to the overall adverse health effects of exposure. Therefore $PM_{2.5}$, the finer size fraction of PM, remains a priority issue for Defra.

2. There are many different sources both natural and man-made that contribute to $PM_{2.5}$ particles in the atmosphere. The main anthropogenic sources are relatively ubiquitous, namely industry and power stations, road transport and residential and shipping sources. Particles can be directly emitted, primary PM, or formed indirectly through chemical and physical processes in the atmosphere, secondary PM. The $PM_{2.5}$ fraction is removed relatively slowly from the atmosphere and the dispersion of $PM_{2.5}$ can effectively be treated like that of a gas.

3. The observations of $PM_{2.5}$ demonstrate the long residence time in the atmosphere and the resultant potential to be transported over large distances. This highlights the need to quantify $PM_{2.5}$ at a regional scale, as much of the urban concentration, around 50-80%, is driven by the regional "background". Measurements indicate that secondary $PM_{2.5}$ is a key feature of this regional "background" and that transboundary influences can be important for the direct import of both $PM_{2.5}$ and its gas phase precursors. Table 6.1 shows a modelled example of the different contributions to UK $PM_{2.5}$ concentrations from different sources.

Table 6.1: Population-weighted mean contributions to urban and rural background annual mean $PM_{2.5}$ in the UK in 2009 from the PCM model (see Chapter 5 and Annex A2.8). Total modelled concentration is 10.7 $\mu g\ m^{-3}$ (the percentages have been rounded to integers).

Component	Estimated contribution
sea salt and residual (natural)	16%
SIA (secondary inorganic aerosol)	38% (of which about 50% is from non-UK sources)
SOA (secondary organic aerosol)	8%
regional primary (contributions to regional PM from non-local emission inventory sources of primary PM (> ~15 km away))	11% (of which about 50% is from non-UK sources)
rural and urban dusts	11%
non-traffic local sources	10%
traffic local sources (primary exhaust emissions and brake and tyre wear)	7%

4. The delivery of air quality policy objectives relies upon the ability to measure pollutants in an accurate, reproducible and reliable way. Currently there are significant challenges associated with the reliable and reproducible measurement of $PM_{2.5}$.

5. Long-term self-consistent records are essential for the fulfilment of policy requirements and to understand the impact of policy actions on the concentration of any given pollutant. At this time, it is not clear that we have measurements sufficient to meet this requirement for $PM_{2.5}$ owing to the nature of the measurement systems used. The answer to the question 'Do we have a robust measure of $PM_{2.5}$?' remains substantially uncertain. A major difficulty for assessment of compliance is that $PM_{2.5}$ measurement methods are still evolving and the reference method is currently being revised. Consequently, measurements made in 2020 may not be directly comparable to those made in the period 2009-2011 (the base period for the EU Air Quality Directive requirement). This sheds serious doubt on our ability to provide evidence that the EU exposure reduction target is being met for $PM_{2.5}$. These measurement difficulties, and also the interpretation of $PM_{2.5}$ data, provide significant challenges for the modelling community. The measurement uncertainty is currently at the limit of being meaningful for interpretation by models and *vice versa*.

6. AQEG strongly recommends that a focused working group is put together to make a short-term assessment of the risks of, and solutions and opportunities to mitigate, measurement uncertainties and of the way that uncertainties impact on our ability to deliver air quality policy in the UK.

7. The second critical requirement concerns the availability and quality of chemically-speciated $PM_{2.5}$ measurements. It is clear these are essential to the development of effective mitigation policy via source apportionment, as they allow the delineation of source–receptor relationships, as well as being a better comparator for models that deal with individual components. Speciated measurements could also be used in epidemiological studies to strengthen the knowledge of the influences of particle size and composition upon toxicity and allow the development of more refined metrics for the prediction of effects on health.

8. Modelling data and some limited measurement data suggest that a large proportion of the regional background is comprised of the secondary inorganic aerosols (SIA) nitrate and sulphate, as well as secondary organic aerosols (SOA). In cities this is enhanced by an urban increment (Chapter 5, Figure 5.6). What do the measurements and models tell us about mitigation options?

    (a) Reducing urban increment alone may not meet exposure reduction targets but there are sources that could be mitigated.

    (b) There is a significant transboundary import and export of SIA into and out of the UK, and therefore there is a need for regional-based action. Modelling estimates indicate that per tonne of sulphur dioxide (SO_2), nitrogen oxides (NO_x) and ammonia (NH_3) emitted by the UK, about 50%, 55% and 35% respectively of the overall resulting population exposure to $PM_{2.5}$ is incurred outside the UK, i.e. results in exposure in other countries. From the UK perspective, only about half the exposure of the UK population to SIA is due to UK emissions, with around 33% arising from other countries and 17% from shipping. Future effects will depend on the control of emissions of SO_2, NO_x and NH_3 in other countries and from shipping as well in the UK.

(c) Control of SIA is uncertain because of the complex non-linear response of SIA concentrations to reductions in precursor emissions owing to chemical interactions between pollutants; in particular, the formation of ammonium nitrate is reversible, temperature dependent and highly dependent on the availability of NH_3. This needs to be borne in mind when considering the effectiveness of further SO_2 and NO_x reductions, with emissions of NH_3 likely to remain broadly constant. Regional ammonia control combined with NO_x and SO_2 control are therefore likely to be critical future factors in future control of $PM_{2.5}$. There are also trade-offs to be considered as, for example, abatement of SO_2 may lead to increase in nitrate aerosol.

9. Looking forward, there is a clear potential policy imperative in terms of meeting future exposure reduction targets for $PM_{2.5}$. The UK is likely to be required to meet a reduction target of around 2 µg m^{-3} in three-year average concentrations across the UK network of urban background sites, currently roughly 13 µg m^{-3} (see Chapter 1), between 2010 and 2020. While the reductions required to meet targets appear to be relatively small, they will still present a substantial challenge, especially in view of the proportion subject to UK control. There are significant non-linearities in PM chemistry that mean that changes in precursor gas emissions can have non-proportional effects on the observed PM concentrations. Interaction between pollutants means that changes in one can affect another; for example, reductions in SO_2 and NO_x over the next decade are expected to reduce ammonium (NH_4^+) concentrations even though NH_3 emissions are projected to remain relatively constant (with a greater proportion of the NH_3 redeposited by dry deposition).

10. The chemistry of secondary organic PM formation is poorly understood and it is not clear which sources should be targeted to reduce PM concentrations (see Table 6.1). Though modelling suggests that the bulk of SOA is biogenic in origin implying limited capacity for reduction, there is considerable uncertainty in the modelling of such complex chemistry with semi-volatile compounds.

11. There is a general and important challenge in the development of emission inventories fit for modelling $PM_{2.5}$ concentrations. Are inventories that have traditionally been constructed for reporting to international bodies following prescribed methods and procedures suitable for use in air quality models? The answer is no because of the importance of the temporal and spatial variability of emissions of primary $PM_{2.5}$ and secondary precursor gases from many varied sources and because of the high uncertainty in the methods used for quantifying emissions from, in particular, the many diffuse fugitive dust sources. Another reason is the absence of certain sources from reported inventories, such as wind-blown dust, resuspension of road dust and biogenic sources.

12. With respect to road traffic emissions, a key future factor is that as reductions in exhaust emissions of PM occur as a consequence of European vehicle emission regulation, non-exhaust components of traffic emissions will become much more important, emphasising the need to introduce measures to control their sources. Emissions from tyre and brake wear, and road abrasion are not well understood, yet current inventory projections predict that if they continue to be uncontrolled they will be responsible for over 70% of total traffic emissions of $PM_{2.5}$ by 2020.

13. Emissions from fugitive dust sources, small-scale wood and waste burning, cooking, agriculture, natural sources and shipping are also poorly understood and difficult to quantify yet can make a significant contribution to $PM_{2.5}$ concentrations. This needs to be addressed, especially if the benefits of mitigation are to be assessed.

14. Models are an important tool for the synthesis of knowledge and prediction of concentrations. Models fulfil an important role in answering questions such as how will PM levels change into the future, which are the most important emission sources to control to reach acceptable air quality and what balance should be struck between policy actions within the UK and abroad? PM models are still developing and have a number of inadequacies and uncertainties. It may be that there are ‘surprises’ before we can be sure that they are completely reliable policy tools. There is a pressing requirement to develop and evaluate PM models in the policy context.

15. The science underpinning the knowledge of $PM_{2.5}$ is rapidly evolving and remains uncertain in many areas. There is a need for rapid translation into the policy arena of the newest results and understanding.

6.1 $PM_{2.5}$ report summary of actions

16. Table 6.2 summarises AQEG’s assessment of the action areas for the current evidence base, highlighting areas which need most attention to improve understanding of $PM_{2.5}$ in the UK.

Table 6.2: Action areas for the science and evidence base on $PM_{2.5}$.

Evidence area	Urgency	Impact/ importance	Addresses recommendation(s) or conclusion
Measurements			
Automatic Urban and Rural Network (AURN) $PM_{2.5}$ measurements	1	H	See Chapter 2 (§2.6) and paras 4-5
Chemically-speciated $PM_{2.5}$ measurements	1	H	See Chapter 3 (§3.10.2) and para 7
Concentrations and composition of $PM_{2.5}$			
Observational analysis	2	M	See Chapter 3 (§3.10.2)
Determination of rural background	1	H	See Chapter 3 (§3.10.2)
Mitigation analysis	2	M	See Chapter 3 (§3.10.2) and para 8

Emissions and receptor modelling

Enhancement of emission inventories:			See Chapter 4 (§4.7) and para 11
• non-exhaust vehicle emissions including tyre and brake wear, road abrasion and road dust resuspension	1	H	See Chapter 4 (§4.7) and para 12
• impact of UK biogenic volatile organic compounds (BVOCs) on formation of SOA	2	H	See Chapter 4 (§4.7)
• fugitive dust emissions from construction, demolition, quarrying, mineral handling, industrial and agricultural processes • PM$_{2.5}$ emissions from domestic and commercial cooking • small-scale waste burning and bonfires • wood burning and the effectiveness of control measures • biogenic emissions of non-methane volatile organic compounds (NMVOCs) • exhaust emissions from off-road machinery used in construction and industry • exhaust emissions from diesel vehicles under real world driving conditions • development of inventories that quantify the spatial and temporal variability in emissions of primary PM$_{2.5}$ and precursor emissions of NH$_3$ from agriculture and methods for their control	2	M	See Chapter 4 (§4.7) and para 13

Modelling and the future

Model evaluation and the link to measurements	1	M	See Chapter 5 (§5.7)
Accuracy of near-term forecast models	3	L	See Chapter 5 (§5.7)
Model availability and ability to address each PM component and mass closure	2	M	See Chapter 5 (§5.7)
Import of transboundary PM (present and future)	1	H	See Chapter 5 (§5.7)
Need for assessment of ability to control future PM$_{2.5}$ concentrations; dependency on ammonia	1	H	See Chapter 5 (§5.7)

Key

§ refers to sections within a specific chapter; references to 'para' numbers are within this chapter.

Urgency

1. Short-term strategic action is required.
2. Mid-term strategic action is required.
3. Longer term action is required either to develop capability or address a large issue.

Impact/importance

H – High impact/importance – Will have a significant immediate impact on policy/evidence.
M – Medium impact/importance – Will have an impact on policy/evidence.
L – Low impact/importance – Will have some impact on policy/evidence.

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