A review of the state-of-the-science relating to secondary particulate matter of relevance to the composition of the UK atmosphere

(Defra Project AQ0732 – Understanding Secondary Inorganic and Organic Aerosol)

Report to Department for Environment, Food and Rural Affairs (Defra)

2015

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Context and Scope

A number of legislative approaches are being taken to control exposure to Particulate Matter (PM) in order to achieve UK 2005 24-hour and annual AQ standards for PM_{10} (PM with diameter less than 10 µm) and subsequent EU 2010 and 2015 and UK 2010 $PM_{2.5}$ (fine particulate matter, with diameter less than 2.5 µm) targets. These include vehicle, industrial and source emission controls and those introduced by local authorities. The UK has set national air quality objectives to comply with European Directive limit and target values of PM_{10} (and $PM_{2.5}$ from 2020) for the protection of human health. These can be found at http://uk-air.defra.gov.uk/documents/National_air_quality_objectives.pdf. From 2015 there is an EU-wide urban background 3-year average exposure concentration obligation (ECO) of 20 µg m^{-3} and from 2020 an average exposure indicator (AEI) reduction target based on the 2010 measured AEI. AEI is determined as a 3-year running annual mean $PM_{2.5}$ concentration averaged over the selected monitoring stations in agglomerations and larger urban areas, set in urban background locations to best assess the $PM_{2.5}$ exposure to the general population. $PM_{2.5}$ comprises both primary and secondary contributions. Since direct primary emissions are more readily understood, increased quantitative understanding of the inorganic and organic fractions of secondary aerosol is necessary to help the UK meet these targets.

In addition to any control of primary particulate matter, the National Emission Ceilings Directive (NECD) (2001/81/EC) sets emission ceilings to be achieved from 2010 onwards for each Member State for the same 4 pollutants as in the 1999 Protocol to Abate Acidification, Eutrophication and Ground-level Ozone (the Gothenburg Protocol); sulphur dioxide (SO_2), nitrogen oxides (NO_x), non-methane volatile organic compounds (NMVOCs), and ammonia (NH_3). These are of direct relevance, being precursors to secondary aerosol as well as ozone. The Convention on Long-range Transboundary Air Pollution, LRTAP adopted amendments to the Gothenburg Protocol in 2012 to introduce emission reduction commitments for 2020 and beyond for the controlled pollutants. Based on a review of EU air policy, in December 2013 the Commission adopted a new Clean Air Programme for Europe with air quality objectives for the period up to 2030, a revised NECD with stricter emission ceilings for six main pollutants, and a proposal for a new Directive to reduce pollution from medium-sized combustion installations. The revised NECD includes new national emission reduction commitments applicable from 2020 and 2030 for SO_2, NO_x, NMVOC, NH_3, $PM_{2.5}$ and CH_4 and intermediate emission levels for the 2025 applicable to the same pollutants. Whilst of direct relevance to secondary aerosol, natural biogenic NMVOC emissions are highly uncertain and not readily controlled by conventional legislative instruments.

In its 2009 report, the Committee on the Medical Effects of Air Pollutants (COMEAP) focussed on particulate matter, represented as $PM_{2.5}$, as the air pollutant most strongly associated with increased risks of mortality. In 2010, using the same data as the report, the impact of human-made $PM_{2.5}$ on the mortality of the UK population, was estimated as a loss of 340,000 years of life in 2008, an effect equivalent to 29,000 deaths. COMEAP speculated that this effect was most likely manifested as a smaller contribution to the earlier deaths of up to 200,000 people. The burden can also be represented as a loss of life expectancy from birth of 6 months (as an average across all births). It was predicted that if the annual average concentration of $PM_{2.5}$ were reduced by 1 microgram per cubic metre, there would be an increase in life expectancy from birth of about 20 days with 4 million years of life gained over the next 100 years by the UK population. Removal of all human-made

particulate matter would lead to a predicted gain of 36.5 million life years over the same time period; an increase in life expectancy from birth of 6 months.

This legislative and public health setting provides the backdrop for the subject of this review. Particulate matter can either be directly emitted as liquid or solid material from a variety of sources, or be formed in the atmosphere from primary pollutants. The latter, so-called secondary aerosol is generated by the transfer of material, either inorganic or organic, from the vapour to the aerosol phase following the chemical processing of emitted gaseous precursor pollutants. A number of processes therefore contribute to secondary aerosol formation, including the emission of precursor species and multiphase chemical and physical processes.

Ammonium sulphate and ammonium nitrate, the major contributors to secondary inorganic aerosol (SIA) are formed by the atmospheric oxidation and reaction of precursor gases (SO_2, NO_x) and subsequent reaction with NH_3 and comprise a major component of fine particulate matter. The much more diverse but no less substantial, secondary organic aerosol (SOA) components are formed by the atmospheric oxidation of precursor gases (e.g. VOCs) emitted from both man-made and natural sources. The mass of organic matter in particulate is significantly enhanced in polluted regions worldwide but the source of organic matter in these areas is currently unknown. The profile of the emission of man-made VOC precursors may be subject to changes in response to legislative controls. Natural emissions may change with environmental conditions and with changes to land-use or biota.

Largely because of the complexity of both the emitted precursors and of the formation and transformation processes, the secondary component of atmospheric particulate matter is diverse and variable and is the most difficult fraction to quantitatively predict or unambiguously quantify from measurements. Furthermore, owing to the long distances over which both precursors and particles may be transported, the mixture of sources contributing to the secondary component is highly variable and dependent on meteorological conditions. The targets required to meet the forthcoming EU and UK legislative obligation to reduce exposure to particulate matter will be difficult to realise without addressing the substantial contribution from secondary matter. It is therefore important to understand how secondary aerosol formation and transformation depends on the emissions and fundamental processes.

The aim of this report is to provide Defra with a review of existing evidence regarding the contribution of secondary organic aerosol and secondary inorganic aerosol to PM concentrations. The work aims to identify and prioritise any knowledge gaps relevant to UK air quality policy and make clear recommendations for further studies which could be undertaken to fill the evidence gaps identified.

Policy Summary

Particulate matter (PM) is the term used to describe condensed phase (solid or liquid) particles suspended in the atmosphere. PM may be directly emitted into the atmosphere (termed primary particles) or formed by the reaction of atmospheric gases (secondary particles). Largely because of the complexity of both the emitted precursors and of the formation and transformation processes, the secondary component of atmospheric particulate matter is diverse and variable. It is the most difficult fraction of PM to quantitatively predict or unambiguously quantify from measurements. It will be difficult to achieve the targets required to meet the forthcoming EU and UK legislative obligation to reduce exposure to particulate matter without reducing secondary particulate matter concentrations.

The aim of this report is to provide Defra with a review of existing evidence regarding the contribution of Secondary Organic Aerosol (SOA) and Secondary Inorganic Aerosol (SIA) to PM concentrations. The work aims to identify and prioritise any knowledge gaps relevant to UK air quality policy and make recommendations for further studies which are required to fill the evidence gaps identified.

The contributions of SIA/SOA to $PM_{2.5}$ are highly variable and dependent on location. As a broad estimate, secondary aerosol might be expected to contribute roughly half of roadside $PM_{2.5}$, increasing to the majority (of the order of 90%) of rural $PM_{2.5}$, with the urban background contribution lying between these values, depending on location, meteorology and season.

Ammonium sulphate and ammonium nitrate, the major contributors to SIA are formed by the atmospheric oxidation and reaction of precursor gases (sulphur dioxide, SO_2 and nitrogen oxides, NO_x) and subsequent reaction with ammonia (NH_3). SIA is a major component of fine particulate matter in the UK. Emissions of SIA precursors are generally well established and reasonably well quantified both in the UK and in Europe.

The Acid Gas and Aerosol Network provides good coverage of the UK measuring the main SIA components, but the inlets have not been characterised so measurements are not fully quantitative. This limits the data from which reliable spatial distributions, temporal trends and fractional contributions to particulate mass can be derived. At the two Defra monitoring sites that measure both total $PM_{2.5}$ mass and SIA components, North Kensington and Auchencorth Moss, the mean monthly percentage contributions show that in 2009 SIA made up between 25% and 100% of measured $PM_{2.5}$. Nitrate generally dominates SIA and there has been no discernable trend in total average nitrate from 2000 – 2009.

Models capture the order of magnitude of SIA but it is unclear whether they capture the non-linear response of SIA concentrations to changes in precursor emissions. It appears that model studies are inconsistent in their sensitivities, some predicting greatest sensitivity to SO_2 abatement, others to NH_3 abatement. There is a need to represent the high spatial and temporal variability of ammonia emissions through flux measurements and inclusion in emission inventories, and to evaluate the effect of such variability on SIA formation. There is an urgent need to understand, if not reconcile, the divergent predicted dependencies of SIA on precursor emissions. Model evaluation (and if necessary representation improvement) of SIA processes is required to reproduce the non-linear responses of SIA to reduced precursor emissions and to fully resolve the contributory processes. The representation and roles of NH_3 and of gaseous versus aqueous sulphate production require particular attention. Model emission of primary sulphate should be clearly reported and considered when attributing emission sensitivities. NO_x emissions from international shipping are projected to make an increasing contribution to European emissions so characterisation of this source should be improved.

Organic aerosol (primary and secondary) frequently forms the dominant fraction of fine particulate matter in the atmosphere. However, measurements indicate that models poorly predict organic aerosol concentrations and underestimate the contribution made by SOA particularly in polluted regions. SOA forms when volatile organic compounds (VOCs), both natural and man-made, undergo gas phase oxidation reactions, forming products that preferentially exist as a liquid or solid rather than a gas either forming new particles or condensing onto pre-existing particles.

Recent studies of the volatility (the tendency of a substance to vaporise, that is to become a gas) of emitted particles have blurred the distinctions between the primary and secondary organic aerosol categories. Under ambient conditions some of the primary particulate matter emissions from combustion can evaporate. The vapours produced undergo oxidation, producing previously unrecognised semi-volatile and intermediate volatility compounds (S/IVOC). These S/IVOCs may be a substantial additional source of SOA. There are still large uncertainties in the concentrations, reaction rates, and SOA yields of S/IVOC precursors. Emissions from biomass burning are gaining attention as a potentially important source of these new compounds and consequently SOA, although field and laboratory studies show highly variable results. Laboratory studies of emission factors for the range of burners used in the UK, including consideration of IVOCs and SVOCs, would improve characterisation and quantification of biomass burning emissions.

The highest priority evidence need is the identification and quantification of the most effective biogenic and anthropogenic SOA precursors. This would include an assessment of the reliability of estimates of IVOC, SVOC and conventional precursor effectiveness, which could be done using chamber measurements under representative conditions where necessary. This is a huge undertaking and will require international collaboration to achieve. Some of this work has been made possible by EU network activities such as EUROCHAMP but the funding period for this network is now over. Enhanced speciated source strengths of anthropogenic VOC emissions targeted to the most effective SOA precursors (including IVOCs and SVOCs) should be included in inventories. There are recently funded UK projects that will contribute to this however the outputs will not be available for a number of years.

The current level of understanding of SOA formation is low. Initially the newly recognised, potentially important, IVOC and SVOC compounds need to be measured. A reliable technique for routine monitoring of chemically-resolved volatility needs to be developed. Such measurements are extremely challenging and will require substantial effort from the current state of the science. There are promising techniques, though it is not currently clear that the science or technology are sufficiently advanced to do this comprehensively, routinely or even successfully. Improved measurements will facilitate the necessary inclusion of some representation of IVOC and SVOC particulate matter precursors in atmospheric models. In the relatively short-term, the most promising approach is to use what are known as lumped representations of these sets of compounds. Lumped representations allow compounds that are sufficiently similar to be represented by one species with properties that are considered reasonably representative of the whole group. This greatly reduces the complexity of the model.

There is no way of directly measuring the SOA fraction of organic aerosol but it can be estimated using numerical techniques. There are few available datasets from which organic aerosol contributions can be derived using these techniques, with a particular lack of roadside studies. Only four network sites measure organic aerosol and so meaningful assessment of SOA trends or spatial distributions cannot be made from measurements. Application of suitable numerical techniques to data collected during intensive research measurement campaigns has provided evidence that there are 24 hour daily mean PM mass exceedances driven by secondary components in the UK. SIA mass is generally greater than SOA at the locations studied.

Models that are not tuned to chamber simulations do not replicate SOA mass loadings and tuned models can give very different predicted sensitivities to environmental conditions. Large-scale models using SOA parameterisations that are tuned to fit with measurements of SOA and its precursors in studies carried out in atmospheric chambers perform better in clean biogenic regions, but fail to capture anthropogenic enhancements to SOA mass and generally under predict in polluted regions. It is unclear that any models predict NO_x, oxidant, temperature or meteorological dependencies well. Models suggest that non-linear interactions exist between reductions in either NO_x or anthropogenic VOCs, or both, and $PM_{2.5}$ SOA. Depending on the model representation and tuning, reductions in NO_x can preferentially increase either biogenic SOA or anthropogenic SOA. Non-UK chemistry-climate feedback studies suggest that an increase in temperature can significantly increase biogenic SOA. There is no central source of UK or EU biogenic VOC emissions information and the huge temporal and spatial variability, and lack of meaningful speciation makes their inclusion in models challenging. Also, factors (such as temperature, light and stress) affecting the release of effective biogenic SOA precursors are poorly understood. A more complete speciation of biogenic VOC emissions is required, targeted towards the most effective SOA precursors.

From a policy perspective the chemical origin of SOA is probably unimportant; the consideration is whether reduction in anthropogenic emissions will beneficially affect SOA loadings. Further chamber studies are necessary to probe the sensitivity of biogenic SOA to anthropogenic VOC reductions, and of both anthropogenic and biogenic SOA to NO_x reductions. Models with a range of SOA representations should be evaluated against the observed dependencies. The concept of biogenic and anthropogenic SOA is not scientifically well justified; the separation can be defined in terms of the biogenic or anthropogenic origin of the precursors of SOA or in terms of the formation of SOA under biogenically- or anthropogenically-dominated atmospheres. Currently it is not understood how or why SOA displays a dependence on anthropogenic input so assessment of the relative importance of biogenic and anthropogenic emissions is not possible. The lack of mechanistic understanding precludes the prediction of effective mitigation measures. Where literature studies exist, the majority consider the dominant precursors to be biogenic VOCs. There is, however, a persuasive argument that this conclusion may result from the high-yield anthropogenic VOCs being extremely difficult to quantify. Owing to the lack of empirical data and reliable predictive capability, it is unclear whether, and by how much, SOA concentrations in the UK would reduce in response to a reduction in anthropogenic VOCs.

A high priority recommendation is to explore the parameter sensitivity of UK SOA predictions using a range of representations to identify those that behave 'most physically'. This is a complex issue; tuned models may capture observations in specific situations well but their predictive capability is reduced by the lack of physical basis for the tuned parameters. Model exploitation of emergent UK networks data, European network measurements and intensive case study data should be encouraged using both online (chemical mechanism coupled to meteorological model) and offline (meteorological model output fed into chemical mechanism but no chemical feedbacks to meteorological model) models in investigations of long-term SOA and SIA relationships. UK sensitivity studies should be conducted using a range of physically reasonable models to evaluate relative contributions to SOA by anthropogenic and biogenic emissions.

Since secondary aerosol is formed from primary precursors, there is a strong need for coordination of network measurements of major primary precursors and SIA and SOA. It will benefit the move to UK compliance with EU directives on daily PM exposure levels to commit to long-term monitoring of the major secondary contributors to $PM_{2.5}$ on time scales that capture episodic events, resolving the contributors using appropriate numerical techniques. This will require use of semi-continuous or continuous analysers for inorganic and organic components at a sufficient number of locations to obtain geographical coverage from which to generate spatial distribution trends. The widespread network use of

semicontinuous analysers (measuring both inorganic and organic carbon/elemental carbon) with reliable, characterised inlets or Aerosol Chemical Speciation Monitors (ACSM), coupled to a comparison of numerical analytical techniques, is essential in identification of areas of uncertainty/disagreement in derivation of the relative contribution of SOA and SIA to PM concentrations. It should be noted that the ACSM does not currently measure $PM_{2.5}$ but transmits and measures components closer to PM1 presenting challenges to interpretation in the context of the $PM_{2.5}$ criterion.

With current evidence, it is not straightforward to draw conclusions about relative impacts of UK and non-UK, or anthropogenic and biogenic emissions on SIA or SOA formation; this would require incorporation of reliable emissions data into appropriate models. Setting UK data in context of European network data with model interpretation could provide evidence for transboundary contributions to the SIA and SOA fractions. There are also ground-based and airborne intensive datasets, which could be used. There are too few sites that measure all relevant parameters to derive clear measurement-based relationships between SOA or SIA and precursors, oxidants and meteorology. To-date, there have been few modelling studies that have exploited the limited amount of UK network data in conjunction with European network data to unambiguously derive relationships for UK SIA and none that have reliably established such relationships for SOA.

The outstanding evidence gaps, particularly in our understanding of SOA, are much larger than UK researchers can achieve alone. Solution of these problems will require coherent investigations by UK researchers within broad collaborative international efforts. Simultaneous expansion of the UK monitoring network capability, comparison of available measurement techniques and incorporation of recent developments in SOA understanding into state-of-the-art models should be encouraged to most efficiently address the outstanding issues.

Type				Recommendation	Capability limited by not following this recommendation	Needs	Helps
A Fundamental	SIA		1	Reduce NH$_3$ emission variability uncertainty through flux measurement and evaluate uncertainty impacts on SIA	Accurately capture nitrate and hence SIA		
			2	Model sensitivity to NO$_x$ emission from shipping; measurement characterisation, projection and impact prediction	Address the influence of shipping on SIA		
	SOA		3a	Identification and quantification of the most effective biogenic and anthropogenic SOA precursors; requires lab and representative chamber data and process modelling	Confidently evaluate present-day SOA or predict future SOA	**A5,A7,A 9,A10**	**A4**
			3b	Assessment of the reliability of estimates of IVOC, SVOC and conventional precursor effectiveness, including chamber measurements	Evaluate or predict the major anthropogenic SOA contributions	**A5**	**A4**
			4	Speciated source strengths of SOA forming anthropogenic VOCs are needed for emission inventories. May require simplification protocol for unconventional precursors.	Evaluate or predict the major anthropogenic SOA contributions	**A3a,A3 b,A4,A5 ,(A6),A7**	
			5	Enhanced knowledge of the fraction of IVOCs and SVOCs in Primary Organic Aerosol (POA) and their transfer between phases is important in understanding SOA formation.	Evaluate or predict the major anthropogenic SOA contributions		**A3a,A3 b**
			6	Development of reliable technique for routine monitoring of chemically-resolved volatility	Constrain and evaluate SOA predictions		**A4,A5**
			7	Characterisation and quantification of organic compound emissions from domestic and commercial cooking and burning of biomass for heating	Address the influence of cooking and biomass burning on SOA		**A4**
			8	More complete speciation of biogenic VOC emissions, targeted towards the effective SOA precursors (mono- and sesquiterpene and green leaf volatile speciation).	Evaluate or predict the major biogenic SOA contributions		
			9	Quantify the sensitivity of biogenic (B)SOA to anthropogenic (A)VOC reductions and of both (A)SOA and (B)SOA to NO$_x$	Predict the natural and	**A3; A8**	

B Measurement	Both SIA and SOA					
			reductions.	manmade SOA contributions		
		10	Quantify the relative contributions of gaseous and aqueous SOA formation pathways.	Confidently evaluate present-day SOA or predict future SOA		
		1a	long-term monitoring of secondary PM$_{2.5}$ contributors on time scales that capture episodic events, resolving them with appropriate numerical techniques.	Evaluate PM contributions and temporal responses or evaluate models	**B1b**	
		1b	(semi-)/continuous analysers for inorganic and organic components to obtain geographical coverage for spatial distribution trends (note[1]). Needs multiple sites for reliable fractional contribution to UK atmosphere.	Evaluate PM contributions and temporal responses or evaluate models		**B1a**
		2	Where SOA is measured, it is essential to make collocated measurement of PM mass, inorganic aerosol components (incl. SIA), primary emission tracers (CO, NO$_x$, BC, K, levoglucosan and diesel tracers), O$_3$ and local met.	Link PM contributions to their individual components for process evaluation		
		3	Systematically compare available numerical techniques within the UK, in particular emphasising roadside locations	Gain confidence in analytical techniques (and uncertainties)and in the provision of measurements as evidence		**B1a**
		4	Coordinate and collocate network measurements of primary precursors with SIA and SOA	Provide geographical variability in SIA and SOA and evaluate models		
		5	Systematically compare available measurement techniques within the UK, again with emphasis on roadside locations	Gain confidence in measurement techniques (and uncertainties) and in the provision of measurements as evidence		**B1a,B1 b**
		6	Targeted expansion of network capability (e.g. expansion of	Improved geographical	**B1a,B1**	

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[1] possible on campaign basis, after a number of year-long cycles of the single existing ACSM. Also, need to establish links with e.g. EU ACTRIS network (http://www.actris.net/)

			Composition and Size network to more urban and rural sites with instrumentation described above, building on AGANet and AURN sites with their extensive historical data)	variability in SIA and SOA and its attribution, plus model evaluation	**b,B2,B4**	
	SOA	7	Intensive research measurements on VOC oxidation products and the semi- and intermediate volatility organic aerosol components for constraint of simplified model SOA treatments	Constrain and evaluate SOA contributions and predictions		
C Modelling	SIA	1a	Priority: Understand and reconcile divergent predicted dependencies of SIA on precursor emissions. Model evaluation (and resultant improvement) of SIA processes is required.	Prediction of process contributions to SIA and consequent response of SIA to precursor emission reduction	**C1b,C1c**	
		1b	Representation and roles of NH$_3$ and of gaseous vs. aqueous sulphate production require particular attention. Emission of primary sulphate should be clearly reported when attributing emission sensitivities.	Prediction of process contributions to SIA and consequent response of SIA to precursor emission reduction		**C1a**
		1c	Model-measurement comparison and evaluation of SIA and precursor vertical profiles to constrain transboundary and UK sources and resolve elevated vs. surface loading to validate SIA processes.	Attribution of local and transboundary SIA		**C1a**
	SOA	3	Priority: Development of air quality models with reasonable skill to replicate SOA mass loadings in the UK with predictive capability.	Confidently predict SOA for policy compliance	**C2 or C3+C4, ideally C5,C6**	
		4	Short term use of semi-empirical methodologies coupled to appropriate UK gaseous schemes to capture SOA mass based on best knowledge of "unconventional" IVOC and SVOC precursors - "VBS" methodology. Exploration of parameter sensitivity in such an approach.	Make any useful prediction of SOA in the short-term	**A5**	**C1**
		5	Medium / long-term development of highly detailed representations of the oxidation chemistry of emitted VOCs, IVOCs and SVOCs to faithfully capture dependencies of	Make improved mechanistic prediction of SOA in the longer-term	**A5**	**C1**

			gaseous precursor concentrations.			
		6	Systematic reduction of detailed gas phase schemes developed in 5 above appropriate for coupled representations of SOA formation	Confidently predict SOA on the UK scale	**A5,C5**	**C1**
		7	Detailed representation of coupled particle microphysics and chemical transformations in all phases is ultimately required.	Detailed prediction of SOA contribution at all particle sizes with realistic lifetimes and deposition patterns		**C1**
		8	Reliable representation of BVOCs to be used in evaluation of BSOA vs ASOA. Ideally BVOC emissions should respond to model conditions, but perturbation studies possible if uncoupled models used.	Confidence in attribution of natural SOA	**C1**	
		9	Evaluate couplings between AVOCs, NO_x and BVOCs with reliable SOA representation	Understand influence of anthropogenic emissions on biogenic SOA	**A9,C1**	
		10	Evaluate relative contributions to SOA by anthropogenic emission sector and from biogenic emissions. Avoid brute force emission perturbation methods if possible to avoid large numbers of simulations.	Attribute SOA to natural and manmade sources	**A1,A2,A 3a,A3b, A4,A7,A 8,C1**	
		11	Exploitation of available EU network data for model boundary condition constraint and comparison and of available and emergent UK data	Improve estimates of transboundary and local contributions and evaluate models	**A6,B1a, B1b,B2, C1**	
		12	Make use of recently developed methodologies for source-receptor studies (including statistical methods embedded within the host model) and improved emissions estimates using inverse modelling approaches.	Improve confidence in attribution of PM from SIA and SOA		

Secondary Aerosols in the UK Atmosphere: State of the Science, Uncertainties, Gaps and Recommendations

This section is based on the current state of knowledge of the processes giving rise to secondary aerosol of relevance to UK air quality. Since secondary aerosol contributing to PM mass comprises both inorganic and organic components and there are common features applying to both, secondary inorganic aerosol (SIA) and secondary organic aerosol (SOA) are considered together wherever appropriate.

The section is divided into three sections for convenience reflecting the approaches used for collection of appropriate evidence and the status of this evidence which is drawn from a distillation of the information provided in Annexes A, B and C of this report. The three sections address:

A. **Underpinning knowledge about processes leading to secondary aerosol formation**

B. **Knowledge about secondary aerosol derived from measurements**

C. **Knowledge about secondary aerosol derived from modelling**

In this section we aim to target a number of specific areas addressing policy requirements to enable evaluation and control of the contribution of secondary aerosol to UK air quality and consequently inform legislative compliance. To this end, the evidence in the Annexes is pulled together to address the following three high level goals:

Explain the current sources of SOA and SIA as currently measured in the UK atmosphere, including the identity and spatial distribution of precursors, taking account of both annual average and episode conditions

Review the current measurements of SOA and SIA in the UK atmosphere, accounting for spatial distribution, site type and measurement technique, and consider what future measurement strategy would best inform the understanding of SOA and SIA formation/concentrations

Identify the key precursor emissions to SOA/SIA concentration relationships and likely impacts on UK secondary aerosol concentrations of possible future changes in spatially-disaggregated emissions

Addressing these goals is important for understanding the degree to which control of secondary aerosol is possible, the means by which such control may be achieved and hence the appropriate policy responses. To this end, the following key has been adopted for clarity.

Statements of the relevant state of knowledge are shaded green. Gaps in the state-of-the-science required to comprehensively inform policy are identified by amber shading. Recommendations to address the gaps and / or ensure optimal understanding of the science necessary to control air quality are shaded red.

A. Underpinning knowledge about processes leading to secondary aerosol formation

Atmospheric aerosol particles, from a few nanometers (nm) to tens of micrometers (µm) in diameter, may be either directly emitted into the atmosphere or formed *in-situ* by the oxidation of precursor gases and are termed primary and secondary, respectively. The secondary fraction comprises variable amounts of sulphate, ammonium, nitrate, chloride, water and carbonaceous material. The sulphate component is derived predominantly from the atmospheric oxidation of anthropogenic and natural sulphur-containing compounds such as sulphur dioxide (SO_2) and dimethyl sulphide (DMS), respectively. Nitrate is formed mainly from the oxidation of atmospheric nitrogen oxides (NO_x). In the UK, since NH_3 is almost invariably in excess, sulphate is normally present completely neutralised as ammonium sulphate, very occasionally being partially neutralised NH_4HSO_4. Nitrate particularly is only formed when there is enough NH_3 to give fully neutralised ammonium nitrate. Chloride can enter particles as a result of ammonia neutralisation of hydrochloric acid (HCl) supplementing the main primary sea salt source of chloride that is present hundreds of miles from the coast. The carbonaceous fraction of the atmospheric aerosol comprises both elemental and organic carbon. Elemental carbon (EC), also called black carbon (BC), is emitted directly into the atmosphere, predominantly from combustion processes. Organic aerosol (OA) has both a primary (POA, e.g. biomass burning and combustion) and secondary (SOA) fraction. The latter process occurs when volatile organic compounds (VOCs) undergo gas phase oxidation reactions, forming products that have low enough volatility to form aerosol via either nucleation or condensation onto pre-existing particles. Recent studies of the volatility of emitted particles has blurred the distinctions between the primary and secondary organic aerosol categories, with ambient evaporation and oxidation of primary particulate emissions yielding previously unrecognised semi-volatile and intermediate volatility compounds (S/IVOC) that produce substantial additional sources of SOA.

Organic aerosol frequently forms the dominant fraction of atmospheric submicron particulate matter in the atmosphere. However, measurements indicate that models poorly predict OA concentrations. Regional and global models using "traditional" tuned SOA parameterisations form SOA mostly from biogenic VOCs and typically underestimate SOA in polluted regions by an order of magnitude or more but not for clean biogenic regions. SOA formation from additional sources has been included in models. Several box, regional and global modelling studies have explored enhanced formation of SOA from semi-volatile and intermediate volatility organic compounds (S/IVOC) from anthropogenic and biomass burning sources, finding them to be important and previously neglected regional and global SOA source. There are still substantial uncertainties in concentrations, reaction rates, and SOA yields of S/IVOC precursors. SOA formed from biomass burning precursors is gaining attention as a potentially important source, although field and laboratory studies show highly variable net addition (or loss) of OA mass by SOA formation and POA aging from this source.

The source of model underestimation of SOA is unclear, although several factors may play a role:

i) SOA remains dynamic, through both reversible partitioning and continued atmospheric oxidation. This atmospheric processing or "ageing" is not well represented in models and involves physical and chemical processes typically not accessed in the laboratory. Atmospheric mixing blends organic aerosol from various sources;

ii) laboratory SOA yields may not be representative of atmospheric conditions; recent research has revised a number of previously estimated SOA yields and identified new SOA precursors. Yields are found to be environmental condition dependent (e.g. relative humidity, acidity, NO_x levels) and can be higher than previously reported;

iii) aqueous-phase chemistry in aerosols and/or cloud droplets may play a larger role than previously thought;

iv) transfer of both inorganic and organic compounds between vapour and condensed phases is generally poorly, inconsistently or erratically represented and may be the source of significant error; and

iv) SOA formation from biogenic VOCs may vary with the level of pollutants.

The global and regional budgets of SOA are very uncertain. Top-down estimates suggest a global source ranging from 120–1820 Tg (SOA) yr^{-1}. Bottom-up estimates combining VOC emission inventories with laboratory SOA yields suggest global formation of 8–110 Tg (SOA) yr^{-1}. This uncertainty (8–1820 Tg (SOA) yr^{-1}) is very substantial. The relative contributions from anthropogenic, biogenic, and biomass burning sources are similarly poorly constrained. Studies using traditional SOA models predict biogenic SOA sources to greatly exceed anthropogenic ones, while newer models predict fractionally greater anthropogenic SOA. A high biogenic fraction appears consistent with the large fraction of non-fossil carbon detected in ambient OA. Even in polluted regions when OA is universally observed to be enhanced, substantial fractions of non-fossil carbon are found implying anthropogenic enhancement of biogenic SOA formation. Potential mechanisms for such enhanced formation include higher aerosol acidity, NO_x levels and speciation, enhanced pollution-related OA and oxidant levels and speciation. Doubling of biogenic SOA by pollution in the US was predicted primarily resulting from enhanced biogenic VOC oxidation with increased NO_x, and through anthropogenic POA availability for biogenic species condensation. Not all of the non-fossil carbon is biogenic, with significant biomass burning, biofuel and non-fossil urban OA contributions.

As mentioned above, secondary aerosol particles are generated by the transfer of material from the gaseous to the condensed (i.e. solid and/or liquid) phase following the chemical processing of emitted gaseous precursor compounds, which may originate from both anthropogenic and biogenic sources. A number of processes therefore contribute to secondary aerosol formation, including the emission of precursor species, their oxidation and subsequent multiphase chemical and physical processes. In the following sections, the current state of knowledge of these processes is summarised for both secondary organic aerosol (SOA) and secondary inorganic aerosol (SIA).

This section is framed loosely around a number of fundamental questions of direct impact to UK Air Quality and hence of interest for policymakers. The answers to the questions will benefit understanding of the degree to which control of secondary aerosol is possible, the means by which such control may be achieved and the implications on future legislative compliance. The evidence enabling the questions to be addressed is provided in Annex A.

The objective of Annex A is to **Explain the current sources of SOA and SIA as currently measured in the UK atmosphere, including the identity and spatial distribution of precursors, taking account of both annual average and episode conditions**.

Annex A is based around a lifecycle description of secondary aerosol and provides a comprehensive summary of the fundamental basis for the current state-of-the-science relating to atmospheric SIA and SOA. Largely following the model successfully employed by Defra to develop the quantitative understanding of secondary gaseous pollutants, it includes identification and description of the emitted precursors that lead to the formation of SOA and SIA, and provides an overview of current understanding and representation of their emissions, including gaps and uncertainties. It covers anthropogenic and biogenic sources within the UK and EU, their spatial and temporal variability, and the classes and speciation of emitted SOA precursors. The Annex incorporates our own knowledge and studies reported in the literature, and draws on information from a number of sources, including the

National Atmospheric Emissions Inventory, NAEI, for UK anthropogenic emissions, the European Monitoring and Evaluation Programme, EMEP, for wider European emissions. For biogenic organic emissions, account is taken of a number of studies relevant to the UK and EU for information on biogenic VOCs. The section also reviews current understanding of the chemical and physical processes that convert the emitted precursors into SOA and SIA, including gaps and uncertainties. This includes consideration of chemical processes occurring in the gaseous and aerosol phases, and gas-to-aerosol transfer processes. The review information incorporates knowledge and studies reported in the literature, and draws on information from expert review groups. There are important differences between secondary gaseous and particulate pollutants related to precursor identification, phase transfer and process complexity that will be covered.

Specific questions of direct impact on Air Quality and hence of interest for policymakers:

1. What are the SIA / SOA precursors?

SIA: Measurements in the UK show that SIA almost solely comprises fully-neutralised sulphate (SO_4^{2-}) and nitrate (NO_3^-); predominantly ammonium sulphate, $(NH_4)_2SO_4$, and ammonium nitrate, NH_4NO_3, but with some sodium nitrate (and possibly a small amount of sodium sulphate) formed by acid displacement from seasalt under marine influenced conditions. The major sulphate aerosol precursors are oxidised sulphur, emitted mainly as sulphur dioxide (SO_2), with some additional reduced sulphur emission contributions, mainly as dimethyl sulphide (DMS, CH_3SCH_3) (A1.2.1). The major nitrate aerosol precursors are nitrogen oxide (NO_x) emissions, made up of nitric oxide (NO) and nitrogen dioxide (NO_2) (A1.2.1). The ammonium aerosol precursor is emitted ammonia (NH_3) (A1.2.1; A2.2.3). Hydrogen chloride (HCl) may play a role as an SIA precursor under specific conditions, through reaction with NH_3 to form ammonium chloride, NH_4Cl, aerosol (A1.2.1; A2.2.3).

SOA: The emitted precursors to SOA formation are gas phase organic compounds. Larger and less volatile emitted molecules are generally better at making SOA. There are both man-made and natural emissions of SOA precursors, which can be classified as "conventional" and more-recently identified "unconventional" precursors. Anthropogenic sources of conventional SOA precursors identified in a wide range of chamber studies include mono-aromatic compounds such as benzene, toluene, xylenes and trimethylbenzenes. VOCs vary widely in their SOA formation potential and SOA formation from anthropogenic precursor emissions is highly sensitive to their speciation (A1.1.2.2). Relatively recently, "Intermediate volatility" and "Semi-volatile" organic compounds (IVOCs and SVOCs) have been shown to require little ambient oxidation to produce components that will form SOA and more readily do so, with higher mass yields and comprise the large part of the unconventional precursor class (A1.1.5). A range of volatility of components can be formed in the oxidation of both anthropogenic and biogenic emitted compounds. Anthropogenic IVOCs and SVOCs include normal alkanes in the approximate ranges C_{13} to C_{16} and C_{17} to C_{26} respectively and polycyclic aromatic hydrocarbons (PAHs) of greater than 2 and 3 rings respectively. Conventional biogenic SOA precursors include monoterpenes and possibly isoprene (A1.1.3). Both have been studied in chamber experiments, with monoterpenes widely ranging in reactivity and SOA formation potential, but all generally more efficient SOA precursors per unit mass emission than the low yield isoprene. There is some evidence that smaller relatively volatile water-soluble oxygenated molecules such as glyoxal may play a role in SOA formation through aqueous processes in cloud droplets or deliquesced particles. It is thought that larger molecular mass components that are frequently present in the organic fraction originate from smaller molecules that undergo condensed phase accretion reactions, though the exact identity of these smaller molecules is unknown. "Unconventional" biogenic SOA precursors include sesquiterpenes and green leaf volatiles (A1.1.3.2). Sesquiterpenes themselves generally fall into the IVOC volatility category and many early

generation products of their generally rapid oxidation can readily condense to form SOA. The effectiveness as SOA precursors of green leaf volatiles is more variable and generally less-well quantified.

There are substantial uncertainties in the identity and emissions of both anthropogenic and biogenic gas phase compounds that may be effective SOA precursors. Considering the larger SOA precursors, whilst inventories of NMVOCs may be relatively comprehensive in terms of their carbon budget, a fraction of the mass from only a small subset of components will contribute to SOA. These are largely difficult to measure and not in current inventories. Smaller soluble oxygenated molecules that may act as aqueous SOA precursors are formed by gaseous fragmentation of very many VOCs. Mechanistic quantification of the process is unavailable and hence the strength (and associated uncertainties) of the relevant emission sources is not quantifiable.

There is a high priority requirement for identification, representation and assessment of the role of "unconventional" SOA precursors such as IVOCs and SVOCs, their emissions, concentrations and SOA forming potential

There is a requirement to evaluate the relative contributions of gaseous and aqueous SOA formation pathways

2. What are the current precursor emission sources which result in SOA and SIA formation (both regional and transboundary – note the UK, EU and non-EU contributions and the biogenic & anthropogenic, conventional and "unconventional" splits)?

i) **SIA:** The sources of major SIA precursors (SO_2, NO_x and NH_3) are much better constrained than SOA precursor sources with UK emissions according to the NAEI (http://naei.defra.gov.uk/) accounting for 10%, 13% and 8% respectively of the EU-27 emissions in 2010 according to EMEP (http://www.emep.int/). Inventories represent emissions in up to 12 source categories. SO_2 and NO_x emissions are dominated by combustion; mainly power generation for SO_2 and power generation and road transport for NO_x. NH_3 is dominated by the agricultural emissions (including animal waste and use of fertilisers), with contributions from waste (e.g. from anaerobic digestion of organic waste) and combustions (e.g. road transport). UK and EU-27 SO_2 and NO_x emissions show a downward trend resulting from EU control measures, with continued projected future reductions. NH_3 emissions show little projected trend. Presenting in molar terms, NH_3 is already the most abundant emitted SIA precursor in the EU-27, and is projected to become the most abundant UK SIA precursor by 2020. NAEI mapped UK emissions by source sector are available at 1 km x 1 km and EMEP domain emissions at 50 km x 50 km resolution both generally sufficient for sulphate and nitrate prediction (though not for primary pollutant emissions close to a receptor), owing to the time and distance scales required for SO_2 and NO_x oxidation. NH_3 emissions possess a large spatial variability and the consequences of its influence on SIA formation through direct reaction on a short timescale is discussed in response to question 12. Uncertainties in emission spatial variation in order of decreasing mapping quality is reported as: SO_2 > NO_x > NMVOCs > PM_{10} > NH_3. It is not straightforward to compare areal emissions to draw conclusions about the relative impacts of UK and non-UK anthropogenic emissions on SIA formation, which requires incorporation of emissions data in appropriate models (A1.2.2.1, addressed more fully in Annex C). Uncertainties in the 2010 UK emissions totals are estimated as ± 4 % for SO_2, ± 10 % for NO_x and ± 20 % for NH_3, with suggested additional uncertainties of about ± 1.7 % for SO_2, ± 7 % for NO_x and ± 7.5 % for NH_3 for 2030. Natural and biomass burning emissions of SIA precursors are generally smaller and more sporadic than anthropogenic emissions. They include marine emissions of DMS, volcanic emissions of SO_2, NO_x produced by lightning, soil emissions of

NO_x as NO and biomass burning emissions of SO_2, NO_x and NH_3, and are detailed in Annex A.

ii) **SOA:** The emissions of most "conventional" SOA precursors are relatively well-quantified in UK and EU inventories. Almost half the anthropogenic UK VOC emissions fall into the "solvents and other product use" category, with notable "fugitive emissions" and "industrial processes" contributions. Although historically a major contributor, road transport emissions are estimated as only about 6 % of the 2011 total. Unconventional IVOCs & SVOC SOA precursors are emitted from both anthropogenic and biogenic sources. Conventional biogenic SOA precursors include monoterpenes and possibly isoprene. However, there is no evidence for SOA from isoprene from measurements in the UK atmosphere. There is isoprenoid tropical atmospheric SOA above the Amazon and Bornean rainforests; however, North America is the only temperate location where there is solid evidence that it contributes. Methods available to estimate biogenic VOC emissions have allowed them to be speciated into isoprene, monoterpenes and other VOCs, with sesquiterpenes becoming increasingly reported. Emissions of biogenic VOCs possess substantial spatial variations across Europe (A1.1.3.3), resulting from variations in land use and conditions (e.g. temperature). Uncertainties in the spatial variation of the VOC emissions are generally not quantified and reported. Mean annual biomass burning VOC emissions for Europe are less than 1 % of the annual anthropogenic VOC emissions for the EU-27. However, because of their sporadic nature, biomass burning events can have short-term impacts on UK air quality.

The relative daytime (via HNO_3 uptake) and night-time (via N_2O_5 hydrolysis vs Cl^- reaction) contributions to aerosol nitrate are poorly constrained by measurements; the interactions with meteorology (in particular to vertical temperature and RH profiles) will vary substantially between the processes.

Whilst the nitrate contribution to $PM_{2.5}$ from acid displacement in seasalt aerosol will likely be modest, nitrate in the coarse aged seasalt mode may be substantial and make sporadic marine contribute to "pollution" episodes as characterised by PM_{10}.

Owing to our inability to fully reconcile the non-linearity in sulphate reduction with SO_2 emission reduction, there is a requirement to more comprehensively understand the controls on SIA, with particular emphasis on the magnitude of aqueous sulphate production and the roles of NH_3 (see section C).

It is not straightforward to draw conclusions about the relative impacts of UK and non-UK anthropogenic emissions on SIA or SOA formation, for which incorporation of emissions data in appropriate models is required. The interpretation of model simulations of SIA and SOA is covered in section C.

The overall uncertainty in the NAEI anthropogenic VOC speciation has not, to-date, been quantified. Combined with highly uncertain propensity for SOA formation of individual precursors, even for "conventional" sources, uncertainties in the profiles of the effective SOA precursors preclude quantitative apportionment across geographical boundaries.

It is likely that emissions of species that contribute to the IVOC and SVOC burden are the least well characterised in the NAEI, because they tend to be made up of small contributions from each of a very large number of species which cannot be resolved by traditional analytical techniques.

There is a need to represent the high spatial and temporal variability of NH_3 emissions, and to evaluate the effect of such variability on SIA formation.

Evaluation of the source strengths of SIA precursor emissions and their trends, through concentration and flux measurements should be made.

Model evaluation to the sensitivity to uncertainties in the emissions of SIA precursors should be conducted to evaluate process skill by comparison with current measurements and provide confidence in scenario projections

Model evaluation (and if necessary representation improvement) of SIA processes is required to reproduce the responses of sulphate to reduced SO_2 emissions and fully resolve the contributory processes with particular attention to the representation of gaseous vs. aqueous sulphate production

Model-measurement comparison and evaluation of vertical profiles of SIA and precursors is required in order to constrain transboundary and UK sources and resolve elevated vs. surface level loadings

Improved measurement constraint of the night-time and daytime oxidised nitrogen budget is required for model evaluation

Model-measurement comparison and evaluation of the concentrations of $NaNO_3$ in marine, non-marine and episode conditions to establish the contribution of aged seasalt

Characterisation of NO_x emissions from international shipping, which are projected to make an increasing European contribution, should be improved

Reliable and consistent representation of the emissions of biogenic VOCs needs to be used in modelling and assessment studies aimed at quantifying SOA formation

An assessment of the reliability of estimates of IVOC, SVOC, GLV and conventional precursor effectiveness is required, with chamber measurements under representative conditions where necessary

Evaluation of the speciated source strengths of anthropogenic VOC emissions through ambient concentrations and flux measurements should include larger and lower volatility species (IVOCs and SVOCs) than are routinely measured by the hydrocarbon network, and should aim to verify contributions from sources additional to road transport (e.g. solvents and other product use)

IVOCs and SVOCs must be fully represented in inventories, or separate inventories for IVOCs and SVOCs should be developed, even if these are at a simplified carbon number level

Enhanced knowledge of the fraction of IVOCs and SVOCs in POA and their transfer between phases is important to a fuller understanding of SOA formation

A more complete speciation of biogenic VOC emissions is required. This should include (i) speciation within the monoterpene class; (ii) better characterisation of OVOC (including GLVs) speciation; and (iii) inclusion of high-yield SOA precursors (e.g. sesquiterpenes) that are not always represented

Improved characterisation and quantification of the emissions of organic compounds from domestic burning of biomass for heating

3. What do we understand about BSOA and what drives BSOA precursor emissions? Can the UK do anything to control these emissions?

Both regional and global models using "traditional" chamber-tuned SOA parameterisations form SOA mostly from biogenic VOCs and typically do fairly well in clean biogenic regions but underestimate SOA in polluted regions by an order of magnitude or more. Recent evidence indicates that SOA formation from biogenic VOCs may be more efficient in polluted air implying anthropogenic enhancement of biogenic SOA formation. Non-linear interactions between reductions in either NO_x and anthropogenic VOCs, or both, and biogenic $PM_{2.5}$ SOA might be expected owing to the effects on gaseous oxidants and pre-existing condensation sink of particles. Emissions rates of biogenic VOCs are sensitive to the type and quantity of vegetation, season and conditions such as temperature, light and soil moisture. As a result the emissions rates are highly variable both spatially and temporally (A1.1.3). The relative importance of biogenic emissions is greater during the summertime, with an average emissions rate approaching 40 % of that due to anthropogenic NMVOC emissions, but much higher in terms of reactivity and SOA production potential (A1.1.3.1). Particle condensation will be reduced and evaporation enhanced at higher temperatures, so offsetting some of the SOA formation by SVOCs.

Unlike the situation for anthropogenic VOCs, there is no central source of information for biogenic VOC emissions in the UK or Europe, although various estimates have been reported (A1.1.3). Because of the very large spatial and temporal variability of the emissions and their lack of meaningful speciation, annual totals are of relatively limited value for modelling applications, although they do allow broad comparisons of the relative emissions of VOCs from biogenic and anthropogenic sources, and how this varies between the UK and Europe as a whole (A1.1.3.1). The estimates from the different studies cover a range of about a factor of four in annual total emissions. The variability provides an initial indication of the level of uncertainty in estimating the annual totals, but is not particularly useful because of the lack of speciation available (A1.1.3.1).

Owing to the lack of data relating the emissions of highly effective biogenic SOA precursors to the factors determining their release, effective control methodologies are unclear.

The most effective BSOA precursors weighted according to their emissions are unknown and should be identified. The factors controlling emission of these precursors are similarly unknown. Without such knowledge there are few ways to control emissions. Identification and quantification is a high priority.

Many green leaf volatiles (GLVs) are released when plants experience mechanical damage (A1.1.3.2), such as grazing or cutting. As such are a class of biogenic compounds over which there is some potential to exert policy controls. The potential for control should be evaluated in the context of studies investigating the SOA production potential and speciated emissions of individual components

The anthropogenic-biogenic interaction processes are poorly understood and require further investigation in order to be included in models

4. Do we understand the processes leading to SOA formation, transformation and fate? Is this the right place for simplification (e.g. VBS, 8-product, 2-product approaches) to start from (if not, how do we get to the right place)? What are the most

promising routes forward for developing accurate predictive capability for incorporation in air quality models?

A2.3.2.1: There are a number of fundamental uncertainties in our understanding of processes related to SOA formation (largely covered in this section above and detailed in Annex A) that preclude quantitative prediction in the real atmosphere at the present time. It is clear that near-explicit bottom-up models of VOC degradation driven by current anthropogenic VOC inventories underpredict SOA in the UK by orders of magnitude. It is not clear that completely explicit models of gaseous oxidation even driven by perfect, fully-comprehensive emission inventories would capture the carbon flux to the condensed particulate using the commonly used equilibrium partitioning approach, for the reasons outlined in Annex A. However, the more explicit representation of the oxidation of a more comprehensive coverage of emitted organic compounds will inevitably improve the predicted flux of potential condensable oxygenated products.

Rather than assuming instantaneous equilibrium of condensing organic compounds to the total mass of particulate, representing their transfer to an evolving particle distribution is more physically reasonable and more consistent with the treatment of inorganic vapours in the most realistic models. Such an approach, including the most important precursors, promises real predictive capability once sufficient constraint is placed on fundamental properties (vapour pressures, activities etc) and possible reactions in the particles. In the first instance this must be for systems much simpler than the UK atmosphere, such as chamber systems since the state-of-the-science in secondary aerosol formation can be likened to that of gaseous oxidation several decades ago.

Unfortunately, given that the secondary carbonaceous mass present in the condensed phase is a very small fraction of gaseous material oxidised, it is very likely that important condensing molecules will never be captured explicitly with sufficient accuracy (either in the inventories or the degradation mechanisms or both). A further difficulty with the explicit representation of condensation of organic components is the computational expense. Large-scale models cannot carry complex representations of SOA formation with thousands of individual gas phase compounds, and reactions between all of these within the particles.

However, there have been a number of important developments of promise that have a good chance of aiding SOA prediction in the short- and medium-term. The identification of IVOCs and SVOCs as "unconventional" but very effective SOA precursors has led to the possibility of their inclusion in empirical SOA treatments in an extension of the way chamber-tuned mechanisms have previously used the equilibrium partitioning approach. These semi-empirical approaches (e.g. lumping by volatility such as the VBS) can be linked to existing gas phase mechanisms supplemented by appropriate emitted parent IVOCs and SVOCs. Whilst none of the semi-empirical approaches capture the important evolving chemical functionality of aerosol particles (or feedbacks on the gas phase chemistry), they can be linked to kinetic treatments of particle evolution and condensed phase reactions or changes of particle phase can be accounted for by parameterisation. The approach is sufficiently flexible that emerging understanding can generally be accommodated or the approach extended, such that the tuners become more faithful to the underlying processes.

Since more "conventional" (chamber tuned) model performance is generally more reasonable in clean biogenically-dominated regions, it is more likely that the overall reactivity and SOA production potential from chamber experiments can be extrapolated more satisfactorily for biogenic emissions. It is, of course, quite possible (even probable) that this result is a fortunate "coincidence". In any case, inclusion of highly reactive known effective precursors such as sesquiterpenes (themselves IVOCs) and other potential candidates such as GLVs in models at any level of simplification can only improve their physical basis, if not

their skill. Incorporating them in flexible semi-empirical approaches is guaranteed to improve the skill.

Ultimately, absolute faith in a model representation of SOA processes will require an explicit treatment of all the important processes. Such models will be useful in the medium term i) in testing out process knowledge of the SOA systems in chamber experiments, ii) for testing the simplifications discussed above on reduced complexity systems and iii) for deriving simpler traceable mechanisms, much as has been done for gaseous degradation mechanisms. They will eventually be useful for atmospheric predictions in air quality models.

There is a pressing requirement for air quality models to predict SOA mass loadings in the UK atmosphere with reasonable skill and to make reliable future projections.

One method to achieve this, following the successful example of gaseous oxidation mechanisms, is to require traceability to, or evaluation against, explicit and accurate models of the determinant processes.

Development of highly detailed representations of the oxidation chemistry of emitted VOCs, IVOCs and SVOCs is required to provide the basis for reference simulations that faithfully capture dependencies of gaseous precursor concentrations. This will require development and application of methodologies for the automated generation of such highly detailed representations.

The details of transfer of organic material to, and from, the particulate matter in an evolving aerosol distribution must be captured in appropriate dynamical frameworks, informed by appropriate laboratory data and coupled to an explicit gas phase scheme, since SOA components evaporate as well as condense, both processes taking finite time.

In the short term, tuned methodologies that most readily capture SOA mass based on our best knowledge of "unconventional" IVOC and SVOC precursors are required in air quality models. They currently exist coupled to specific gaseous mechanisms, but require development of appropriate precursor inventories, probably requiring new measurement technologies (see Annex B).

In the short-term, semi-empirical approaches should be coupled to the most appropriate UK gaseous schemes.

Pathways for aqueous SOA formation are currently unclear and too poorly constrained by measurement to allow clear recommendation

Systematic reduction of detailed gas phase schemes appropriate for coupled representations of SOA formation is required

# B.	Knowledge about secondary aerosol derived from measurements

This section summarises the measurement-derived evidence related to secondary aerosol. So far as possible, definitive conclusions are drawn from long-term operational measurements made across the UK (and European) network sites. However, owing to the lack of routine quantitative $PM_{2.5}$ SIA and SOA measurements and the interpretation challenges related to the state of our fundamental understanding and associated uncertainties, evidence is supplemented by measurements made on a more intensive case study basis under research conditions.

The section is framed loosely around a number of measurement-related questions of direct impact to UK Air Quality and hence of interest for policymakers. The answers to the questions will benefit understanding of the degree to which control of secondary aerosol is possible, the means by which such control may be achieved and the implications on future legislative compliance.

Annex B provides a comprehensive summary of the current technological state of the art relevant for the study of atmospheric SIA and SOA, including a description of measurement techniques and some of the data analysis methods, along with recent findings. The interpretation of secondary aerosol processes requires measurements beyond those that are routinely deployed to develop our fundamental understanding as detailed in section A and provide constraint required for the models outlined in section C. These are also detailed in Annex B, subsection B1. This section is largely drawn from the evidence provided in Annex B subsection B3, referring to measurement techniques described in B1 and numerical interpretation tools described in B2.

The objective of Annex B is to **Review the current measurements of SOA and SIA in the UK atmosphere, accounting for spatial distribution, site type and measurement technique, and consider what future measurement strategy would best inform the understanding of SOA and SIA formation / concentrations**.

Annex B is delivered in three subsections:

Subsection B1 covers the current in-use measurement techniques. Various instruments exist for the quantification of the aerosol components that make up SIA and SOA. In addition to offline (i.e. not automated) methods, multiple techniques exist for the automated, online quantification of aerosol composition with a high time resolution (1 hour). In addition, techniques for advanced offline analysis (to inform fundamental understanding) are also summarised. The only gaps in the technology identified are the lack of measurements of the semivolatile fraction. The current UK DEFRA network capability is summarised in terms of the available instrumentation. Currently, only four sites (Harwell, Auchencorth Moss, North Kensington and Marylebone Road) are adequately equipped to make reasonable assessments of SIA and SOA, with room for improvement at each.

Subsection B2 covers the data analysis methods used to process the data generated to estimate SIA and SOA based on the measurement data. No instrumental technique is capable of directly quantifying primary and secondary particulate matter. For SIA, this quantification is relatively straightforward with few assumptions necessary, however this is not as straightforward for SOA. Techniques are summarised for the apportionment of OA to primary and secondary sources, the main ones being the application of positive matrix factorisation (PMF) and EC tracer techniques dependent on the measurements used in the analysis, however neither of these techniques can claim to be completely accurate or unambiguous.

The limitations of these techniques are discussed. There are also techniques to further apportion the SOA according to the types of precursor VOCs, using either organic tracers or carbon isotope analysis, however these too have limitations. Recommendations include the complementation of aerosol measurements with a suite of other measurements to reduce ambiguity and further intensive characterisation work.

Subsection B3 covers the findings from recent work studying SIA and SOA in the UK, employing the techniques covered in B1 and B2. While the data from the AGAnet network may not be absolutely quantitative, it does give UK coverage for the geographical and long-term trends in SIA. There are fewer studies into SOA and these are mainly limited to intensive measurement periods rather than long-term monitoring, which are summarised. Certain recent measurements are expanded upon, which includes measurements using the FAAM BAe-146 large research aircraft, which offers insights into transboundary pollution and vertical distribution of secondary aerosol components, and the recent ClearfLo intensive measurement campaign in London in 2012, which also included a year-long aerosol mass spectrometer dataset. These results underscore the importance of nitrate in SIA and also the episodic nature of SIA and SOA events. This in turn shows the usefulness of automated online measurements in capturing such features.

Specific questions of direct impact on Air Quality and hence of interest for policymakers

5. What measurements exist? What are the spatial & temporal patterns from long-term data? Can better use be made of existing particle measurements undertaken in the UK and/or other European countries to provide further evidence of the relative contribution of SOA and SIA to PM concentrations?

Within the UK, the Delta systems (B1.1.3) used in the AGANet network (B1.7.1.3) represent good measures of the 4 main components of SIA. This provides mean annual trends dating back to 2000 and provides geographical concentration maps (B3.1). However, the inlet is uncharacterised and there is a lack of co-located $PM_{2.5}$ total mass at the majority of the sites. Furthermore, the reported monthly means from the AGANet network are unable of capturing episodic events owing to the monthly reporting frequency (B3.4.1). Currently, there are 4 sites (Harwell, Auchencorth Moss, North Kensington and Marylebone Road) running semicontinuous analysers suitable for SIA study (B1.5), of which the first 2 measure $PM_{2.5}$ SIA in addition to PM_{10} (B1.7.1).

There is no equivalent network for SOA within the UK (B1.7.1), outside of the Number and Composition network, which measures Elemental and Organic Carbon (EC/OC; B1.6.2) at four sites and has a continuous Aerosol Chemical Speciation Monitor (ACSM) at one (B1.4.2).

The UK networks alone provide little data on transboundary transport of pollutants. The Europe-wide EMEP and ACTRIS networks (B1.7.2) can be utilised to this end (B3.2), however these data must be interpreted in conjunction with regional chemical transport models (C1.5.8, C3.5.1, C3.5.2). There are also many historical NERC and Met Office-funded intensive composition studies, including both ground and aircraft based for both SIA and SOA, archived on the British Atmospheric Data Centre (BADC; http://badc.nerc.ac.uk) that can be used to develop and validate models on a case study basis (B3.2). Vertical profiles of SIA data from aircraft highlight the importance of understanding the processes and precursors involved in SIA and SOA formation and transport, with measurements at surface level are not representative of concentrations aloft (B3.2).

SIA mass is comprised almost completely of ammonium, nitrate and sulphate (B3.1) with a more minor contribution from chloride and can dominate the total $PM_{2.5}$ mass, accounting for over 69% in episodes (B3.1; B3.4). AGANet measurements (B3.1) show mean annual sulphate varying across the UK with lowest concentrations averaging <0.3 µg m^{-3} in NW Scotland, increasing to >0.9 µg m^{-3} in SE England. Nitrate generally dominates the SIA mass and shows a similar distribution but at higher concentrations ranging from <0.9 to >2.7 µg m^{-3}. The spatial distributions and levels were similar in 2006 and 2009. There has been no discernable trend in total average nitrate from 2000 to 2009, but there has been a steady decrease in sulphate in the 30 sites annual average from 1.9 µg m^{-3} in 2000 to 0.7 µg m^{-3} in 2009. NO_3^- has a clear spring peak, with lower loadings in the warmer summer and it can account for over 50% of the total SIA mass (B3.4). Sulphate shows lower concentrations in the winter months with a peak around March-April. Fractional contributions of SIA to $PM_{2.5}$ are only available where there are co-located SIA and mass measurements with $PM_{2.5}$ inlets. For Auchencorth Moss the mean monthly fractional contribution of SIA ranged from 0.25 to 0.5 (SIA mass ranging from 1 to 2.5 µg m^{-3}) in 2009, and for Harwell the monthly mean SIA fraction ranged from 0.4 to 1 (SIA mass ranging from 3 to 8 µg m^{-3}).

There is currently no way of directly measuring the SOA fraction of OA, so it must be estimated using numerical techniques, which carry inherent uncertainties (B2; B2.2; B2.4). No spatial distributions are available for SOA from long-term networks owing to the limited coverage. Similarly, there are no meaningful long-term trends that can be extracted for SOA.

Two recent year-long analyses of secondary particulate (B3.2; B3.4) have demonstrated the usefulness of the EC tracer method and the continuous Aerosol Mass Spectrometer (AMS) measurements respectively. The first, from Birmingham between 2004 and 2006, showed SOA:$PM_{2.5}$ ratios of 0.16 - 0.21 (as well as 0.27 to 0.46 SIA:$PM_{2.5}$ ratios) for roadside, urban background and rural sites. The second, urban background (North Kensington), dataset was used to derive SOA:$PM_{2.5}$ of between 0.08 and 0.25 (and SIA:$PM_{2.5}$ of between 0.22 and 0.49) for 2012. SOA is always present in the total condensed OA and can dominate the OA mass even in urban environments (B3.2; B3.3), with the ratio of SOA to total OA generally being higher in the summer than the winter. It is noteworthy that the combined, daily average secondary aerosol PM_1 mass (SOA and SIA) has been found to exceed the EU PM_{10} 24 hour directive of 50 µg m^{-3} for a polluted winter event in London in 2012, with NO_3^- contributing the majority at 34.4 µg m^{-3} (B3.4.1). SOA tends not to show a diurnal pattern (or has an extremely weak diurnal cycle), unlike the POA, which is influenced more by vehicle emissions, and (in winter), residential heating demands (B3.2). A range of UK analyses from shorter-term intensive studies (B3.2) presents snapshot evidence for SIA and SOA as a fraction of the total organic material from point locations between 2001 and 2012, but no UK spatial distribution or single-location long-term trends.

Whilst there is good coverage for long-term SIA concentrations, the number of network sites making accurate high frequency SIA measurements is limited. There are only two that measure SIA components and mass with the same inlet cutoff, limiting accessibility of the SIA fraction. The UK network capability for SOA is even more limited than for SIA, with only the four sites (as outlined above) making any long-term measurements of organic aerosol, limiting our ability to make meaningful statements about SOA trends or spatial distributions from measurements. With the paucity of data, it is important that available resources are efficiently exploited and there has been little effort to interpret UK SIA and SOA loadings measured by UK networks in terms of the transboundary contributions, utilising appropriate models validated with European network data. Furthermore, little use has been made of data from ground-based or airborne intensive case study data to interpret process contributions to UK SIA and SOA loadings.

It will benefit the move to UK compliance with EU directives on daily PM exposure levels to commit to long-term monitoring of the major secondary contributors to $PM_{2.5}$

on time scales that capture episodic events, resolving the contributors using appropriate numerical techniques. This will require use of semi-continuous or continuous analysers for inorganic and organic components with at a sufficient number of locations to obtain geographical coverage from which to generate spatial distribution trends.

Since secondary aerosol are formed from primary precursors, there is a strong need for coordination of network measurements of major primary precursors and the SIA and SOA.

6. How do fractions of SOA and SIA differ at roadside, urban, urban background and rural sites in different parts of the UK?

The fractional contribution of secondary aerosol is a complex continuum away from its contributing precursor sources in any particular airmass. The secondary fraction can vary between 30% to almost 100% of PM at urban background and polluted rural locations. There are fewer assessments of UK roadside secondary fractions published (B3.2). It is generally assumed that the roadside fraction is likely to be lower, however this will depend on the specific site and its local roadside increment and there is limited published evidence for this contention. The SIA fraction is predominately greater than the SOA fraction at all UK sites and seasons based on the limited data available. A direct comparison of the relative contribution of secondary aerosol to PM mass across types of location in different parts of the UK suffers from a paucity of appropriate measurement data, not only from network sites but even from case studies where there is limited coverage.

Only at Harwell and Auchencorth are there network data to establish the SIA : $PM_{2.5}$ fraction for long term trends. There are no network sites where similar trends for SOA : $PM_{2.5}$ can be derived directly, nor have they been indirectly derived. It is therefore not possible to evaluate the fractional contributions at roadside, urban and urban background from long-term data. There is currently a general lack of UK-based comparisons of indirect numerical retrieval even from intensive case studies for comparison between different location types and few studies in general performed in roadside locations (B3.2; B3.3)

Multi-instrument comparisons should be conducted, along with comparisons of multiple analytical techniques of co-located measurements to enable evaluation of techniques to retrieve SIA and SOA contributions to $PM_{2.5}$.

Multi-instrument measurements are necessary to characterise the SIA and SOA loadings and thereby fractional contributions. In order to evaluate the relative contributions in different environments, many more such characterisations are required, especially at a representative number of roadside locations.

7. How do SOA formation respond to changes in precursor gases, oxidant concentrations and meteorology?

It must be remembered that there is currently no way of directly measuring the SOA fraction of OA, so it must be estimated using numerical techniques (B2; B2.2; B2.4), which carry inherent uncertainties. From the available measurements, evidence for trends in SOA loading with meteorology has been reported. Specifically, dramatic increases have been observed during anticyclonic conditions in the summer months. During these conditions, observations show that levels of precursors increase as do oxidant concentration due to increase photochemical activity. However, transboundary influences contribute to the SOA loading and covariance with the meteorological conditions rather than any simple direct

causality is obviously occurring. It is clearly not possible to elucidate SOA response to changes in meteorology, precursor gases and oxidants with measurements alone and requires the use of models under particularly challenging conditions.

There are, however, a number of observational sources of evidence that can clarify the SOA response to these factors. The year-long North Kensington AMS measurements show that SOA and sulphate mass both have very weak annual trends. Increases are often associated with long-range transport of pollutants from continental Europe and neither SOA nor sulphate strongly follow nitrate (B3.1; B3.2; B3.4). Meteorology is an important determinant of secondary aerosol concentrations at a receptor site, both in terms of bringing in transported pollution (B3.2) from other regions (important for SOA and sulphate) and lower temperatures favouring semi-volatile condensation (important for certain SOA components and nitrate). SOA increases can occur *in situ* from processing under the right meteorological conditions (summer time, anticyclonic). Under these conditions, the high levels of photochemistry coupled with the build-up of pollutants in a stagnant, non-venting environment leads to an increase in SOA mass. The limited AMS data that ratio of SOA to total OM is generally higher in summer than winter months indicates that the SOA emission sources have a greater influence on the loadings than the temperature, where cooler conditions would favour condensation of vapours. However, temperature will increase both biogenic emissions and oxidation rates, so causality is not straightforward to infer. Increases can occur *in situ* from processing under particular meteorological conditions (e.g. summer time, anticyclonic), where fast oxidation chemistry coupled with the build-up of pollutants in a stagnant, non-venting environment leads to an increase in secondary aerosol mass. Furthermore, the trend is not well-reflected by the limited amount of EC tracer evidence (B3.2) so great caution is required. Modelling studies aiming to resolve the relevant secondary aerosol relationships are extremely limited, but emerging evidence suggests that there may be substantial feedbacks between chemistry and meteorological components on secondary pollutants including PM and that an appropriate treatment of such feedbacks and interactions is necessary.

There is an insufficient number of network sites that are well-enough instrumented to measure all relevant parameters to derive clear measurement-based relationships between SOA (or SIA) and precursors, oxidants and meteorology. To-date, there have been few modelling studies that have exploited the limited amount of UK network data in conjunction with European network data to unambiguously derive relationships for UK SIA and none that have reliably established such relationships for SOA. This is partly attributable to the inadequate measurements, but inadequacy of SOA treatments in models is largely responsible. There is evidence that pollution - meteorology couplings in online models predict significant differences in secondary PM to offline models and that these interactions should be fully explored.

Co-located continuous or semi-continuous measurements of SOA and of emitted precursors and parameters controlling *in situ* oxidant concentrations should be provided across long-term monitoring networks.

Model exploitation of emergent UK network data, European network measurements and intensive case study data should be encouraged using online and offline models in systematic investigations of long-term SOA (and SIA) relationships under varying conditions.

8. How are fractions of organic aerosol (OA) defined / inferred from measurement data (e.g. SOA, biomass burning organic aerosol (BBOA), cooking aerosol (COA) and hydrocarbon aerosol (HOA)) and how reliable are these procedures in estimating these fractions?

Whilst it is possible to quantify OA, there is no measurement technique that directly quantifies the different fractions of OA so far as they relate to source. This is particularly true of the SOA contributions, owing to their pathways to formation from the diverse contributions of condensing vapours, such that conservative tracer methods are not generally applicable to secondary components. To a degree, this is also true for the primary components where there is an incomplete availability of unambiguous tracers (B3.1). Various numerical techniques to quantitatively estimate the different fractions exist, principally Positive Matrix Factorisation (PMF), Elemental Carbon Tracer (ECT) and Primary Organic Tracer methods (POT), such as chemical mass balance (CMB). These techniques carry inherent uncertainties detailed in B.2. While each technique has been employed in the UK, there are few publications featuring systematic comparisons between the techniques (B2.2; B2.4.1). Confidence in any output can be increased by comparison with other co-located measurements.

No instrument is capable of directly quantifying primary and secondary organic components as separate entities nor, therefore, capable of directly attributing secondary components to discrete sources. Combinations of techniques are more powerful, but ambiguity will always remain in quantifying SOA. Modern numerical techniques markedly improve the resolving capabilities, but the limitation must be recognised. There are very few available datasets (from Birmingham and London only for relatively short durations) from which to derive fractional contributions to OA using available numerical techniques with a particular lack of studies at roadside locations (B3.2; B3.3).

Establishment of long-term OA measurement capability at more network sites is necessary to reliably infer the fractional contributions to the UK atmosphere, with particular attention paid to collocated measurements of both gas phase and particle phase tracers

Particle phase tracers could be obtained through general purpose organic analyses on filter samples obtained through the existing networks (B1.2; B1.7.1)

To increase confidence in these estimates, more systematic comparisons between available numerical techniques need to be performed within the UK to supplement the few currently available (in particular emphasising roadside locations)

9. What are the current areas of uncertainty / disagreement regarding the measurement and/or estimation of the relative contribution of SOA and SIA to PM concentrations?

The UK measurement network is a useful resource that could be appropriately instrumented to address many of the measurement-related secondary aerosol challenges. Currently, the lack of data and lack of intercomparison between retrieval techniques preclude any estimate of the uncertainty and disagreement in loading, but there is the potential to make appropriate measurements to make such an evaluation with the network infrastructure (B1.1.3, B1.7.1, B3.1, B3.4.1).

Currently, the UK network capability presents five major areas of limitation / uncertainty:

i) a lack of co-located $PM_{2.5}$ total mass measurements with the SIA measurements, only 4 sites (Harwell, Auchencorth Moss, North Kensington and Marylebone Road) running semicontinuous analysers suitable for SIA study, of which only the first two measure $PM_{2.5}$ SIA in addition to PM_{10} (B1.5, B1.7.1);

ii) a lack of representative SOA measurements across the UK, with only 4 sites capable of measuring OA by offline the EC/OC technique (Harwell, Auchencorth Moss, North

Kensington and Marylebone Road) which, in itself is incapable of distinguishing SOA components, along with one ACSM instrument at North Kensington (B1.4.2, B1.6.2, B1.7.1);

iii) a lack of characterised and consistent size selective inlets, especially for the Delta system used in AGANet;

iv) uncertainty associated with estimating SOA. Since it cannot be measured and distinguished directly, the SOA contribution must be estimated numerically with the (quantifiable) uncertainties associated with the techniques, as discussed above (B2.2, B2.4.1);

v) low time resolutions (days or longer) of many measurements leads to missed episodic events. Long term trends in total SIA mass are accessible through AGAnet, however, the uncharacterised inlet and low time resolution of the Delta system means it is not possible to obtain quantitative data relevant to $PM_{2.5}$ and it is not able to study episodic events.

The widespread network use of semicontinuous analysers (both inorganic and OC/EC) with reliable characterised inlet or ACSM[2]s, coupled to a comparison of numerical analytical techniques, is essential in identification of areas of uncertainty / disagreement in derivation of the relative contribution of SOA and SIA to PM concentrations.

10. What additional measurements could the UK undertake to improve its understanding of secondary aerosol formation / emission precursors?

There is a low capability for measuring secondary aerosol components across the network at present. Where there is the capability, there is sometimes simultaneous measurement of complementary measurements required for interpretation. Technique availability varies across the network, but frequently includes offline measurements with long integration times. There is no routine measurement of SOA properties that can relate the components to likely production processes for comparison with models. The emission of SVOC and IVOC components and the importance of component volatility in the formation of SOA make measurements of particle component volatility a promising route towards characterising likely SOA sources.

Many of the network sites have no capability for measuring OA or SIA. Where there is the capability, there are frequently inadequate supplementary measurements such that only incomplete interpretation is possible. Few measurements are made by automated continuous or semi-continuous methods with high time resolution. Owing to the likely inability to explicitly model SOA formation in the foreseeable future and emerging recognition that volatility of emitted precursors is likely the dominant driver, it is necessary to measure aerosol volatility with appropriate time resolution for model constraint and model-measurement comparison. Suitable techniques for such measurements are not immediately available.

Increase the number of sites making measurements of SOA. This will be ideally through more than one of the following techniques: EC/OC, ACSM, speciated offline organic analysis (for both process-level understanding and SOA budget quantification via CMB)

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[2] It should be noted that the ACSM does not currently measure $PM_{2.5}$, and transmitting and measuring components closer to PM_1 (B1.4.2; B1.7.1) which will present challenges to interpretation in the context of the $PM_{2.5}$ criterion until an appropriate inlet is available.

Additionally, it would be of great benefit to the UK capability if the current network capability was expanded. Expansion of the current Composition and Size network to include more urban and rural sites, using the instrumentation recommended above. This can be achieved by upgrading sites within existing networks such as AGANet and AURN with their historical aerosol composition and PM$_{2.5}$ data

It is vital that sites used for measuring SOA should include the following to either help elucidate key processes or to reduce uncertainty in the SOA estimations: PM$_{2.5}$ mass, inorganic aerosol (including SIA) composition, primary emissions tracers, including CO, NO$_x$, BC, potassium, levoglucosan and diesel tracers, O$_3$, local meteorology

Where possible, long-term measurements should be automated, continuous and with a time resolution of hours to capture episodic events

More research-oriented intensive measurements with a focus on VOC oxidation products and the semi- and intermediate volatility organic aerosol components will facilitate this and allow model constraint where models resort to this representation to obtain sufficient mass flux to the particles

Since IVOCs and SVOCs will be partially incorporated into SOA, their measurement requires resolution in both phases. A reliable technique for routine monitoring of chemically-resolved volatility needs to be developed

C Knowledge about secondary aerosol derived from modelling

This section summarises the modelling-derived evidence related to secondary aerosol. A number of models with secondary aerosol treatments have been used for simulating air quality in the UK atmosphere. Ranging from box models running in a pseudo-Lagrangian sense driven by offline trajectories, through to sophisticated online coupled meteorology-chemistry models run on Eulerian grids, they have had varying levels of success.

So far as possible, conclusions in this section are drawn from modelling studies based around simulations of the UK (and European) atmosphere. There have been comparatively few large-scale modelling efforts with models of appropriate structural capability to comprehensively address SIA and SOA processes in the UK, so the section necessarily draws evidence from non-UK investigations as appropriate.

This section is framed loosely around a number of modelling-related questions of direct impact to UK Air Quality and hence of interest for policymakers. The answers to the questions will benefit understanding of the degree to which control of secondary aerosol is possible, the means by which such control may be achieved and the implications on future legislative compliance.

Annex C provides a comprehensive summary of the state of the art relevant for the modelling of atmospheric SIA and SOA, including a description of modelling frameworks (in subsection C1) and some of the interpretive techniques (subsection C2), along with recent findings (in subsection C3).

The objective of Annex C is to **Identify the key precursor emissions to SOA/SIA concentration relationships and likely impacts on UK secondary aerosol concentrations of possible future changes in spatially-disaggregated emissions**

Models use a range of treatments of PM$_{2.5}$, SIA and SOA, with a wide range of complexity (or conversely of simplification). They either assume a bulk mass of condensed material, or make some assumption of a dynamically-evolving distribution of particles. The latter is

obviously more physically based; the former can be considerably cheaper since with increasing complexity there is generally an increase in computational expense. Mass transfer of material between the vapour and condensed phases is similarly approximated. The simplest approaches assume that inorganic and organic components instantaneously equilibrate between phases in either the bulk or dynamically-evolving treatments. Such approaches include the simplest implementations of 2-product or VBS treatments of SOA by absorptive partitioning. More complex approaches allow mass transfer of components to an evolving distribution either of compounds explicitly generated by a gas phase oxidation mechanism or surrogates (e.g. binned by volatility) linked to one. Currently, limited knowledge of the identity and emission strength of precursors and limited understanding of the process of SOA formation prevent clear improvement in model skill from the inclusion of explicit scheme. Indeed, tuned treatments and semi-empirical approaches currently predict much more SOA than explicit schemes in better agreement with observations. Models of SIA formation are better able to capture the observed magnitude of material condensed from the vapour phase with more widespread treatment of explicit linkage to gas phase mechanisms, but there is still considerable uncertainty presented by the treatment of aqueous processes. Empirical approaches for secondary aerosol include incorporation of interpolated data from measurement sites or the use of pre-calculated source receptor relationships. Such approaches are cheap and can reasonably faithfully reproduce average behaviour, but with no process knowledge and hence poor reliability for future prediction.

Combinations of model frameworks across a range of scales can be useful in air quality predictions since it is impractical to make long simulations at high resolution over large domains. In choosing the model resolutions, there is an inevitable trade-off between ability to account for detailed local dispersion and explicit emission sources and the ability to treat larger domains incorporating local and long-range sources and transformation mechanisms across a range of timescales in larger scale models. Too coarse a resolution limits the ability to resolve concentrations of pollutants to accurately assess exposure. Increased model resolution requires increased resolution of gridded emissions. Similarly, vertical resolution and boundary layer representation is likely to be important in secondary aerosol processes, particularly for semi-volatile components, which have strong temperature dependences. There are advantages to both Eulerian and Lagrangian models. The latter are less computationally expensive, though their lack of close integration with NWP models could become increasingly important. It is increasingly possible to include complex secondary aerosol treatments in Eulerian models and there appears to be no reason not to adopt such frameworks where resolution of more realistic physics of relevance to aerosol processes is possible.

Couplings between aerosol and meteorology (only possible in Eulerian approaches) have received recent attention and coupled models (including, for example, resolved aerosol-cloud interactions and interactive wet and dry deposition) have shown up to 5 μgm^{-3} difference in UK surface level secondary PM. Recent studies have indicated possible effects of future temperature increases on planned abatement strategies with changes to parameters relevant to SOA and SIA formation that include temperature effects on reactions rates, aerosol dynamics, gas / particle partitioning and boundary layer stability and vertical transport.

Evaluating model uncertainties is important when evaluating effectiveness of control strategies for $PM_{2.5}$. Traditional brute force sensitivity analyses have been used to investigate the impact of emission abatements, typically, though not always, using trajectory models in the UK. Such 'one at a time' approaches can be accurate, but only where predictions are directly and predictably related to inputs or where more qualitative overview of effects between model components is required. Recent developments include approaches where model diagnostics are embedded within the model to extract complex source-apportionment relationships. Defining structural model uncertainties, rather than those in

model parameters, is more challenging and often relies on model intercomparisons. Owing to the large number of uncertainties in the SOA production, such methods are inevitably required in evaluating the effectiveness of control strategies.

There is apparently contradictory evidence relating to the sensitivity of SIA to emission perturbations. UK PTM studies have indicated that NH_3 emission reduction can have the largest effect in reducing levels of SIA $PM_{2.5}$ through combined impact on $(NH_4)_2SO_4$ and NH_4NO_3 with marked seasonal differences. In contrast, Eulerian modelling has found that sulphate mass loadings respond to reductions in SO_2 emissions such that they have the largest effects on reducing total UK $PM_{2.5}$ SIA, again with strong seasonal variability. Nitrate was shown to respond non-linearly to SO_2 abatement with subsequent reduced sensitivity to NO_x reductions as NH_4NO_3 formation becomes favourable and is predicted to dominate under episodic conditions. Contributions from transboundary sources are not insignificant. In European studies, it has been suggested that EU regulatory strategies should focus on reductions in NO_x rather than NH_3 as, unlike the UK, continental SIA is thought to be NO_x limited for nitrate formation. It should be noted that many Eulerian models introduce some of the primary emissions of SO_2 directly as sulphate to account for underprediction normally attributed to aqueous processes. It is unclear why this is required only in some models and is not broadly documented.

UK studies are largely focused on a limited number of measurement sites for model validation. While speciated SIA data for model constraint and comparison is becoming increasingly available, there is relatively patchy coverage and a number of remaining uncertainties associated with existing measurements (Annex B).

Predicting the effects of VOC abatement strategies on SOA $PM_{2.5}$ is extremely difficult. In contrast to SIA, these processes are highly uncertain (see Annex A) leading to correspondingly large uncertainties in their simplifications included in large-scale models. Such primitive process representation suggests that conclusions should be drawn on existing studies only with caution. While mechanistic models perform poorly with regards to total mass, they should offer the ability to better constrain composition dependencies should speciated SOA data become available (Annex B). Semi-empirical SOA models that are tuned to chamber simulations can better predict observed SOA mass, though have better skill for biogenically rather than anthropogenically dominated conditions (see Annex A). There is an implicit assumption that the yields extracted from the chamber simulations are representative of atmospheric conditions. With either mechanistic or semi-empirical model, quality of emission inventory needs improvement. Whilst precursor emission regulations generally only target anthropogenic emissions, it is essential to understand how effects of biogenic emissions affect air quality standards via their interactions with anthropogenic species. Such interaction occurs include the impact on oxidant levels (O_3, OH, NO_3) thus impacting production of semi-volatile products in the gas phase. European studies have predicted that most of the SOA mass is biogenic in origin and elimination of the biogenic sources would therefore have the largest effect in reducing SOA mass by over ~80%. Through effects on oxidant levels and pre-existing absorbing mass however, elimination of anthropogenic organic emissions would reduce SOA by less than~20%.

Specific questions of direct impact on Air Quality and hence of interest for policymakers

11. What is the relevant significance of SOA and SIA precursor emission sources now and in the future?

SIA (C2.2, C3.5, C3.5.1.1): Observational evidence coupled to limited modelling studies suggests that reductions in SO_2, NO_x and NH_3 have resulted in non-linear reductions in

particulate sulphate, nitrate and ammonium. Such non-linear responses are captured to varying degrees in models and so future predictions are divergent. The confidence with which we can predict these non-linearities is related to our fundamental understanding of the SIA formation, transformation and loss processes. Modelling evidence appears contradictory. Eulerian studies using WRF-CMAQ found that reduction in SO_2 can have the largest effect in reducing levels of SIA $PM_{2.5}$ in the UK. Nitrate responded non-linearly to SO_2 abatement and dominated in future scenarios, leading to SIA loading becoming less sensitive to SO_2 reduction. The reduction in sulphate led to conditions favouring NH_4NO_3 formation with low NO_x emission reduction sensitivity. In this study, reducing NO_x and NH_3 had the smallest effects on PM loadings. It should be noted that many Eulerian studies have emitted a fraction (from 1.2% to 5%) of SO_2 as primary sulphate to account for underprediction attributed to missing aqueous processes (C3.5.1). It might be expected that there will be large sensitivity of SIA to SO_2 perturbation in such studies. Contributions from transboundary sources are not insignificant. European simulations using the Eulerian PMCAMx model suggested that EU regulatory strategies should focus on reductions in NO_x rather than NH_3 as, unlike the UK, continental SIA is thought to be NO_x limited for nitrate formation. In contrast, UK PTM work has suggested that reduction of NH_3 emission by 30% can have a larger effect than reducing NO_x, SO_2, VOCs or CO in reducing levels of SIA $PM_{2.5}$ through combined impact on $(NH_4)_2SO_4$ and NH_4NO_3 with marked seasonal differences. Sulphate mass concentrations responded linearly to SO_2 emission reduction and increased slightly as NO_x emissions decreased. Nitrate non-linearly reduced with reducing NO_x emissions owing to competing changes in gas phase HNO_3 production, but linearly reduced with NH_3 emission reduction. Further PTM work reported that the recent reduction in SIA is attributable largely to a fall in the sulphate concentration, with low sensitivity of nitrate to the NO_x emission reductions that have occurred and an increase in nitrate from decreasing SO_2 emissions (consistent with the very small recent changes in UK nitrate, despite substantial reduction in NO_x emissions). Further SO_2 abatement increased the NO_3^- contribution and reduced NO_3^- sensitivity to further NO_x emission reduction. A projected reduction in SO_2, NO_x and NH_3 of 64%, 75% and 96% led to a reduction of 2 μgm^{-3} of SIA. NAME studies found little effect on NH_4NO_3 of increased and decreased NH_3 emissions by 30%, finding NH_3 emission reduction by a factor of ten did produce a dramatic reduction but an increase by a factor of ten did not have such a significant effect. Depending on the model treatment of aqueous processes, reductions in NH_3 can induce large sensitivities for predicted particulate sulphate due to the effect of NH_3 on balancing acidity of in-cloud production when accounted for in models.

SOA (C.3.4, C3.5.2.1): Any abatement in anthropogenic VOC emissions might be expected to have an indirect impact on subsequent biogenic aerosol productions through the availability of oxidants and the removal of ASOA on which BSOA precursors can condense. Models suggest that there will be non-linear interactions between reductions in either NO_x or anthropogenic VOCs, or both, and $PM_{2.5}$ SOA. Depending on the model representation and tuning, reductions in NO_x have been predicted to specifically increase SOA derived from α and β-pinene whereas anthropogenic SOA have been predicted to have greatest response to a projected 30% reduction in both NO_x and anthropogenic VOCs. This obviously depends on the process dependencies hardwired into the model. Non-UK Chemistry-climate feedback studies suggest that an increase in temperature can significantly increase biogenic VOC emissions and ozone concentrations, raising biogenic SOA by around 35% across Europe.

There is an inconsistency in existing model representation of SIA processes and it is unclear that we quantitatively understand the reasons for the non-linearities in the response of the SIA loadings to reduced precursor emissions. Limited one-at-a-time perturbation studies have been conducted. However, systematic evaluation of the predicted SIA response across the possible range of conditions (and uncertain parameters) needed to understand the response to precursor emission changes has not been reported.

There are no untuned model representations of SOA that can replicate mass loadings. Explicit SOA models are not envisaged in the short or medium term. Accordingly it is unclear whether any of the determinant dependencies are captured in any model. Tuned models can give very different predicted sensitivities to changed environmental conditions. This gives little to no confidence in future predictions.

No UK chemistry-climate feedback studies using coupled models have been carried out for **the UK.**

There is an urgent need to understand, if not reconcile, the divergent predicted dependencies of SIA on precursor emissions. Well-constrained model-measurement intercomparisons with accurate representations of SIA processes are required to replicate the spatial and temporal variation in loadings and to give confidence in future predictions of non-linear SIA responses to emissions.

For accurate prediction of sulphate loadings, cloud processes must be well represented at an appropriate scale. Model emission of primary sulphate should be clearly reported and considered when attributing emission sensitivities.

Further chamber studies are required to probe the sensitivity of BSOA to anthropogenic VOC reductions and of both ASOA and BSOA to NO_x reductions in mixed precursor chamber experiments. Models with a range of SOA representations should be evaluated against the observed dependencies.

A high priority recommendation is to explore the parameter sensitivity of SOA predictions using a range of representations. This will help to identify those that behave most physically in e.g. reproducing observed trends, capturing observed loadings and covariances (e.g. establishing whether the modelled SOA varies more like modelled NO_3^- or SO_4^{2-}).

In the absence of coupled chemistry-climate studies, a minimum requirement is to conduct BSOA precursor perturbation studies for the UK with the most physically reasonable SOA model available.

12. If the UK wished to reduce PM concentrations, reducing which precursor(s) would have the greatest impact and where? What are the likely responses to precursor emission increases/reductions? What measures can the UK undertake to effectively control SOA and SIA formation?

SIA (C2.2; C3.5; C3.5.1.1): Based on limited UK and EU studies, reducing NH_3 can have largest effect in reducing levels of SIA $PM_{2.5}$, the response dependent on season studied nitrate predicted to dominate in future scenarios. As noted above, other studies are apparently contradictory, finding that SO_2 abatement can have the largest effect and other studies predicting significant impact from NO_x reduction. Reductions in NH_3 emissions will effect particulate sulphate via in cloud processing such that a 30% reduction in NH_3 has been noted to cause differences of over 1 μgm^{-3} in particulate sulphate. The predicted contribution from transboundary sources is not insignificant, the contributions from continental Europe dependent on the proposed mitigation strategies imposed there, northern European conditions favouring the predominance of NH_4NO_3. When comparing contributions from both the UK and EU, one UK PTM study attributes a larger sensitivity of $PM_{2.5}$ NO_3^- to EU emissions reductions in NO_x and NH_3 emissions.

SOA (C.3.4; C3.5.1; C3.5.2.1): Any reductions in anthropogenic VOCs are predicted to have indirect impacts on levels of biogenic SOA, in some cases significantly increasing concentrations depending on the interplay between NO_x and relevant oxidants. Limited

studies suggest largest contributor is from the solvent sector, followed by the chemical industry and traffic. Extreme scenarios modelled in the EU and US suggest complete removal of all anthropogenic sources would reduce total SOA by only 15%, with larger decreases near to emission sources. In contrast, elimination of all biogenic emissions led to reductions in SOA between 72-90% over the EU and US (C3.5.2). Choice of the gas phase model is important, as is the modelled interaction with changing meteorological conditions and influences from transboundary sources.

Whilst there have been a number of limited studies perturbing SIA precursors in one-at-a-time studies, a comprehensive series of perturbation experiments aiming to capture the non-linearities and contributions by sector and geographical location has not been reported. Only such studies using reliable models can reliably inform policy.

Organic precursor contributions are highly problematic. It is unclear how SOA precursor inventories are to be improved given the lack of quantitative identification of the determinant precursors. There are a very limited number of studies prescribing SOA components from specific sectors. Source-receptor relationships are using increasingly outdated statistical methods whereas non-UK models are now benefitting from new developments in online model diagnostics and inverse modelling approaches.

There are no UK perturbation studies using physically reasonable models to evaluate relative contributions to SOA by anthropogenic emission sector or from biogenic emissions.

Whilst underpinning quantitative understanding of SIA formation is well developed, the non-linearities and strong sensitivities to emissions and environmental conditions still present challenges in supporting policy decisions. It is a matter of highest priority to establish reliable sensitivity estimates using reasonable perturbation simulations with a well validated model tool (preferably a multi-model study).

UK secondary aerosol knowledge would benefit from the use of more recently developed methodologies for establishing source-receptor relationships (including statistical methods embedded directly within the host model) and improved emissions estimates using inverse modelling approaches.

UK sensitivity studies should be conducted using a range of physically reasonable models to evaluate relative contributions to SOA by anthropogenic emission sector and from biogenic emissions. By preference, avoidance of brute force emission perturbation methods is advised to avoid large numbers of simulations necessary to capture non-linear dependencies on varied parameters.

13. What is our current understanding of the roles of ammonia in SIA formation and how are PM concentrations affected by spatial and temporal variations in emissions of ammonia and other SIA precursors? What impact would a reduction in UK and non-UK ammonia emissions have on PM concentrations?

Ammonia is clearly the precursor to particulate ammonium (and is not present to any significant degree as undissociated dissolved ammonia). NH_3 is the most abundant alkaline gas in the atmosphere (A2.2.3), and because of its dominant role in neutralising acids, is the most abundant secondary cation in UK atmospheric aerosol (H^+ being dominant in high acidity atmospheres, such as parts of the US)[3]. It is efficiently taken up into any acidic aqueous particles and NH_3 uptake serves to regulate the acidity of aerosol and cloud droplets (which, in turn, influences the solubility and oxidation rate of species such as SO_2).

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[3] Under heavily marine-influenced conditions, Na^+ and K^+ may dominate the coarse mode, but NH_3 will still dominate the accumulation mode (and largely $PM_{2.5}$)

In NAME it has been found that in-cloud SO_4^{2-} production is very dependent on NH_3 control of droplet acidity, which is strongly dependent on the chemical scheme. A 30% increase or decrease in ammonia could lead to change in particulate sulphate of over 1 μgm^{-3}. Where it occurs in the atmosphere, NH_3 may also play a role in the ternary nucleation of sulphate particles. As with ammonium sulphate ($(NH_4)_2SO_4$), the equilibrium thermodynamics of ammonium nitrate (NH_4NO_3) under dry and moist conditions are extremely well established. The existence of NH_4NO_3 in aerosol particles is strongly favoured at low temperature and high relative humidity, and can therefore be influenced by normal daily cycles in humidity and temperature, and loading will vary strongly with altitude (as discussed in Annex B)

Whilst at a fundamental level the processes by which NH_3 impact SIA are well known, the strong dependencies of NH_4NO_3 equilibration and vertical temperature and RH gradients lead to high sensitivity to accurate representation of the boundary layer height and its physical properties. The non-linear aerosol nitrate response to reductions in SO_2 and NO_x occurs through changes in gas phase concentrations and thermodynamic changes favourable production of NH_4NO_3. Reductions in NH_3 can induce large sensitivities for predicted particulate sulphate resulting from the effect of NH_3 on balancing acidity of in-cloud production when accounted for in models. This has important implications for the representation of cloudiness and the coarseness of model grid resolution. Indeed, there is a growing body of evidence that domain size and grid resolution are important to resolving SIA processes. Along with the non-linearities in equilibration, the dynamics of aerosol microphysical processes will be important in determining whether a grid resolution is sufficiently fine. In addition, NH_3 emissions possess a large spatial variability, and it influences SIA formation through direct reaction on a short timescale (A1.2.2.3). Emission grid resolution should be sufficiently high to resolve the spatial variability. The MADE/SORGAM aerosol model coupled to RADM2 in WRF-Chem was found to underestimate sulphate by a factor of 2, and overestimate nitrate and ammonium by a factor of 2 compared with the EMEP surface stations in February 2007. The discrepancies were attributed to missing aqueous sulphate production and the thermodynamic treatment in the model.

UK PTM studies have found varying responses to projected emissions reductions, finding reduction of SO_2, NO_x and NH_3 of 64%, 75% and 96% can lead to a reduction of 2 μgm^{-3} of SIA. A second UK PTM perturbation study attributed a larger sensitivity of $PM_{2.5}$ NO_3 to 30% EU emissions reductions in NO_x and NH_3 than to UK reductions of the same magnitude. European studies have found greater sensitivity to EU NO_x emissions, though it is unclear whether this is a regional difference in sensitivity. WRF-CMAQ studies have found less of a sensitivity to NH_3 emissions, but it is unclear whether this is a result of primary sulphate emissions (without any sensitivity to NH_3) being used as reported in US studies. It should be noted that NH_3 is very heterogeneous in its emissions and is taken up directly and rapidly without a need for atmospheric reaction. As such, coarse representation of emissions can directly translate to inaccuracy in SIA production unlike emissions of SO_2 and NO_x.

It is unclear how accurately some models can represent aqueous phase processing and impact of oxidant concentration perturbations in future scenarios. Uncertainties in the spatial variation of the emissions are not quantified and reported. However, the NAEI "data quality confidence ratings" for each pollutant map in order of decreasing mapping quality for the major pollutants is reported as: SO_2 > NO_x > NMVOCs > PM_{10} > NH_3 (A1.1.2.3; A1.2.2.3). There are few evaluations of the relative SIA precursor contributions using reliable models and none that comprehensively map the possible parameter space.

A treatment of its emissions at high spatial resolution (i.e. much finer than 50 km x 50 km) is therefore ideally required for its role in SIA formation to be fully represented.

An NH_3 emission perturbation sensitivity study is required, using different model treatments (equilibrium, hybrid and fully kinetic, with various thermodynamic

treatments) of SIA evaluated against UK measurements, where possible. This should be rolled into the multi-pollutant analysis recommended above. NH$_3$ is only one of many contributory species in a non-linear interactive system. The study should reflect the current uncertainty in emission spatial distribution as well as future uncertainties in emissions and environmental conditions (see section A for a discussion of the emission uncertainties).

14. What impact would a reduction in UK and non-UK SO$_2$ emissions have on PM concentrations (including the changes to shipping emissions due to MARPOL Convention)?

In addition to the limited sensitivity studies to SO$_2$ emission reduction presented in response to questions 11 and 12, there have been a very limited number of studies investigating the impacts on UK SIA of a reduction in shipping emissions resulting from the MARPOL Convention. Only a comparison of 2020 projections using the PCM and UKIAM models has been reported. The PCM uses measurement-interpolated relationships and UKIAM used source-receptor relationships from more complex models. It is noted that both approaches are limited in the reliability of future projections, but the PCM predicted 15% SIA reduction and the UKIAM 33% for 2020. The UKIAM model used 85% reduction in North Sea SO$_2$ emissions in addition to reduction in EU land-based emissions whilst the PCM only considered land-based reductions (C3.5.1.1). The comparison was used to infer a reduction of the order of 18% SIA mass attributable to MARPOL, notwithstanding the substantial potential inaccuracies in the calculation.

There have been no systematic investigations solely perturbing shipping emissions as expected to occur following the MARPOL convention.

The SIA emission sensitivity simulations recommended previously should include a reasonable reduction in the shipping emissions into future scenarios and perturbation experiments solely directed at MARPOL mediated emission reductions is required

Technical Annexes

Introduction

Atmospheric aerosol particles, from a few nanometers (nm) to tens of micrometers (μm) in diameter, may be either directly emitted into the atmosphere or formed in-situ by the oxidation precursor gases and are termed primary and secondary, respectively. The secondary fraction comprises variable amounts of sulphate, ammonium, nitrate, chloride, water and carbonaceous material. The sulphate component is derived predominantly from the atmospheric oxidation of anthropogenic and natural sulphur-containing compounds such as sulphur dioxide (SO_2) and dimethyl sulphide (DMS), respectively. Nitrate is formed mainly from the oxidation of atmospheric nitrogen oxides (NO_x). In the UK, since NH_3 is almost invariably in excess, sulphate is normally present completely neutralised as ammonium sulphate, very occasionally being partially neutralised NH_4HSO_4. Nitrate particularly is only formed when there is enough NH_3 to give fully neutralised ammonium nitrate. Chloride can enter particles as a result of ammonia neutralisation of hydrochloric acid (HCl) supplementing the main primary seasalt source of chloride which is present hundreds of miles from the coast. The carbonaceous fraction of the atmospheric aerosol comprises both elemental and organic carbon. Elemental carbon (EC), also called black carbon (BC), is emitted directly into the atmosphere, predominantly from combustion processes. Organic aerosol (OA) has both a primary (POA, e.g. biomass burning and combustion) and secondary (SOA) fraction. The latter process occurs when volatile organic compounds (VOCs) undergo gas phase oxidation reactions, forming products that have low enough volatility to form aerosol via either nucleation or condensation onto pre-existing particles. Recent studies of the volatility of emitted particles has blurred the distinctions between the primary and secondary organic aerosol categories, with oxidation of primary emissions as well as previously unrecognised semi-volatile and intermediate volatility compounds (S/IVOC), producing an additional source of SOA (Robinson et al., 2007; Jimenez et al., 2009; de Gouw et al., 2011).

Organic aerosol frequently forms the dominant fraction of atmospheric submicron particulate matter in the atmosphere (Zhang et al., 2007; Jimenez et al., 2009; Hallquist et al., 2009). However, measurements indicate that models poorly predict OA concentrations. Regional and global models using "traditional" tuned SOA parameterisations form SOA mostly from biogenic VOCs and typically underestimat SOA in polluted regions by an order of magnitude or more (e.g. Heald et al., 2005; Volkamer et al., 2006; Hodzic et al., 2010a) but not for clean biogenic regions (Tunved et al., 2006; Chen et al., 2009; Hodzic et al., 2009; Slowik et al., 2010). SOA formation from additional sources has been included in models. Several box (Dzepina et al., 2009), regional (Hodzic et al., 2010a; Tsimpidi et al., 2010) and global (Pye and Seinfeld, 2010) modelling studies have explored enhanced formation of SOA from semivolatile and intermediate volatility organic compounds (S/IVOC) from anthropogenic and biomass burning sources (Robinson et al., 2007), finding them to be important and previously neglected regional and global SOA source. There are still substantial uncertainties in concentrations, reaction rates, and SOA yields of S/IVOC precursors. SOA formed from biomass burning precursors is gaining attention as a potentially important source, although field (Capes et al., 2008; Yokelson et al., 2009; DeCarlo et al., 2010) and laboratory (Grieshop et al., 2009; Heringa et al., 2011) studies show highly variable net addition (or loss) of OA mass by SOA formation and POA aging from this source.

The source of model underestimation of SOA is unclear, although several factors may play a role:

i) SOA remains dynamic, through both reversible partitioning and continued atmospheric oxidation. This atmospheric processing or "ageing" is not well-represented in models and

involves physical and chemical processes typically not accessed in the laboratory. Atmospheric mixing blends organic aerosol from various sources.

ii) laboratory SOA yields may not representative atmospheric conditions; recent research has revised a number of previously estimated SOA yields and identified new SOA precursors (Shilling et al., 2008; Ng et al., 2007b; Kroll et al., 2005; Volkamer et al., 2007; Lim and Ziemann, 2009). Yields are found to be environmental condition dependent (e.g. RH, acidity, NO_x levels) and can be higher than previously reported (Ng et al., 2007a; Iinuma et al., 2004; Surratt et al., 2007b; Hildebrandt et al., 2009).

iii) aqueous-phase chemistry in aerosols and/or cloud droplets may play a larger role than previously thought (Lim et al., 2005; Carlton et al., 2006; Sorooshian et al., 2007; Volkamer et al., 2007; Tan et al., 2010),

iv) Transfer of both inorganic and organic compounds between vapour and condensed phases is generally poorly, inconsistently or erratically represented and may be the source of significant error and

v) SOA formation from biogenic VOCs may be more efficient in polluted air (Spracklen et al., 2011; de Gouw et al., 2005; Goldstein et al., 2009).

The global and regional budgets of SOA are very uncertain. Top-down estimates suggest a global source ranging from 120–1820 Tg (SOA) yr^{-1} (Goldstein and Galbally, 2007; Hallquist et al., 2009). Bottom-up estimates combining VOC emission inventories with laboratory SOA yields suggest global formation of 12–70 Tg (SOA) yr^{-1} (Kanakidou et al., 2005), though this has recently been revised to 8-110 Tg (SOA) yr^{-1} (Farina et al., 2010). This uncertainty (8–1820 Tg (SOA) yr^{-1}) is very substantial. The relative contributions from anthropogenic, biogenic, and biomass burning sources are similarly poorly constrained. Studies using traditional SOA models predict biogenic SOA sources to greatly exceed anthropogenic ones (Tsigaridis et al., 2006; Tsigaridis and Kanakidou, 2007; Heald et al., 2008; Henze et al., 2008), while newer models predict fractionally greater anthropogenic SOA (Farina et al., 2010; Pye and Seinfeld, 2010). A high biogenic fraction appears consistent with the large fraction of non-fossil carbon detected in ambient OA (e.g., Hodzic et al., 2010b). Even in polluted regions when OA is universally observed to be enhanced, substantial fractions of non-fossil carbon are found (e.g. Schichtel et al., 2008) implying anthropogenic enhancement of biogenic SOA formation (de Gouw et al., 2005; Goldstein et al., 2009; Weber et al., 2007; Hoyle et al., 2011). Potential mechanisms for such enhanced formation include higher aerosol acidity (e.g. Jang et al., 2002; Surratt et al., 2010), NO_x levels (Ng et al., 2007a; 2008) and speciation (e.g. Chan et al., 2010), enhanced pollution-related OA and oxidant levels (Tsigaridis and Kanakidou, 2007), and oxidant speciation (e.g. Ng et al., 2008). Doubling of biogenic SOA by pollution in the US was predicted primarily resulting from enhanced biogenic VOC oxidation with increased NO_x, and through anthropogenic POA availability for biogenic species condensation (Carlton et al., 2010). Not all of the non-fossil carbon is biogenic, with significant biomass burning, biofuel and non-fossil urban OA contributions (Hodzic et al., 2010b).

Technical Annex A - Process Understanding

Secondary aerosol is generated by the transfer of material from the gaseous to the condensed (i.e. solid and/or liquid) phase following the chemical processing of emitted precursor compounds, which may originate from both anthropogenic and biogenic sources. A number of processes therefore contribute to secondary aerosol formation, including the emission of the precursor species, their oxidation and subsequent multiphase chemical and physical processes. In this Annex the current state of knowledge of these processes is summarised for both secondary organic aerosol (SOA) and secondary inorganic aerosol (SIA).

Subsection A1 identifies the emitted precursors to SOA and SIA formation, and summarises information on their sources and emissions in the UK and Europe. Current understanding of these sources and associated emissions estimates is reviewed, including consideration of their spatial and temporal variability and projected trends.

The emitted precursors to SOA formation are gas phase organic compounds, many thousands of which are potentially emitted from a variety of anthropogenic, biogenic and natural sources. Mapped estimates of anthropogenic emissions of organic compounds that can potentially act as SOA precursors are provided by the non-methane volatile organic compound (NMVOC) inventories compiled by the NAEI and EMEP. Biogenic emissions are believed to play a particularly important role, but there are no similar central sources of information for biogenic NMVOC emissions in the UK or Europe. Various estimates have been reported and are available, but the biogenic source strengths are subject to considerable uncertainty.

Organic compounds emitted from both anthropogenic and biogenic sources possess a wide range of properties, such that the SOA formation potential is very sensitive to the emitted speciation. They are often broadly categorised as volatile organic compounds (VOCs), intermediate volatility organic compounds (IVOCs) and semi-volatile organic compounds (SVOCs) to reflect their very wide range of volatilities. The lower volatility components (IVOCs and SVOCs) are expected to have a generally higher propensity to generate SOA upon oxidation, but are made up of a potentially enormous number of larger and more complex species that are not well-defined or resolved by traditional analytical techniques. They are therefore also not well represented in existing anthropogenic non-methane volatile organic compound (NMVOC) inventory speciations, which (purposely) focus on the more abundant volatile components.

The major components of SIA are sulphate (SO_4^{2-}) and nitrate (NO_3^-), usually fully neutralised by ammonium (NH_4^+) under UK conditions. The major emitted SIA precursors are sulphur dioxide (SO_2) for sulphate aerosol, nitrogen oxides (NO_x) for nitrate aerosol, and ammonia (NH_3) for ammonium aerosol, which derive mainly from anthropogenic sources in the UK and Europe. Natural sources may also make a contribution, including marine emissions of dimethyl sulphide (DMS) for sulphate and soil emissions of NO for nitrate.

Because of the dominance of anthropogenic sources, and the relatively simple speciation of the emitted precursors, the emissions of SIA precursors are generally much better defined than those of SOA precursors, with mapped emissions estimates compiled by the NAEI and EMEP. The least well represented is NH_3, for which the major source emissions (from agriculture) are characterised by high spatial and temporal variability. Important contributions to SO_2 and NO_x emissions are also made by international shipping, which are not included in national inventory totals. In the case of NO_x, international shipping emissions are projected to become comparable to those from land-based sources in the EU from about 2020.

Subsection A2 provides an overview of the gas phase chemical processing of the emitted SOA and SIA precursor species, to form products that can transfer to the

condensed phase; and the mechanisms by which this transfer occurs. A discussion of the representation of these processes in atmospheric mechanisms is also provided.

The atmospheric oxidation of SOA precursors may be initiated by a number of reactions, including reaction with the photochemically-generated hydroxyl radical (OH) and with ozone (O_3). They possess a wide range of reactivities and associated atmospheric lifetimes, and are generally oxidised more rapidly during summertime regional-scale photochemical episodes, when the concentrations of both OH and O_3 are elevated. They are oxidised by highly complex gas phase mechanisms that form a very large number of partially oxidised intermediates, prior to ultimate conversion of the emitted carbon into carbon dioxide (CO_2). SOA is formed from the transfer of this partially oxidised organic material to the condensed phase, occurring in competition with its further oxidation to CO_2 in the gas phase.

The gas phase chemistry of SOA precursors in atmospheric mechanisms is generally highly simplified, producing a limited set of products for which transfer to and from the condensed phase is represented. This chemistry is therefore usually decoupled from the traditional gas phase chemistry describing the role of VOCs as O_3 precursors. However, general understanding of the gas phase processing of organic compounds is sufficiently well-advanced to allow future development of explicit, highly detailed representations of the chemistry that could be used as benchmark representations with coupled gas phase chemistry and SOA formation.

The transfer of oxidised organic products from the gas phase to the bulk condensed phase involves a number of transport and kinetic processes, including gas phase diffusion, accommodation at the gas-particle interface, and bulk phase diffusion; with the additional possibility of chemical reactions occurring, either at the interface or in the bulk phase. Because of this complexity, explicit process representations are seldom employed in air quality models, with most models using a simplified approach that describes the vapour-pressure driven equilibrium partitioning of the oxidised organic products between the gaseous and condensed phases. The yields and vapour pressures of the partitioning products are usually empirically optimised on the basis of chamber observations. These methodologies are reviewed, and limitations and shortcomings are discussed.

The chemical processing of SIA precursors is generally better understood and represented than that of SOA precursors, because SIA derives from a smaller set of well-defined emitted precursor compounds. The oxidation of SO_2 to sulphate proceeds via both gas phase and aqueous phase ("in-cloud") pathways, which are very well characterised. The aqueous phase route dominates on average, although gas phase oxidation (initiated by reaction with OH) is more important under summertime photochemical episode conditions.

The processes involved in the oxidation of NO_x to nitrate are well-characterised. The chemistry initiated by reaction of OH with NO_2 (which is most important during the day) leads directly to the formation of gas phase nitric acid (HNO_3), which can transfer to the condensed phase to form nitrate aerosol. This can occur either by reaction with NH_3 to form condensed phase ammonium nitrate (NH_4NO_3), or by direct uptake, often as part of an acid-displacement reaction with sea-salt aerosol to form condensed phase sodium nitrate ($NaNO_3$). The night-time oxidation of NO_x (via reaction of NO_2 with O_3) leads to the formation of dinitrogen pentoxide (N_2O_5), which can undergo a surface reaction with H_2O to form condensed phase HNO_3, or react with sea-salt aerosol to form condensed phase $NaNO_3$. On average, the day time and night time oxidation routes are of comparable importance, with the rate of both increased under summertime regional-scale photochemical episodes, when the concentrations of both OH and O_3 are elevated.

NH_3 is efficiently taken up into acid sulphate aerosols to form condensed phase ammonium sulphate (($NH_3)_2SO_4$). As indicated above, condensed phase ammonium nitrate (NH_4NO_3) is also formed from the reversible reaction of gas phase NH_3 and gas phase HNO_3, for which

the position of the equilibrium depends on the prevailing conditions (e.g. temperature and relative humidity).

A1: Emissions of secondary aerosol precursors

Summary

Introduction

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A1.1.2: Anthropogenic emissions of SOA precursors

A1.1.3: Biogenic emissions of SOA precursors

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A1.2: SIA precursors

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A1.2.3: Natural emissions of SIA precursors

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A2: Chemical and physical processes forming secondary aerosol

A2.1: Processing of SOA precursors

A2.1.1: Gas-phase oxidation of emitted organic compounds

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A2.2: Processing of SIA precursors

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A1: Emissions of secondary aerosol precursors

A1.1: SOA precursors

A1.1.1: Classification of SOA precursors

The emitted precursors to SOA formation are gas phase organic compounds. Many thousands of such compounds are emitted into the atmosphere from a variety of anthropogenic and biogenic sources, with each compound potentially contributing differently per unit emission to secondary pollutant formation, due to differences in physico-chemical properties. These organic compounds cover a very wide range in volatility, with non-volatile components being present entirely in the condensed phase and therefore being classed as primary organic aerosol (POA). The remaining compounds are emitted either wholly or partially in the gaseous phase under relevant atmospheric conditions, and these can all be classed as SOA precursors (although the lower volatility components also contribute to POA).

SOA precursors are sometimes broadly separated into three categories on the basis of volatility (e.g. Robinson et al., 2007; Huffman et al., 2009; Pye and Seinfeld, 2010), namely volatile organic compounds (VOCs), intermediate volatility organic compounds (IVOCs) and semi-volatile organic compounds (SVOCs), as defined more fully below. Although these distinctions are not made in national inventories (which report all organic compound emissions potentially contributing to secondary pollutant formation as "non-methane volatile organic compounds, NMVOCs") these different categories can be helpful in identifying sets of lower volatility compounds with a generally higher propensity to generate SOA, and ensuring that their emissions and subsequent processing is adequately represented in modelling assessments.

Volatile organic compounds (VOCs) have been loosely defined as organic compounds with saturation concentrations (C_0) that are greater than about 10^6 g m^{-3} (Pye and Seinfeld, 2010), although other broadly compatible definitions also exist[4]. They are emitted entirely in the gas phase, and include (for example) all normal alkanes up to dodecane (n-$C_{12}H_{26}$). The category also includes "traditional" SOA precursors such as aromatic hydrocarbons up to ~C_{11} (including toluene, xylenes and trimethylbenzenes), isoprene and monoterpenes (e.g. α-pinene). However, a large proportion of the emitted VOC burden is expected to be relatively inefficient at generating SOA upon further oxidation, owing to a dominance of relatively more volatile species, e.g. light alkanes and oxygenates (Passant, 2002).

Intermediate volatility organic compounds (IVOCs) have been loosely defined as organic compounds for which C_0 lies in the approximate range 10^4 - 10^6 µg m^{-3} (Pye and Seinfeld, 2010). They are partially present in the condensed phase at very high organic aerosol loadings (e.g. in a tailpipe), but become essentially entirely gas phase species upon dilution to relevant ambient conditions. They are expected to have a high propensity to form SOA upon further oxidation in the atmosphere (e.g. (Chan et al., 2009; Presto et al., 2010; Aumont et al., 2012). They include (for example) the normal alkanes from tridecane (n-$C_{13}H_{28}$) to hexadecane (n-$C_{16}H_{34}$). The category also includes small polycyclic aromatic hydrocarbons (PAHs) such as the two-ring PAH naphthalene and some 3-ring PAHs (e.g. acenaphthene), and sesquiterpenes (e.g. β-caryophyllene).

Semi-volatile organic compounds (SVOCs) have been loosely defined as organic compounds for which C_0 lies in the approximate range 10^{-1} - 10^4 µg m^{-3} (Pye and Seinfeld, 2010). They are partitioned between the gaseous and condensed phases under relevant

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[4] The VOC Solvents Directive (1999/13/EC) defines a VOC as having a vapour pressure ≥ 0.01 kPa at 293.15 K. The amended Paints Directive (2004/42/EC) defines a VOC as having a boiling point ≤ 250 °C at a standard pressure of 101.3 kPa.

ambient conditions. They include (for example) the normal alkanes from heptadecane (n-$C_{17}H_{34}$) up to about hexacosane (n-$C_{26}H_{54}$). The category also includes 4-ring PAHs such as pyrene and some 3-ring PAHs (e.g. anthracene). Oxidation of the gas phase component of SVOCs is likely to generate non-volatile products at the first oxidation step, which reside entirely in the aerosol phase.

## A1.1.2: Anthropogenic emissions of SOA precursors

Estimates of anthropogenic emissions of organic compounds that can potentially act as SOA precursors are provided by the non-methane volatile organic compound (NMVOC) inventories compiled by the National Atmospheric Emissions Inventory (NAEI: http://naei.defra.gov.uk/) for the UK, and collated with corresponding data from an extended domain that includes the whole of the Europe by the European Monitoring and Evaluation Programme (EMEP: http://www.emep.int/). Although the primary role of such inventories is to report on compliance to the EU and other international bodies in relation to national annual emissions totals and trends, the information also provides valuable and comprehensive sources of input data for air quality modelling studies, and is widely used in scientific and policy assessments.

A1.1.2.1: Annual totals and trends in anthropogenic NMVOC emissions

The total annual emissions of NMVOCs, historical annual trends and future annual projections are generally available from the NAEI and EMEP. Figure A.1 shows examples of such data for the UK and collectively for the 27 member states of the EU (EU-27). These show the tail end of a downward trend in NMVOC emissions resulting from EU control measures, implemented since the early 1990s, but indicate only modest future changes in total NMVOC emissions. Corresponding information for NO_x emissions is also shown, which displays a stronger projected trend and a progressive increase in the NMVOC/NO_x emissions ratio in the future. This indicates that conditions will become more NO_x-limited, which may have implications for some features of the chemical processing of emitted SOA precursors (see section A2.1.1).

The data in Figure A.1 show that the UK emissions account for about 11 % of the total emissions of NMVOCs from the EU-27 in 2010, which corresponds to an average emissions density in the UK that is about a factor of two greater than that in the EU-27 (based on respective areas of 2.44×10^5 km^2 and 4.33×10^6 km^2). The 2010 NMVOC emissions total from the extended EMEP domain (which includes the whole of Europe and neighbouring parts of Asia and North Africa) is about a factor of two greater than that for the EU-27, over an area that is about a factor of five larger. However, it is not straightforward to use such comparisons to draw conclusions about the relative impacts of UK and non-UK anthropogenic emissions on SOA formation, for which incorporation of emissions data in appropriate models is required (see section C).

Uncertainties in the UK annual emissions totals are estimated by the NAEI, as described for example in AQEG (2013), with the uncertainties for the 2010 totals being ± 10 % for both NMVOCs and NO_x. When changes in methodology are implemented, totals for previous years are recalculated consistently so that the same uncertainty can reasonably be assigned to historical totals. The uncertainty in future projections is assessed by running a number of probable scenarios, as described by Misra et al. (2012), leading to an additional uncertainty that increases with time. The spread of results for 2030 suggests additional uncertainties of about ± 1.3 % for NMVOCs and ± 7 % for NO_x.
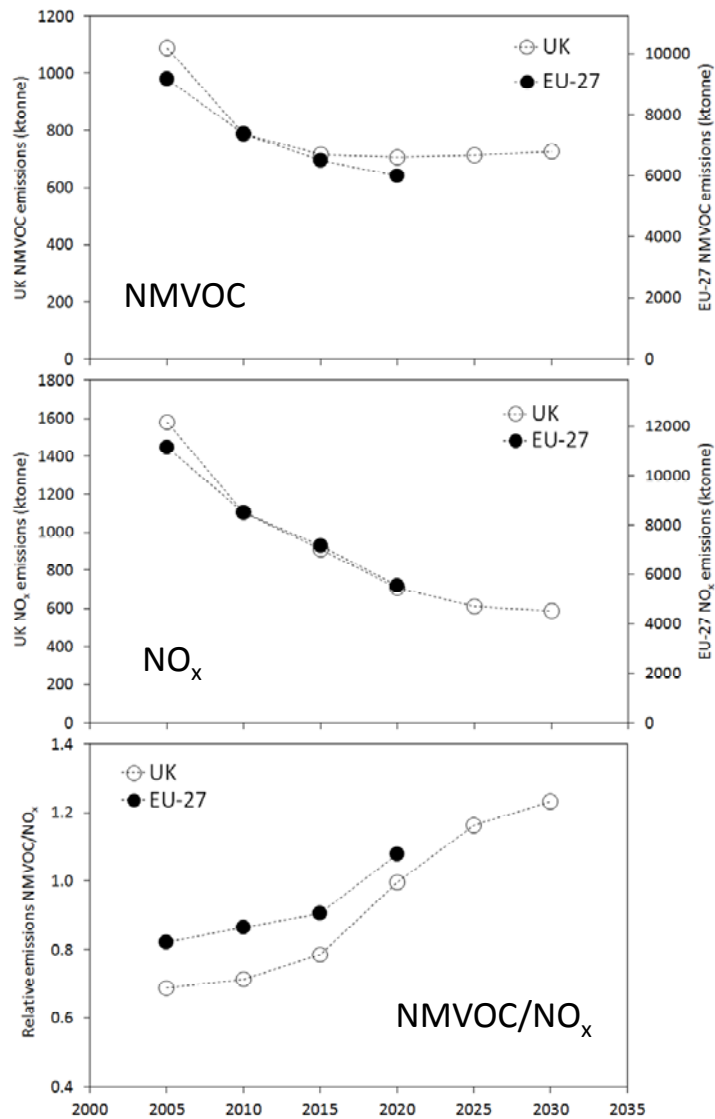
Figure A.1: Historical and projected annual total anthropogenic emissions of NMVOCs and NO_x for the UK (taken from Misra et al., 2012) and the EU-27 (AQEG, 2012), and the corresponding trend in the emissions ratio NMVOC/NO_x. The scales for the emissions from the UK and EU-27 in the top two panels have been set so that the data points for 2010 are superimposed.

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A1.1.2.2: Anthropogenic NMVOC source categories and speciation

The emissions inventories represent NMVOC emissions in terms of 11 broad source categories (e.g. see Table A.1). It should be noted that the reported national totals exclude contributions from a number of additional sources (denoted "Memo Items", for example international shipping and aviation), which total an additional 14 % for the UK in 2011 (see Table A.1).

Almost half the emissions of NMVOCs in the UK national total fall into the "solvents and other product use" category, with notable contributions from "fugitive emissions" and "industrial processes". Although historically a major contributor, road transport emissions are estimated to account for only about 6 % of the UK national total in 2011.

The 11 broad source categories are further subdivided into a total of 295 anthropogenic sources in the NAEI (e.g. Passant, 2002). The NAEI currently defines 111 species profiles

representative of different sets of these sources, which result in a full speciation which contains 664 NMVOC species (Passant, 2002). Although the inventory nominally represents NMVOCs, the individual components of the speciation include examples of IVOCs (e.g. the normal alkanes from n-$C_{13}H_{28}$ to n-$C_{16}H_{34}$, and naphthalene) and SVOCs (e.g. n-$C_{17}H_{36}$ and anthracene); and some species that are expected to be sufficiently non-volatile to remain in the condensed phase (e.g. benzo(a)pyrene) and contribute only to POA. The species profiles are updated periodically, but have remained unchanged since those reported by Passant (2002).

Table A.1: Total UK anthropogenic emissions of NMVOCs in 2010 and 2011, and contributions of the relevant source sectors (source: NAEI, from Defra National Statistics Release: Emissions of air pollutants in the UK, 1970 to 2011, 18th December 2012: https://www.gov.uk/government/publications/emissions-of-air-pollutants).

SNAP	Source sectors	2010	2011
1	Energy industries (Combustion in power plants and Energy Production)	0.6%	0.6%
2	Manufacturing Industries and Construction	3.1%	2.9%
3	Road Transport	7.0%	5.8%
4	Non-road transport	1.4%	1.5%
5	Other sectors (Commercial, residential , agriculture and fishing, stationary and mobile combustion)	4.9%	4.8%
6	Other, Mobile (Including military)	0.3%	0.3%
7	Fugitive emissions	19.9%	19.1%
8	Industrial Processes	13.9%	14.1%
9	Solvent and other product use	44.5%	46.5%
11	Waste	4.3%	4.3%
12	Other (included in national total for entire territory) [a]	0.2%	0.2%
	National Total (ktonne)	771.44[b]	752.08[b]
	Memo Items (ktonne) [b]	104.39[b]	105.57[b]

Notes: [a] Emissions from Gibraltar are included in the UK national total. [b] National totals exclude additionally-reported contributions from Memo Items, which are: International & National Aircraft (cruise), International Shipping, emissions from forest fires, and Natural Emissions (volcanoes).

The overall uncertainty in the NAEI VOC speciation has not been quantified. As discussed in more detail elsewhere (e.g. AQEG, 2013), the species profiles are better known for some sources than others, and generally more precise for the more abundant components within a given source, which tend to be the smaller, more volatile species. It is likely that species that contribute to the IVOC and SVOC burden are the least well characterised, because they tend to be made up of small contributions from each of a very large number of species which cannot be resolved by traditional analytical techniques, and with these species therefore usually collectively referred to as the "unresolved complex mixture, UCM" (e.g. Knipping and Dabdub, 2012).

For example, the NAEI speciation contains 23 of the 75 possible isomers of $C_{10}H_{22}$, but only one of the 4347 possible isomers of $C_{15}H_{32}$. In addition to this, the (probable high concentration) conditions under which many profiles are likely to have been characterised may underestimate the gas phase contributions of IVOCs and SVOCs, and therefore their contribution to SOA precursor emissions as represented in a speciated NMVOC inventory. The UCM emitted from combustion processes is thought to be composed of a very complex mixture of branched and cyclic compounds that are C_{10} and higher and which are therefore present in the aerosol and gas phases.

As a result, the NMVOC speciation is likely to contain a generally good representation for emitted VOCs (as originally intended), but a rather incomplete representation for the lower-volatility IVOCs and SVOCs that contribute to the UCM. The complexity of the sources of

IVOCs can be inferred the likely contributing sources – in urban environments including evaporative and combustion emission of diesel and kerosene fuels which cover the carbons ranges C_{12}-C_{22} and C_9-C_{15} respectively. While it is recognised that a representation of the full speciation of these classes would be prohibitively complex and impractical, an assessment is required of the level of omission and misrepresentation of the UCM in emissions inventories. It is important to understand the chemical character and emission rates of the UCM from major sources and to elucidate the atmospheric fate of these compounds (Knipping and Dabdub, 2012).

A1.1.2.3: Spatial variation in anthropogenic NMVOC emissions

Mapped emissions for the NMVOC source sectors given in Table A.1 are available from the NAEI for the UK at a resolution of 1 km x 1 km. Similarly, those for the extended EMEP domain are available from EMEP, at a resolution of 50 km x 50 km. Although these spatial resolutions cannot resolve the variation of primary pollutant emissions close to a receptor, they are generally sufficient for applications related to the formation of SOA, because of the time and distance scales required for multi-generational chemical processing of most precursor organic compounds (see section A2).

Uncertainties in the spatial variation of NMVOC emissions are not quantified and reported, although the NAEI does report "data quality confidence ratings" for each pollutant map (Bush et al., 2008), based on an assessment of the combination of contributory sources for each pollutant. Within this rating the ranking in order of decreasing mapping quality for the major pollutants is reported as: SO_2 > NO_x > NMVOCs > PM_{10} > NH_3.

A1.1.2.4: Temporal variation in anthropogenic NMVOC emissions

The temporal breakdown of annual NMVOC emissions is not officially reported as part of the NAEI and EMEP inventories. However, associated studies have defined temporal profiles for NMVOCs emissions for the source sectors in Table A.1 by time-of-day, day of the week and month of the year (Jenkin and Clemitshaw, 2000; Friedrich and Reis, 2004), which are used in modelling applications (e.g. Utembe et al., 2005; Simpson et al., 2012). An updated assessment of the temporal variation of emissions sources is also currently being carried out by the NAEI (AQEG, 2013).

It is probable that the speciation of NMVOC emissions shows temporal variations (e.g. resulting from known changes in fuel formulation that occur with time of year), but this information is not readily available. It should also be noted that the partitioning of SVOCs between the gaseous and condensed phases possesses a strong temperature dependence, such that they are likely to play a more important role as SOA precursors at higher temperatures, when oxidation of the gaseous component is more favoured.

A1.1.2.5: Verification of emissions rates using measurements

As discussed in detail by AQEG (2013), measurements of species concentrations and fluxes can in principle be used to verify emissions rates in published inventories, although such studies are not carried out regularly and systematically.

Since 1993, routine monitoring of NMVOCs in the UK has been carried out via Defra's Automatic Hydrocarbon Network (e.g. Derwent et al., 2000; Dollard et al., 2007), using automated GC-FID instrumentation to make hourly measurements of up to 31 light (C_2-C_8) hydrocarbons. These data, and similar measurements conducted elsewhere, provide the potential for evaluating emissions of some of the more volatile components of the NAEI NMVOC emissions inventory, although there is no overlap with IVOCs and SVOCs.

A limited number of analyses of UK Automatic Hydrocarbon Network data have been carried out, which have determined the relative source strengths and long-term trends for each of

the measured hydrocarbons at the monitoring locations (Derwent et al., 2000; Dollard et al., 2007; Murrells et al., 2012). All these studies have demonstrated a dominance of road transport sources, but have not clearly revealed contributions from sources in the dominant "solvents and other product use" category (see Table A.1). Likely reasons for this include that the sites are better located to characterise road transport sources (which are relatively well-defined spatially and temporally), compared with more diffuse solvent emissions; and that the monitored light hydrocarbon set is estimated to cover only 19 % of the aggregated solvent speciation, compared with 65 % of the road transport speciation (AQEG, 2013).

Campaign measurements made at specific locations or times also provide information that can be used to evaluate emissions data. For example, recent measurements made in London as part of the NERC-funded Clean Air for London (ClearfLo) project provide information on the ambient concentrations of larger hydrocarbons than covered by the Automatic Hydrocarbon Network. The winter average concentrations confirm an important contribution from larger molecular weight hydrocarbons that may not be fully represented in the NAEI speciation, with the observed mass concentration of C_{13} aliphatic hydrocarbons (i.e. alkanes, alkenes and alkynes) being similar to that of C_4 aliphatic hydrocarbons. This re-emphasises the need for a full evaluation of the contribution and representation of IVOCs and SVOCs to anthropogenic organic compound emissions.

A1.1.3: Biogenic emissions of SOA precursors

Emissions of SOA precursors from biogenic sources are expected to play an important role, based on OA source apportionment studies derived from ^{14}C measurements in the UK (Heal et al., 2011) and elsewhere in Europe (e.g. Szidat et al., 2006; Szidat et al., 2009), as discussed further in section B.

Biogenic sources are defined as emissions from vegetation. Although such emissions can be regarded as due to human activities (e.g. crop growing and other managed land use) to varying extents, such emissions are not usually included in anthropogenic source inventories. Emissions rates of biogenic NMVOCs are sensitive to the type and quantity of vegetation, season and conditions such as temperature, light and soil moisture (e.g. Guenther et al., 1995). As a result the emissions rates are highly variable both spatially and temporally. They are usually estimated for modelling purposes using mapped emission potentials, based on land-cover datasets for emitting vegetation, and environmental correction factors that depend on the prevailing meteorological conditions. The emission potentials define the emissions rate under standard reference conditions, and the environmental correction factors describe how the emissions rate varies with conditions, with key variables being leaf surface temperature and the intensity of photosynthetically active radiation, PAR (e.g. Guenther et al., 1995). Unlike the situation for anthropogenic NMVOCs, there is no central source of information for biogenic NMVOC emissions in the UK or Europe, although various estimates have been reported (e.g. Simpson, 1995; 1999; Winiwarter et al., 2001; Dore et al., 2003; NATAIR, 2007; Steinbrecher et al., 2009; Karl et al., 2009). The applied emissions rates may therefore vary from one model to another, depending on the sources of the emission potentials and meteorological data, and the methods and assumptions used to infer leaf surface temperature and the intensity of PAR (and the effects of shading) from standard meteorological parameters (e.g. see Simpson et al., 2012).

The methods available to estimate biogenic NMVOC emissions have generally allowed them to be speciated into isoprene, monoterpenes and other VOCs (OVOCs)[5], with a further

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[5] The term OVOCs is used here as an abbreviation for "other VOCs", as is the convention in studies reporting emissions of organic compounds from biogenic sources. It is noted that the same

category of sesquiterpenes becoming increasingly reported (Duhl et al., 2008; Steinbrecher et al., 2009; Karl et al., 2009). With the exception of isoprene (2-methyl-buta-1,3-diene, C_5H_8), these categories represent potentially complex mixtures of species. As discussed further below, monoterpenes ($C_{10}H_{16}$) and sesquiterpenes ($C_{15}H_{24}$) are isomeric classes of hydrocarbon, containing two and three isoprene units respectively. The "OVOCs" category consists of a large number of species, including hydrocarbons, and a variety of oxygenated compounds such as alcohols, aldehydes, ketones and acids (e.g. Helmig et al., 1999) and green-leaf volatiles (Hamilton et al., 2009).

A1.1.3.1: Annual totals and seasonal variability in biogenic NMVOC emissions

Emissions of NMVOCs from biogenic sources are not included in the national totals reported by the NAEI and EMEP. Because of the very large spatial and temporal variability of the emissions, annual totals are of relatively limited value for modelling applications, although they do allow broad comparisons of the relative emissions of NMVOCs from biogenic and anthropogenic sources, and how this varies between the UK and Europe as a whole.

Table A.2 compares estimates of annual biogenic NMVOC emissions totals for the UK (or Great Britain) for a number of years, with the totals broken down into the broad speciation categories identified above, where available. The estimates from single studies that cover a number of years demonstrate a modest level of year-to-year variability, which results mainly from the variability in meteorological conditions. The estimates from the different studies cover a range of about a factor of four. This is partly because the studies of Winiwarter et al. (2001) and OSRM (2006) only include emissions from trees (usually denoted forests). However, the variability also provides an initial indication of the level of uncertainty in estimating the annual totals. The uncertainty in these studies is typically reported to be about a factor of four for isoprene and monoterpenes, with greater uncertainties of about an order of magnitude for sesquiterpenes and OVOCs.
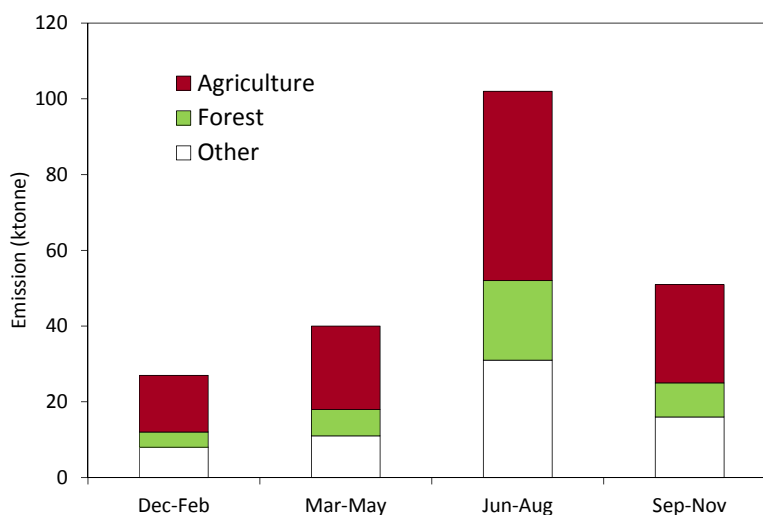
Table A.2: Reported estimates of annual total biogenic NMVOC emissions (ktonne) for the UK (or Great Britain), subdivided into isoprene, monoterpenes (MT), sesquiterpenes (SQT) and other VOCs (OVOCs). Where the estimates are year-specific, the current NAEI estimate of anthropogenic NMVOC emissions is also given (where readily available).

Study	Year	isoprene	MT	SQT	OVOC	total	Anthropogenic
Simpson et al. (1999)	-	58	31	-	89	**178**	-
Winiwarter et al. (2001)	-	-	-	-	-	**67** [a]	-
CORINAIR (2002)	-	53	39	-	27	**119**	-
Stewart et al. (2003)[b]	1998	9 [c]	94 [c]	-	-	**103** [c]	-
OSRM (2006) [d]	1997	6.7	49.0	-	34.8	**90.5** [a]	-
OSRM (2006) [d]	1998	5.7	46.0	-	33.0	**84.7** [a]	-
OSRM (2006) [d]	1999	6.6	47.0	-	33.4	**87.0** [a]	-
OSRM (2006) [d]	2000	6.3	46.0	-	32.8	**85.1** [a]	1496
OSRM (2006) [d]	2001	6.5	45.8	-	32.7	**85.0** [a]	1411
OSRM (2006) [d]	2002	6.3	48.4	-	34.5	**89.3** [a]	1326
OSRM (2006) [d]	2003	7.1	51.7	-	36.7	**95.5** [a]	1207
NATAIR (2007)	1997	-	-	-	-	**280.3**	-
NATAIR (2007)	2000	-	-	-	-	**254.6**	1496
NATAIR (2007)	2001	-	-	-	-	**252.5**	1411
NATAIR (2007)	2003	-	-	-	-	**281.4**	1207
Karl et al. (2009)[b]	2005	*53.7* [e]	*64.7* [e]	*1.4* [e]	*99.1* [e]	**219**	1049

Notes: [a] Emissions from trees and forests only. [b] Emissions reported for Great Britain. [c] Scaled and rounded from reported totals of 8 and 83 ktonne C for isoprene and MT. [d] Calculated using PELCOM land use data (Winiwarter et al., 2001) within the Ozone Source Receptor Model (OSRM), as reported in AQEG (2009). [e] Component totals estimated here from land use

abbreviation is also widely used to mean "oxygenated VOCs". Although some of the OVOC burden being discussed here is oxygenated, it also includes non-oxygenated material.
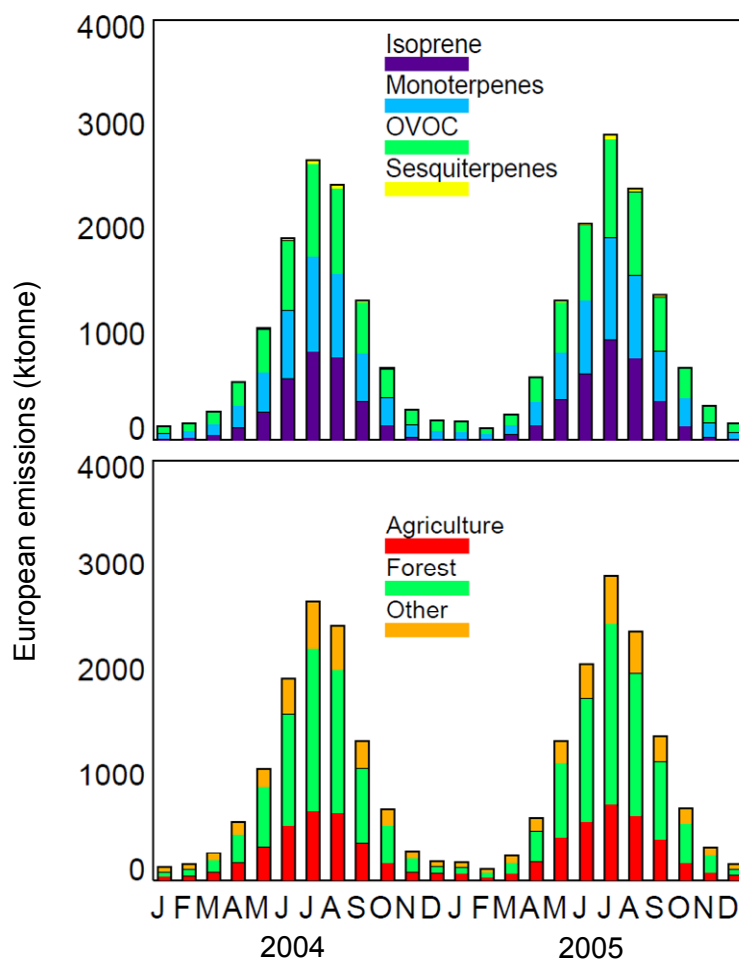
Figure A.2: Seasonal variation of biogenic NMVOC emissions and contributing sources in Great Britain in 2005, as reported by Karl et al. (2009).

Table A.3: Reported estimates of annual total biogenic NMVOC emissions (ktonne) for Europe, subdivided into isoprene, monoterpenes (MT), sesquiterpenes (SQT) and other VOCs (OVOCs).

Study	Year	isoprene	MT	SQT	OVOC	total
Simpson et al. (1999)	-	-	-	-	-	**10706** [a]
Winiwarter et al. (2001)	-	-	-	-	-	**13037** [a]
CORINAIR (2002)	-	4000	3700 6100	-	6000	**13700 16100** [a]
NATAIR (2007)	1997	3310 [b]	4440 [b]	200 [b]	3640 [b]	**11590**
NATAIR (2007)	2000	3640 [b]	4590 [b]	200 [b]	3670 [b]	**12100**
NATAIR (2007)	2003	3960 [b]	5040 [b]	200 [b]	4010 [b]	**12940**
Karl et al. (2009)	2004	3286 [c]	3867 [c]	97 [c]	4350 [c]	**11600**
Karl et al. (2009)	2005	3485 [c]	4100 [c]	102 [c]	4613 [c]	**12300**

Notes: [a] Emissions reported for forests only. [b] Taken from Figure 5 in NATAIR (2007). [c] Component totals based on approximate contributions of 3400, 4000 and 4500 ktonne for isoprene, MT and OVOC, out of a total of 1200 ktonne, given at the start of the section 3.1 text in Karl et al. (2009). The remaining 100 ktonne is assigned to SQT and is consistent with the $\approx$ 1% contribution given later in the section.

Figure A.3: Seasonal variation of biogenic NMVOC emissions, contributing sources and broad speciation in Europe in 2004 and 2005, as reported by Karl et al. (2009). The figure is adapted from Figures 4 and 5 in Karl et al. (2009).

The average of the reported annual totals is about 150 ktonne (where multi-year studies are represented by a single average value). This is about 20 % of the UK anthropogenic total for 2011. Thus, the biogenic NMVOC annual emissions total is greater than that for road transport emissions (for example) by a factor of about three. As shown in Figure A.2, the emissions vary strongly with season, based on data presented by Karl et al. (2009) for Great Britain, with approximately 50 % of the annual emissions occurring in June, July and August. This illustrates that the relative importance of biogenic emissions is greater during the summertime, with an average emissions rate approaching 40 % of that due to anthropogenic NMVOC emissions (based on the 2011 UK total with little seasonal variability).

Table A.3 compares estimates of annual biogenic NMVOC emissions totals for Europe. In this case, the estimates from the different studies show a reasonable level of consistency (covering a range of about 11000 - 16000 ktonne), although the estimated uncertainties are essentially the same as those indicated above. The average reported value is about 12500 ktonne, indicating that the UK emissions account for about 1.2 % of the total emissions of biogenic NMVOCs in Europe, which corresponds to an average emissions density in the UK that is about a factor of two smaller than the European average.

Figure A.3 shows the estimated seasonal variation of biogenic NMVOC emissions. This is based on data presented by Karl et al. (2009), which is comparable with data for Europe given in other studies (e.g. NATAIR, 2007).

A1.1.3.2: Biogenic NMVOC source categories and speciation

The reported studies have generally used relevant land use data with highly-detailed plant species distributions to categorise biogenic NMVOC emissions from trees (usually denoted forests), agriculture (i.e. crops) and other land use, which includes shrubland, wetland and grassland. Figure A.2 shows the contributions of these contributing sources in Great Britain in 2005, as estimated by Karl et al. (2009), which suggest that about 20 %, 50 % and 30 % of the annual emissions result from forests, agriculture and other sources, respectively. Other parts of Europe show elevations in emissions from forests, leading to corresponding estimates of about 60 %, 25 % and 15 % for the Europe as a whole, as shown in Figure A.3 (based on Karl et al., 2009).

Tables A.2 and A.3 and Figure A.3 also show the breakdown of the emissions estimates in terms of the broad NMVOC speciation categories. All studies show that isoprene, monoterpenes and OVOCs all make relatively large contributions to the UK and European totals, with sesquiterpenes making a small contribution, where this has been reported (NATAIR, 2007; Karl et al., 2009). The generalised source categories possess different propensities to emit the different species, as shown in Table A.4 for the European Atlantic zone, based on Karl et al. (2009).

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Table A.4: Reported estimates of annual total biogenic NMVOC emissions (ktonne) by source for the European Atlantic zone (Belgium, Denmark, France, Ireland, the Netherlands, United Kingdom) in 2005, reported by Karl et al. (2009). The emissions are subdivided into isoprene, monoterpenes (MT), sesquiterpenes (SQT) and other VOCs (OVOCs), and the source subtotals reported for Great Britain in the same study are also shown.

Source	isoprene	MT	SQT	OVOC	Atlantic zone total (ktonne)	GB total (ktonne)
Agriculture [a]	6.8 %	28.5 %	0.9 %	63.8 %	221	**113**
Forests [b]	66.0 %	22.7 %	0.4 %	11.0 %	282	**40**
Other sources [c]	29.2 %	17.9 %	0.4 %	34.6 %	92.4	**65**

Notes: [a] Emissions from crops. [b] Emissions from trees. [c] Emissions from other land use, including shrubland, wetland and grassland.

As indicated above, monoterpenes, sesquiterpenes and OVOCs are classes of compounds that potentially include a large number of component species with varying abilities to generate SOA. Sesquiterpenes are generally reactive IVOCs with high SOA-forming propensities (e.g. Alfarra et al., 2012), such that their small contribution to the total emissions is still potentially significant. A variety of structurally-different monoterpenes are known to be emitted (e.g. Owen et al., 2001), with the speciation varying with vegetation type and other factors (e.g. season: Llusia and Penuelas, 2000). They possess a wide variability in reactivity, but the applied speciation in assessment studies is usually determined by the representation of chemical processing that is available. The OVOC category potentially includes an enormous variety hydrocarbons and oxygenated compounds, and is likely to contain many currently unidentified species (e.g. Helmig et al., 1999; NATAIR, 2007; Goldstein and Galbally, 2007). It is often represented by small oxygenated compounds (e.g. methanol, ethanol, acetaldehyde and acetone) in modelling applications (e.g. NATAIR, 2007), with these species possessing low propensities to form SOA, although contributions from larger species up to C_{14} have been reported in observational studies (Helmig et al., 1999). Green leaf volatiles (GLVs) are a sub-class of OVOCs that, according to some estimates, may contribute 1-5 Tg yr^{-1} to global SOA yields, around one third of that estimated to be produced by isoprene. Many GLVs are released when plants experience mechanical damage, such as grazing or cutting. As such they a class of biogenic compounds over which there is some potential to exert policy controls.

A1.1.3.3: Spatial variation in biogenic NMVOC emissions

Emissions of biogenic NMVOCs possess substantial spatial variations across the European domain, resulting from variations in land use and conditions (e.g. temperature). Mapped emissions for biogenic NMVOCs are reported at relatively high spatial resolution, e.g. 12 km x 12 km for Great Britain (Stewart et al., 2003) and 0.089° x 089° for Europe (Karl et al., 2009), but are often aggregated to 50 km x 50 km for modelling applications (e.g. Vieno et al., 2010). These spatial resolutions cannot resolve the variation of primary pollutant emissions close to a receptor, but are generally sufficient for applications related to the formation of SOA, because of the time and distance scales required for the chemical processing of most precursor organic compounds (see section A2). However, a possible exception is rapid SOA formation from the oxidation of reactive seqsuiterpenes (e.g. β-caryophyllene).

Uncertainties in the spatial variation of the NMVOC emissions are generally not quantified and reported.

A1.1.3.4: Temporal variation in biogenic NMVOC emissions

In addition to the broad seasonal variability illustrated in Figures A.2 and A.3, emissions of biogenic NMVOCs possess enormous shorter timescale temporal variability resulting from their dependence on temperature and light, and other environmental factors such as water stress and disease. The methods discussed above, based on mapped emission potentials and environmental correction factors, intrinsically include representation of the temporal variability and capture elevations in emissions under episodic heat wave conditions. They are therefore a more appropriate method of representing biogenic emissions than other approaches, e.g. based on annual totals and default temporal profiles, as used for anthropogenic emissions.

A1.1.3.5: Verification of emissions rates using measurements

Measurements of species concentrations and fluxes can in principle be used to verify emissions rates. In the UK, hourly measurements of isoprene concentrations have been carried out routinely as part of Defra's Automatic Hydrocarbon Network (e.g. Derwent et al., 2000; Dollard et al., 2007). These observations have identified an increasingly important contribution of biogenic sources, as anthropogenic emissions in vehicle exhaust decline (AQEG, 2007, 2009; von Schneidemesser et al., 2011). They have also demonstrated the dependence of the emissions rate on conditions, and its elevation at higher temperatures, as has also clearly been shown in campaign studies at specific locations and times (e.g. Lee et al., 2006). Such observations have been used evaluate isoprene emissions rates, as used in the EMEP4UK model (Vieno et al., 2010), which are based on the representation of Simpson et al. (1999). The comparison suggested that the emissions were underestimated by a factor of about 2 in the locality of the observations, which is well within the estimated uncertainty.

There have been no published measurements of ambient concentrations or trends of monoterpenes, sesquiterpenes or GLVs in the UK. Very recently, monoterpene measurements have been made in London during the Clearflo project in 2012, and these give some indications of typical winter and summer abundances in an urban environment. Interpretation of urban observations of monoterpenes has to take account of the fact that these chemicals are also now widely used in consumer and industrial cleaning products, and a notable anthropogenic source now potentially exists, particularly for limonene (dipentene).

A1.1.4: Emissions of SOA precursors from biomass burning

Emissions from sporadic biomass burning events, such as forest fires, are not usually included in national inventories, although information sources are available. For example,

the Global Fire Emissions Database (GFED) provides a comprehensive source of emissions estimates since 1997, including those of non-methane hydrocarbons, NMHCs (http://www.globalfiredata.org/index.html; van der Werf et al., 2010; Giglio et al., 2010; van Leeuwen and van der Werf, 2011). It makes use of satellite information on fire activity and vegetation productivity to estimate gridded monthly burned area and fire emissions, as well as providing scalars that can be used to calculate higher temporal resolution emissions. The information is reported at a spatial resolution of 0.5° × 0.5°.

Table A.5 shows GFED estimates of annual total NMHC emissions, for selected regions (Europe and North America) and globally. The global emissions are dominated by wildfires in Africa, Asia and South America, with the European contribution being only about 0.3 % (where this excludes contributions from Russia). The mean annual total for Europe is thus less than 1 % of the annual total anthropogenic NMVOC emissions for the EU-27 (see above). However, because of their sporadic nature, biomass burning events can have short-term underlying impacts on air quality in the UK, e.g. as reported for wild fires in Portugal in 2003 (e.g. Tressol et al., 2008).

The speciation of organic emissions from biomass burning has been investigated, both in controlled studies on different types of vegetation under various conditions (e.g. Hays et al., 2002) and through atmospheric observations in biomass burning plumes (e.g. Yokelson et al., 2007; Simpson et al., 2011; Lewis et al., 2013). These studies indicate that the emitted speciation contains a greater proportion of larger VOCs, IVOCs and SVOCs (both hydrocarbons and oxygenates), than the generally more efficient and controlled combustion-related emissions that are included in national anthropogenic inventories. Wildfire burning observations show significant emissions of aromatic containing compounds.. As a result, biomass burning emissions are likely to have a greater propensity per unit mass emission to form SOA.

Domestic burning of biomass for heating is a very understudied area, and little is known about emissions from materials and burners used in the UK. Extrapolating from wildfires, however, would suggest that the impact of changes in domestic burning will be sensed through the Automatic Hydrocarbon Network, via the growth in ambient benzene concentrations.

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Table A.5: Global and selected regional estimates of annual total NMHC emissions (ktonne) from biomass burning, from the Global Fire Emissions Database (GFED) v 3.1 (http://www.globalfiredata.org/index.html). The years of the minimum and maximum emissions are shown in brackets.

	Minimum	**Maximum**	**Mean (1997 2011)**
Europe [a]	30 (2002, 2009, 2010)	120 (2000)	60
Boreal North America	60 (2001)	1650 (2004)	660
Temperate North America	20 (1997)	240 (2007)	110
Global	15210 (2001)	30270 (1997)	20650
Notes: [a] Excluding Russia.			

A1.1.5: Recommendations

- A reliable and consistent representation of the emissions of biogenic VOCs and IVOCs needs to be used in modelling and assessment studies aimed at quantifying SOA formation.
- A more complete speciation of biogenic emissions is required. This should include (i) the subdivision of the monoterpene class into individual species, to characterise the most important contributors and to allow their wide variability in

reactivity and SOA-forming potential to be represented; (ii) better characterisation of the component species making up the OVOC category; and (iii) Inclusion of contributions of additional classes of species with a general high propensity to form SOA (e.g. sesquiterpenes and GLVs) that are not always represented.

- Evaluation of the variability in UK source strengths of biogenic VOC emissions and their contribution to gaseous carbon budget, through speciated ambient measurements of concentrations and fluxes, and with particular emphasis on monoterpenes, GLVs and sesquiterpenes.

- The formation of SOA from anthropogenic precursor emissions is highly sensitive to their speciation. The contributions of IVOCs and SVOCs to the NMVOC total should be better quantified, to ensure that they are fully represented, or separate inventories for IVOCs and SVOCs should be developed, even if these are at a simplified carbon number level.

- Evaluation of the source strengths of anthropogenic VOC emissions and their speciation through ambient measurements of concentrations and fluxes. This should include larger and lower volatility species than are routinely measured by the hydrocarbon network, and should aim to verify contributions from sources additional to road transport (e.g. solvents and other product use).

- Improved characterisation and quantification of the emissions of organic compounds from domestic burning of biomass for heating.


## A1.2: SIA precursors

A1.2.1: Classification of SIA precursors

Observational studies in the UK indicate that the SIA contribution to $PM_{2.5}$ is comprised almost exclusively of sulphate (SO_4^{2-}) and nitrate (NO_3^-), fully neutralised by ammonium (NH_4^+), such that sulphate and nitrate are mainly present as ammonium sulphate, $(NH_4)_2SO_4$, and ammonium nitrate, NH_4NO_3 (AQEG, 2012). Nitrate may also be present as sodium nitrate ($NaNO_3$), particularly in the coarse aerosol fraction.

The major precursors to sulphate aerosol formation are oxidised sulphur emissions, mainly as sulphur dioxide (SO_2), with additional contributions from reduced sulphur emissions, mainly as dimethyl sulphide (DMS, CH_3SCH_3). The major precursors to nitrate aerosol formation are nitrogen oxide (NO_x) emissions, made up of nitric oxide (NO) and nitrogen dioxide (NO_2). The only emitted precursor to ammonium aerosol formation is ammonia (NH_3).

Hydrogen chloride (HCl) may play a role as an SIA precursor under specific conditions, through its reaction with ammonia to form ammonium chloride, NH_4Cl, aerosol.
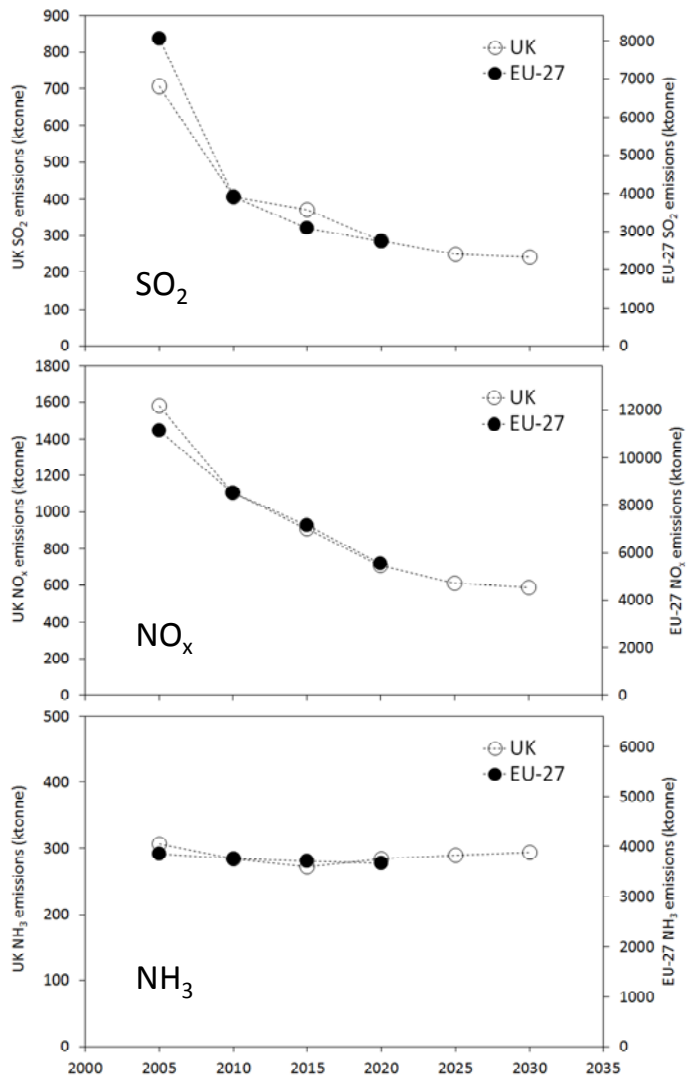
Figure A.4: Historical and projected annual total anthropogenic emissions of SO_2, NO_x and NH_3 for the UK (taken from Misra et al., (2012)) and the EU-27 (AQEG, 2012). The scales for the emissions from the UK and EU-27 have been set so that the data points for 2010 are superimposed.
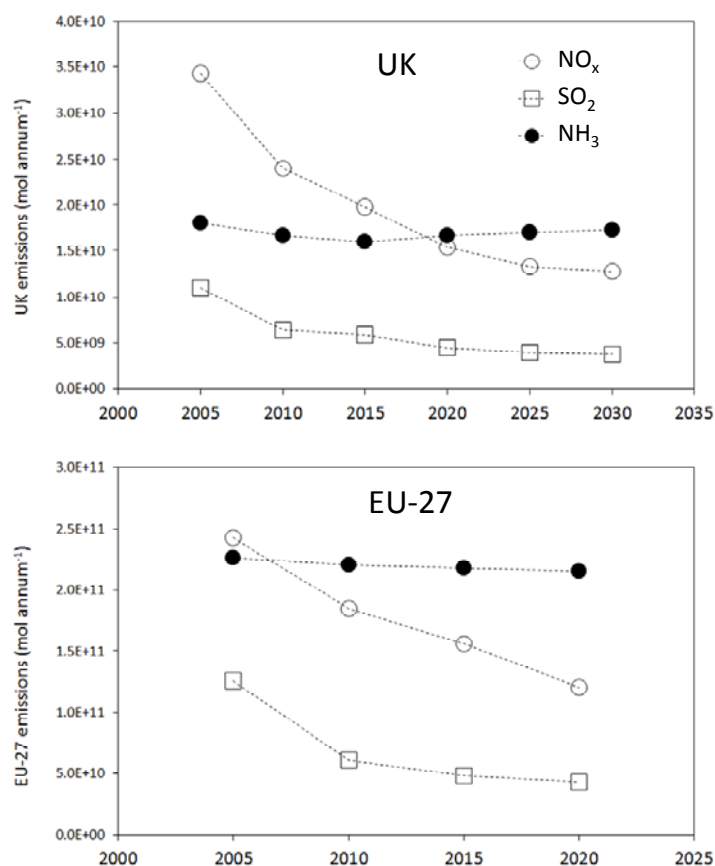
Figure A.5: Historical and projected annual total anthropogenic emissions of SO_2, NO_x and NH_3 for the UK (taken from Misra et al., 2012) and the EU-27 (AQEG, 2012). The data are the same as shown in Figure A.4, but with the annual emissions presented in molar units instead of mass units.

A1.2.2: Anthropogenic emissions of SIA precursors

Estimates of anthropogenic emissions of the major SIA precursors (SO_2, NO_x and NH_3) are provided by the inventories compiled by the National Atmospheric Emissions Inventory (NAEI: http://naei.defra.gov.uk/) for the UK, and collated with corresponding data from an extended domain that includes the whole of Europe by the European Monitoring and Evaluation Programme (EMEP: http://www.emep.int/). The NAEI also provides estimates of HCl emissions. Although the primary role of such inventories is to report on compliance to the EU and other international bodies in relation to national annual emissions totals and trends, the information also provides valuable and comprehensive sources of input data for air quality modelling studies, and is widely used in scientific and policy assessments.

A1.2.2.1: Annual totals and trends in anthropogenic emissions

The total annual emissions of SO_2, NO_x and NH_3, historical annual trends and future annual projections are generally available from the NAEI and EMEP. Figure A.4 shows examples of such data for the UK and collectively for the 27 member states of the EU (EU-27). For SO_2 and NO_x, these show a downward trend in emissions resulting from EU control measures, with continued reductions projected for the future. In contrast, the emissions of NH_3 show little projected trend. Figure A.5 shows the same data, but with the annual emissions presented in molar units instead of mass units to provide a general indication of the relative availability of the precursors to participate in chemical reactions (noting that SO_2 and NO_x first need to be oxidised to form the acidic reagents). This indicates that, on average, NH_3 is already the most abundant emitted SIA precursor in the EU-27, and is projected to become the most abundant precursor in the UK by 2020.

The data in Figure A.4 show that the UK emissions account for about 10 %, 13 % and 8 % of the respective total emissions of SO_2, NO_x and NH_3 from the EU-27 in 2010. This corresponds to average emissions densities in the UK that are greater than in the EU-27 by factors of about 1.8, 2.3 and 1.3 (based on respective areas of 2.44×10^5 km^2 and 4.33×10^6 km^2). The 2010 emissions totals from the extended EMEP domain (which includes the whole of Europe and neighbouring parts of Asia and North Africa) are greater than those for the EU-27 by factors of 6.1, 2.4 and 2.1 for SO_2, NO_x and NH_3, over an area that is about a factor of five larger. However, it is not straightforward to use such comparisons to draw conclusions about the relative impacts of UK and non-UK anthropogenic emissions on SIA formation, for which incorporation of emissions data in appropriate models is required (see section C).

Uncertainties in the UK annual emissions totals are estimated by the NAEI, as described for example in AQEG (2013), with the uncertainties for the 2010 totals being ± 4 % for SO_2, ± 10 % for NO_x and ± 20 % for NH_3. When changes in methodology are implemented, totals for previous years are recalculated consistently so that the same uncertainty can reasonably be assigned to historical totals. The uncertainty in future projections is assessed by running a number of probable scenarios, as described by Misra et al. (2012), leading to an additional uncertainty that increases with time. The spread of results for 2030 suggests additional uncertainties of about ± 1.7 % for SO_2, ± 7 % for NO_x and ± 7.5 % for NH_3.

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Table A.6: Total UK anthropogenic emissions of SO_2, NO_x and NH_3 in 2010 and 2011, and contributions of the relevant source sectors (source: NAEI, from Defra National Statistics Release: Emissions of air pollutants in the UK, 1970 to 2011, 18th December 2012: https://www.gov.uk/government/publications/emissions-of-air-pollutants).

SNAP	Source sectors	2010			2011		
		SO_2	NO_x	NH_3	SO_2	NO_x	NH_3
1	Energy industries (Combustion in power plants and Energy Production)	58.0%	29.8%	0.3%	61.4%	30.3%	0.3%
2	Manufacturing Industries and Construction	18.1%	16.2%	0.1%	16.3%	16.3%	0.2%
3	Road Transport	0.2%	33.3%	3.6%	0.2%	32.8%	3.1%
4	Non-road transport	2.9%	8.0%	-	2.8%	8.8%	-
5	Other sectors (Commercial, residential , agriculture and fishing, stationary and mobile combustion)	10.4%	9.1%	0.7%	10.1%	8.2%	0.7%
6	Other, Mobile (Including military)	1.9%	2.5%	0.0%	1.5%	2.5%	0.0%
7	Fugitive emissions	3.2%	0.2%	0.1%	2.2%	0.2%	0.2%
8	Industrial Processes	5.0%	0.7%	1.4%	5.3%	0.7%	1.6%
9	Solvent and other product use	-	-	0.4%	-	-	0.4%
10	Agriculture	-	-	87.3%	-	-	86.2%
11	Waste	0.2%	0.1%	6.1%	0.2%	0.1%	7.3%
12	Other (included in national total for entire territory) [a]	-	0.0%	0.1%	-	0.0%	0.1%
	National Total (ktonne)	406.92[b]	1106.58[b]	285.69[b]	378.77[b]	1033.08[b]	290.15[b]
	Memo Items (ktonne) [b]	93.93[b]	341.18[b]	8.16[b]	86.55[b]	373.14[b]	8.16[b]

Notes: [a] Emissions from Gibraltar are included in the UK national total. [b] National totals exclude additionally-reported contributions from Memo Items, which are: International & National Aircraft (cruise), International Shipping, NH_3 emissions from wild animals and humans, and Natural Emissions (volcanoes).

It should be noted that the reported national totals exclude contributions from a number of additional sources, denoted "Memo Items" (e.g. from international aviation and shipping: see Table A.6). For SO_2 and NO_x, these items are collectively quite significant, representing an additional 23 % and 36 % in the UK in 2011; whereas for NH_3, they are comparatively minor,

representing an additional 3 %. Emissions from international shipping within the extended EMEP domain (i.e. from the Baltic Sea, Black Sea, Mediterranean Sea, North Sea and north-east Atlantic Ocean) are reported to be about 2400 and 4000 ktonnes in 2010, for SO_2 and NO_x respectively (EMEP, 2002). International shipping therefore accounts for about 10 % and 20 % of the total emissions of these precursors within the extended EMEP domain, with these totals only being factors of 1.7 and 2.1 lower than those for land-based sources in the EU-27 in 2010 (shown in Figure A.4). Because of the projected decreases in NO_x emissions from the EU-27 (Figure A.4), and projected increases from international shipping in European seas (EEA, 2013), it is estimated that the land-based and shipping NO_x totals will be comparable from 2020 onwards (EEA, 2013), such that emissions from international shipping will potentially be a major contributor to regional-scale pollution in Europe. For SO_2, existing legislation on the sulphur content of marine fuels is projected to result in substantial decreases in SO_2 emissions from international shipping (EEA, 2013), such that both these and the land-based emissions are predicted to decline.

HCl represents a very minor precursor to SIA formation. The NAEI quantifies its total UK emissions as 12 ktonne in 2011, which is therefore considerably lower than those of the other SIA precursors discussed above. Emissions of HCl have decreased by more than a factor of 20 since 1990, as a result of a decrease in coal combustion and the implementation of flue gas technologies.

A1.2.2.2: Anthropogenic source categories

The emissions inventories represent emissions in terms of up to 12 broad source categories (e.g. see Table A.6). SO_2 and NO_x emissions are dominated by combustion sources, in particular power generation for SO_2 and power generation and road transport for NO_x. Emissions of NH_3 are dominated by the agricultural emissions (including animal waste and use of fertilisers), but with small notable contributions from waste (e.g. from anaerobic digestion of organic waste) and combustions sources (e.g. road transport).

A1.2.2.3: Spatial variation in anthropogenic emissions

Mapped emissions for the source sectors given in Table A.6 are available from the NAEI for the UK at a resolution of 1 km x 1 km. Similarly, those for the extended EMEP domain are available from EMEP, at a resolution of 50 km x 50 km. These spatial resolutions cannot resolve the variation of primary pollutant emissions close to a receptor, but they are generally sufficient for representing the formation of sulphate and nitrate, because of the time and distance scales required for chemical processing of SO_2 and NO_x (see section A2). However, NH_3 emissions possess a large spatial variability, and it influences SIA formation through direct reaction on a short timescale (see section A2). A treatment of its emissions at high spatial resolution (i.e. much finer than 50 km x 50 km) is therefore ideally required for its role in SIA formation to be fully represented (e.g. Hellsten et al., 2008; Skjøth et al., 2011).

Uncertainties in the spatial variation of the emissions are not quantified and reported, although the NAEI does report "data quality confidence ratings" for each pollutant map (Bush et al., 2008), based on an assessment of the combination of contributory sources for each pollutant. Within this rating the ranking in order of decreasing mapping quality for the major pollutants is reported as: SO_2 > NO_x > NMVOCs > PM_{10} > NH_3.

A1.2.2.4: Temporal variation in anthropogenic emissions

The temporal breakdown of the annual emissions is not officially reported as part of the NAEI and EMEP inventories. However, associated studies have defined temporal profiles for SO_2 and NO_x emissions for the source sectors in Table A.1 by time-of-day, day of the week and month of the year (Jenkin et al., 2000; Friedrich and Reis, 2004), which are used in modelling applications (e.g. Simpson et al., 2012). An updated assessment of the temporal variation of emissions sources is also currently being carried out by the NAEI (AQEG, 2013).

The source strength of NH_3 emissions depends strongly on conditions. For the major agricultural sources (i.e. related to animal waste), the emission rate can depend on a number of factors such as the temperature, pH and total ammonium nitrogen (TAN) content of the emitting medium, and wind speed (e.g. Skjøth et al., 2011). As a result it potentially possesses an enormous temporal variability, and an attempt to represent this needs to be made in modelling studies. Although methods using default temporal profiles have been applied and compared (e.g. de Meij et al., 2006), the development of methods involving mapped emissions potentials and appropriate environmental correction factors may provide a more reliable representation of the temporal variation and dependence on conditions (e.g. Skjøth et al., 2011).

A1.2.2.5: Verification of emissions rates using measurements

As discussed in detail by AQEG (2013), measurements of species concentrations and fluxes can in principle be used to verify emissions rates in published inventories, although such studies are not carried out regularly and systematically.

A1.2.3: Natural emissions of SIA precursors

Emissions of from natural sources may also have an impact on SIA formation. Volcanic emissions of SO_2 are reported to be 2627 ktonne within the EMEP domain in 2010 (EMEP, 2012). This represents 11 % of the domain total, and is a factor of six greater than the UK anthropogenic total for 2010. However, the majority of volcanic emissions are emitted either in Sicily or Iceland, such that the impact on the UK is likely to be limited.

Emissions of reduced sulphur, mainly as dimethyl sulphide (DMS, CH_3SCH_3), have an important impact on the global biogeochemical sulphur cycle. Produced by marine phytoplankton, DMS is a ubiquitous component of seawater, and readily undergoes sea-to-air exchange. It has been observed at coastal locations in the UK, such as north Norfolk (e.g. Carslaw et al., 1997), and Brittany (e.g. Putaud et al., 1999) and has been shown to have an impact on chemical processes at those locations. Marine sulphur emissions are reported to be 743 ktonne (as an SO_2 equivalent) for the EMEP domain in 2010 (EMEP, 2012). This represents 3 % of the domain total, and is approaching a factor of two greater than the UK anthropogenic total for 2010. In addition to DMS, the total may also have smaller contributions from other reduced sulphur compounds, such as hydrogen sulphide (H_2S), carbonyl sulphide (OCS), methanethiol (CH_3SH) and dimethyl disulphide (DMDS, CH_3SSCH_3).

NO_x is also emitted from soil, in the form of NO (e.g. Simpson et al., 1999). Emissions from the EU-15 are reported to be 99.2 ktonne N from forest soils and 98 ktonne N from agricultural soils, in 2000 (NATAIR, 2007). This equates to a total of 648 ktonne (as an NO_2 equivalent), which is about 8 % of the 2010 anthropogenic NO_x total for the EU-27. For the UK, NATAIR (2007) estimates agricultural soil emissions to dominate, at 10 ktonne N in 2000. This equates to 33 ktonne (as an NO_2 equivalent), which is about 3 % of the UK anthropogenic NO_x totals in 2010 and 2011.

Lightning and corona discharge during thunderstorms result in the formation of NO_x in the atmosphere, mainly as NO. Annual emissions from the EU-27 are estimated to be about 10 ktonne (NATAIR, 2007), where this figure relates to NO produced at an altitude < 1000 m. This therefore represents only a minor source of NO_x, compared with other anthropogenic and natural sources.

1.2.4: Emissions of SIA precursors from biomass burning

Emissions from sporadic biomass burning events, such as forest fires, are not usually included in national inventories, although information sources are available. For example, the Global Fire Emissions Database (GFED) provides a comprehensive source of emissions estimates since 1997, including those of SO_2, NO_x and NH_3

(http://www.globalfiredata.org/index.html; van der Werf et al., 2010; Giglio et al., 2010; van Leeuwen et al., 2011). It makes use of satellite information on fire activity and vegetation productivity to estimate gridded monthly burned area and fire emissions, as well as providing scalars that can be used to calculate higher temporal resolution emissions. The information is reported at a spatial resolution of 0.5° × 0.5°.

Table A.7 shows GFED estimates of annual total SO_2, NO_x and NH_3 emissions, for selected regions (Europe and North America) and globally. The global emissions are dominated by wildfires in Africa, Asia and South America, with the respective European contributions being only about 0.2 %, 0.2 % and 0.8 % (where this excludes contributions from Russia). The mean annual totals for Europe are thus about 0.1 %, 0.3 % and 1.4 % of the annual total anthropogenic SO_2, NO_x and NH_3 emissions for the EU-27 (see above). However, because of their sporadic nature, biomass burning events can have short-term underlying impacts on air quality in the UK, e.g. as reported for wild fires in Portugal in 2003 (e.g. Tressol et al., 2008).

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Table A.7: Global and selected regional estimates of annual total emissions of SO_2, NO_x and NH_3 (ktonne) from biomass burning, from the Global Fire Emissions Database (GFED) v 3.1 (http://www.globalfiredata.org/index.html). The years of the minimum and maximum emissions are shown in brackets.

		Minimum	**Maximum**	**Mean (1997 2011)**
Europe [a]	SO_2	2 (2002, 2008)	11 (2000)	5
	NO_x	10 (2002)	45 (2000)	22
	NH_3	22 (2010)	128 (2001)	53
Boreal North America	SO_2	9 (2001)	288 (2004)	114
	NO_x	31 (2001)	986 (2004)	394
	NH_3	20 (2001)	492 (2004)	199
Temperate North America	SO_2	2 (1997)	33 (2007)	14
	NO_x	9 (1997)	122 (2007)	55
	NH_3	10 (1997)	102 (2007)	63
Global	SO_2	1665 (2001)	3358 (1998)	2318
	NO_x	7410 (2009)	13929 (1998)	9763
	NH_3	4662 (2011)	9102 (1998)	6278

Notes: [a] Excluding Russia.

A1.2.5: Recommendations

- There is a need to represent the high spatial and temporal variability of NH_3 emissions, and to evaluate the effect of such variability on SIA formation.
- Evaluation of the source strengths of SIA precursor emissions, and their trends, through ambient measurements of concentrations and fluxes. This should include improved characterisation of NO_x emissions from international shipping, which are projected to make an increasing European contribution.

# A2: Chemical and physical processes forming secondary aerosol

A2.1: Processing of SOA precursors

A2.1.1: Gas-phase oxidation of emitted organic compounds

A2.1.1.1: Overview of understanding

SOA is formed when the gas-phase chemical processing of emitted VOCs, IVOCs and SVOCs generates oxygenated products that undergo gas-to-aerosol transfer. As described above (section A1), many thousands of different organic compounds are potentially emitted from anthropogenic and biogenic sources, such that the gas phase chemical system is highly complex. The gas phase oxidation of each emitted organic compound may be initiated by one or more reactions, including reaction with hydroxyl (OH) radicals (which are mainly produced by photolysis processes during the day), reaction with nitrate (NO_3) radicals (which are most abundant during the night) and reaction with ozone (O_3) (e.g. Jenkin and Clemitshaw, 2000; Atkinson and Arey, 2003; Atkinson et al., 2006). VOCs may also react with halogen atoms although the effect has not been reported to be significant in the UK atmosphere. Other initiation reactions may contribute under specific conditions (e.g. reaction with halogen atoms), although these have not been reported to be significant in the UK atmosphere. The relative importance of these reactions depends on the structure of the given organic compound and on the ambient conditions (see below).

As a result of the complexity of the emitted VOC, IVOC and SVOC mixture, and of the oxidation chemistry, the atmosphere contains an enormous number of structurally different oxygenated organic compounds, possessing a very wide range of properties (e.g. reactivity, photolability, volatility and aqueous solubility) and different propensities to participate in gas-to-aerosol transfer mechanisms. As described further below (section A2.1.2), these mechanisms may be available to varying degrees for most oxygenated organic products, and the ability of a product to transfer to the aerosol phase can be influenced by further chemical reactions, either on the aerosol surface or in the bulk aerosol which, in turn, are influenced by the composition of the aerosol. However, a major factor influencing gas-to-aerosol transfer is product volatility, because this determines the extent to which a product is partitioned between the phases in the absence of condensed-phase chemical reactions. The following general description of the gas phase oxidation chemistry therefore highlights current understanding of the impacts of the chemistry on the volatility of the products formed.
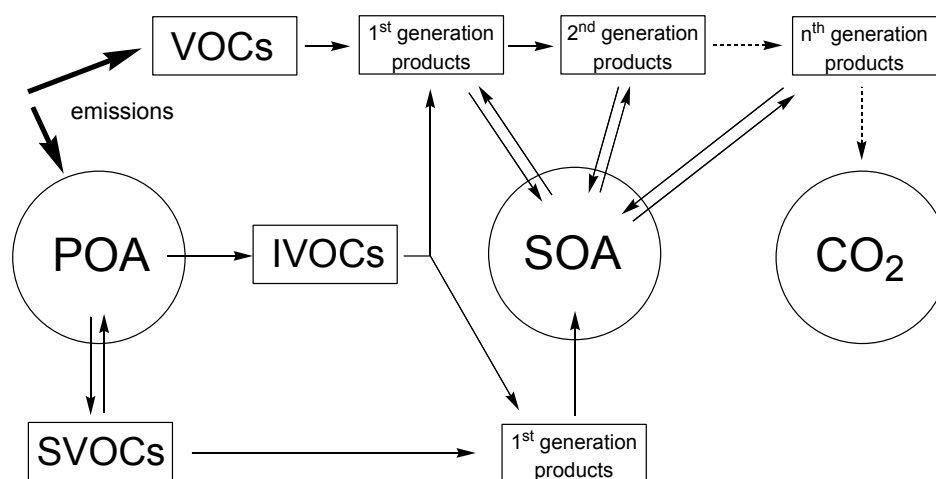
Figure A.6: Schematic representation of the emission and chemical processing of emitted organic material.

As described in more detail elsewhere (e.g. Jenkin and Clemitshaw, 2000; Kroll and Seinfeld, 2008; Hallquist et al., 2009), the initial oxidation chemistry leads to the production of a set of organic products containing one or more polar oxygenated functional groups, which tend to make the products less volatile than the parent. Further oxidation may introduce additional functional groups, such that the "second generation" set of products

(and subsequent generations) may be of even lower volatility. However, the oxidation mechanisms also lead to fragmentation of the carbon chains to form lower molecular weight oxygenates (which tend to be more volatile), and the gas phase oxidation ultimately converts all the carbon in the emitted organic compounds into carbon dioxide (CO_2). This therefore differs to the situation for the major SIA precursors, SO_2 and NO_x, for which the ultimate products of gas phase oxidation (i.e. H_2SO_4 and HNO_3) are the forms that are most associated with the condensed phase. SOA is therefore formed from the gas-to-aerosol transfer of partially oxidized organic material, occurring in competition with further oxidation in the gas phase, as shown schematically in Figure A.6. The formation of SOA can also be inhibited by removal of the gas phase oxygenated products by deposition processes.

For all classes of emitted organic compound, the propensity for SOA formation (per unit emission) tends to increase as the size of the organic compound is increased. This arises partly because the reactivity of larger organic molecules in a given class is generally greater than that of smaller ones (i.e. the rate of accumulation of oxidised products increases with the size of the parent organic compound), and partly because the volatility of the oxidation products formed from the larger organic compounds is lower. Consequently, the oxidation of larger organic compounds is more likely to generate high concentrations of lower volatility products. As a result, IVOCs and SVOCs can potentially have an important collective impact of SOA formation, even if their total emissions are much less than those of VOCs (e.g. Pye and Seinfeld, 2010). As shown in Figure A.6, oxidation of the gas phase component of SVOCs (and to some extent IVOCs) is likely to generate non-volatile products at the first oxidation step, which reside entirely in the aerosol phase. Because of the incorporation of oxygenated functional groups, the vaporisation of compounds that are initially in the POA phase, followed by oxidation and condensation leads to a net increase in organic aerosol mass.

Certain classes of emitted organic compound are also more likely to lead to SOA formation, by virtue of their general high reactivity and types of oxidation product formed. Of particular significance are cyclic compounds, since the products of fragmentation (i.e. ring opening) processes are often of the same (or similar) carbon number as the parent compound. Furthermore, in the cases of aromatic compounds and cycloalkenes (which include many monoterpenes and sesquiterpenes), oxidation occurs predominantly by an "addition" mechanism, so that the first generation products contain two (or more) polar functional groups. Consequently, the oxidation of these classes of compound is more likely to lead to the generation of low-volatility products than the oxidation of similar-sized compounds in other classes. The characterisation of SOA formation from the degradation of aromatic hydrocarbons, monoterpenes and sesquiterpenes has therefore been the focus of numerous chamber investigations over the years (e.g. Hallquist et al., 2009 and references therein).

The distribution of products formed from the oxidation of VOCs, IVOCs and SVOCs also depends on the prevailing ambient conditions. This is partly because the relative contribution of the initiation reactions varies with conditions, as a result of the differing effects on the ambient levels of OH, NO_3 and O_3 (see below). However, the oxidised product distribution is also generally dependent on the availability of NO_x, such that this can be an important factor in determining the influence that a given precursor organic compound has on the formation of SOA, as evidenced by the NO_x-dependence of SOA yields in chamber investigations (e.g. Johnson et al., 2004; Presto et al., 2005; Ng et al., 2007a).

It should be noted that the gas phase oxidation of organic compounds also impacts on the formation of O_3 and on the availability of oxidising free radicals, such as OH (e.g. see Jenkin and Clemitshaw, 2000). As a result, the gas phase chemistry has an indirect effect on SOA formation, by virtue of its influence on the oxidation rates of organic compounds in general. Equally, the formation of SOA removes organic material from the gas phase, and therefore potentially has a feedback on the formation of O_3 and the availability of free radicals. Consequently, a sound understanding of multiphase atmospheric organic chemistry, and its

adequate representation in models, is important for assessing the formation of both SOA and O_3.

Table A.8: Atmospheric lifetimes of example VOCs, IVOCs and SVOCs, with respect to reaction with OH, NO_3 and O_3 at: (a) representative average levels, and (b) representative episodic levels. Lifetimes are based on reagent levels given in the footnotes, and measured or estimated rate coefficients given in Calvert et al. (2002; 2008) and Atkinson and Arey (2003). A blank entry means the reaction is uncompetitive.

Compound	Class		OH		NO_3	O_3	
			(a)	(b)	(a)	(a)	(b)
decane (n-$C_{10}H_{22}$)	alkane	VOC	26 h	2.6 h	240 d	-	-
pentadecane (n-$C_{15}H_{32}$)	alkane	IVOC	16 h	1.6 h	150 d	-	-
cosane (n-$C_{20}H_{42}$)	alkane	SVOC	11 h	1.1 h	110 d	-	-
α-pinene ($C_{10}H_{16}$)	alkene [c]	VOC	5.3 h	32 min	11 min	6.6 h	2.2 h
β-caryophyllene ($C_{15}H_{24}$)	alkene [d]	IVOC	1.4 h	8.5 min	3.5 min	2.9 min	58 s
toluene (C_7H_8)	aromatic	VOC	49 h	4.9 h	-	-	-
naphthalene ($C_{10}H_8$)	aromatic [e]	IVOC	12 h	1.2 h	-	-	-
pyrene ($C_{16}H_{10}$)	aromatic [f]	SVOC	5.0 h	30 min	-	-	-

Notes: [a] Based on representative average reagent levels, as follows: [OH] = 1 x 10^6 molecule cm^{-3} ($\approx$ 0.04 ppt); [NO_3] = 2.5 x 10^8 molecule cm^{-3} ($\approx$ 10 ppt); [O_3] = 5 x 10^{11} molecule cm^{-3} ($\approx$ 20 ppb). These concentrations are typical of those in the UK, based on both observational and modelling studies (Jenkin and Clemitshaw, 2000). [b] Based on representative episodic reagent levels, as follows: [OH] = 1 x 10^7 molecule cm^{-3} ($\approx$ 0.4 ppt); [O_3] = 1.5 x 10^{12} molecule cm^{-3} ($\approx$ 60 ppb). The concentration of OH is typical of peak values in a regional scale photochemical pollution event, as simulated for the TORCH-2003 campaign using PTM-CRI v2 (Jenkin et al., 2008). The O_3 concentration is typical of that currently observed in regional scale photochemical pollution events. [c] -pinene is a monoterpene. [d] -caryophyllene is a sesquiterpene. [e] Naphthalene is a 2-ring PAH. [f] Pyrene is a 4-ring PAH.

Table A.9: Atmospheric lifetimes of selected octane and monoterpene isomers (all VOCs), with respect to reaction with OH and O_3 at: (a) representative average levels, and (b) representative episodic levels. Lifetimes are based on reagent levels given in Table A.8 footnotes, and measured rate coefficients given in Atkinson and Arey (2003). A blank entry means the reaction is uncompetitive.

Compound	Class	OH		O_3	
		(a)	(b)	(a)	(b)
octane (n-octane)	alkane: octane isomers (C_8H_{18})	1.4 d	3.4 h	-	-
2,3,4-trimethylpentane		1.8 d	4.2 h	-	-
2,2,4-trimethylpentane ("iso-octane")		3.5 d	8.3 h	-	-
2,2,3,3-tetramethylbutane		12 d	1.2 d	-	-
-pinene [c]	alkene: monoterpene isomers ($C_{10}H_{16}$)	5.3 h	32 min	6.6 h	2.2 h
-pinene [d]		3.5 h	21 min	1.5 d	12 h
limonene [e]		1.6 h	9.6 min	2.9 h	58 min
-terpinene [f]		46 min	4.6 min	1.7 min	34 s
ocimene [g]		1.1 h	6.6 min	1.0 h	20 min

Notes: [a] See Table A.8. [b] See Table A.8. [c] Bicyclic monoterpene with endocyclic double bond. [d] Bicyclic monoterpene with exocyclic double bond. [e] Monocyclic diene monoterpene with endocyclic and exocyclic double bonds. [f] Monocyclic conjugated diene monoterpene with endocyclic double donds. [g] Acyclic triene monoterpene.

Oxidation lifetimes of VOCs, IVOCs and SVOCs

The reactivity of emitted organic compounds has an influence on the temporal and spatial scales over which they generate oxygenated products. VOCs, IVOCs and SVOCs cover an enormous range of reactivity, such that their oxidation lifetimes typically vary from minutes to

months under average conditions. Table A.8 shows the lifetimes of selected emitted organic compounds with respect to their reactions with OH radicals, NO_3 radicals and O_3. This illustrates a number of features:

- The lifetimes of organic compounds in a given class generally become shorter as the size of the compound increases.
- Alkenes (including monoterpenes and seqsuiterpenes) are generally more reactive than other classes of organic compound, with oxidation potentially initiated significantly by reaction with OH, NO_3 and O_3.
- The lifetimes of the organic compounds decrease under episodic conditions (i.e. regional scale photochemical pollution events), when concentrations of OH and O_3 are typically elevated.

The lifetimes given in Table A.8 indicate the timescale over which the precursor VOC, IVOC or SVOC is converted into its first-generation oxidation products in the gas phase. For SVOCs (and to some extent for IVOCs), this is also likely to be characteristic of the timescale over which the compound forms SOA, because the first-generation products are of sufficiently low volatility to transfer completely to the aerosol phase. For VOCs (and to some extent for IVOCs), it is likely that no products are formed that transfer completely to the aerosol phase, but that products formed over several generations may be partitioned between the phases to varying degrees, and subject to continued gas-phase chemical processing. As a result, any impact the oxidation of a given VOC has on SOA formation occurs over a much longer timescale than the initial oxidation step. This is similar to the impact of VOC oxidation on O_3 formation, which is known to occur over a multi-day timescale under the conditions of regional-scale photochemical pollution events that influence the UK (e.g. Derwent et al., 2005).

The above discussion provides information on general trends in reactivity and lifetime for organic compounds, and how these vary with compound size and class. In addition to this, there can also be considerable variability in the reactivity (and other properties) for isomeric compounds within the same class (see Table A.9). For example, highly branched alkanes tend to have a lower reactivity (i.e. longer lifetime) than the normal alkanes, or slightly branched isomers, as shown for the example of isomers of octane (i.e. C_8H_{18}) in Table A.9. However, of particular significance for SOA formation is the wide variability in reactivity for biogenic hydrocarbons, such as monoterpenes (i.e. isomers of $C_{10}H_{16}$), as also shown in Table A.9. This further illustrates the importance of a fully resolved emissions speciation, as discussed in section A1.

A2.1.1.2: Representation of gas phase organic chemistry in atmospheric models

Detailed explicit mechanisms

As indicated above, the chemistry involved in the gas phase oxidation of the emitted VOC, IVOC and SVOC mixture is highly detailed. In practice, only a very small fraction of the reactions occurring in the atmospheric oxidation of organic compounds has been studied experimentally. Only for the simplest light hydrocarbons and oxygenates (e.g. methane, ethane, ethene, methanol, acetaldehyde, acetone and dimethyl ether) have the kinetics and products of the majority of the elementary reactions involved in their complete degradation to CO_2 and H_2O been investigated (Atkinson et al., 2006), and those data continue to be refined (http://iupac.pole-ether.fr/). For a number of larger and more complex VOCs (including isoprene, selected terpenes and aromatic hydrocarbons), some important aspects of their degradation chemistry have been studied experimentally, and information continues to be reported in the literature. This information provides a partial basis for defining their oxidation chemistry, which can be supplemented by the inclusion of reactions and associated parameters which are inferred from the more detailed understanding of the chemistry of the smaller compounds. For many other VOCs, IVOCs and SVOCs little or no

experimental information exists, and their degradation chemistry (if represented in a mechanism) needs to be defined almost exclusively by inference. Although the reaction parameters assigned to many individual reactions cannot (are unlikely to be) verified experimentally, the global performance of oxidation mechanisms developed in this way is usually evaluated or optimised using appropriate data from environmental chambers (e.g. Stockwell et al., 1997; Pinho et al., 2007; Pinho et al., 2005; Carter, 2008).

A variety of explicit chemical mechanisms describing the oxidation of emitted organic compounds have been developed for use in models, although these have traditionally been designed to represent the role of VOCs as precursors to O_3 formation. There have been relatively few attempts to assemble chemical mechanisms that represent the detail and complexity of atmospheric organic chemistry, and which may provide an indication of the distribution of oxygenated products available to participate in gas-to-aerosol transfer mechanisms. A widely used example is the Master Chemical Mechanism (MCM: http://mcm.leeds.ac.uk/MCM/), the current version of which (MCM v3.2), treats the gas phase oxidation of 143 emitted organic compounds, and contains about 17,000 elementary reactions of about 6,700 species. Of the 17,000 chemical reactions, only about 500 have measured parameters, such that the kinetics and products of the large number of unstudied chemical reactions are estimated on the basis of the known reactions of a comparatively small number of similar chemical species using rules and methods defined in a published protocol (e.g. Jenkin et al., 1997; Wagner et al., 2003; Saunders et al., 2003).

Although the MCM (coupled with a representation of gas-aerosol product partitioning) has been used in number of assessments of SOA formation with some degree of success (Johnson et al., 2006a; 2006b; Utembe et al., 2009; Derwent et al., 2010b; Barley et al., 2011), there are a number of gaps in the gas phase representation that have a likely impact on the results:

- The MCM necessarily includes a level of simplification, so that its size remains practical and manageable (e.g. Jenkin et al., 1997). As a result, it is not an exhaustive representation of the gas phase chemistry. The simplification is partly achieved by generally omitting reaction channels of less than 5 % probability, and by imposing greater simplifications on the chemistry of certain product types for which the chemistry was traditionally less well characterised. This has the effect of omitting the formation of an extremely large number of products (probably at least 10^{12}) formed in very low yields, which would otherwise have a collectively significant contribution. These products would likely be highly functionalised (e.g. Aumont et al., 2005), and would therefore have a strong propensity to transfer to the aerosol phase.

- The emitted organic compounds treated MCM v3.2 are almost all VOCs, such that there is generally no consideration of IVOCs or SVOCs. For example, the largest alkane is dodecane (n-$C_{12}H_{26}$), and the largest alkenes are the monoterpenes, α-pinene, β-pinene and limonene ($C_{10}H_{16}$); and the sesquiterpene, β-caryophyllene ($C_{15}H_{24}$), which is the sole IVOC represented.

- The mechanism only includes a limited number of isomers of the larger VOCs, so that differences in reactivity and SOA-forming propensity from one isomer to another cannot be fully represented. For example, Owen et al. (2001) reported contributions from about 20 different monoterpenes emitted from biogenic sources, which would need to be represented by α-pinene, β-pinene and limonene when applying MCM v3.2. Similarly, the NAEI anthropogenic NMVOC speciation includes contributions from 23 isomers of $C_{10}H_{22}$ (Passant, 2002), which would need to be represented by the single isomer, decane (n-$C_{10}H_{22}$) when applying MCM v3.2.

These omissions can be addressed by using automated mechanism construction methods that are based on a well-developed set of rules (e.g. as defined in the MCM protocol), as shown by Aumont et al. (2005). In principle, such methods can be used to generate fully

explicit mechanisms for any set of emitted organic compounds, as demonstrated recently in relation to SOA formation from a series of IVOCs and SVOCs up to n-$C_{24}H_{50}$ (Aumont et al., 2012). In accurately reflecting the true complexity of atmospheric organic chemistry, however, it is clear that such mechanisms are prohibitively large, and unsuitable for application in practical atmospheric models – which is also generally the case for MCM v3.2. These approaches therefore ideally need to be used as benchmark representations of the oxidation chemistry, against which reduced representations can be tested using sets of scenarios in zero-dimensional models.

Reduced mechanisms

A large variety of reduced mechanisms have been used to describe organic chemistry more economically in science and policy models (e.g. see Annex B of Derwent et al., 2010a), with most mechanisms originally being developed to describe O_3 formation from the oxidation of VOCs. The methods traditionally used to reduce these gas phase oxidation mechanisms have usually involved either or both of:

(a) A systematic reduction in the complexity of the chemistry for the considered suite of organic compounds (i.e. "lumped chemistry"), and/or;

(b) The lumping of emissions, so that the chemistry for one organic compound can be used to represent that of a number of organic compounds (i.e. "lumped emissions").

These methods are not necessarily ideal for producing mechanisms that can maintain the SOA-forming propensity of the chemistry relative to that of a detailed explicit reference mechanism, and which can therefore provide a consistent coupled representation of SOA formation. Lumped chemistry intermediates, developed using method (a), usually each represent a large number of species in a detailed mechanism which have a similar impact upon O_3 formation when they react, but which possess a very wide range of physical properties (e.g. vapour pressure). As a result, they are not appropriate to represent SOA formation. Reduced mechanisms developed by emissions-lumping (i.e. method (b)), tend to represent a number of emitted compounds in a given class (e.g. alkanes) by a single compound, usually the smallest, because it invariably has the simplest chemistry. Clearly this procedure does not preserve the SOA-forming propensity of the set of emitted compounds.

Although most widely-used reduced mechanisms have subsequently been adapted to include a representation of SOA formation, these representations have usually been decoupled from the gas phase chemistry forming O_3, because of difficulties associated with the above limitations. A series of emitted organic compounds is used to represent SOA precursors, with some or all of these compounds being complementary to those used as O_3 precursors (e.g. as is usually the case for monoterpenes and sesquiterpenes). The emitted SOA precursors are oxidised to form a separate set of SOA-forming products. The gas phase oxidation rates of the emitted compounds and products are calculated using the concentrations of reagent species, such as OH, NO_3 and O_3, generated by the standard gas phase chemistry scheme. The yields and gas-to-aerosol partitioning properties of the SOA-forming products are usually empirically-based, and have been derived using the results of chamber studies (e.g. Kroll and Seinfeld, 2008; Hallquist et al., 2009). These methods are described further in section A2.1.2 below.

There are very few reduced mechanisms for which coupled representations of SOA formation and gas phase oxidation have been developed (e.g. Griffin et al., 2005; Utembe et al., 2009). One example is the Common Representative Intermediates mechanism, CRI v2, which was initially developed using systematically lumped chemistry (i.e. method (a) above) to provide a representation of the gas phase oxidation chemistry with a performance that is traceable to that of MCM v3.1 (Jenkin et al., 2008). The subsequent development of an SOA module (Utembe et al., 2009) was subject to some of the difficulties outlined above, in

relation to assigning properties to the lumped intermediates. However, it was shown that the results of reference simulations of SOA formation carried out with MCM v3.1 for a range of conditions, could be broadly recreated by including gas-to-aerosol partitioning for a limited number of carefully-selected oxidised intermediates, and empirically optimising their partitioning parameters. Although further development is clearly required, this showed the potential for generating coupled reduced SOA schemes by systematic reduction of detailed explicit chemistry.

A2.1.2: Recommendations

- Development of highly-detailed representations of the oxidation chemistry of emitted VOCs, IVOCs and SVOCs is ideally required to provide the basis for reference simulations that fully represent the true detail of atmospheric organic chemistry, and the dependence of SOA formation on emitted precursor identity and ambient conditions.

- Development and application of methodologies for the automated machine generation of such highly-detailed representations.

- Development and application of methodologies for the systematic reduction of detailed gas phase schemes, to produce reduced mechanisms appropriate to for coupled representations of SOA formation.

- Development of coupled representations of SOA formation from both detailed and reduced schemes.

A2.2: Processing of SIA precursors

A2.2.1: Oxidation of SO_x to sulphate

As discussed above in section A1.2.2, the major emitted precursors to sulphate aerosol formation are sulphur dioxide (SO_2), emitted from both anthropogenic and natural sources, and dimethyl sulphide (DMS, CH_3SCH_3) emitted from marine sources.

Oxidation of SO_2

The oxidation of emitted SO_2 can occur by both gaseous phase and aqueous phase routes, as illustrated in Figure A.7. The predominant gas phase reaction for SO_2 is reaction with the hydroxyl radical (OH), which initiates a sequence of reactions that generate gaseous sulphuric acid, H_2SO_4. Consequently, the fractional conversion of SO_2 to gaseous H_2SO_4 is determined by how efficiently the gas-phase oxidation route, initiated by the reaction with OH radicals, competes with the alternative oxidation or removal routes for SO_2 (e.g. aqueous phase oxidation or dry deposition). H_2SO_4 is sufficiently non-volatile to generate SIA by the processes of nucleation and condensation. The gas phase oxidation of SO_2 may therefore result in the formation of new aerosol particles, or the growth of existing ones. At a typical average OH concentration of 10^6 molecule cm^{-3} (0.04 ppt), SO_2 is oxidized to H_2SO_4 at a rate of about 0.3 % hr^{-1} (i.e. lifetime $\approx$ 2 weeks) although the conversion rate is correspondingly greater at elevated OH concentrations consistent with a photochemical episode.

Although the gas phase oxidation of SO_2 can dominate under specific conditions, oxidation in the aqueous phase is generally more important. This is largely governed by how frequently polluted air masses encounter clouds, and typically occurs at a rate of about 1 % hr^{-1}, under UK conditions (e.g. Metcalfe et al., 1995). As shown in Figure A.7, the solvated

form of SO_2 (i.e. $SO_2.H_2O$) is present in equilibrium with the ionic species HSO_3^- and SO_3^{2-}. In all these species, sulphur is in the +4 oxidation state, and they are usually collectively denoted S(IV). Oxidation to the +6 oxidation state (i.e. S(VI) or "sulphate") is promoted by the presence of aqueous phase oxidants and catalysts. As described in detail elsewhere (e.g. Finlayson-Pitts and Pitts, 2000), dissolved hydrogen peroxide (H_2O_2) and ozone (O_3) are believed to be particularly important, although oxidation by O_3 becomes progressively less efficient with increasing acidity of the cloud droplets. The chemical processing of SO_2 by the cloud therefore leads to the oxidation of S(IV) to S(VI) and, upon evaporation, the resultant particles contain additional sulphate. Unlike the gas-phase oxidation route, however, aqueous phase oxidation cannot result in nucleation of new aerosol particles.
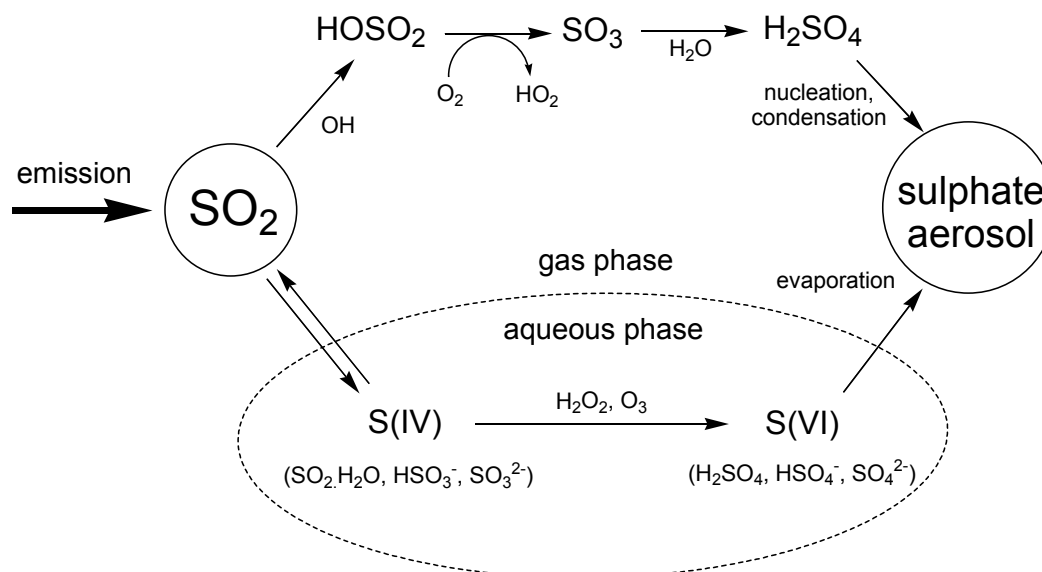

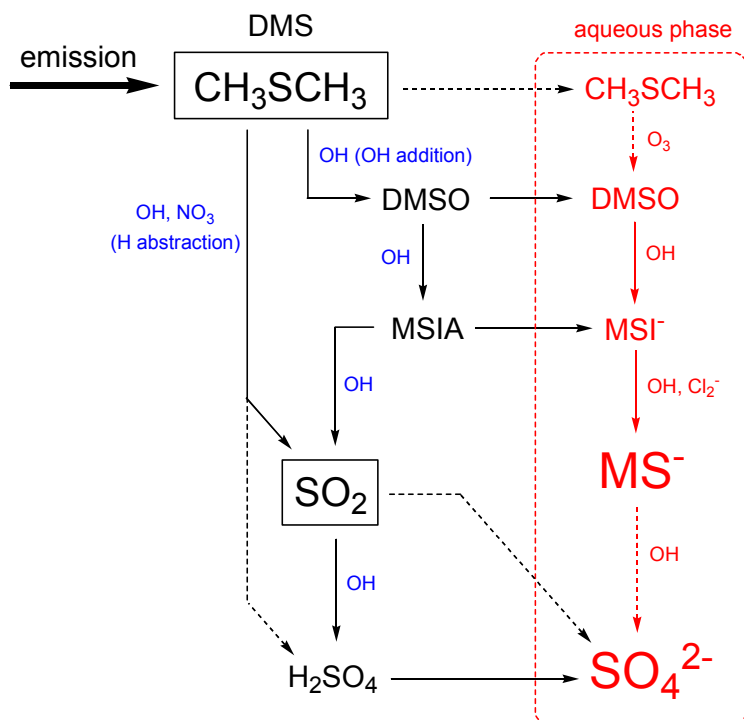Figure A.7: Major chemical processes involved in the oxidation of SO_2 to sulphate aerosol.

Figure A.8: Main features of the atmospheric oxidation mechanism of DMS, showing processes occurring in the gaseous and aqueous phases.

Oxidation of DMS

The oxidation of DMS in the gas phase is initiated mainly by its gas phase reactions with OH radicals (which are mainly produced by photolysis processes during the day) and reaction with NO_3 radicals (which are most abundant during the night). Reaction with the bromine oxide radical (BrO) is also reported to make a significant global contribution to DMS oxidation (e.g. Breider et al., 2010), with BrO derived mainly from bromine release from sea-salt aerosols.

The lifetime of DMS with respect to removal by reaction with OH radicals is about 40 hours, at a typical average OH concentration of 10^6 molecule cm^{-3} (0.04 ppt). The reaction with NO_3 is about equally important when NO_3 concentrations are about an order of magnitude greater than those of OH, and reported budget calculations over wide geographical scales suggest that this is generally the case (e.g. Lucas and Prinn, 2005). However, NO_3 levels as high as about 10 ppt have been reported at some coastal locations, including the UK (e.g. Carslaw et al., 1997). Under such conditions, NO_3-initiated oxidation potentially dominates DMS removal, with an associated DMS lifetime of about 1 hour.

The gas phase degradation chemistry potentially generates a large number of intermediate products (e.g. as reviewed in detail by Barnes et al., 2006). Figure A.8 shows a simplified representation of the chemistry, which identifies some of the main products formed from the OH and NO_3 initiated chemistry. Current understanding predicts SO_2 to be the ultimate dominant product of gas phase oxidation, with its further oxidation leading to the formation of sulphate aerosol, as described above. Sulphuric acid (H_2SO_4) is also formed directly (but in low yield) from the gas phase oxidation of DMS.

Aqueous phase chemical processes are predicted to have a significant influence on the product distribution, with these leading predominantly to the formation of methane sulphonate (MS^-, $CH_3SO_3^-$) in the aerosol phase (e.g. Zhu et al., 2006). The direct aqueous phase ozonolysis of DMS potentially makes a small contribution to its removal under tropospheric cloud conditions, particularly at lower temperatures. However, as shown in Figure A.8, the aqueous phase oxidation of the soluble intermediates dimethyl sulphoxide (DMSO) and/or methane sulphinic acid (MSIA), formed from the gas phase chemistry, are believed to represent the major route to MS^- formation. In the presence of sufficient cloud/aerosol water, therefore, the gas phase initiation reactions lead to significant formation of both sulphate (SO_4^{2-}) aerosol and methane sulphonate (MS^-) aerosol. MS^- is estimated to be further oxidized to SO_4^{2-} in aqueous solution, on a characteristic timescale of about 2 days (e.g. Zhu et al., 2006).

A2.2.2: Oxidation of NO_x to nitrate

Nitrate aerosol is formed from the oxidation of emitted nitrogen oxides (NO_x). As shown in Figure A.9, nitrate aerosol is formed from the oxidation of nitrogen dioxide (NO_2), which is itself mainly derived from the oxidation of emitted nitric oxide (NO). The predominant daylight oxidation route for NO_2 is initiated by its reaction with OH, which leads to quantitative formation of gaseous nitric acid, HNO_3. At a typical background OH concentration of 0.04 ppt, NO_2 is converted to HNO_3 at about 5 % hr^{-1} (i.e. lifetime $\approx$ 20 hours) by this reaction, although the conversion rate is correspondingly more rapid at elevated OH concentrations consistent with a photochemical episode. HNO_3 is highly soluble, and also shows a strong affinity for surfaces. It is therefore scavenged by existing aerosol particles and droplets to form nitrate aerosol, in competition with removal by deposition to the ground. The uptake of HNO_3 into sea-salt aerosol

proceeds via an acid-displacement reaction, leading to the formation of condensed phase sodium nitrate ($NaNO_3$) and release of gaseous hydrogen chloride (HCl). As described further below, HNO_3 can also combine with emitted ammonia (NH_3) to form ammonium nitrate aerosol (NH_4NO_3).
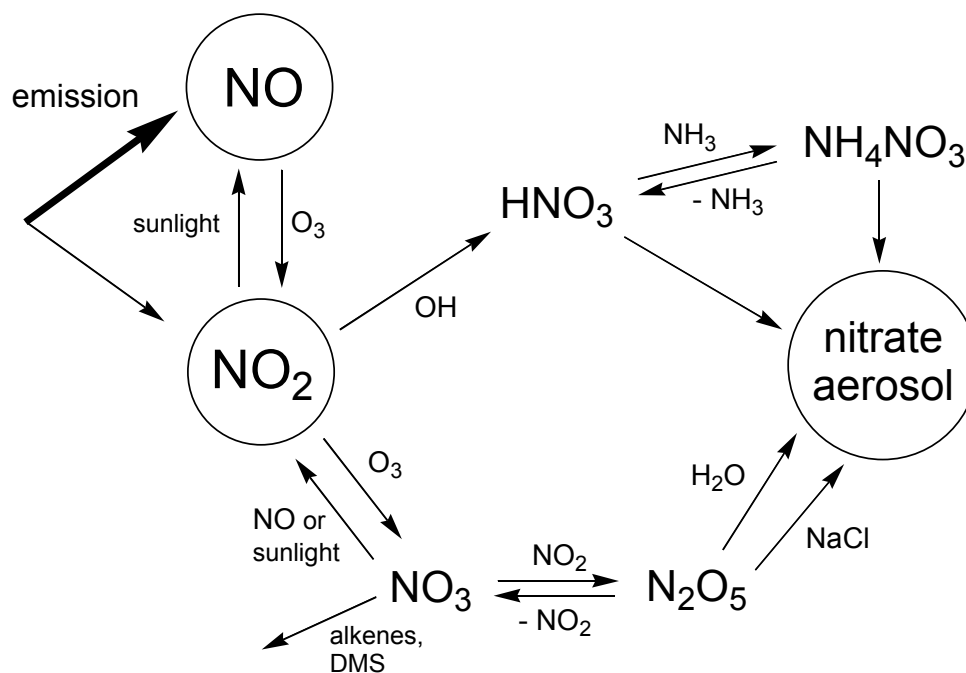

Figure A.9: Major chemical processes involved in the oxidation of NO_x to nitrate aerosol.

Nitrate aerosol is also generated via the formation of the higher oxide, N_2O_5, which is formed following the reaction NO_2 with O_3 to form the nitrate radical, NO_3 (see Figure A.9). However, this reaction sequence is very inefficient during the day, and at higher levels of NO, because the intermediate NO_3 radical photolyses and reacts with NO rapidly, leading to NO_x regeneration. Because N_2O_5 is in equilibrium with NO_3, it also cannot persist at significant concentrations under these conditions. During the night, significant NO_2 to N_2O_5 conversion can occur, with the potential for nitrate aerosol generation from the reaction of N_2O_5 with H_2O on the surfaces of existing aerosol particles and droplets. The reaction of N_2O_5 with sea-salt aerosol, also leads to the formation of condensed phase sodium nitrate ($NaNO_3$) and gas phase $ClNO_2$, which photolysis to result in partial regeneration of NO_2, and release of chlorine atoms.

The conversion of NO_2 to nitrate aerosol, via N_2O_5, potentially occurs at a comparable rate to that from OH initiated oxidation during daytime. However, its efficiency can be reduced by the reaction of NO_3 with residual night-time NO, or as a result of its reactions some organic compounds (e.g. alkenes and DMS), as described in previous sections.

A2.2.3: Conversion of NH_3 to ammonium

The precursor to ammonium aerosol formation is ammonia (NH_3). NH_3 is the most abundant alkaline gas in the atmosphere, and therefore plays a significant role in neutralizing acids. It is efficiently taken up into acidic sulphate aerosols, formed by the processes described

above, leading to the formation of ammonium sulphate ($(NH_3)_2SO_4$) aerosol. As a consequence, NH_3 uptake also serves to regulate the acidity of aerosol and cloud droplets, which, in turn, influences the solubility and oxidation rate of species such as SO_2. NH_3 also plays a role in the ternary nucleation of sulphate aerosols.

As indicated above, ammonium nitrate (NH_4NO_3) aerosol is formed from the reversible reaction of gas phase NH_3 and gas phase HNO_3 (see Figure A.9), which is highly complex and dependent on the prevailing conditions. The equilibrium ratio for NH_3, HNO_3 and NH_4NO_3 depends on temperature, and is also strongly influenced by relative humidity above the deliquescence point of NH_4NO_3, because NH_4NO_3 then dissolves into an aqueous solution and its thermodynamic properties are changed. The existence of NH_4NO_3 in aerosol particles is strongly favoured at low temperature and high relative humidity, and can therefore be influenced by normal daily cycles in humidity and temperature (Allen et al., 1989).

NH_3 can also participate in a reversible reaction with gas phase hydrogen chloride (HCl), to form ammonium chloride (NH_4Cl) aerosol (e.g. Pio and Harrison, 1987). As indicated in section A1.2.2, emissions of HCl are very minor compared with those of the other SIA precursors, and typically too low to sustain an atmospheric concentration of HCl that results in significant formation of NH_4Cl aerosol.

A2.3: Mass transfer between phases and condensed phase processes

A2.3.1: Gas-to-aerosol transfer of oxidation products

Gaseous compounds undergo oxidation in the atmosphere resulting in low volatility products that could either nucleate to form new particles or, more commonly, condense on pre-existing particles changing their composition and increasing their size and mass. This condensation process is highly dynamic and driven by the difference between the actual vapour pressure of the condensing molecules and their equilibrium vapour pressure over the particle surface. There are a number of fundamental restrictions in extrapolating this behaviour from a single particle to wider scales.

A2.3.1.1 Fundamental processes controlling gas-to-particle transfer

Mass Transfer (incl. gaseous diffusion and accommodation)

The interaction of a trace gas molecule with the surface of a droplet or particle involves multiple transport and kinetic processes, including gas phase diffusion to the surface, thermal accommodation with the surface, adsorption to and desorption from the surface, possible reaction at the gas/surface interface, and, for liquids and some amorphous solid surfaces, interfacial mass transport of trace species (mass accommodation), solvation, bulk phase diffusion and bulk phase reaction (Kolb et al., 1995; 2010). Figure A.10 provides a simplified illustration of key processes and flux terms used to describe atmospheric gas uptake by atmospheric particles: gas kinetic flux of surface collisions (J_{coll}), the adsorption onto the particle surface (J_{ads}), absorption into the particle bulk (J_{abs}), desorption from the surface (J_{des}), and net uptake by the condensed phase (J_{net}). The red arrows indicate production and loss of chemical species by reactions at the particle surface (P_s, L_s) or in the particle bulk (P_b, L_b).
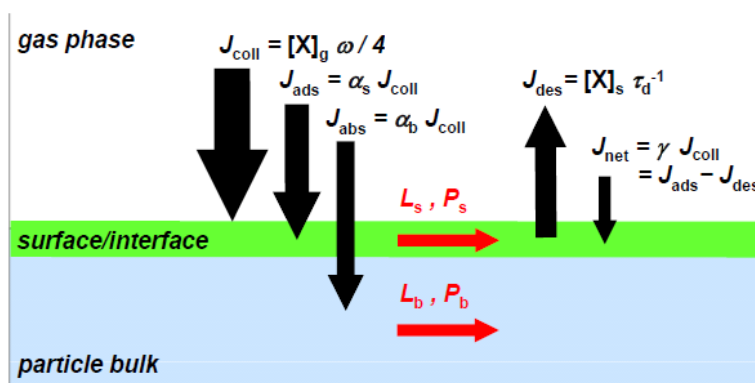
Figure A.10: Schematic illustration of key processes and flux terms describing gas uptake by atmospheric particles (taken from Kolb et al. (2010)).

The terms mass accommodation and thermal accommodation are generally used to describe the transfer of chemical species (molecules, radicals, atoms) and thermal energy from the gas phase to the condensed phase (aerosol or cloud particles). Thermal accommodation represents energy transfer and it is a process during which gaseous molecules collide with the surface and equilibrate with the surface in all degrees of freedom (kinetic and internal energy), typically on a time scale of $\sim 10^{-11}$ s. The thermal accommodation coefficient is expressed as the number of molecules equilibrated with the surface divided by the total number of molecules colliding with the surface. Surface accommodation, or adsorption, is the process where gaseous molecules may collide with a surface and not be immediately scattered, staying at the surface for longer than the duration of direct scattering processes ($>10^{-12}$ s). Unlike thermal accommodation, surface accommodated molecules may retain part of their collisional kinetic energy. The accommodated or adsorbed molecule is bound to the surface by relatively weak forces, such as van der Waals forces or hydrogen bonds. The surface accommodation coefficient is the number of molecules accommodated at the surface divided by the total number of molecules colliding with the surface. After surface accommodation gaseous molecules may be incorporated into the bulk of the condensed phase by interfacial mass transport processes involving their solvation in the interface region. This is known as bulk accommodation, or absorption. The bulk accommodation coefficient is the number of molecules incorporated into the particle bulk divided by the total number of molecules colliding with the surface. Note that for liquid surfaces the bulk accommodation coefficient is often described as the mass accommodation coefficient.

The net gas uptake is an experimentally derived quantity, and the uptake coefficient for a trace gas is determined as the ratio of the number of trace gas molecules removed from the gas phase (net loss) divided by the total number of trace gas collisions with the surface. It is the result of the accommodation processes described above and possible subsequent processes such as surface reaction and bulk diffusion and reaction. It is often difficult to experimentally determine which, if any, of the accommodation coefficients defined above are actually controlling the uptake of trace gas species in either laboratory experiments or the atmosphere. The uptake coefficient is the net probability that a molecule undergoing a gas-kinetic collision with a surface is actually taken up at the surface. The coefficient often depends on time as uptake may be limited by: adsorption equilibrium on the surface; a limited number of reactants on the surface; solubility; a limited number of reactants in the bulk of the particles. The coefficient may also depend on the gas phase concentration of the molecule. Therefore, the uptake coefficient is not a constant and its values reported from laboratory measurements often cannot be transferred directly to other conditions. This must be done through a proper parameterisation of the processes at the interface and beyond. Most measurements determine the rate of loss of trace gas phase species and/or the rate of

gain of condensed phase trace species to or through a known or estimated liquid or solid surface area. In the case of unreactive gases, the resulting uptake coefficient can be identified with some combination of surface accommodation (adsorption) and bulk accommodation (absorption). For reactive molecules, the various types of reversible and irreversible surface reactions may proceed in series with surface adsorption and in parallel with absorption by the bulk phase.

Given the complexity of the trace gas uptake processes, phenomenological models are usually necessary both to evaluate the results of laboratory experiments and to model the impacts of trace gas uptake on atmospheric processes. Phenomenological models currently used include:

1. Continuum flux model: Coupled differential rate equations of mass and heat transport using continuum flow formulations with correction factors for kinetic effects at gas-particle interface (Kulmala and Vesala, 1991; Vesala et al., 1997; Winkler et al., 2004).
2. Kinetic resistance model: Linear combination of flux resistances (decoupled and normalized fluxes) in analogy to resistances in electric circuits (Jayne et al., 1990; Ammann et al., 2003; Davidovits et al., 2006; Pöschl et al., 2007).
3. Kinetic flux model: Coupled differential rate equations of mass transport and chemical reactions using gas kinetic formulations with correction factors for gas phase diffusion effects (Ammann and Pöschl, 2007; Pöschl et al., 2007).

A gaseous molecule may be taken up into a liquid due to its solubility. This is expressed in terms of the Henry's law constant, which relates the partial pressure of the trace gas and its molar concentration in the condensed phase at equilibrium. In reactions on solid or liquid surfaces the equivalent measure of phase partitioning is the Langmuir equilibrium constant for surface adsorption. Under some conditions the uptake flux is also determined by diffusive transport in either the gas or condensed phase, requiring values for diffusion coefficients in either phase. The rate constants of condensed phase reactions may also determine uptake rates. On solid particles adsorbed molecules cannot transfer to the bulk by diffusion, as diffusion is too slow through the solid medium. A molecule colliding with the surface of solid condensed matter can undergo adsorption, in which case it accommodates into a weakly bound state. The term "surface accommodation coefficient" is used for the probability of adsorption on a clean surface. Adsorbed molecules may leave the surface through thermal desorption and at ambient temperatures a surface equilibrium is established when the flux for adsorption equals the desorption flux.

Vapour Pressure

The equilibrium vapour pressure of each aerosol constituent is determined by its pure component saturation vapour pressure, which depends on the molecular properties. Saturation vapour pressures of organic components are currently poorly known, particularly for the least volatile compounds (Barley and McFiggans, 2010). Uncertainty in this parameter is already known to introduce 4 orders of magnitude uncertainty in predicted mass (McFiggans et al., 2010)!

Increased attempts to predict secondary organic aerosol (SOA) formation from near-explicit (e.g. Johnson et al., 2004; 2006b) and explicit (e.g. Lee-Taylor et al., 2011) models of oxidative VOC degradation have led to a substantial interest in techniques for the prediction of vapour pressures of each aerosol component. Barley and McFiggans (2010) conducted an evaluation of some of the widely-used and some more recent techniques. Whilst a reasonable assessment was possible (and a test set of low vapour pressure data was assembled and provided for evaluation), it was clear that there is a scarcity of experimental data on heavily functionalised and highly oxygenated compounds representative of semi-volatile and low volatility material found and predicted to be in the atmosphere. There have

been a large number of research efforts in recent years to measure such compounds using a range of techniques. There has been no recent compilation or review of vapour pressure measurements, but vapour pressure data have been measured using a variety of techniques for atmospheric purposes (Booth et al., 2009; 2010; 2011; Bilde and Pandis, 2001; Bilde et al., 2003; Mønster et al., 2004; da Silva et al., 2001). The methods include i) direct techniques for measurement of solid phase compounds along with corrections to the preferred sub-cooled liquid state and ii) indirect techniques for determination of the sub-cooled liquid vapour pressure.

Knudsen Effusion Mass Spectrometry (KEMS) allows probing only the volatility without raising issues of aerosol kinetics (Booth et al., 2009). KEMS consists of a temperature controlled cell with an effusing orifice i.e. the size of the orifices is much smaller than the mean free path of the effusing molecules. The sample effuses creating a molecular beam proportional to the vapour pressure inside the cell, without disturbing the thermodynamic equilibrium in the cell. Vapour pressures are then derived by calibrating the mass spectrometer signal to a sample of known volatility. It is frequently necessary to have (sub-cooled) liquid vapour pressures (e.g. Cappa et al., 2008), rather than the solid state measured by KEMS. They can be inter-converted using Differential Scanning Calorimeter (DSC) data (Booth et al., 2010) and the Prausnitz equation (Prausnitz et al., 1986). There are relatively few measurements of highly oxygenated multifunctional low-volatility compounds (Barley and McFiggans, 2010) and many of those that are present are extrapolated down from much higher temperatures than those relevant for atmospheric science. This lack of data causes estimation methods to remain inaccurate for many atmospherically relevant multifunctional organics (Booth et al., 2010; 2011). Revision and extension of the basis set used to evaluate vapour pressures predictive methods is crucial, only 45 compounds being used By Barley and McFiggans (2010). Work using KEMS has extended the volatility dataset for low-volatility atmospherically important compounds, a necessary step for both evaluation and improvement of vapour pressure estimation methods.

Activity Coefficients

The vapour pressure of a component over a particle containing a mixture including that component will be lower than the vapour pressure of the pure component and dependant on how much there is of it in the mixture. It will also depend on how it interacts with other components in the mixture. This is expressed in terms of the components' activities in the mixture, which can be calculated in a number of ways. Activity coefficients are complex functions of the solution composition. Calculating activity coefficients is complicated, with a large number of approaches discussed extensively in the literature (e.g. Clegg and Seinfeld, 2006 and references therein). For inorganic aqueous solutions, there are various options available; however the most accurate are semi-empirical thermodynamic models (Topping et al., 2005a). In solution mixtures of strong electrolytes where association of ions is assumed not to occur, an ion-interaction rather than ion-pairing model is the appropriate choice (Clegg and Brimblecombe, 1988). Pitzer's molality based model (Pitzer, 1973; 1975; Pitzer and Mayorga, 1973; Pitzer and Silvester, 1976) had been the most powerful and widely used, yet the severe concentration limitations associated with it prevent its use for predictions in low RH regions where aerosols may exist in states of very high aqueous concentrations (Topping et al., 2005a). Many of these concentration limitations are overcome by using the Pitzer, Simonson and Clegg mole fraction based approach (PSC, Clegg and Pitzer, 1992; Clegg et al., 1992). For inorganic systems, the Pitzer-Simonson-Clegg models (PSC) (Clegg et al., 1998a; 1998b) are regarded as the most accurate and robust inorganic activity coefficient model available for atmospheric purposes. Predictions from this set of models across the composition space of H^+ - NH_4^+ - Na^+ - $SO_4 2^-$ - NO_3^- - Cl^- - H_2O can be performed online at (www.aim.env.uea.ac.uk). Models designed to calculate solute activities in multi-component organic solutions include the group contribution method UNIFAC

(Fredenslund et al., 1975). There are inherent limitations to the UNIFAC model that are important to consider, though methods that exist for circumventing these problems are discussed by Topping et al., (2005b). Originally designed for chemical separation processes where the chemical components of interest are short chain mono functional compounds, its estimates for properties of multifunctional compounds that are common in the atmosphere can be uncertain (Koo, 2003). Sources in the literature do not recommend UNIFAC for compounds in which 2 strongly polar groups are separated by less than 3 to 4 carbon atoms because the interaction between these groups are not accounted for (Saxena and Hildemann, 1997). There are however ways of improving UNIFAC. Whilst there have been numerous attempts to modify the original equations for studies outside of the atmospheric field (modified UNIFAC (Dortmund) (Gmehling et al., 1993; 1998; Weidlich and Gmehling, 1987), and modified UNIFAC (Lyngby) (Larsen et al., 1987)), effort has since been directed to improving predictions for atmospheric systems, including the updated parameter matrix of Ninni et al., (2000) and Peng et al., (2001). Peng et al., (2001) used an electro-dynamic balance to modify the functional group interaction parameters of the COOH-H2O, OH-H2O, and OH-COOH pairs. These groups were chosen as they are most affected by hydrogen bonding (Peng et al., 2001).

A main problem with applications for atmospheric systems is the ability to treat mixed inorganic-organic systems. Attempts have been made to formulate a coupled thermodynamic approach, namely the models of Ming and Russell (2002) and Clegg et al., (2001). In the model of Ming and Russell (2002) ions were treated as new groups within UNIFAC, whereas Clegg et al., (2001) formulated a molality based model for coupling the two separate fractions. Both utilised the same activity coefficient models for the separate fractions (organics – UNIFAC; inorganics – mole fraction based activity model of Clegg and Pitzer (1992), Clegg et al., (1992)). Unfortunately, these coupled models were hampered by a severe lack of experimental data from which important interaction parameters can be derived. As such, it became necessary to neglect this coupling with the future intent to improve the description as and when the data becomes available, or indeed as new-coupled models are developed (Topping et al., 2005b). Regarding the latter, activity coefficient models available for organic-inorganic mixtures include X-UNIFAC (Erdakos et al., 2006), LIFAC (Yan et al., 1999), AIOMFAC (Zeund et al., 2008), and extended-ZSR (Clegg et al., 2003). The first three are group contribution methods, the last a compound specific model built on the ZSR mixing rule. Whilst these methods remained largely unevaluated apart from small subsets of organic functionality (Marcolli et al., 2004; Chan and Chan, 2003; Choi and Chan, 2002; Cruz and Pandis, 2000), recent work by Zuend et al., (2011) has extended the parameter set used in the AIOMFAC model for organic-inorganic mixtures containing carboxyl, hydroxyl, carbonyl, ether, ester, alkenyl, alkyl, and aromatic functional groups (http://www.aiomfac.caltech.edu/). The broad range of inorganic ions and organic functional groups that AIOMFAC can account for is displayed in Figure A.11.

group name	ions → main groups ↓	H^+	Li^+	Na^+	K^+	NH_4^+	Mg^{2+}	Ca^{2+}	Cl^-	Br^-	NO_3^-	HSO_4^-	SO_4^{2-}
alkyl	CH_n	19	31	184	68	90	16	35	256	35	43	5	104
alkyl bonded to hydroxyl group	$CH_n^{[OH]}$	10	19	91	40	43	13	20	140	21	23	1	51
hydroxyl	OH	10	19	91	40	43	13	20	140	21	23	1	51
carboxyl	COOH	4	9	47	33	48	6	6	66	9	18	4	56
ketone	CH_nCO	4	2	40	9	3	2	2	37	4	7		14
aldehyde	CHO		1	4	1	1	1	1	4	1	2		2
ether	CH_nO	2	7	24	14	4	1	5	45	5	2	1	4
ester	CCOO		4	14	2			5	19	4	1		1
alkenyl	C=C	1	1	4	1	7	1	1	6	1	4	1	4
aromatic hydrocarbon	ACH_n	7	8	19	26	4	5	2	40	8	6	1	16
aromatic carbon-alcohol	ACOH	3	7	14	24	1	5	1	32	6	4		13

Figure A.11: Distribution of datasets for the determination of organic main group ↔ ion interaction parameters (taken from Zuend et al., (2011)).

Full complexity activity coefficient models remain too slow to be used in large-scale atmospheric chemistry models (Wexler and Clegg, 2002). Empirical mixing rules are available (Bromley,1973; Kusik and Meissner, 1978). These schemes are much faster than the PSC models, are used extensively in atmospheric studies and have been shown to predict activity coefficients over a range of molalities fairly well, the method of Bromley (1973) incorporated into the ISORROPIA model used in the CMAQ and PTM model described in section C (Nenes et al.,1998). However, the applicability of these mixing rules for saturated and super-saturated multicomponent solutions is limited by maximum ionic strengths up to which the mean binary activity coefficient parameterizations are valid. Also, their use usually entails expensive, repeated evaluations of the binary activity coefficients as the ionic strength changes in an iterative numerical solution for gas-liquid/solid partitioning. Metzger et al. (2002a; 2002b) formulated empirical equations for the activity coefficients of solutes as a function of relative humidity in the EQSAM model. This is employed in the EMEP4UK model discussed in section C. However, Metzger et al., (2002a; 2002b) note how these equations break down for a sulfuric acid solution. More recently, Zaveri et al., (2005) developed the multi-component Taylor expansion method (MTEM), based on the series expansion rule used for dilute alloy solutions and extended this to aqueous electrolyte solutions at any concentration. The basis of the use of a Taylor Series expansion within MTEM is that variation of the natural logarithm of the activity coefficient with ionic mole fractions appears to be almost linear over the entire RH range. Thus the choice of concentration scale is based on the empirical behavior of the given multicomponent system rather than on ion solution thermodynamic theory (Zaveri et al., 2005). This method is employed within the WRF-CHEM model disussed in section C. Following this, Topping et al., (2012) used the same empirical basis to fit the PD-FiTE model model to output from the thermodynamic model ADDEM (Topping et al., 2005a; 2005b), deriving optimised polynomial expressiobs to specifically calculate the equilibrium vapour pressure of NH_3, HCl and HNO_3 above an aqueous inorganic solution. This model was similarly designed for use in the WRF-CHEM framework (see section C), but applicable to any model framework. Reduced complexity frameworks for mixed inorganic-organic solutions remain elusive. Whilst Topping et al., (2012) presented an organic version of the PDFiTE framework and Donahue

et al., (2011) presented a 2D basis set with prescribed activity coefficients as a function of volatility using the SIMPOL vapour pressure method as a basis (Pankow and Asher 2008), there is no general recommendation for reduced complexity inorganic-organic frameworks at this time.

The Kelvin Effect

A key aspect that distinguishes the thermodynamics of atmospheric particles is their curved interface. This curvature has an important effect on the vapour pressure of the compounds forming these particles over their surfaces. The Kelvin equation (Seinfeld and Pandis, 2006) states that the vapour pressure over a curved interface always exceeds that of the same substance over a flat surface. The vapour pressure of a liquid is determined by the energy required to separate a molecule from the attractive forces exerted by its surrounding molecules and bring it to the gas phase. When a curved interface exists, as in a small droplet, there are fewer molecules immediately adjacent to a molecule on the surface than when the surface is flat. Consequently, it is easier for the molecules on the surface of a small drop to escape into the vapour phase and the vapour pressure over a curved interface is always greater than that over a plane surface. The Kelvin equation determines the minimum possible particle size, and it relates the equilibrium radius of a droplet of pure substance to the physical properties of the substance and the saturation ratio of its environment.

Phase State and condensed phase diffusion limitation

Recent evidence indicated that aerosols may exist in metastable amorphous states, rather than simple liquid/solid mixtures (Virtanen et al., 2010). Indeed, empirical evidence suggests that particles can form glass like substances (Zobrist et al., 2008). As the glass transition temperature is approached, an increase in viscosity leads to a reduced rate of molecular diffusion and an arrested non-equilibrium structure (Tong et al., 2011). Viscosity is a measure of the resistance (typically of a fluid) to deformation by stress. Materials are generally considered liquids when they have a viscosity in the range of 10^{-3} –10^2 Pa s. Rubbers, gels and ultra-viscous liquids (such as pitch) are in the range 10^2–10^{12} Pa s and glassy solids $>10^{12}$ Pa s. Koop et al., (2011) show that for markedly slowed down equilibration times of 1 min - 1h in 100 nm particles viscosities of 10^5 - 10^7 Pa s are needed. Partitioning between the gas and condensed phase is kinetically limited in such amorphous states. Traditional organic aerosol models do not account for this, they assume that 1) the aerosol phase is a well-mixed non-viscous liquid; 2) the aerosol phase instantaneously equilibrates with the gas phase constituents. This adds significant uncertainty to predictions of gas/particle mass transfer as mixing timescales are ultimately governed by the diffusion coefficients of the aerosol constituents in the aerosol, which, on the other hand, are connected to the viscosity of the particulate matter. For typical aerosol sizes, the characteristic time for mixing could increase from a few milliseconds to hours or even days (Shiraiwa et al., 2011; Shiraiwa and Seinfeld, 2012). This has several important implications for organic and multicomponent aerosol formation, as the low diffusivity of individual organic molecules in solid/amorphous organic mixtures could directly affect their mass transfer, and thus the loading and composition.

Assessment of the current state-of-knowledge

To assess the atmospheric importance of the above phenomena, modelling approaches that treat the organic condensation/evaporation as a dynamic process and couple the gas phase transport to the condensed phase diffusion are urgently needed. Whilst these remain almost non-existent, some progress has been made (Shiraiwa et al., 2011). To develop these tools, quantitative information on the molecular properties governing the transport in both the gas and condensed phases are required. Presently, there is a fundamental lack of data and modelling tools that underpin our ability to resolve these topical issues. Viscosity as a function of temperature is widely known for common liquids (~ 200 in CRC, ~5000 in YAWS

(2003)), most references for glassy material is pharmaceutical polymers (Cui, 2007). For condensed-phase diffusion there is very little quantitative information available for non-aqueous systems, except for a handful in non-viscous common organic solvents (benzene/acetone/hexane) (Grossmann and Winkelmann, 2007). As aerosol particles exist as complex mixtures, the lack of data for even binary systems is critical. For vapour pressures, most of the data that models are based on are collected for structurally simple compounds (particularly hydrocarbons) and most of the compounds found in the atmosphere will not have vapour pressure data available in the standard databases (Barley and McFiggans, 2010). Predictive models for all three properties exist, but as they were originally developed for industrial engineering purposes, they are not typically applicable to atmospherically representative systems (Barley and McFiggans, 2010) and, for diffusivity and viscosity, remain entirely unevaluated. Dynamic modelling of gas-aerosol partitioning requires quantitative estimates on the accommodation coefficients of the evaporating or condensing compounds. Unfortunately direct measurements are scarce for atmospherically relevant compounds – although significant progress has been made recently in designing experiments to constrain these values (e.g. Miles et al., 2010). By measuring actual growth rates of a single droplet with model predictions, accurate information on the saturation vapour pressures and diffusion coefficients will help constraining accommodation coefficients for the studied compounds.

Poling et al., (2001) have reviewed predictive techniques available for multi-component solutions. Available methods include group contribution schemes based on the UNIFAC model (Gastonbonhomme et al., 1994; Wu, 1986). To replicate the measured glass transition of mixtures there are mixing rules available such as the Gordon–Taylor approach and the Couchman–Karasz equation (Koop et al., 2011) that is based on thermodynamic concepts. However, as Koop et al., (2011) states, at present, none of these different approaches seems superior in accurately predicting the glass transition of multi-component mixtures, which is in part due to the fact that only limited data sets exist to which the models can be compared and improved.

There is a need to develop models that couple the condensational transport of molecules from the ambient gas phase to/aerosol particles (see Figure A.12) using diffusion theory and kinetic theory of gases (see e.g. Riipinen et al., 2011). The diffusion coefficients, viscosities, saturation vapour pressures, and surface accommodation coefficients will need to be used as input to these models, as they are crucial in determining the rate of molecular transport between the gas and condensed phases. In addition to the mass transport equations, the heat transport resulting from the release/absorption of latent heat upon condensation/evaporation will be simulated (see e.g. Vesala et al., 1997). The models will need to be evaluated with observations of dynamic evaporation/condensation and diffusional transport of atmospherically relevant compounds.

Treatments of the gas/aerosol partitioning of individual organic compounds often rely on structure-based predictive models of thermodynamic properties such as sub-cooled liquid vapour pressures, as well as models to predict activities in multicomponent organic mixtures and in aqueous solutions (see Raatikainen and Laaksonen, 2005) for a comparison of models in mixed organic/inorganic systems and Zuend et al., (2011; 2008) for more recent developments of a comprehensive multicomponent activity coefficient model framework). Current atmospheric models of coupled transformation of gases and particles are necessarily highly simplified in their treatment of the organic components of aerosols, and gas/aerosol partitioning, and tend to use 'lumping' schemes in which broad classes of compounds are considered as single components within the model. The development of schemes that are both relatively simple, but have both predictive power and have a clear basis in the physical and thermodynamic properties of the underlying chemical compounds, is an active field of research.
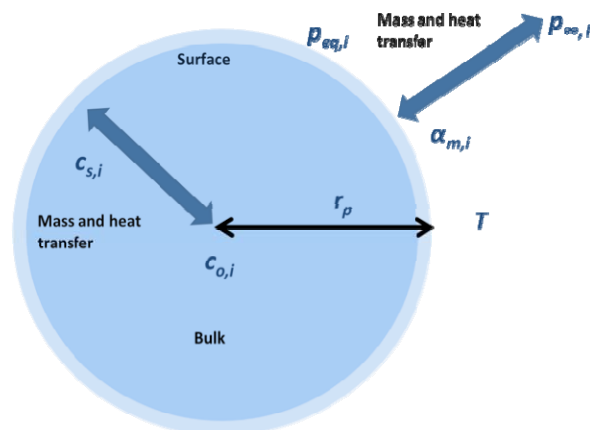
Figure A.12: A schematic illustrating the coupled aerosol and gas phase transport processes described in the microphysical models. r_p refers to particle radius, T the temperature, $p_{eq,i}$ the equilibrium vapour pressure of the condensing or evaporating species i at the particle surface (which is determined by the saturation vapour pressure, liquid phase activity and particle curvature), $p_{\infty,i}$ is the partial vapour pressure (or concentration) of i far away from the particle, and $\alpha_{m,i}$ the mass accommodation coefficient. $c_{s,i}$ is the condensed phase concentration of i at the particle surface, and $c_{0,i}$ at the centre of the particle – the difference in which is the

Large-scale prognostic models cannot carry complex representations of SOA formation with thousands of individual gas phase compounds. As such, in an attempt to mitigate these problems, empirical SOA models that neglect any detailed chemistry have been incorporated into atmospheric chemical transport and general circulation models for a number of years (e.g. Heald et al., 2005; Lane and Pandis, 2007; Henze et al., 2008). These models attempt to represent the organic aerosol are comprised of separate volatility fractions rather than individual compounds. However, this simple approach cannot account for the complexity and dynamics of SOA systems (Hallquist et al., 2009), and do not consider the evolving chemical functionality explicitly (Jimenez et al., 2009). Attempts to derive basic volatility-composition relationships rely on parameterised forms of the previously mentioned single component vapour pressure models (Donahue et al., 2011). As such there is currently no accurate semi-empirical way of developing reduced complexity process models that can capture the important evolving chemical functionality of aerosol particles. Whilst explicit and semi-explicit models are capable of capturing this complexity, they suffer from huge uncertainties in fundamental parameters, both approaches ultimately currently hindering our ability to accurately predict SOA mass concentrations.

A2.3.1.2 Equilibrium partitioning of components between gaseous and condensed phases

Gas-particle partitioning theory

The key assumption underlying many current treatments of SOA is that it is composed largely of semi-volatile compounds that partition between the gas and condensed phases. The equilibrium absorptive partitioning of SOA is described using the theoretical foundations on organic aerosol phase partitioning developed by Pankow (1994b, a) and extended by Odum et al., (1996) to SOA formation. Partitioning of each compound is described by an equilibrium partitioning coefficient $K_{p,i}$ (m^3 µg m^{-1}), or equivalently (Donahue et al., 2006) its inverse, the saturation vapour concentration, C_i^* (µgm^{-3}):

$$\frac{c_i^p}{c_i^g} = K_{p,i}\, C_{OA} = \frac{C_{OA}}{C_i^*} \tag{1}$$

where c_i^g is the mass concentration of species i per unit volume of air (μgm^{-3}) in the gas phase, c_i^p is the mass concentration per unit volume of air (μg m^{-3}) in the particulate phase, and C_{OA} is the mass concentration per unit volume of air (μgm^{-3}) of the total absorbing particle phase. Both $K_{p,i}$ and c_i^* can in theory be derived from the saturation vapour pressure of the pure compound if its activity coefficient in the absorbing phase can be determined (Bowman and Karamalegos, 2002; Chang and Pankow, 2006), although Donahue et al. (2006) have suggested that this formulation can be simplified with a modified version of Raoult's law. C_{OA} refers only to the particulate matter participating in absorptive partitioning, which can be an organic aerosol into which semivolatile organics can partition, and possibly the aqueous portion of the particles in the case of highly water-soluble organics. This means that as long as some absorbing mass is present, some fraction of a given semivolatile compound will partition into the particle phase, even if its gas-phase concentration is below its saturation concentration, c_i^*. The fraction of a semivolatile compound in the particle phase can be derived based on a variation of equation (1) and as the amount of absorbing material (C_{OA}) increases, compounds of greater volatility (larger c_i^*, smaller $K_{p,i}$) will increasingly partition into the particle phase. When $c_i^* = C_{OA}$ half of the semivolatile mass of species i resides in the particle phase. If $c_i^* \gg C_{OA}$, essentially all of the semivolatile species i is in the particle phase.

Odum et al., (1996) applied this basic partitioning model to SOA formation in reaction chambers (smog chambers) and showed that SOA yield, defined as the mass of aerosol formed per mass of hydrocarbon reacted, can be expressed in terms of the formation of a collection of semi-volatile compounds. The volatility distribution of the oxidation products is represented by the product yields and partitioning coefficients. A two-product version of this model was used by Odum et al., (1996) because adding more products did not improve the fit to the yields obtained from the chamber studies. Consequently, the two-product model has been used as the standard means of representing laboratory SOA yield data in many experimental and modelling studies (Seinfeld and Pankow, 2003; Kanakidou et al., 2005; Hallquist et al., 2009). Recently, Chan et al. (2007) have presented a framework to extend the simple product model to take into account the kinetics of both gas- and aerosol-phase processes. In their framework the initial oxidation products may react further to generate second generation products, semivolatile aerosol products may react to generate non-volatile products.

The volatility basis set (VBS) approach

With increasing understanding of the nature and complexity of SOA formation, the limitations of representing laboratory data with a two-product model are now evident. There are two major issues: the wide range of C_{OA} in the atmosphere and the ongoing oxidation of semivolatile organics in both the gas and particle phases. Donahue and co-workers (Donahue et al., 2006; 2011; Presto and Donahue, 2006; Pathak et al., 2007) have proposed the use of a "volatility basis set" (VBS) to address these issues, where they have demonstrated that partitioning over abroad range of organic aerosol mass, including typical ambient levels, 0.1 – 20 μg m^{-3}, is better represented by a larger number of products. The VBS consists of a group of lumped compounds with fixed C^* values, comprising up to 9 "bins" separated by one order of magnitude each in C^* at 300K. Using the VBS, different SOA-forming reactions can be mapped onto the same set of bins over the range of organic aerosol mass concentration typical of ambient conditions while maintaining mass balance for more volatile co-products as well. Aging reactions within the VBS can be added easily if the kinetics and volatility distribution of the products can be measured or estimated.

Unresolved challenges with partitioning approaches

The implementation of the gas-to-particle partitioning approaches to experimental and modelling data, as well as in the atmosphere is challenged by several unresolved factors, including:

1. In the absence of consideration of the kinetics of gas-aerosol mass transfer (as discussed in 2.1.2.1), the gas-to-particle approaches will be incapable of fully resolving the dynamics of SIA or SOA formation.
2. A serious limitation of current partitioning approaches is that reactions of either gas or condensed phase compounds will displace the equilibrium described in Eq (1). This will lead to the mean that the fraction of a semi-volatile compound in the particle phase is not just a function of K*p, i* (or C_i^*) and C_{OA}, but also of the rate at which C_i^g or C_i^p are reduced during reactions. Both condensed-phase and heterogeneous reactions may play a role (e.g., Chan et al., 2007; Kroll and Seinfeld, 2008).
3. The composition of SOA can be extremely complex, where the identity and properties of the participating gaseous and condensed phase components, with the exception of possibly a small fraction, is not currently possible. The compounds relevant to SOA formation are sometimes minor products with yields of only a few percents. These are especially difficult to parameterise in simplified chemical mechanisms.
4. The portion of the total organic aerosol mass that represents the mass of the condensing phase, C_{OA} is not well established. The role of water-uptake and of inorganics in C_{OA} is difficult to quantify. It is also not clear whether primary organic aerosol mass should be considered (Song et al., 2007), or how amorphous or possibly solid fractions affect the absorption and mixing of the available organic carbon.
5. Laboratory experiments suffer from artefacts and difficulties including the loss of particles and vapours to chamber surfaces, making it more difficult to correctly achieve mass balance.
6. It is often assumed that C^* varies with temperature according to the Clausius-Clapeyron equation (Chung and Seinfeld, 2002; Takekawa et al., 2003). However, the enthalpies of vaporisation values are highly uncertain (Saathoff et al., 2009; Pathak et al., 2007; Chung and Seinfeld, 2002; Bilde and Pandis, 2001). Donahue et al. (2006) showed that these values can be reconciled, and concluded that models should not confuse two possible approaches; models with few semivolatile components should use artificially low values, while models covering a wide range of values for C^* should use more realistic enthalpy of vaporisation values.
7. Vapour pressures, molar activity coefficients and the mean molecular weights of the condensing phase species are all difficult properties to measure or estimate, even for those compounds whose identity is known (e.g., Clegg et al., 2008a, b). This can be complicated further when considering the role of relative humidity on organic partitioning (Chang and Pankow, 2006). The thermodynamics of mixtures in a laboratory experiment and in the atmosphere may also differ, as atmospheric mixtures are presumably much more diverse.

Assessment of the current gas-particle partitioning approaches

For convenience, the formation of condensed material in the ambient atmosphere is frequently considered to have occurred through the instantaneous attainment of the equilibrium between the phases. This assumption is implicit in the commonly used absorptive partitioning of organic material. Such an assumption can facilitate the use of yield data from photochemical smog chambers in models of atmospheric aerosol formation, from the original 2-product yield approach of Odum et al., (1996) through to the fitted original volatility basis

set (VBS) of Donahue et al., (2006) and onwards to the 2-D VBS of Donahue et al., (2011). Whilst fitting an equilibrium aerosol to an observed yield is widespread and straightforward, it provides little mechanistic information and its wider use inevitably relies on valid extrapolation to ambient conditions from those of the laboratory. Chamber yields also implicitly incorporate the kinetic limitations experienced in the particular experiment which will be specific to the dynamical evolution of the aerosol and not generally the same as ambient conditions to which the yields are applied.

Use of absorptive partitioning theory based on fundamental property data can theoretically provide a more solid basis for predicting the equilibrium loading of condensed material, provided the underlying assumptions are valid. In practice, however, first principles prediction of gas-particle partitioning of semi-volatile components has proven difficult. In order to improve such predictions (or to quantitatively evaluate the reasons for their failure) requires appropriate and comprehensive pure component saturation vapour pressure data (as a function of temperature) and activity coefficient data for the multicomponent aerosol particles. In reality, direct application of absorptive partitioning under most conditions is dubious, since the equilibrium is seldom attained and readily perturbed; condensable vapour concentrations are rapidly changing, transfer of mass in the condensed phase and between phases may be diffusionally limited and it is unlikely that condensed components do not react. Nonetheless, absorptive partitioning provides a limit to the predicted condensed mass for unreactive particulate material, an equilibrium prediction as the reference point for more physical treatments and an easily accessible zeroth-order approximate prediction of condensed component mass.

A2.3.2: Condensed-phase reactions

A2.3.2.1 Aqueous phase reactions

Prediction of the SOA mass in the atmosphere has been mostly based on the implementation of the gas-to-particle partitioning approach in models, implying that SOA compounds are formed in the gas phase and then partition to an organic phase. However, discrepancies in predicting organic aerosol oxidation state, size and product (molecular mass) distribution, relative humidity (RH) dependence, and vertical profile suggest that additional SOA sources and aging processes may be important or that a reversible equilibrium partitioning approach is not applicable and that condensing components are "locked away" during growth of solid particle (see discussion in 2.1.2.1 about condensed phase diffusional limitation). The formation of SOA in cloud and aerosol water is not considered in these models even though water is an abundant medium for atmospheric chemistry and such chemistry can form dicarboxylic acids and "humic-like substances" (oligomers, high-molecular-weight compounds), i.e. compounds that do not have any gas phase sources but comprise a significant fraction of the total SOA mass (Decesari et al., 2000; Gelencser et al., 2000a; 2000b; Kiss et al., 2002). There is increasing direct evidence from both laboratory (Carlton et al., 2007) and field measurements (Sorooshian et al., 2007; 2010;Hennigan et al., 2009) for aqueous phase formation of SOA, however the importance of this pathway to the global source of organic aerosol is currently unclear. Fu et al. (2008) estimated a global source of 11 Tg yr^{-1} of SOA formed through the irreversible uptake of dicarbonyls in clouds and aerosols, comparable to the source of SOA from the gas phase pathway. Inclusion of this additional source of SOA in the GEOS-Chem model eliminated the low bias previously seen during a specific model/measurement comparison study, with a small improvement in the ability of the model to capture the observed variability in water soluble organic carbon (Fu et al., 2009). Similarly, Carlton et al. (2008) found that including a detailed aqueous phase SOA mechanism in the CMAQ model modestly improved the correlation of the same model/measurement study. Comparing the GEOS-Chem global model simulation of the vertical profile of organic aerosol with 17 measurement datasets including remote, polluted and fire-influenced conditions, Heald et al., (2011) found that

aqueous phase SOA made up more than 20 % of total organic aerosol at all altitudes, with a pronounced enhancement from 2–6 km, where contributions vary from 40–80 % of total simulated OA. This mid-tropospheric enhancement was not supported by the measured vertical profiles, nor was the model-observation discrepancy (when aqueous SOA was not included) larger in this region of the troposphere. The authors stated that the addition of the aqueous phase source, as it was described in the GEOS-Chem model, was unlikely to improve the model simulation, beyond a mean reduction in bias. They concluded that their analysis did not offer definitive evidence for the importance of aqueous phase SOA, but it did not preclude it and recommended that additional chemical constraints were clearly required to investigate the importance of this source to the global OA budget.

Understanding of the aqueous phase process has been increasing based on conducted laboratory investigations determining kinetic and mechanistic parameters of reactions in aqueous solutions (see Zellner and Herrmann, 1995; Herrmann, 2003). Ervens et al., (2011) reviewed the current knowledge on aqueous phase organic reactions and combined evidence that pointed to a significant role of aqueous phase SOA formation in the atmosphere. In their review, a modelling-based comparison was made between aqueous and gas phase SOA yields and mass predictions for selected conditions. These simulations suggested that the aqueous phase SOA might contribute almost as much mass as gas phase SOA to the SOA budget, with highest contributions from biogenic emissions of volatile organic compounds (VOC) in the presence of anthropogenic pollutants (i.e. NO_x) at high relative humidity and cloudiness. It was previously hypothesised that organic compounds are oxidised in the aqueous phase of cloud and fog droplets and products remain in the particle phase upon water evaporation (Blando and Turpin, 2000). More recently, it was hypothesised that chemical processes in the aqueous phase of hygroscopic particles (aerosol water) can also efficiently contribute to aqueous phase SOA mass (Volkamer et al., 2007). Aqueous phase processes start with water-soluble, polar precursors and form SOA that is more oxygenated than gas phase SOA as they lead to functionalisation or accretion (e.g. acid formation, oligomerisation) rather than to breakage of the carbon structure as in gas phase reactions. Laboratory studies have shown that at low, cloud-relevant aqueous phase concentrations, organic acids (e.g. oxalate) are formed from small aldehydes and related compounds. At the higher solute concentrations associated with aerosol water, "high-molecular weight compounds" (HMWC) tend to preferentially form (Lim et al., 2010). It has been shown that the organic fractions of atmospheric aerosol particles have properties consistent with such aqueous laboratory studies (Ervens et al., 2011). A host of organic acids has been observed in ambient particles, with oxalate globally ubiquitous throughout the tropospheric column (e.g. (Kawamura and Sakaguchi, 1999; Kawamura et al., 2003)). The atmospheric dynamics of oxalate suggests that it is predominantly secondary, and yet its abundance has not been explained by gas phase chemistry. Laongsri and Harrison (2013) have recently reported measurements of oxalate at urban and rural sites in the UK and inferred that it had a predominantly secondary source with advection from mainland Europe being important.

A2.3.2.2 Macromolecules, HULIS and Oligomers

There is additional interest in condensed phase reactions because they might help to explain the formation of high molecular weight products detected in atmospheric aerosol particles (Gelencser et al., 2002; Limbeck et al., 2003). Studies have reported that macromolecular species contribute significantly to the mass of organic compounds present in atmospheric aerosol particles (Decesari et al., 2000; Gelencser et al., 2000a; 2000b;Kiss et al., 2002). The largest fraction of these species showed considerable similarities in structural properties to humic and fulvic acids and were as a result termed humic-like substances (HULIS). HULIS is an operationally defined fraction of the aerosol and its quantification depends to some extent on the applied extraction, isolation and detection method. This fraction consists of polyacidic compounds of aliphatic and aromatic structures with additional substituted

functional groups. Their molecular mass was determined to be between 150–500 Da (Kiss et al., 2003). In a comprehensive review, Graber and Rudich (2006) concluded that, although it is difficult to distinguish atmospheric HULIS from terrestrial and aquatic humic substances on a chemical level, there are significant differences in physical properties such as hygroscopicity and cloud condensation nuclei (CCN) activity (e.g. Dinar et al., 2006a; 2006b; Asa-Awuku and Nenes, 2007). There is indication that HULIS can be of primary origin, e.g., wood combustion, but may also be associated with secondary particle-phase production (Gelencser et al., 2002; Surratt et al., 2007a; 2008). Higher-MW reaction products (i.e., products with MWs higher than those of first- and higher-generation oxidation products) have been identified in laboratory SOA produced from the atmospheric oxidation of a wide range of compounds, including 1,3,5-trimethylbenzene, cycloalkenes, α-pinene and isoprene (Gao et al., 2004a; 2004b; Iinuma et al., 2004; Kalberer et al., 2004; Tolocka et al., 2004; Dommen et al., 2006; Hamilton et al., 2006), as well as the hydration of glyoxal (Hastings et al., 2005). In addition to these classical SOA precursor systems, other compounds which are present in atmospheric aerosols have also been investigated as possible contributors to oligomers, such as levoglucosan (Holmes and Petrucci, 2006).

Numerous laboratory studies have shown evidence for the reactive uptake of volatile organic species during SOA formation as well as the formation of higher-MW organics in SOA. The first studies were based on indirect evidence, i.e., increased SOA mass concentration observed in the presence of acidic seed aerosol (Tobias and Ziemann, 2000; Jang et al., 2002; Jang et al., 2004; Limbeck et al., 2003). Although it was proposed that polymerisation reactions of volatile carbonyls may account for the observed SOA mass increase, there was no direct evidence to support this at the time. Subsequent studies utilised mass spectrometry for the direct detection of higher-MW products, and showed that oligomers, characterized by a highly regular mass difference pattern of 12, 14, 16 or 18 Da, constituted a considerable portion of the SOA (Kalberer et al., 2004; Tolocka et al., 2004; Gao et al., 2004a; 2004b). It should be noted that the terms *oligomer* and *oligomerisation*, as opposed to *polymer* and *polymerisation*, are normally used in this context because, in the reaction systems studied to date, the MW range of the products is limited (IUPAC, 1996).

Technical Annex B - Secondary Aerosol Measurements

The purpose of section B is to summarise the current technological state of the art that is relevant for the study of SIA and SOA in the atmosphere, including some of the data analysis methods, and to summarise recent findings. The primary measurement objective considered for this section is the quantification and apportionment of SIA and SOA on an operational and long-term basis. However, due to the complex nature and lack of fundamental understanding in many aspects of this area of study, attention is also paid to research-grade instrumentation that is typically used for short intensive studies. In addition, there are certain other measurements that while not measurements of SIA and SOA, can be used in support of these measurements to either further fundamental understanding as detailed in section A or to help constrain or validate the models described in section C. Section B specifically focuses on the contribution of the total SA to $PM_{2.5}$, as it has been shown this is where the majority of the SA mass resides. The noticeable exception is coarse nitrate, which is discussed in section B2.7.

This section is separated into three subsections, which are summarised as follows:

Subsection B1 covers the current in-use measurement techniques. Various instruments exist for the quantification of the aerosol components that make up SIA and SOA. In addition to offline (i.e. not automated) methods, multiple techniques exist for the automated, online quantification of aerosol composition with a high time resolution (1 hour). In addition, techniques for advanced offline analysis (to inform fundamental understanding) are also summarised. The only gaps in the technology identified are the lack of measurements of the semivolatile fraction. The current UK DEFRA network capability is summarised in terms of the available instrumentation. Currently, only four sites (Harwell, Auchencorth Moss, North Kensington and Marylebone Road) are adequately equipped to make reasonable assessments of SIA and SOA, with room for improvement at each.

Subsection B2 covers the data analysis methods used to process the data generated to estimate SIA and SOA based on the measurement data. No instrumental technique is capable of directly quantifying primary and secondary particulate matter. For SIA, this quantification is relatively straightforward with few assumptions necessary, however this is not as straightforward for SOA. Techniques are summarised for the apportionment of OA to primary and secondary sources, the main ones being the application of positive matrix factorisation (PMF) and primary organic tracer (POT) techniques, however neither of these techniques can claim to be completely accurate or unambiguous. The limitations of these techniques are discussed. There are also techniques to further apportion the SOA according to the types of precursor VOCs, using either organic tracers or carbon isotope analysis, however these too have limitations. Recommendations include the complementation of aerosol measurements with a suite of other measurements to reduce ambiguity and further intensive characterisation work.

Subsection B3 covers the findings from recent work studying SIA and SOA in the UK, employing the techniques covered in B1 and B2. While the data from the AGAnet network may not be absolutely quantitative, it does give UK coverage for the geographical and long-term trends in SIA. There are fewer studies into SOA and these are mainly limited to

intensive measurement periods rather than long-term monitoring, which are summarised. Certain recent measurements are expanded upon, which includes measurements using the FAAM BAe-146 large research aircraft, which offers insights into transboundary pollution, and the recent ClearfLo intensive measurement campaign in London in 2012, which also included a year-long aerosol mass spectrometer dataset. These results underscore the importance of nitrate in SIA and also the episodic nature of SIA and SOA events. This in turn shows the usefulness of automated online measurements in capturing such features.

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B1.7: Monitoring Networks

B1.7.1: UK based monitoring networks

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B2: Data Analysis Techniques

B2.1: Factorisation of organic matter

B2.2: Positive Matrix Factorisation (PMF)

B2.3: ME-2

B2.4: Primary organic tracer techniques (POT)

B2.4.1: Use of Tracers for Specific Primary Organic Aerosol Sources

B2.5: Secondary tracer techniques

B1 Measurement Techniques

The following section details the techniques available to measure SIA and SOA, and will include examples of instruments that are used in the existing UK networks and in the wider research community. The list may not be exhaustive, but will be a broad representation of the described technique. This section will not cover instruments or techniques that are limited to the laboratory. Such instruments are discussed in Annex A, where they contribute to the fundamental understanding of SOA or SIA.

Measurement approaches can be separated into two main categories: offline and online. Offline methodologies take samples which are subsequently analysed in a laboratory, whilst online instruments perform simultaneous collection and chemical characterisation *in situ*, although further data analysis may still be required. Offline techniques predominately rely on particles being collected on a filter medium, and some consideration to the types of samplers available and filter substrate material needed are discussed here.

There is a subset of instruments that collect bulk samples online, which can either be stored for later analysis or analysed offline within the instrument. These semi-continuous instruments provide flexibility as they can be easily integrated into a network for providing online information, whilst offering the ability to perform more detailed offline analysis.

There are other measurements that need to be considered when discussing SOA and SIA. These measurements either allow an indirect assessment of the SOA/SIA mass to be evaluated or they are used to enhance our fundamental scientific understanding and inform models. For example, if the total masses of $PM_{2.5}$ and primary aerosol are known, then the difference between the two is the mass of secondary material. The measurements needed to perform this calculation and other indirect approaches are detailed in section B1, whilst the analysis required is detailed in section B2.

B1.1 Sampling systems for offline analysis

Many of the analytical techniques described in the following sections require a sample to be taken and stored so it can be analysed offline. Described below are some of the common techniques for sampling aerosol, including examples used in the monitoring networks.

B1.1.1 Filters

The most well-established method of collecting aerosol samples is to pass the sampled air through a filter, which is subsequently analysed in the laboratory. Providing the right pore size is used, all of the particulate matter within the air can be assumed to be collected on the filter. Many commercial samplers are available from a number of manufacturers that hold the filter in a controlled and monitored flow and record the start and stop times of sampling. A number of different filter media are available such as PTFE, glass fibre, quartz, polycarbonate and cellulose and are suited to different applications. The most basic form of analysis is the weighing of collected samples, which forms the basis of PM_{10} and $PM_{2.5}$ measurements when the filter is run downstream of a suitable impactor. However, for the purposes of the measurement of SIA and SOA, other procedures are available, which are all based around analytical chemistry techniques.

The main disadvantage of using filters to perform aerosol measurements is that in order to collect enough material for analysis, the air must be sampled through the filter for an

extended period of time, typically a day, although this varies according to the detection limit of the analytical procedure and the ambient mass concentrations. This can be mitigated by using higher flow rates than the standard 16.7 l min^{-1} used by most aerosol sampling equipment (so-called 'high volume' samplers), but this necessitates the use of larger pumps, filters and impactors, which in turn means that the sampler is larger and requires more power. Generally speaking however, filter samplers are likely to not capture processes that occur on timescales of less than a day (See section B3.3.1), such as oxidation chemistry and the change in condensation rate that occurs between day and night as outlined in Annex A.

Another disadvantage of the technique is that the act of changing the filters and analysing the samples in the laboratory is a labour-intensive process, which increases the cost of performing the measurement and can make sampling in remote locations difficult. There are commercial samplers available that automate the collection process from a number of manufacturers, compliant with the US EPA PM$_{2.5}$ and PM$_{10}$ reference methods. A notable example is the Partisol 2025 manufactured by Thermo Scientific, which is used extensively within the UK. This can collect samples on 16 standard 47 mm filters at 16.7 l min^{-1} sequentially, thus meaning daily site visits to change substrates are not needed. A similar system, the Leckel Sequential Sampler SEQ47/50, is operated at the 2 UK EMEP sites and enables up to 17 samples to be taken, with sample times ranging from 1 - 168 hours. Other manufacturers of samplers include Digitel, Tecora and URG.

As regards the investigation of secondary aerosols, a major limitation with filter samplers is the fact that semivolatile aerosol components (see A2.1.1) can interact with the sampled particles during or after sampling (Zhang et al., 1992; Schauer et al., 2003; Chow, 1995). This can lead to either positive or negative artefacts when dealing with particle components such as ammonium nitrate and semivolatile organics. Because the partitioning effects are related to temperature, this can be mitigated by keeping the sample medium at a temperature close to ambient during sampling and freezing the sample after exposure. This is obviously difficult where there are strong temperature gradients across the sampling period such that particulate matter sampled during a cool night is evaporated the following day, for example. Positive artefacts can also be mitigated by placing a suitable denuder upstream of the filter and negative sampling artefacts can be estimated by placing a denuder or chemically treated filter downstream of the filter (Schauer et al., 2003).

B1.1.2 Cascade Impactors
A further limitation of filter sampling is that information regarding the relationship between particulate matter and particle size is limited to the size cut provided by an upstream impactor or cyclone (Chow et al., 1995). The usual preferred technique for collection of size-selected samples is the use of a cascade impactor. This places multiple impaction stages in series with sequentially decreasing size cuts and collection substrates placed on each impaction surface to collect the particulates at each size interval (McMurry, 2000). A number of commercial samplers exist, such as the Micro Orifice Uniform Deposit Impactor (MOUDI) manufactured by MSP, the Electrical Low Pressure Impactor (ELPI) by Dekati and the Andersen impactor by Thermo Scientific. This allows data to be collected on composition as a function of size, for instance in separating the fine and coarse aerosols or assessing lung deposition potential. However, there are disadvantages compared to filter sampling. Because the sample is split into multiple stages, greater sampling times must be used to

satisfy a given analytical technique's detection limit. Also, for the purposes of the analytical techniques discussed here, it is currently not possible to automate the substrate changes, so the sampling system is inherently more labour intensive.

B1.1.3 The Delta system

Another instrument of note is the Delta system. This system, as described by Sutton et al. (2001), measures gas phase NH_3 and particulate NH_4^+. Particle laden air is sampled through two denuder tubes coated in an acid to strip out the NH_3 and then the NH_3 free air is sampled through a filter. The filter is coated in a citric acid-methanol mix to retain the potentially volatile NH_4^+. The instrument samples at 0.3-0.4 l/min and provides monthly averages. An extended version is also used for precursor gases (HNO_3, HONO, HCl and SO_2) and SIA components (NO_3^-, NO_2^-, Cl^-, SO_4^{2-}). The Delta system is currently employed on the AGANet sites (see section B1.6.1 below).

The main limitation to the Delta system is the time resolution. The average filter sample time is 1 month. It is also labour intensive and requires preparation of filter samples in common with other offline methods. The final issue with the Delta network is the lack of size segregation. The inlet consists of tube with a funnel to prevent water ingress. Therefore, it is not conforming to any true PM definition and has a cut-off of 4 – 5 μm (unpublished). However, it has been shown that the majority of the SIA mass is in the size fraction less than 2.5 μm, so the measured SIA mass is likely to be close to the total $PM_{2.5}$ SIA mass.

B1.2 Off-line analysis methods

Generally the detailed analysis of SOA is done in the laboratory using aerosol samples collected onto filters and the organic compounds extracted using techniques such as solvent extraction (Cheng and Li., 2004), supercritical fluid extraction (Chiappini et al., 2006) or thermal desorption (Greaves et al., 1985;Veltkamp et al., 1996) to release the semi-volatile species. A range of solvents and pre-treatments can be used, such as derivatisation, to increase the range of species analysed and often the solvent used can be used as a definition of the species present i.e. water soluble organic compounds (WSOC). Thermal desorption has gained increasing popularity over the last few years for the measurement of semi-volatile, thermally stable organic aerosol components and can be used without any sample preparation when combined with high resolution techniques (Hays and Lavrich., 2007). Particle into liquid samplers (PILS) grow aerosol particles in a supersaturated water environment and then impact them onto a surface over which water is continuously flowed (Weber et al., 2001; Orsini et al., 2003).

B1.2.1 Gas Chromatography – Mass Spectrometry

Gas chromatography is a separation technique that allows species to be separated based on their volatility or polarity. The simplest instruments use a flame ionisation detector, which is low cost and reliable. However, it has poor selectivity and can only be really be used for species at high concentrations.   For aerosol analysis, detection is usually performed using a mass spectrometer that allows the structure of the molecule to be identified. Generally electron ionisation at 70 eV is used for comparison to extensive mass spectral databases, such as the NIST library. Gas chromatography coupled to mass spectrometry (GC-MS) is one of the most widely used techniques to separate, identify and quantify individual species within aerosol particles (Kotianova et al., 2004) and references therein.

Particles collected onto filters can be extracted using solvent or analysed directly by thermal desorption. Detection limits are in the pg- g range depending on the molecule functionality, with hydrocarbon species found in POA generally having the greatest sensitivity. Unfortunately, the complexity of OA can be a barrier to this type of analysis resulting in constantly overlapping peaks, also known as an unresolved complex mixture or hump.

The oxidised nature of SOA makes it unsuited to conventional GC analysis, resulting in poor performance. The range of amenable species can be increased using derivatization ((Surratt et al., 2006; Docherty and Ziemann., 2001;Ho and Yu., 2002)), allowing typical oxidation products found in SOA, as outlined in Annex A, including acids, alcohols and carbonyl species to be measured and allowing further of understanding of the oxidation processes described in A2.1.1. However, involves extensive sample preparation and increases analysis time.

B1.2.2 Comprehensive Two-Dimensional Gas Chromatography (GCXGC)

GCXGC is a more advanced version of gas chromatography, where species can be separated on the basis of two chemical properties, usually volatility and polarity. This results in large increases in the amount of separation that can be achieved for complex mixtures. A modulator is used to transfer material between GC columns and commercial systems generally involve cryogenic trapping. GCXGC is generally coupled to either a flame ionisation detector (for quantification) or a mass spectrometer (for identification). Initial studies resulted in the separation of over 10,000 organic species in urban aerosol samples, many of which could be mechanistically linked to aromatic oxidation processes (Hamilton et al., 2004; Welthagen et al., 2003).

GCXGC has recently been incorporated into a field deployable thermal desorption aerosol GCXGC with a flame ionisation detector (2D-TAG) which operates on a 1 hour cycle, providing detailed OA composition at a higher time resolution than previously studied (Worton et al., 2012).

GCXGC is a powerful tool for identifying compounds that can be linked to specific sources. For instance it has been used to identify chemicals emitted from manufacturing processes, (Alam et al., 2013), SOA from aromatics (Hamilton et al., 2004) and biogenic SOA (Kallio et al., 2006). Its uptake as a routine instrument has been slow, in part due to difficulties with quantification and also the huge number of species that can separated creates data handling problems. It has recently been coupled to a nitrogen specific detector (Nitrogen Chemiluminescence Detector) that only produces a signal for organic compounds that contain nitrogen (Ozel et al., 2011).

B1.2.3 High Performance Liquid Chromatography (HPLC)

HPLC separates compounds on the basis of interaction with a stationary phase and the majority of studies separate compounds on the basis of polarity. HPLC works well for polar, water-soluble species and high molecular weight compounds and is becoming increasingly popular for the analysis of SOA compounds in aerosol. It is routinely used for the analysis of small carboxylic acids. It gives complementary information to GC (that works well for non-polar POA) and the combination of both techniques, offers real potential to characterise the organic species described in section A2.1.

HPLC can be coupled to MS using electrospray ionisation or atmospheric pressure chemical ionisation. Both techniques ionise molecules without fragmenting them, allowing the molecular mass to be determined. Using a tandem MS, that allows further fragmentation of the molecule, provides additional structural information and is becoming the standard technique for tracer analysis.

Recently ultra high-performance liquid chromatography (UHPLC) has been used, which decreases analysis times (1 hour to 10 minutes), increasing sample throughput without losing the amount of separation of components.

B1.2.4 Capillary electrophoresis

Capillary electrophoresis (CE) can be used for the analysis of charged species or compounds that are in equilibrium with a charged form, thus they are generally suited to carboxylic acids. CE can also be coupled to mass spectrometry and has been used to investigate the organic acids and acidic oligomers in SOA formed through the processes described in section A2.1.3 in a range of smog chamber simulations (Muller et al., 2007;Krivacsy et al., 2000; Rudolph and Stupak., 2002; Adler et al., 2003; Iinuma and Herrmann., 2003; Gao and Rudolph., 2004).

B1.2.5 Ion Chromatography

Ion chromatography (IC) is a common analytical procedure that can be used to quantify the concentrations of ions in solution, although other techniques can be used, such as Inductively Coupled Plasma – Atomic Emission Spectrometry (ICP-AES) for metal cations. This is the most common technique used for the offline identification and quantification of the soluble inorganic component, which represents all the major components of SIA. Samples are obtained by dissolving the sample on a filter or impactor substrate in water. This technique can also be used for the separation of organic aerosol components, especially for the analysis of very acidic, short-chain carboxylic or dicarboxylic acids, such as oxalic acid and glyoxylic acid (Kerminen et al., 2000;Jaffrezo et al., 1998;Rohrl and Lammel., 2001). Mass spectrometric detection is usually not applied with IC because of the necessity to use buffers that are often not suitable for MS-detection. However, there exist methods for the coupling of IC with mass spectrometric detection that have been used to investigate chamber SOA and the corresponding gas phase (Fisseha et al., 2004).

B1.2.6 High-resolution Mass Spectrometry

High-resolution mass spectrometry involves very accurate mass measurements of molecules in aerosol (up to 0.00001Da), which allows the elemental composition to be determined. This increases the amount of molecular information that can be obtained, which can provide insights into the degree of oxidation and chemical make up of SOA. Instruments used include Fourier Transform Ion Cyclotron Mass Spectrometry (FTICR-MS) and Orbitrap mass spectrometry. Without a separation technique, it cannot isolate isomers (compounds with the same atoms present but different structures). However, data analysis strategies can allow information on the degree of oxidation (through the O:C ratio) and allow unparalleled compositional information to be obtained.

These techniques can also be coupled to liquid chromatography to allow both the mass and structure to be determined, but this is difficult due to the slow speed of the mass spectrometer and the very large data sets obtained (5 Gb). The cost of instrumentation is

high and there are only few systems available in the UK, all used for multiple research activities.

B1.2.7 Nuclear Magnetic Resonance (NMR)

NMR can be used for a quantitative functional group analysis, but provides limited molecular information, due extensive overlapping of peaks in the spectrum. Generally proton NMR is used (^{1}H-NMR) as this has the necessary sensitivity and allows different functional groups of aerosol to be determined, such as CH, CHO, OH and COOH. It requires large samples similar to the other offline analysis and can take many hours for a single analysis.

One way to reduce the complexity of the NMR analysis is to look at the bulk composition of water soluble OA (which is assumed to be representative of SOA away from biomass burning sources), simplifying the analysis of large data sets. Ion exchange chromatography has been used to separate WSOC into three fractions depending on polarity, (a) neutral/basic compounds, (b) mono and di-carboxylic acids and (c) polycarboxylic acids, followed by subsequent analysis using proton nuclear magnetic resonance (HNMR) (Decesari et al., 2000). Unlike chromatography, which provides data on specific compounds, this can offer insight into the overall functionality of the bulk SOA (McFiggans et al., 2005)

B1.2.8 Rare isotope mass spectrometry

The analysis of rare isotopes in atmospheric aerosols allows the "age" of the particulate to be differentiated in a manner analogous to radiocarbon dating. 14C is the most useful isotope in this regard but it is difficult to isolate due to the presence of N2 at the same nominal mass and the sensitivity needed at parts per trillion levels. Generally aerosol samples are converted to CO2 and then graphitised, possibly after separation using an EC/OC protocol (see B1.5.2). The samples are ionised using a caesium ion beam and analysed using an accelerator mass spectrometer, involving a tandem Van der Graff generator. The MS is very expensive, with UK access available as part of the Scottish Universities Environmental Research Centre. Additionally, 13C can also be quantified using this technique. The techniques used to interpret these data are discussed in section

B1.3 Limitations of offline techniques

In addition to the instrument specific limitations highlighted above, the main limitation of offline techniques is their poor sensitivity, which requires large amounts of particulate mass to be collected, although the exact detection limits depend on the specific technique and the ambient mass concentrations. Using high-volume impactors allows the time resolution of filter analysis to be reduced, with some recent studies analysing at 6 hour time resolution. Tracer methods described in section B2 such as CMB, often require the very high separation that can be achieved by offline methods and obtaining quantitative data for high complexity datasets is often expensive, as a large number of calibration standards are needed.

B1.4 Online Aerosol Mass Spectrometry

Over the past two decades, there have been significant advancements in online aerosol mass spectrometry (Murphy, 2007; Nash et al., 2006; Laskin et al., 2012). Broadly speaking, the techniques can be separated into two categories. The first is laser desorption and ionisation and the second is thermal desorption and subsequent ionisation.

B1.4.1 Laser Desorption and Ionisation (LDI)

Laser desorption techniques introduce aerosol particles into a vacuum chamber, where individual particles are struck with a high energy laser pulse which simultaneously desorbs the particles and ionises the resulting gas. The ions are then analysed with time-of-flight mass spectrometry (ToF-MS). However, these techniques yield all components of PM, and not just the SOA and SIA fractions. There are further challenges with this methodology, such as the ability to be quantitative, which make them unsuitable for determining the mass of SOA and SIA. These are discussed in detail in Laj et al., 2009. In some of cases, the laser desorption techniques have been used to explicitly identify different types of secondary aerosol (e.g. Dall'Osto et al., 2009a, b), but the total mass of SOA and SIA was measured by other instruments. Examples of these instruments can be found in Laj et al., 2009 and Laskin et al., 2012, but as the requirement for this report is to quantify SOA and SIA mass, they are not discussed here. However, one advantage of the single particle techniques is that they can provide qualitative information about the distribution of SOA and SIA within an aerosol population. This may be of benefit for any emerging policy pertaining to, for example, health effects of SOA or SIA where composition of individual particles is required rather than bulk or ensemble information.

B1.4.2 Thermal desorption

The mostly widely available thermal desorption aerosol mass spectrometer is the Aerosol Mass Spectrometer (AMS) supplied by Aerodyne Research Inc and the related Aerosol Chemical Speciation Monitor (ACSM) (Canagaratna et al., 2007; Ng et al., 2011). These instruments are capable of measuring both the SOA and SIA fractions of PM. The instruments consist of three differentially pumped vacuum chambers. The first houses an aerodynamic lens (Zhang et al., 2002; 2004) that focuses the particles down to a narrow beam, and a skimmer cone which removes the majority of the air molecules. The second chamber allows the particles to be sized vacuum aerodynamically, and the third is the detection region, consisting of a tungsten surface held at ~600C, known as the vaporiser, and finally the mass spectrometer. The aerosol particles impact on the heater and those with a flash vaporisation temperature of 600 °C or less are desorbed to form a gas. The gas is then ionised by 70 eV electron ionisation before being analysed using a mass spectrometer.

There are two types of detector that are normally fitted to the AMS: a quadruple mass spectrometer (Q-AMS: Jimenez et al 2003; Jayne et al., 2000) and a Time-of-Flight mass spectrometer (ToF-AMS). There are two sub-types of ToF-AMS, the Compact ToF-AMS (C-ToF-AMS: Drewnick et al., 2005) and the high resolution ToF-AMS (HR-ToF-AMS: Decarlo et al., 2006). The different detectors allow different mass resolutions, limits of detection etc, and are summarised in table B.1.

	Detection Limit (ng m^{-3})		Mass Resolving Power (m/Δm)	Mass Range (m/z)
	NO$_3$	Organics		
Q-AMS	32[a]	320[a]	UMR[c]	1-300

C-ToF-AMS	1.2[a]	12[a]	800	1-1000
HR-ToF-AMS (V mode / W mode)	2.9/32[a]	29/320[a]	2500/5000	1-1200
ACSM	12[b]	148[b]	UMR[c]	1-200

[a] based on 1 minute averaging time (http://www.aerodyne.com/products/aerosol-mass-spectrometer)
[b] based on 30 minute averaging time (Ng et al., 2011)
[c] Unit Mass Resolution, i.e. a resolution of 1 Da throughout the entire mass spectrum.

Due to its high cost of operation, the standard AMS is most suited for intensive studies. A new AMS designed for long term monitoring, the Aerodyne Aerosol Chemical Speciation Monitor (ACSM: Ng et al., 2011), is a smaller, low cost version. It also provides real time, quantitative mass loadings and chemical composition of the non-refractory aerosol, which includes SOA and SIA. Unlike the other AMS, this instrument does not provide size information and has a lower sensitivity detector, .however, the basic principle of operation is the same.

B1.4.2.1 Limitations of the AMS and ACSM
The AMS is quoted as measuring the submicron fraction of the PM. The inlet transmission is 100% between ~0.06 and 0.7 µm, with low penetration between 1 - 2µm. However, comparisons between the AMS and other instrument measuring $PM_{2.5}$ mass, shows that the AMS is capturing the majority of the SOA and SIA mass. For example, Ng et al. 2011 showed that the ACSM recorded ~70% of the total $PM_{2.5}$ nitrate and sulphate mass as measured by a PILS. The instrument is also only capable of measuring the fraction of particulate that will desorb on the vaporiser surface, which is operationally defined as 'nonrefractory'. In practice, this means it is capable of quantifying ammonium nitrate, ammonium sulphate, ammonium chloride and organic matter and comparisons with other instruments have been favourable (Takegawa et al., 2005). However, the instrument in its standard configuration is not capable of detecting sea salt, dust and black carbon. It also appears that the AMS is less efficient as measuring nitrate from sodium nitrate, although part of the discrepancies reported may also be due to mismatches in the size selectivity of the different instruments (Allan et al., 2004a). While some of the organic matter that comprises SOA is not volatile enough to be detected in its natural state, the AMS instead detects the thermal decomposition products produced on the vaporiser surface, such as CO_2 (McFiggans et al., 2005). While this means SOA can be quantified, a certain amount of information regarding its chemical nature is lost.

The collection efficiency (CE) of the AMS systems is defined as the fraction of particles which are sampled into the inlet and are measured by the detector. The CE is a combination of 3 components (Huffman et al., 2005): lens transmission; non-sphericity and; particle

bounce. Several authors have produced parameterisations to calculate the collection efficiency based different factors such as chemical composition and sample line RH (Crosier et al., 2007; Matthew et al., 2008). These corrections have been validated by independent, co-located measurements. A recent review by Middlebrook et al. (2013), compares the different approaches and provides a new parameterisation taking all the different conditions into account, validated by independent measurements. The work concludes that the error in CE is of the order 30%, and that sample lines are dried to RH < 20% to remove the effect of RH on the final CE.

B1.5 Semi-continuous inorganic measurements

A common technique for determining the SIA mass of PM is to mix ambient aerosol particles with steam to either activate or scavenge the particles into droplets, and impact them to produce a flow of water which is then either stored for later analysis or analysed offline within the instrument with an ion chromatograph (IC). These techniques have shorter sample times than the offline filter methods, but not as short as the aerosol mass spectrometry approaches. The methods do not yield any size information and it is important to remove any gas phase components which make be absorbed by the water and produce readings in the IC. Fitted with the appropriate cyclone inlet, the instruments measure the majority of the $PM_{2.5}$ inorganic mass. Examples of commercially available units include the Particles into Liquid Sample (PILS, or PILS-IC when configured with an IC. Weber et al., 2001; Orsini et al., 2003), Monitor for Aerosols and Gasses in Ambient Air (MARGA, Trebs et al., 2004) and the URG Ambient Ion Monitor (Khlystov et al., 1995; Wu et al., 2007). Table B.2 summarises the main operating parameters and limits of detection

	Typical species measured	Typical limits of detection (ng m^{-3})	Typical sample length
PILS	Na^+, NH_4^+, K^+, Ca^{2+}, Mg^{2+}, Cl^-, NO_3^-, NO_2^-, SO_4^{2-}	100	15 mins
MARGA	Na^+, NH_4^+, K^+, Ca^{2+}, Mg^{2+}, Cl^-, NO_3^-, SO_4^2	50-100	I hour
URG- AIM	Na^+, NH_4^+, K^+, Ca^{2+}, Mg^{2+}, Cl^-, NO_3^-, NO_2^-, SO_4^{2-}	50	1 hour
R&P 8400N/8400S	NO_3 / SO_4	400	8.5 mins
Delta (extended)	NH_4^+, NO_3^-, NO_2^-, Cl^-, SO_4^{2-}	100	1 month

Sunset Analyser	OC (and EC)	400	1 - 2 hours

Table B.2. Summary of semi-continuous measurement techniques

Two species specific monitors, the R&P 8400N and 8400S, measure the mass concentration of nitrate and sulphate respectively (Stolzenburg et al., 2000; Drewnick et al., 2003). The principle of operation is to sample air through a cyclone and through a denuder to remove any potential gas phase contaminants. The particle laden air is then humidified and impacted on a volatilisation cell. After a typical sample time of 8.5 minutes, the instrument switches to an analysis mode, with a particle free air stream flowing over the volatilisation cell into a detector. For the 8400N this is a nitrogen oxide analyser and for the 8400S, a sulphur dioxide analyser. The cell is then flash heated in the order of 100ms, and the resulting evolved oxides of nitrogen and sulphur are measured by chemiluminescence and UV fluorescence, respectively.

B1.5.1 Limitations of the semi-continuous techniques

Most of the techniques listed above are robust at delivering bulk analysis of the major ions which contribute to the total $PM_{2.5}$ SIA mass. Developments have been made in measuring total water soluble organic carbon (WSOC) and simple acids (Sullivan et al., 2004), however this does not specifically quantify the secondary fraction explicitly. It has also not seen extensive use outside of research projects

There are differing results in the literature for the R&P devices. For example, Drewnick et al., 2003 report good agreement with other semi-continuous methods for sulphate and an average mass recovery of 85% when compared with a filter based method and Markovic et al., 2012 reports good agreement with an AMS. In contrast, EPA et al., 2008 report recoveries as low as 65% for nitrate and propose the differences are a non-linear function of concentration. The EPA report recommends only the IC methods (e.g. PILS-IC) be used for major SIA ions. Furthermore, the R&P instruments only measure one compound of the SIA mass, and miss the other major compound, ammonium and to a lesser extend chloride.

The steam jet aerosol samplers rely on the total ion signal in solution to be from the aerosol particles. This is achieved by passing the sample stream though a denuder. Wu et al., 2007, report that under high SO_2 and NO_x conditions, URG AIM measured more nitrate and sulphate than filter based measurements, due to the positive interference from the gas phase. It is therefore important to ensure that an adequate denuder is fitted and that regular blanks are taken.

Similar to the high gas phase conditions, Wu et al., 2007 also reported large deviations from the filter based methods under high loadings of nitrate and sulphate (>~ 20 µg m^{-3}). The authors concluded that this was due to insufficient steam to dissolve the available ions and that more research was needed, although the loading here are likely to only be experienced in the UK in extreme pollution events.

B1.6 Other measurements

As mentioned in the introduction, this section is divided into two categories: those which can be used as an indirect means to determine SOA or SIA, those that support the measurements and those which enhance fundamental scientific understanding and inform models.

B1.6.1 Mass Measurements

Mass measurements are discussed here, as these are commonplace on the monitoring networks (e.g. AURN) and are the most common methods used when attempting to calculate secondary mass fractions. The Filter Dynamic Measurement System (FDMS) used in the UK (Thermo Scientific, model 8500) is based on the Tapered Element Oscillating Microbalance (TEOM), but has two modes of operation, namely non-volatile and volatile mass. Air is sampled through a $PM_{2.5}$ head, dried and continuously sampled onto a filter at the end of the tapered element. The frequency of oscillation of the element is directly related to the mass on the filter. In the non-volatile mode, the sample chamber is held at 30C, which differs from the TEOM which samples at 50°C. The 20°C difference is known to have produced a loss of some volatile material, which led to the development of the FMDS. The volatile mode cools and filters the air for all PM before it is passed to the filter. This allows any volatile material that was collected during the non-volatile cycle to evaporate. The change in mass during this cycle is recorded as the volatile mass. There are considerations to be borne in mind when utilising PM data for calculating secondary fractions. As discussed in section A, a large fraction of both SIA (principally ammonium nitrate) and SOA are semivolatile, so this must be considered when comparing these data with the reported volatile and non-volatile masses. It must also be borne in mind that when analysing older TEOM data, the behaviour of semivolatile secondary material may not be captured at all. A more comprehensive assessment of the FDMS and associated issues is given in the AQEG (2012).

An alternative online method, which like the FDMS, has been approved for PM monitoring, is the Beta Attenuation Monitor (BAM), where air is sampled onto a filter and exposed to beta radiation and a scintillation detectors on the other side of the filters measures the attenuation in the particle beam. Once the attenuation for an unloaded filter is accounted for (the zero), the total mass can be calculated. Commerical units include the Met One BAM 1020. Although the BAM has been shown to be equivalent by EU and EPA standards, the main limitation is in the data inversion as the conversion to mass makes an assumption about the composition (Turpin et al. 2001).

B1.6.2 Offline or Semicontinuous EC/OC

Thermal optical OC/EC analysis is a form of evolved gas analysis whereby a sample collected on a quartz substrate is heated and carbonaceous matter is emitted as a gas either through vaporisation, pyrolysis or burning and the total amount of carbon is quantified. The OC/EC instrument manufactured by Sunset Labs (Birch and Cary, 1996) is a commercial and automated application of this technique and comes in versions for offline or in situ semicontinuous analysis.

The differentiation between organic carbon (OC) and elemental carbon (EC) is based around the assumption that OC can be liberated through vaporisation or pyrolysis whereas EC can only evolve through burning. This is done by ramping the temperature (up to 550-900°C depending on the protocol) while the substrate is in an inert atmosphere (normally helium) and monitoring the amount of carbon evolved. Once all the OC has been measured, the temperature is ramped again (between 500-650°C to 800-920°C, again depending on protocol) in the presence of oxygen to burn off any remaining EC. Because a fraction of the OC will char (effectively transforming to EC) during heating, a light source (e.g. laser) is used

to monitor the filter during heating. Any darkening of the filter is ascribed to charring OC, which is used to correct the data.

While the technique is very accurate for the quantification of the total carbon, there are a number of confounding factors that can affect the 'split' between OC and EC. Certain organic species may behave differently and their vaporisation and/or charring may behave unexpectedly for a given temperature profile. Additionally, there may be interactions between the different particulate components that may also alter the evolution of carbon. Because of this, a temperature programme and optical correction method developed for the measurement of an aerosol in a given environment may not be as applicable to another. It is fundamentally difficult to define a truly objective and universal differentiation between OC and EC, particularly when large PAHs are present that blur the line between organic and graphitic carbon on a molecular level. By this token, any definition of OC and EC using this technique will be operationally defined and be dependent on the measurement protocol. It is therefore important that a defined temperature programme and optical correction method is chosen and used consistently between samples in order that they be comparable.

In the USA, the protocols most commonly used are the IMPROVE (Chow et al., 1993) and EPA/NIOSH (Peterson and Richards, 2002) protocols, depending on the sampling network. In Europe, the EUSAAR 2 protocol was developed in 2010, based on the optimal analysis of samples collected in various rural locations across the continent (Cavalli et al., 2010). Within the UK, the QUARTZ protocol is used on the Numbers and Composition network, which is similar to the NIOSH protocol and has been shown to give equivalent data to other protocols used within Europe (Emblico et al., 2012).

B1.6.3 Supporting measurements

B1.6.3.1 Number size distributions

Number size distributions (particle number concentration vs particle diameter) are often needed to inform detailed models of secondary aerosol formation, as described in A2.1.2. The most common tool for this purpose is the Scanning Mobility Particle Sizer (SMPS). This separates particles electrostatically before counting them using a Condensation Particle Counter (CPC) and by scanning the separation voltage, a complete size distribution can be built up. While other counting and sizing instruments exist such as optical particle counters and aerodynamic particle sizers, the SMPS is preferred as it detects particles in the approximate size range of relevance to the accumulation mode particles involved in secondary formation (30 – 500 nm). Manufacturers include TSI (models 3080 and 3034) and GRIMM and specifications for the use of these for ambient sampling have been developed for EUSAAR and published by Widensohler et al. (2012).

B1.6.3.2 Gas phase precursors, intermediates and tracers

A range of precursor gases are associated with the formation of SOA and SIA and the observation of these gas phase species is central to evaluating the likely yields of secondary matter particulate matter. Key gas phase inorganic species, that on chemical transformation provide mass to SIA, are SO_2, NO_x (sum of NO and NO2) and NH_3. Volatile and semivolatile organic compounds (VOCs and SVOCs) provide feedstock material for the growth of SOA and cover a wide range of chemical functionalities and volatilities. The transformation of inorganic and organic gas phase chemicals is mediated by the oxidants O_3, hydroxyl radical (OH) and nitrate (NO_3) radical.

Measurements of NO_x are made widely in the UK as part of the Defra AURN air quality compliance monitoring network. The standard technique is based on chemiluminescence, whereby NO is excited via ozone reaction to give NO*, which relaxes to yield a photon. The technique is robust for NO and good traceable standards exist. The measurement of NO2 is more complex since this species requires conversion to NO prior to measurement (Kleffman et al., 2013). In the AURN network this is achieved via catalytic means, and the process may also convert other oxidized nitrogen species to give a NO signal - for example peroxyacetylnitrate. AURN network data is therefore something approaching an operationally defined version of NO_x, which approximates closer to NOy (the sum of all gas phase oxidized nitrogen species). Research instruments use a wavelength-specific photolytic degradation of NO2 to NO prior to measurement, and this gives a more true measurement (Fuchs et al., 2010). The lack of adoption of this methodology in compliance monitoring is an artefact of the instrumental methods described in the associated EC Directives. Other direct measurements of NO2 include Laser Induced Fluorescence (LIF). Sensor-based approaches for the measurement of NO_x are at an experimental phase, however have been trialed recently at Heathrow Airport (Mead et al., 2013).

Observations of SO_2 are typically made using a pulsed fluorescence technique, and these instruments also form part of the UK AURN, albeit with a diminishing number of measurement locations as ambient levels of SO_2 reduce. The technique is relatively robust with good quality traceable standards. Modern instrumentation has detection limits around 0.1 nmol mol-1 which is adequate for urban and rural detection, but sometime insufficient to determine SO_2 in clean marine air or aerosol nucleation studies. In these instances chemical ionization mass spectrometry is often used for measurement, although these are specialist research instruments. Chemical ionization is also an appropriate method for the detection of the by-products of NO_x and SO_2 precursor oxidation in the gas phase including HNO_3 and H_2SO_2 (Speldel et al., 2007).

Ammonia in the gas phase is generally measured for monitoring purposes using chemical stripping via wall reaction with, for example, citric acid following a denuder stage to remove aerosols. The technique is used in a number of monitoring programmes with samples typically returned to a central laboratory for ion chromatography detection. Whilst somewhat manually intensive and with low time resolution, the technique is well proven at urban and background abundances. The literature contains many alternative research grade approaches to NH_3 measurement including spectroscopic and mass spectrometric and chemi-sensors (Williams et al., 1992).

The diversity of organic compounds that can partition to the SOA means to no single technique can resolve all species (Hamilton and Lewis, 2006). The most straightforward measurement of VOC precursors is for smaller C2- C7 non-methane hydrocarbons. These species are very volatile and do not partition under ambient conditions to aerosol, but on oxidation can form secondary products that are associated with SOA. There are around 50 species commonly reported in this class including long lived VOCs such as ethane and acetylene, and short-lived species such as isoprene and 1,3 butadiene. The standard measurement method is gas chromatography flame ionization detector (GC-FID) coupled with thermal desorption. Four locations in the UK have online measurement of C2-C7 NMHCs as part of the Defra automatic hydrocarbon monitoring network. Other research instruments exist and are used on a campaign basis and for the analysis of whole air samples from taken from aircraft. The methodology is robust and accurate with pmol mol^{-1}

sensitivity, but is relatively expensive to operate and has a substantial data work-up associated with it.

Higher molecular weight SVOCs and polar VOCs (including oxygenated and nitrated species) are measured less frequently. A range of different instrumental techniques exist however, mostly based around mass spectrometric detection. Small carbonyl molecules, plus a limited range of hydrocarbon-like species can be measured at high-time resolution using proton transfer reaction mass spectrometry (PTR-MS). This commercially available instrumentation achieves 1-10 s time resolution at sub nmol mol-1 sensitivities (Lindinger et al., 1998). This type of observation is extremely valuable when determining the temporal evolution of VOCs, direct emissions from vehicles, fluxes or fast reactions in the laboratory. Whilst not used in compliance monitoring, a substantial number (>20) of instruments are used for research in the UK. A chemical ionization MS variant on this technique is capable of measuring organic acids, based on an instrument commercially available from the US. The limiting factor with most direct mass spectrometry measurements is that of isobaric interference; compounds with the same molecular mass but different chemical structure give an indistinguishable signal in the instrument.

The benchmark method for higher molecular weight organic compounds, including for example monoterpenes, monoaromatics, higher carbonyls and multifunctional species, is GC-MS. This is a well-established technique that can typically resolve gas phase compounds of equivalent volatility to C18 (Miller et al, 2008). The limiting factor above this becomes the sampling capabilities of thermal desorption. This is a key group of species to determine in SOA studies since some may directly partition to aerosol, which others such as terpenes and aromatics are major global precursors. Whilst the technique is well understood, a limiting factor in application is a lack of traceable calibration materials. Monoterpene gas standards for example have only very recently become available from NIST. Standards for higher hydrocarbons and carbonyls must generally be generated dynamically on demand. This creates a substantial experimental overhead.

Higher gas phase hydrocarbons released from incomplete kerosene and diesel combustion are often in the carbon range C8-C18 and form a highly complex grouping, reflecting the petrochemical source materials. For complete speciation of this class of compound variants of GC-MS are required which have either greater GC peak capacities or MS mass resolution. GCxGC-MS or GC-HRT-MS are research grade tools that can achieve complete molecular characterization of such mixtures, but they are used only infrequently, and generate very large datasets (Lewis et al., 2000).

A small sub-set of polar organic compounds are not amenable easily to direct GC or MS analysis techniques. Some of these species are of particular importance to SOA, such as glyoxal and methyl glyoxal. Here a whole range of different research techniques have been reported for measurements including optical spectroscopic, sensor, liquid chromatography and chemical derivitisation .

Finally it is worth considering those oxidant species in the atmosphere responsible for the conversion of primary material into condensable secondary products in SIA and SOA. Of these oxidants ozone is the most easily measured, and indeed forms a substantial part of the AURN network. A very robust methodology exists for O_3 measurement based on UV absorption, with direct calibration via Beer-Lambert law. The other key oxidants OH and

NO$_3$, are also directly measureable using research grade instrumentation. OH is generally measured using low-pressure on-resonance LIF, however this is highly complex instrumentation and perhaps only 5-6 instruments exist world-wide (Heard, 2006). NO$_3$ can be detected directly using optical methods such as cavity ring down spectroscopy, but again this is a highly specialist endeavour. Indirect estimation of NO$_3$ has been proposed from selective hydrocarbon degradation (McLaren et al., 2010).

In summary therefore, the key inorganic precursors to SIA can be measured relatively easily, with high confidence, and data is readily available from online networks. Organic precursors are more complex, and whilst methods exist for almost all types of organic, they require a range of different techniques to be applied simultaneously, restricting observations to short intensive research experiments. The key gas phase radical species that drive oxidative processes can also be detected directly, but the instrumentation is highly specialized and used only infrequently for research campaigns.

B1.6.3.3 Aerosol Volatility
As discussed in sections A component volatility is crucial to the understanding of SOA formation and as discussed in section C, there are model implementations that use volatility as a basis for parameterising precursors and secondary organic components (Robinson et al., 2007). It is greatly desirable to be able to quantify the volatility of the organic aerosols in the ambient atmosphere, both to further understanding and to develop the models. While FDMS measures a semivolatile fraction, this is comprised of both semivolatile organic and inorganics and as it only measures at one temperature, does not provide sufficient detail to constrain the models in question and there are no suitable routine measurements of organic volatility available.

One technology that has been employed is thermal denuders, whereby an instrument (often an AMS) samples aerosols downstream of a heated tube (Huffman et al., 2009). Data can be gained by cycling the temperature of the denuder and measuring the speciated particulate matter depletion as a function of temperature. However, linking volatility by temperature to the saturation concentrations required by the models is not straightforward and questions have been raised regarding the fundamental reliability of this technique (Fuentes and McFiggans, 2012). If such a measurement was available that was easily comparable with volatility models, this would greatly improve scientific understanding and model development. The technique of selectively trapping and releasing gases presented by Cross et al., (2013) shows some promise, but this is currently not fully developed.

Recommendation – A reliable technique for routine monitoring of chemically-resolved volatility is developed

B1.7 Monitoring Networks
The majority of the instruments described in the previous sections provide point measurements. i.e. they provide information from a single location. To understand SOA and SIA on larger scales and to build up a picture of the distribution of these particles across the UK, a system of spatially distributed measurements is needed. This can be achieved either by a network of fixed measurement sites or with mobile measurements. As previously discussed, assessments of SOA and SIA can be made using a range of different instruments but the quality varies depending on the specific deployment and the suite of data available from a single site. As a result, data that would contribute to assessments of SIA and SOA

are spread across a number of different measurement networks, with the suitability and quality of the data varying from site to site. This is compounded by the fact that data from multiple instruments should be taken into consideration and assessments are generally improved by the depth of data available.

B1.7.1 UK based monitoring networks

The UK has several long term monitoring networks for recording selective atmospheric pollutants. The sites are predominately set up to monitor if statutory air quality standards and targets set by the various EU Directives are being met and measures combinations of PM (10 and 2.5), black carbon, gases and some chemical composition of the aerosol. For the purpose of this report, some of the networks report the mass of SIA by measuring the main constituents, namely NH_4^+, SO_4^{2-}, NO_3^- and Cl^-. However, only one monitoring network (Particles Numbers and Concentrations) includes a measurement of organic aerosol.

The sites often serve more than one network, with several different measurements being taken.

B1.7.1.1 Automatic Urban and Rural Network (AURN)

AURN (http://uk-air.defra.gov.uk/networks/network-info?view=aurn) is the largest UK network, with over 100 sites with data going back to the 1970's. Around 100 of these sites monitor $PM_{2.5}$, predominately by FDMS, but also BAM and gravimetric measurements (collected with a Partisol). Similar stations are also operated by local authorities, research institutes and industry, providing a comprehensive data coverage across the UK (Any insight into how Defra could tap into the research networks would be helpful).

B1.7.1.2 London Air Quality network (LAQN)

The London Air Quality network (http://www.londonair.org.uk/LondonAir/Default.aspx) operates 115 sites across the capital, 14 of which belong to the AURN network. The network is maintained by Kings College London (KCL). The metric of interest for this report is $PM_{2.5}$ mass.

B1.7.1.3 UK Eutrophying and Acidifying Pollutants (UKEAP)

The UKEAP monitoring project (http://uk-air.defra.gov.uk/networks/network-info?view=ukeap) has 4 elements for monitoring pollutants, two of which are discussed here. The other two are exclusively gas monitoring stations. The first is the National Ammonia Monitoring Network (NAMN: http://pollutantdeposition.defra.gov.uk/ammonia_network), which consists of 85 sites, established in 1996. However, only a subset of these provide particulate NH_4^+. The second network included in UKEAP is the Acid Gas and Aerosol Network (AGANet: http://pollutantdeposition.defra.gov.uk/aganet), which provides monthly averages of particulate NO_3^-, SO_4^{2-} and Cl^-. This network has 30 sites and was established in 1999. The AGANet is seen as an extension to the NAMN sites for particulates. The sites employ a Delta system for NH_4^+ and an extended system for NO_3^-, Cl^- and SO_4^{2-}.

B1.7.1.4 Black Carbon

The black carbon network (http://uk-air.defra.gov.uk/networks/network-info?view=ukbsn) is managed for DEFRA by the National Physical Laboratory (NPL). The network builds on the black smoke network and has data dating back to the 1920's. The black carbon network was established in 2006, replacing the old offline black smoke metric with online 2-wavelength

Magee Aethalomters (Quincey et al., 2011). As of 2012, there are now 14 sites in the network, 12 of which form part of the AURN network.

B1.7.1.5 Particle Numbers and Concentrations Network

The UK Particle Numbers and Concentrations Network (http://uk-air.defra.gov.uk/networks/network-info?view=particle) is a network of offline measurements that augments 6 existing monitoring sites. The exact deployment at each site varies, but includes automated filter samples for offline composition analysis (including EC/OC) and semicontinuous inorganic analysers at four sites (Harwell, Auchencorth Moss, Marylebone Road and North Kensington).

Table B.3: Summary of available secondary aerosol composition measurements

Instrument	Inorganics	Organics	High time resolution	$PM_{2.5}$ capable	Network or sites	
Automated filter samplers	X	X		X	Particle Numbers and Concentrations Network	
Online EC/OC		X	X	X		
AMS / ACSM	X[1]	X	X	[2]	North Kensington (ACSM)	
Ruprecht and Patashnick	X[3]		X	X	Marylebone	
PILS / AIM / MARGA	X		X	X	Particle Numbers and Concentrations Network	
Delta	X				AGANet	

Notes:

[1]Can measure all SIA except sodium nitrate

[2]Approximate PM1

[3]Can only measure nitrate or sulphate, depending on the specific instrument

B1.7.2 European wide networks

There are two main European monitoring networks in which the UK is currently involved. They both provide a distributed network of aerosol measurements and can be used by scientists and governments alike when considering, for example, The Convention on Long-range Transboundary Air Pollution (LRTAP).

B1.7.2.1 European Monitoring and Evaluation Program (EMEP)

EMEP (http://www.emep.int/index.html) is a comprehensive network bringing together measurements, emissions and modelling to better understand air pollution on scales up to hemispherical scales. The network operates in 40 countries, including the UK. The UK has several EMEP sites, but only two are being operated as level II supersites. These are at Auchencorth Moss and Harwell. Both these sites are part of the UKEAP, black carbon and particle networks. In addition to the Delta system for monthly means of the main SIA components, they also have a MARGA installed for hourly means of both PM_{10} and $PM_{2.5}$ ions.

B1.7.2.2 Aerosols, Clouds, and Trace gases Research InfraStructure Network (ACTRIS)

ACTRIS is a Framework 7 European project aimed at integrating ground based atmospheric monitoring stations. The project was started on the 1st April, 2011 and will run for 4 years. In addition, ACTRIS promotes transnational access via travel and subsistence grants to researchers to the sites that will enrich and enhance the scientific data being collected at the site.

ACTRIS integrated 1 new and 3 existing networks, one of which was the European Supersites for Atmospheric Aerosol Research (EUSAAR), which operated 20 sites from 2006 – 2011. ACTRIS now has approximately 30 aerosol measurements sites, two of which are based in the UK. The two sites in the UK are the same two in the EMEP network: Authencorth Moss and Harwell. Indeed, the ACTRIS sites are shared with other networks, such as EMEP.

B2 Data Analysis Techniques

In section B1, a range of instruments have been identified that are capable of delivering quantitative data on various aspects of aerosol composition. However, these measurements, either in isolation or in combination, do not necessarily quantify the relative contributions of primary and secondary components to the different chemical fractions of the aerosol, as many of the components can have multiple sources, both primary and secondary. Indeed, no instrument is capable of directly quantifying primary and secondary organics as separate entities.

With the study of secondary particulate matter in mind, the goal of a data analysis technique covered in this section is to quantitatively apportion a fraction of measured particulate matter to secondary processes and then, if possible, attribute the secondary material to a given precursor type or chemical process. Most techniques are based around standard receptor modelling, i.e. assuming that the aerosol ensemble is a combination of primary and secondary aerosols that create a linear, additive response in the analytical technique being used (Hopke et al., 2006). By identifying characteristic signatures and applying a priori knowledge of the different sources under investigation, measured particulates can be assigned to the different classes. Note that other analytical techniques are often applied for the purposes of investigation of fundamental processes, however these are not necessarily useful for quantification and are not considered here.

However, there are a number of different approaches that can be used and while the results are similar in nature, each has its own issues and ambiguities that must be borne in mind when interpreting the data. Many of these techniques can be considered quite mature when

applied to the investigation of primary aerosols, particularly where a given source emits particulates with a consistent profile that is not modified between source and receptor. However, the situation with secondary organic aerosols in particular is complicated in that by definition, the particulates under investigation must have undergone a chemical transformation in the atmosphere, so the condition for ideal receptor modelling that the factor profile is not modified may not be satisfied.

Note that most of this section is concentrated on the techniques used to quantify the SOA contributions. As discussed in section A, the majority of SIA in the UK is composed of ammonium, nitrate and sulphate. As the processes governing these are substantially less complex than SOA and there are relatively few primary sources to confound these measurements, the analysis is more straightforward. As such, the SIA analysis is confined to section B2.6

B2.1 Factorisation of organic matter

For the purposes of this report, 'factorisation' is used to describe the technique whereby a multivariate dataset is reduced to a discrete number of 'factors', each expressed as a representative profile within the variable space of the analytical technique and a quantitative contribution to each sample. If the samples are taken sequentially at a given receptor site (e.g. by an automated instrument), the contribution data will represent a time series of the aerosol component. Note that because factorisation is limited to the variables used within the analysis, it can only apportion the total particulate matter that is quantifiable by a given analytical technique. Therefore, if these techniques are to be used to quantify SOA, they must be applied to an analytical technique that quantifies the total organic aerosol. For example, this could not be applied to the organic fraction quantified by IC, as this would only deliver information on a limited subset of the organic matter.

Not all multivariate techniques are necessarily suited for the purposes of receptor modelling. For example, while principle component analysis (PCA) is highly effective at reducing a dataset to distinct core trends, the derived factors can be abstract, containing a certain amount of negative values, and therefore difficult to relate to physical quantities. By necessity, receptor models normally explicitly specify that a give factor must be non-negative in terms of both its mass concentration within a sample and its profile of contributions to the individual variables. While meaning that the solutions are physically meaningful, this introduces the complication that the factors are unlikely to be numerically orthogonal, which can increase the ambiguity of solutions.

B2.2 Positive Matrix Factorisation (PMF)

PMF is a popular non-negative factorisation technique originally developed at the University of Helsinki and is currently additionally available through the US EPA. Note that this is not the only factorisation method supported by the EPA; an alternative algorithm, UNMIX, is also available, however this is not widely used for the purposes of SOA retrieval. The two dimensional PMF2 algorithm works by taking a two-dimensional multivariate dataset and deriving a predefined number of factors, each in the form of two vectors, as follows:

$$x_{i,j} = \sum_{p} g_{i,p} f_{p,j} + e_{i,j}$$

Where x is the 2D data matrix (e.g. mass spectra vs. time), g and f are non-negative vector factor profiles (e.g. a mass spectrum and a time series), p is the number of factors and e is a residual matrix.

The solutions are derived iteratively using a chi-squared minimisation, so in addition to the instrumental data, the algorithm must also be provided with measurement precision data. There are various ways of estimating this quantity, ranging from empirically deriving the noise associated with a measurement to modelling the instrumental function. PMF does not generally use any a priori factor profiles, instead using a randomly-populated data matrix at the start of the fitting, with a user-defined 'seed'.

PMF (Paatero, 1997) has been used with great success in various forms of receptor modelling for primary aerosols, particularly when applied to the analysis of trace metals (Pekney et al., 2006). As with other factorisations, it is only useful for SOA quantification when applied to a technique that quantifies all of, or a clearly defined fraction of, the organic fraction. The technique has been applied to bulk spectroscopic techniques such as FTIR and HNMR with some success (Decesari et al., 2011; Hawkins et al., 2010), however these techniques are not particularly widespread, so are not detailed here. In the field of SOA analysis, the technique has been most successful when applied to the organic data reported by the AMS and latterly the ACSM.

The application of PMF to AMS data was first reported by Lanz et al. (2007), however the use of the technique proliferated with the introduction of an open-source software suite called PMF Evaluation Tool (PET) developed at the University of Colorado at Boulder and detailed in Ulbrich et al. (2009). This does not exist as a PMF algorithm in itself, but as a front-end to the precompiled PMF2 executable code that can be obtained under licence from the University of Helsinki. In addition to the PET software, Ulbrich et al. (2009) also introduced data pretreatment and interpretive procedures that have since become the accepted as standard for AMS analysis.

The usual approach is to apply the algorithm to the organic fraction of the mass spectral data extracted according to Allan et al. (2004), using precision estimates based on a modified version of the error model presented by Allan et al. (2003). More recently, the data has also been applied to the high-resolution data outputs described by DeCarlo et al. (2006), which discriminates the peaks according to elemental composition, thereby increasing the number of variables and therefore increasing the resolving power of the technique.

In a typical polluted environment, this technique quantitatively resolves a number of different organic aerosol types including hydrocarbon like (HOA), biomass burning (BBOA), oxygenated (OOA) and cooking (COA). As all but OOA can be ascribed to POA, it is standard practice to assume that the OOA is representative of the sum total SOA. Furthermore, the algorithm often reports multiple OOA factors, given names such as OOA1 and OOA2 or LV-OOA and SV-OOA. It should be noted that these are not discrete OA types, but rather the manifestation of the variability within SOA within the receptor model; as this explicitly provides data on factors with fixed profiles, the two OOA factors represent end members within a continuum of varying composition. The transitions between the different types of OOA can be taken as indicative of the amount of chemical processing that the OA has undergone, as described by Jimenez et al. (2009).

The PMF algorithm is not without limitations and ambiguities. A given run requires the user to specify the number of factors to use and as there are no fixed rules, the choices can become subjective. Common to many factorisation techniques, there is a level of ambiguity owing to rotational freedom within the factors, which results in quantitative uncertainty. While the use of the 'fpeak' parameter can be used to explore this ambiguity, this is limited in scope, as this reduces a multidimensional area of ambiguity to a single parameter (Paatero et al., 2002). This ambiguity is reduced when high-resolution data is used, due to the additional variables available. Confidence in the outputs can also be increased through the comparison with other data sources, in particular combustion tracers (Allan et al., 2010). There have also been attempts to combine the AMS data directly with other sources such as organic gas phase data from a PTR-MS during the fitting process (Slowik et al., 2010), but these methods are not widespread. There have also been attempts to apply PMF to the size-resolved PTOF data, but this has yet to yield tangible benefits.

It is difficult to objectively quantify the accuracy of this technique in determining the SOA fraction because of the lack of external comparisons that can be made. Allan et al. (2010) estimated an uncertainty of up to 7% due to rotational ambiguity, but this was done by varying the FPEAK parameter, which as stated above has limitation. The accuracy will also be highly dependent on the specific dataset. Factors will include the time interval over which data was taken, the distinctiveness of the time series (in particular if any of them reduce to close to zero independently of the others) and the instrument used, which in turn dictates the signal-to-noise of the data and the availability of high-resolution data products. When assessing the reliability of a given factorisation, one must pay close attention to a number of technical details described by Ulbrich et al. (2009). It is standard practice to explore these details in the supplementary material accompanying publications, however the nature and exact amount of detail varies between authors.

B2.3 ME-2

In an attempt to reduce the ambiguity in the fitting process, attempts have been made to use the ME-2 algorithm as an alternative to PMF2. Also developed at the University of Helsinki, this is a computationally more expensive but more generic solver that can be applied to the receptor model. This differs from PMF in that it allows more a priori information to be provided to guide the solutions. When applied to AMS data, this allows 'target' factor profiles to be specified (e.g. for HOA, BBOA), based on previous data. This reduces the amount of rotational freedom within the potential solutions and allows for a greater number of factors to be derived, thereby providing more accurate data. This is of particular use for lower signal-to-noise data or when high-resolution data is not available, such as when applied to ACSM data. As the factor profiles are known to vary slightly between instruments and campaigns (particularly for BBOA), the profiles are not stuck to rigidly, with a certain amount of variation allowed through the alteration of relaxation parameters. This technique was first introduced by Lanz et al. (2008) but recently, a software front-end has been released by the Paul Scherrer Institut. This method can produce improved results, but the use of a priori information can diminish the objectivity of the analysis. A standardised approach is currently being developed such that data can be consistently compared. Because this technique is in its relative infancy, it is difficult to objectively assess its accuracy.

B2.4 Primary organic tracer techniques (POT)

The EC tracer method has been very widely applied, not only in the UK but internationally, and is a straightforward and easy to apply method of deriving POA and SOA fractions, although recent work has cast some doubt over its reliability.

The technique was pioneered in Europe by Castro et al. (1999) who first applied it to air samples collected at various sites in Portugal and in Birmingham, UK. The basic principle of the method is illustrated by Figure B.1. Concentrations of organic carbon are plotted against simultaneously measured concentrations of black carbon, or more commonly elemental carbon. These show a considerable scatter but the basic premise is that there is a lower limit line as seen in Figure B.1 which describes samples which contain zero secondary organic carbon. The gradient of the line (OC/BC = 1.1 in the case of Figure B.1) describes the OC/BC or OC/EC ratio of primary organic aerosol. All points above the line contain secondary organic matter whose mass can be estimated from the distance of the point to the minimum ratio line. Therefore,

$$OC_{prim} = BC \times (OC/BC)_{minimum}, \text{ and}$$

$$OC_{sec} = OC_{total} - (OC/BC)_{minimum} \times BC$$

Castro et al. (1999) noted that rural sites tended to show a higher minimum OC/BC ratio than urban sites but did not look further into this phenomenon. This topic was revisited by Pio et al. (2011) who examined data (now for OC and EC rather than BC) from a much wider range of sites including roadside and a busy roadway tunnel. They found that the highest minimum ratios were in samples from remote and rural sites while urban background sites show spatially and temporally consistent minimum ratios of around 1.0 for PM_{10} and 0.7 for $PM_{2.5}$. However, in roadside and road tunnel samples, the OC/EC ratio was more typically in the range of 0.3-0.4, and in data from Birmingham, the ratio of OC/EC in roadside increment air (roadside minus urban background) also lay within this range. They concluded that the ratio of primary OC/EC in road traffic emissions lies typically within the range 0.3-0.4 which is consistent with ratios measured in studies of diesel exhaust. The observation of higher ratios at suburban sites and even greater ratios at rural and remote sites is indicative of other sources of organic carbon. These could be primary, including sources such as woodsmoke and plant waxes etc., or the elevated ratios might simply reflect the fact that all atmospheric samples contained some secondary organic aerosol.
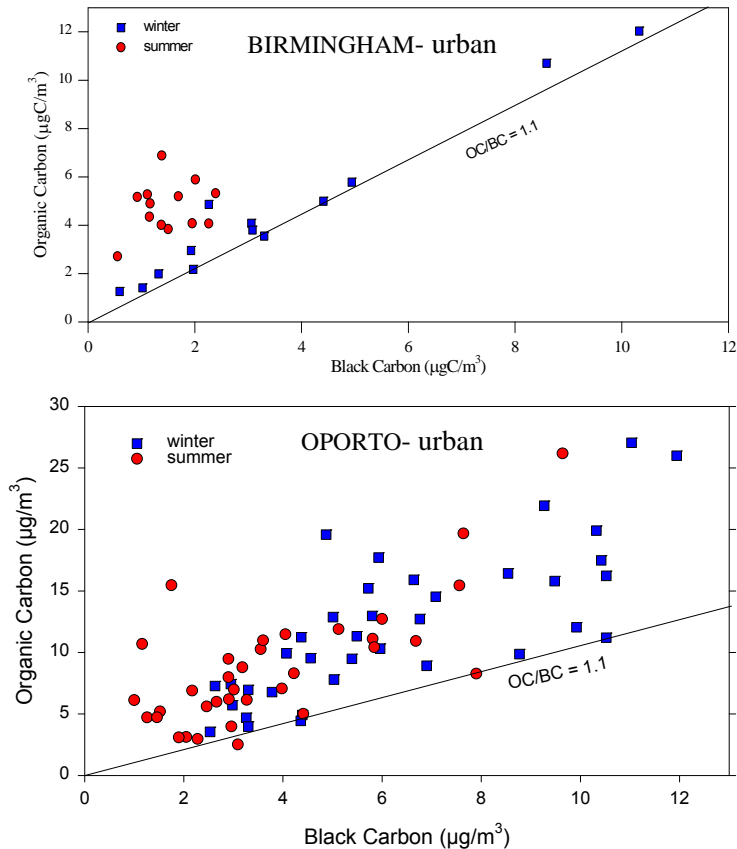
Figure B.1: Relationships between black and organic carbon

Critical examination of the assumptions behind the elemental carbon tracer method raises many questions. Elemental carbon/black carbon is not generated by secondary formation mechanisms and consequently it should be a good tracer of primary emissions. However, the OC/EC ratio of different primary emissions sources is rather variable. For traffic, as indicated above, the OC/EC ratio is typically 0.3-0.4 although it can be much higher in physically constrained environment where greater partitioning of organic compounds onto the particulate matter takes place (Chirico et al., 2011). The OC/EC ratio for wood burning is very much higher, typically of the order of 10, while for cooking aerosol it is expected to be larger and for vegetative particulate matter there is not expected to be any EC associated. Consequently, if the mix of source contributions to primary organic aerosol is relatively invariant from day-to-day, then the concept of a lower limit line on the OC/EC plot is a realistic possibility. However, it is more difficult to eliminate the possibility of SOA contributing carbon to all samples and that consequently the OC/EC ratio expected for primary organic aerosol is never attained. There does not appear to be a viable way of correcting for this error. Assuming that the OC/EC ratio of fresh traffic exhaust is representative of POA and using this rather than the minimum ratio to calculate the SOA/POA split is liable to over-estimate SOA by not accounting for non-traffic sources of POA, while use of the minimum ratio method as described above is liable to under-estimate the contribution of SOA to total organic aerosol.

B2.4.1 Use of Tracers for Specific Primary Organic Aerosol Sources

There are organic compounds which either individually or in combination can be used as tracers of individual sources of primary organic aerosol. The most common use of a single compound as a source tracer is the use of levoglucosan as a wood combustion tracer. Biomass burning releases a number of anhydrosugars of which levoglucosan is the most abundant representing around 10% of the mass of carbonaceous emissions from burning of wood. If an assumption is made as to the ratio of total particulate matter to levoglucosan in wood combustion emissions, then a concentration of woodsmoke in air can be estimated from analytical data for levoglucosan. This is not however straightforward as the ratio of total particle mass to levoglucosan is dependent upon wood type and combustion conditions tending to be lower in smouldering combustion and higher in hot flaming combustion which gives a more efficient burn-out (Harrison et al., 2012). The figure of 10.7 for woodsmoke-levoglucosan mass has been very widely used but is based upon burning wood in Austrian wood stoves and sampling from the early stages of the combustion (Schmidl et al., 2008) which may give a biased estimate.

There tend not to be individual characteristic markers for other sources of primary organic aerosol such as cooking, traffic and oil burning. Rather, a combination of tracer compounds is used to establish a source profile which can then be used in a Chemical Mass Balance (CMB) Model (e.g. Yin et al., 2010; Zheng et al., 2002) alongside the chemical profiles for other sources in order to give a breakdown of contributions to the entire particulate mass. This CMB algorithm is available through the US EPA (http://www.epa.gov/scram001/receptor_cmb.htm). Generally speaking, the accuracy of such assessments is improved through the availability of a wide range of markers within a given dataset, usually from GC analysis. The technique also requires the use of emissions profiles relevant to the measurement location, of which a number exist in the literature (e.g. Schauer et al., 2002).

B2.5 Secondary tracer techniques

Molecular characterization of organic aerosol allows insights into aerosol sources and mechanisms of aerosol formation, transformation and loss. Secondary organic aerosol compounds that can be mechanistically linked to precursors, can provide evidence of chemical processing and sources. The advancement of analytical instrumentation described in B1, over the last 20 years has lead to considerable progress in the characterization of aerosol components, with a great deal of new knowledge about SOA formation being produced, as a result of smog chamber simulations of atmospheric oxidation processes, and subsequent measurement of tracers in ambient aerosol.

One of the major difficulties in using SOA tracer compounds for source apportionment is in ensuring that their only source is from the oxidation of the specified precursor and is not emitted from primary sources or produced from other precursors.

B2.5.1 Biogenic SOA

A number of tracer molecules have also been identified for monoterpene SOA. The majority of studies involve α- and β-pinene, in part due to their high emissions from pine and other forests and in part due to the ease of obtaining commercial standards. *Cis*-pinonic acid and *cis*-pinic acid have been known as major oxidation/ozonolysis products from α-pinene oxidation, and are tracers characteristic of short ageing timescales. More recently 3-methyl-1,2,3-butanetricarboxylic acid (MBTCA) has been discovered as a tracer of more aged α-

pinene SOA and it has been measured in a range of forested and suburban areas influenced by local forests. It has recently been identified in PM$_{2.5}$ collected in North Kensington, London during the Clearflo project. Representative SOA tracers identified in ambient aerosol are summarized in table B.4.

The importance of isoprene as a SOA precursor was made through the measurement of 2-methyl tetrols, 2-methylglyceric acid and number of other aerosol constituents which could be mechanistically linked to isoprene in the Amazon Basin using GC/MS. Subsequent chamber studies also identified isoprene organosulfate tracer compounds, formed via the interaction of SOA and SIA, which have since been measured in a range of environments (Claeys et al., 2004; Surratt et al., 2010). One such tracer, methyl furan, has also been shown to have a distinctive marker within AMS mass spectra (Robinson et al., 2011). However, while this has recently shown the presence in tropical rainforests and areas of North America (Slowik et al., 2011), no evidence has yet been published showing this to be present to any significant degree in the UK. While it has yet to be thoroughly investigated, if isoprene SOA was found to be insignificant in the UK, this would be consistent with the theory that acidic seed aerosol are needed, as aerosols in the UK are typically neutralised by ammonium (Lin et al., 2012).

B2.5.2 Anthropogenic SOA tracers

There is considerably less information available for specific tracers that can be linked to anthropogenic SOA. The major anthropogenic precursors to SOA are from transport related emissions, including evaporative and tailpipe emissions of petrol and semi-volatile diesel exhaust (as described in section A1). Although many anthropogenic SOA species have been measured in smog chamber simulations, only a few have been measured in ambient aerosols.

Petroleum products contains a complex mixture of hydrocarbons and a small number of tracer species have been identified for the alkanes, aromatics and polyaromatic hydrocarbons. Many of the oxidation products identified have multiple precursors and in some cases have primary emission sources also. 2,3-digydroxy-4-oxobutanoic acid and 2,3-dihydroxy-4-oxopentanoic acid have been suggested as suitable markers of toluene or related aromatic SOA. Phthalic acid has also been suggested as tracer of SOA from polyaromatic hydrocarbons.

Another major SOA source in urban areas is from food cooking, with a significant amounts of fatty acids released during cooking of meat. SOA tracers for cooking aerosol have also been identified in ambient aerosols. Some examples of species identified in ambient aerosol are shown in Table B.4.

Precursor type	Sources	Oxidation Product types identified in SOA	Examples observed in ambient aerosol
Anthropogenic			
Aromatics	Gasoline, Solvent usage	Cyclic anhydrides Aromatic nitro-phenols	Furandione[a] 5-methyl-2-nitrophenol 2,3-dihydroxy-4-oxopentanoic

		Carboxylic acids	acid
Alkanes	Gasoline, Diesel	Aldehydes	Nonanal
		Carboxylic acids	Decanoic acid
		Furanones	Dihydro-5-ethyl-2(3H)-furanone
Fatty Acids	Meat cooking	Dicarboxylic acids	Azealic acid[b]
		Esters	*iso*-propyl palmitate[c]
		Oxo-acids	9-oxononanoic acid
Polyaromatic Hydrocarbons	Combustion sources	O-PAH	9-fluoren-9-one
		Dicarboxylic acids	Phthalic acid[i]
		N-PAH	Nitro-chrysene
Plasticisers	Plastics	Phthalates	Dibutyl-phthalate
Biogenic			
Isoprene	Vegetation	Methyl tetrols	2-methyl-threitol[d]
		Dicarboxylic acids	2-hydroxymethylsuccinic acid
		Organosulfates	IEPOX sulfate esters[e]
Monoterpenes	Vegetation	Aldehydes	Pinonaldehyde[f]
		Carboxylic acids	Pinonic acid, Pinic acid, terpenylic acid[k]
		Tricarboxylic acid	3-methyl-1,2,3-butanetricarboxylic acid (MBTCA)[j]
Sesquiterpenes	Vegetation	Carboxylic acids	-caryophyllinic acid[h]

[a]Hamilton et al., 2004; [b]Pol et al., 2006; [c]Goldstein et al., 2008; [d]Claeys et al., 2004; [e]Surratt et al., 2007; [f]Williams et al. 2007; [g]Tentative identification in Wozniak et al., 2008 ; [h]Lewandowski et al., 2007; [i]Kleindienst et al., 2012 ; [j]Muller et al., 2012 ; [k]Claeys et al., 2009.

B2.5.3 Biomass Burning SOA

There is very limited information on biomass burning SOA tracers. Possible tracers include methyl-nitrocatechols and methoxy-nitrophenols (Mohr et al., 2013). However, both of these species can form from aromatic oxidation and so may not be suitable in highly polluted areas (IInuma et al., 2010)

B2.6 Carbon isotope techniques

While it does not offer any additional information on the quantification of SOA, the analysis of 14C can be used to determine the fraction of 'fossil' carbon in a manner similar to radiocarbon dating. This isotope is produced naturally in the atmosphere from cosmic rays and decays with a halflife of 5,730 years. Carbon originating from the modern biosphere will have a 14C/12C ratio representative of the atmospheric CO_2 (around one part per trillion), and will be present in carbonaceous aerosols arising from biomass/biofuel combustion, biogenic SOA, primary biological particles (e.g. spores, pollen) and cooking. The analysis typically models the carbon as being composed of a mixture of 'fossil' and 'modern' carbon in proportions that can be determined by inspecting the 14C/12C ratio. If the carbon is pre-separated according to EC/OC analysis and emissions profiles associated with POA/SOA assumed as with POT, this can be used to apportion the SOA into modern and fossil carbon. By making further assumptions concerning the origins of the different types of carbon, this can then be extended to an attribution of anthropogenic vs biogenic.

This technique is not without confounding factors. Biomass 14C released through wood burning will be a reflection of the atmospheric 14C concentrations over the lifetime of the tree rather than current concentrations. This is an issue because atmospheric concentrations increased in the mid-20th century due to atmospheric nuclear weapons testing, so this can add an element of uncertainty to the isotopic ratio assumed for biological carbon. The technique can also be impacted by sources of radioisotopes impacting a receptor site, e.g. medical facilities. There are also inherent problems when trying to relate biogenic and anthropogenic sources to modern and fossil carbon. Vehicles are increasingly using biofuels, either in their entirety (e.g. biodiesel) or as an additive (e.g. ethanol). There is also an inherent uncertainty when estimating biogenic SOA from modern OA in areas affected by biofuel combustion as this produces both primary and secondary OA that will similarly be classed as 'modern'. Perhaps the biggest drawback of this technique relates to the sensitivity and linearity of measurement needed to detect variations on sub-ppt levels. Even in polluted environments, samples must be collected over long times using high-volume samplers. The expense and labour intensity of these measurements means that this technique is inherently limited to intensive studies rather than monitoring or extensive model comparisons.

Unlike 14C, 13C is a stable isotope of carbon, present in both atmospheric and fossil carbon in quantities of around 1% of 12C and is much easier to quantify. Modern terrestrial C4 vegetation (e.g. corn, salt marsh plants) has a 13C defect of between -14 and -12‰, modern marine plants between -22 and -18‰ and modern C3 vegetation (most terrestrial plants) and fossilised carbon between -30 and -23‰ (Wozniak et al., 2012, and references therein). Used to complement the 14C analysis, this can be used to further apportion the carbon to vegetation types.

B2.7 Primary inorganic subtraction

The majority of ammonium, nitrate and sulphate detected in continental environments tends to be secondary in nature, although there can be contributions from sea salt or dust produced by the action of the wind. When estimating SIA based on on- or offline measurements of inorganic aerosols, corrections can be made to account for primary nitrate or sulphate. Subtractions of primary sulphate in sea salt can easily be made by estimating this contribution based on measured concentrations of sodium and the known ionic ratios in

seawater, which are constant (Millero, 1974). Similarly, contributions of nitrate and sulphate from dust can be estimated based on mineralogical profiles of the dust sources, where known. While this can be more ambiguous than the sea salt fraction, this mainly impacts the coarse fraction, whereas the majority of the secondary material is in the fine fraction. The exception to this is the coarse nitrate fraction, which is formed when nitric acid condenses onto sea salt particles and displaces chloride as HCl (Putaud et al., 2004). This will increase the mass of particulate, as NO_3^- has a greater molecular weight than Cl^-, which will in effect contribute to anthropogenic secondary PM_{10}, although the net increase in mass will not be as much as ammonium nitrate. This increment can be easily elucidated from the inorganic analysis of PM_{10} samples or semicontinuous analysers by calculating the chloride that would have been present at the point of emission, again based on the sodium concentrations.

Note that observational composition data alone cannot determine the formation route of SIA, e.g. gas vs heterogeneous processing of nitrate or sulphate, as the final product is the same. These processes can only be investigated in conjunction with a model of some description.

B3 Understanding

The following section will take the information from B1 and B2 to describe what measurements of SIA and SOA are currently undertaken in the UK and, importantly, what measurements are lacking in the UK. Based on the state of knowledge and the gaps in the UK capability, this will lead to recommendations for long term strategy for monitoring SOA and SIA and the precursors leading to their formation. Data is presented from the networks in the UK and from research programs.:

B3.1 Data from networks

The UK has a very well establish network for monitoring the major ions forming the bulk of SIA (NH_4^+, NO_3^-, Cl^- and SO_4^{2-}). AGANet has provided information on SIA (and other species) since 1999 and provides monthly means from 30 sites across the UK. The network is part of UKEAP and as such has strict QA/QC protocols for any data made public and ensures that there is little site by site variability of the quality of the data. The data are available on the UKair database and is published in the UKEAP reports and also in the Review of Transboundary Air Pollution (RoTAP) produced by CEH and which is publically available (RoTAP, 2012).
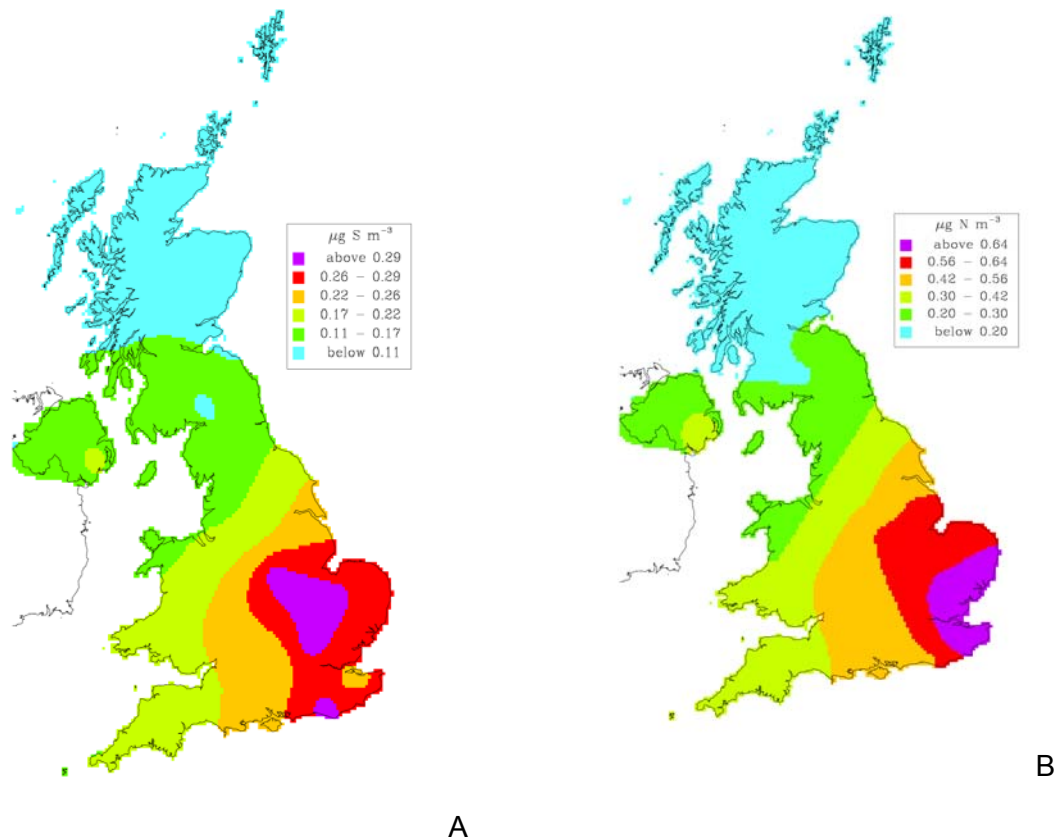
Figure B.2 (A) Average annual SO_4^{2-} from 2006. (B) Average annual NO_3^- aerosol concentrations from 2006. Data taken from RoTAP (2012), provided by Prof. D. Fowler, CEH.

Figure B.2 A shows the mean annual SO_4^{2-} map for the UK, with a concentrations averaging 0.2 µg m^{-3} in NW Scotland, increasing to 0.6 µg m^{-3} in SE England. NO_3^- shows a similar spatial distribution. The UKEAP 2010 report (Conolly et al., 2012) has similar concentration maps from the AGANet site, shown below in figure B.3. Broadly, the spatial distributions are the same in 2009, as are the concentrations for nitrate, noting that the RoTAP data reports ug of N and UKEAP reports the total NO_3^-, hence the difference in scales. Concentrations across the UK peak in the SE in excess of 3 µg m^{-3}. The UKEAP report also reports the Cl- concentrations for 2009.
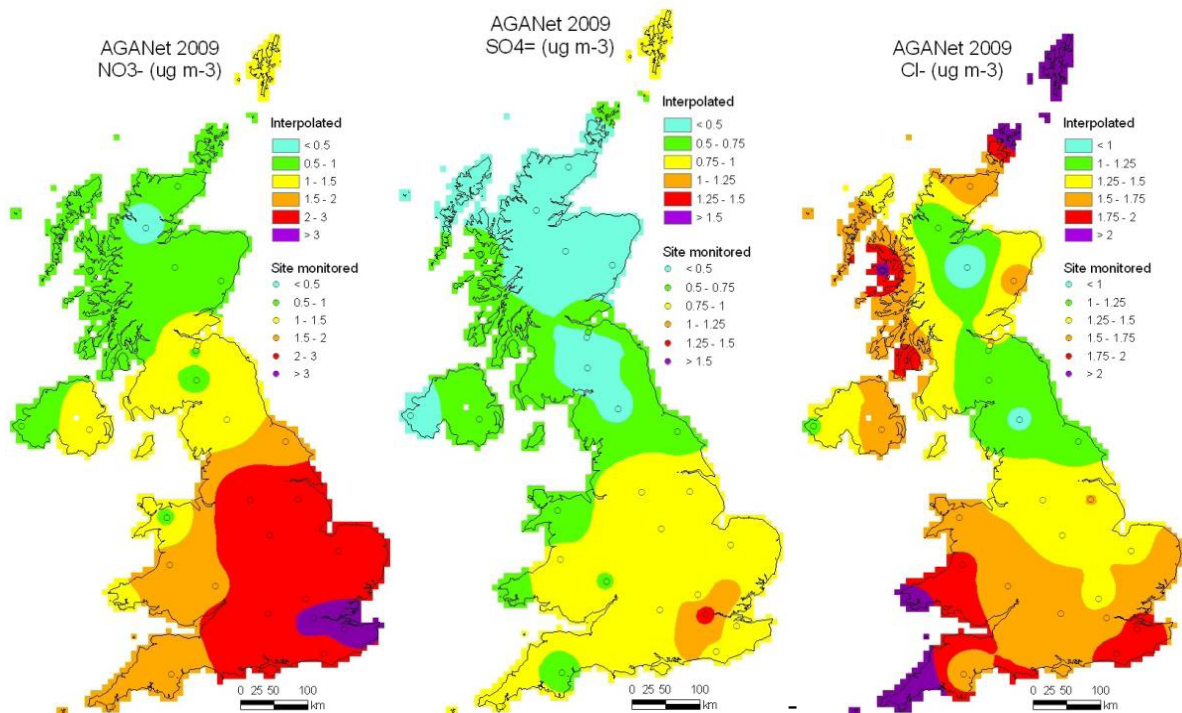
Figures B.3. taken from the Conolly (2011).

These data are useful for mapping the SIA pollutants across the UK. By averaging the concentrations from each of the 30 stations over a year, the UK average annual trends can be seen. UKEAP concludes that there are no discernable trends in nitrate from 2000 – 2009, whilst there has been a steady decrease in sulphate in the 30 sites annual average from 1.9 $\mu g\ m^{-3}$ in 2000 to 0.7 $\mu g\ m^{-3}$ in 2009. However, the trend has not matched the decreases in SO_2 emissions, as might be expected (Jones and Harrison, 2011), so sulphate appears to be adopting the role of a 'background' aerosol. No trends are reported for Cl^-, but the spatial distribution is clearly different. However, the Cl^- data does not discriminate between secondary Cl^-, from NH_4Cl and Cl^- from NaCl.

The data can also be averaged to monthly means so the annual variation can be assessed. These data show a clear peak in the NO_3^+ in the spring months, decreasing in the warmer summer months. Sulphate shows lower concentrations in the winter months with a peak around March-April. The nitrate trends are seen in the CLEARFLO dataset presented in section B3.4 below.

There are some limitations to using the AGANet data set. Firstly, the total $PM_{2.5}$ is not normally reported alongside the AGANet data, so there is no published data on the relative contribution the major SIA ions make, and only the EMEP supersites measure both. In figure B.4 below, the monthly mean SIA and fraction of the total $PM_{2.5}$ is plotted from 2009 from Authencorth Moss and Harwell, two sites with AGANet that also form part of the AURN network (and EMEP).
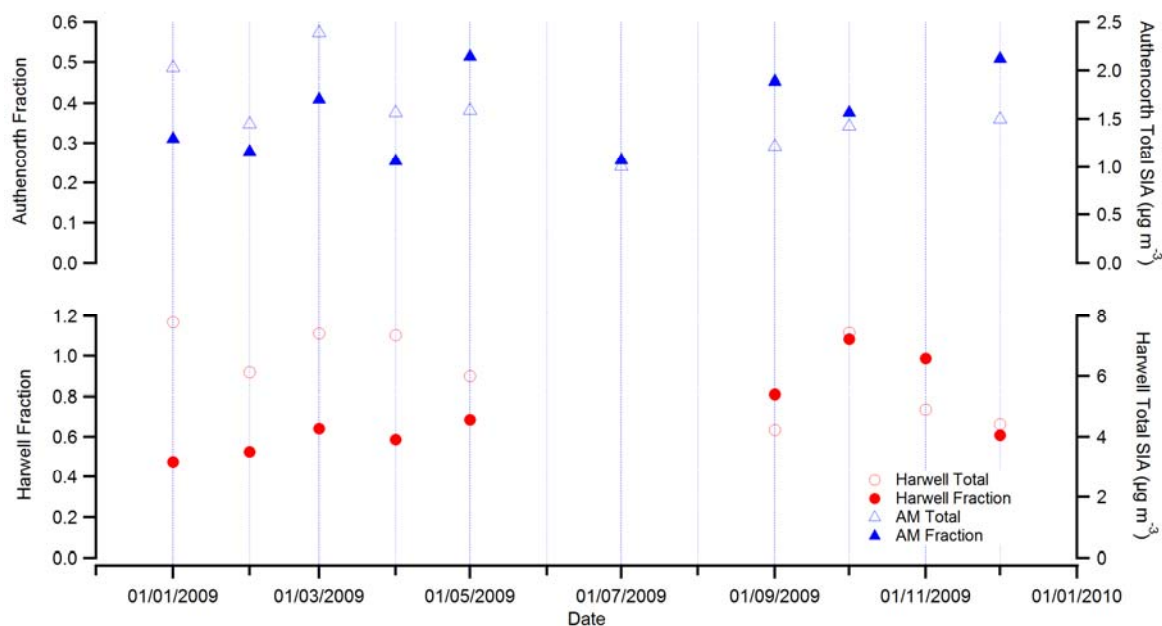
Figure B.4 Total SIA from Authencorth Moss and Harwell and the relative fraction of the total PM$_{2.5}$

The data shows for AM, that the fraction of PM$_{2.5}$ which is attributable to SIA is between ~0.3 and 0.5. The Harwell data raises some questions, as the fraction of SIA mass to total goes above 1. This could be a data quality issue, or it could also be due to the Delta system having an uncharacterised inlet, with a cut off between 4 - 5 µm.

Recommendation – either the AGANet sites should be upgraded to include a PM$_{2.5}$ mass measurement, or AURN sites should be upgraded to included SIA measurements using either a semicontinous analyser or ACSM. The inlet for the Delta system must be upgraded if true PM$_{2.5}$ mass is to be reported.

A second problem with the AGANet data sets is its inability to capture episodes. This is discussed below in section B3.4, which looks at a year long case study of SIA and SOA in London.

B3.2 Data from research

There are limited data sets from the UK which have detailed compositional analysis. These data sets provide and excellent means to further the understanding of the processes involved in the production or transport of SIA and SOA, but do not provide information on the trends. Table B.5 below summaries the prominent data from the UK research community.

City (Classification)	Season Year	SIA:SOA	SOA: Total OM	SIA: PM$_{2.5}$	SOA: PM$_{2.5}$	SA: PM$_{2.5}$	Analysis	References
Manchester (urban)	Winter 2007	2.07	0.29	0.32	0.15	0.47[a]	PMF-AMS	Allan et al., 2010
Manchester (urban)	Autumn 2001	3.13	0.61	No Data[b]	No Data[b]	No Data[b]	PMF-AMS	Jimenez et al., 2009

Location	Period						Method	Reference
London (urban background)	Autumn 2006	2.36	0.53	0.67	0.28	0.95	PMF-AMS	Allan et al., 2010; Harrison et al., 2012
London (urban background)	Autumn 2007	5.58	0.29	No Data[b]	No Data[b]	No Data[b]	PMF-AMS	Allan et al., 2010
Chelmsford (Rural)	Summer 2003	1.63	0.69	No Data[c,d]	No Data[c,d]	No Data[c,d]	PMF-AMS	Jimenez et al., 2009
Edinburgh (Urban)	Autumn 2000	0.92	0.63	No Data[c]	No Data[c]	No Data[c]	PMF-AMS	Jimenez et al., 2009
Chilbolton (Rural)	Spring 2009	4.38	0.51	No Data[d]	No Data[d]	No Data[d]	PMF-AMS	Unpublished
North Kensington (urban background)	All of 2012	1.81 – 5.36[d]	0.27 – 0.54[d]	0.22 – 0.49[e]	0.08 – 0.25[e]	0.33 – 0.69[e]	PMF-AMS	Unpublished
Birmingham (urban roadside)	May 2004 - May 2005	2.21[f,g]	0.52	0.36	0.16	0.53	POT	Yin and Harrison, 2008
Birmingham (urban background)	May 2005 - Nov 2005	1.28[f,g]	0.53	0.27	0.21	0.47	POT	
Birmingham (rural)	Nov 2005 - May 2006	2.21[f,g]	0.50	0.46	0.21	0.66	POT	
London Marylebone Road (Roadside)	2002-2004	0.42[f,g]	No Data[h]	0.49	No Data[h]	No Data[h]	POT	Charron et al., 2007
Birmingham (urban background)	May 07 – Apr 08	0.51 – 5.42[e,f,g]	0.11 – 0.74[e]	0.18 – 0.63[e]	0.07 – 0.44[e]	0.28 – 1.00[e]	POT / CMB	Yin et al., 2010
Birmingham (rural)	May 07 – Apr 08	0.28 – 3.94[e,f,g]	0.13 – 0.71[e]	0.15 – 0.63[e]	0.08 – 0.78[e]	0.35 – 1.02[e]	POT / CMB	Yin et al., 2010
Harwell (rural)	July – Nov 2010	1.31[f,g]	0.87	No Data[h]	No Data[h]	No Data[h]	POT	Charron et al, 2013

Birmingham (urban background)	July – Nov 2010	1.16[f,g]	0.87[f]	No Data[h]	No Data[h]	No Data[h]	POT	Charron et al, 2013

Table B.5: Summary of the SIA and SOA measurements in the UK. [a] Data from AURN Manchester Piccadilly, ~700m from AMS measurements and vertically separated by 35m. [b] No representative AURN monitoring station nearby. [c] No $PM_{2.5}$ data that year. [d] no $PM_{2.5}$ monitoring station within 20km of measurement. [e] data based on min-max of the monthly means. [F]total SIA from assuming full neutralisation of SO_4 and NO_3 as no measured NH4 data. Cl- not measured, but based on other data represents a mean contribution of 3.9% to SIA. [g]assuming a OC to OM conversion factor of 1.85 (mid-point from Polidori et al., 2008). [h] data not supplied in publication.

It should be noted that while there are a large number of studies within the UK to use either the PMF-AMS and POT techniques for the estimation of SOA, there are no studies that have critically compared the two techniques, owing to the lack of collocated studies to date. Comparisons have been performed elsewhere, particularly in the USA. Docherty et al. (2008) presented one such comparison in Riverside, CA, comparing POT using EC, CO and GC (using the CMB algorithm) as tracers, the assumption that PILS-WSOC represented SOA and PMF-AMS. They concluded that the different methods gave largely similar results for the campaign period, PMF-AMS, CMB and PILS-WSOC estimated 74, 78 and 69% SOA/OA respectively. The EC and CO tracer methods were also in broad agreement, although these were highly sensitive to the emission ratios used. While results such as this are encouraging, comparisons such as this should be repeated for the UK, as differences in emissions profiles can be expected based on differences in fuel usage and vehicle fleets. Allan et al., (2010) were able to get good correlations between PMF-AMS POA and CO and NO_x for London and Manchester, implying that these could be used as tracer, but also noted stark differences in ratios with other studies, highlighting the need to validate the emissions profiles for specific lotions. For example, CO is mainly emitted mainly by petrol engines, but the POA is mainly emitted by diesel engines, so the relationship will be governed by the relative local abundance of the different engines. It should be noted that measurements were taken during Clearflo suitable for a systematic CMB and PMF-AMS comparison, however, at the time of writing, the combined analysis is still in progress.

The $PM_{2.5}$ data from Manchester, 2007 is taken from a road side site, situated approximately 700m from the aerosol measurement site. The aerosol site was also made from roof top, approximately 35m from the ground. This adds a large uncertainty in the predicted SA : $PM_{2.5}$ ratio, and it likely to represent a lower limit as road side measurements of $PM_{2.5}$ are likely to be higher than those aloft, above the street canyon.

The data from Charron et al., 2013 (Harwell and EROS) has certain assumptions. Firstly, the method of calculating sulphate does not account for sulphate from sea salt. However, the authors estimate this leads to, at most, an over estimation of 8%. Secondly, the total SIA does not include Cl-. Of the dataset presented here, the average Cl- contribution to the total SIA is ~3%. Finally, the NH_4^+ is not measured, but predicted assuming a fully neutralised aerosol, which is reasonable for continental environments without an excess of sulphate. It is assumed the Cl- from non-sea salt sources is in the form of NH_4Cl, giving another uncertainty of 3%. This gives a total uncertainty in the figures of 9.05%.

Mean concentrations of primary and secondary organic carbon measured in Regents Park during REPARTEE I were 1.51 μg m^{-3} and 1.43 μg m^{-3} respectively (Harrison et al., 2012). Concentrations on the BT Tower were estimated as 0.96 μg m^{-3} for primary organic carbon and 1.40 μg m^{-3} for secondary organic carbon, the latter being almost equal to that measured at ground-level indicating the regional nature of SOA. These results for Regents Park were broadly consistent with those derived from the AMS measurements. In the case of SIA, concentrations of sulphate on the BT Tower were insignificantly different from those at ground-level in Regents Park for the majority of the REPARTEE I campaign and measured fluxes of sulphate on the BT Tower were generally near zero. However, during a regional pollution episode, concentrations on the Tower exceeded those at ground level giving a clear indication that regionally transported sulphate was driving the concentrations measured at ground level. There was no evidence for significant formation of sulphate within the atmosphere of London itself. The results presented from the same project by Allan et al. (2010) showed that the SOA had little or no diurnal trend in winter, implying a regional source, whereas traffic emissions, cooking and solid fuel burning all showed diurnal trends consistent with emissions and boundary layer mixing.

Martin et al. (2011) presented a meta-analysis of AMS measurements in Manchester and looked for patterns relating to source region, synoptic meteorology and local conditions. The study found that the conditions that favoured the highest concentrations of secondary organic and inorganic matter were those where anticyclonic conditions caused pollution to be imported from mainland Europe. However, as these conditions were also associated with lower wind speeds and therefore enhanced processing times of UK emissions, the additional mass cannot be ascribed to transboundary pollution in its entirety. In particular, this study found that high ammonium nitrate concentrations were associated with the colder temperatures that occur during these synoptic conditions in the winter, which is likely to be at least partly driven by the semivolatile nature of nitrate, as described in section A.

Measurements on board aircraft platforms can offer additional insight into transboundary transport. Within the UK, the measurements provided by the FAAM BAe-146 are particularly useful, as this often features an AMS in conjunction with a large suite of other in situ measurements. Because this is operated on a campaign basis, it does not offer the extensive temporal coverage offered by the network measurements, but it does allow the vertical structure of the boundary layer to be characterised and also the horizontal extent and evolution of plumes from cities and regions to be mapped. These data are presented in Morgan et al., (2009; 2010a; 2010b) and show the importance of transported material from Europe during easterly conditions. In particular, nitrate is enhanced towards the top of the boundary layer, owing to the lower temperatures. This could causer higher mass concentrations at the surface during the night. The same trend can be extended to semivolatile SOA, although the observational evidence for this is not as strong.
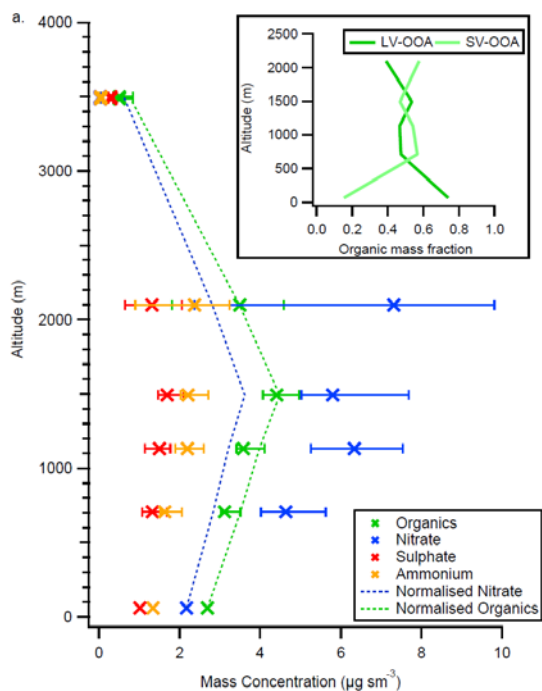
Figure B.5: Vertical profile of aerosols above Europe, from Morgan et al. (2010a)

There are few published assessments of secondary fractions available from UK roadside sites, owing to the difficulty in deploying a large enough suite of specialist instruments at such sites, as space is often limited. Charron et al., 2007 provided estimates for the Marylebone Road site based on network data obtained from 2002 to 2004 that indicated secondary material was a major contributor to PM_{10} exceedences, even at a site with a strong primary contribution. However, the site lacked the state-of-the-art instrumentation at the time that is currently available for more accurate assessments of SOA. The Marylebone Road dataset from CLEARFLO shows much promise in this regard, but at the time of writing, analysis is ongoing. However, it should be noted that the primary/secondary fraction at roadside receptors is known to be highly variable and dependent on a wide range of factors, including (but not limited to) traffic type and density, local micrometeorology and street canyon effects. It may be possible to estimate the enhancement of the primary fraction by using more abundant measurements (e.g. NO2 from diffusion tubes) as a proxy, however this will require more intensive measurements such as that performed at Marylebone Road to characterise other sites more thoroughly.

The secondary aerosol fraction can vary between 30% to almost all of PM at urban background and polluted rural locations. The roadside fraction is likely to be less, however this will depend on the specific site.

Recommendation – More multi-instrument characterisation work to be performed at a number of roadside locations.

B3.3 Current SOA capability

The UK currently has OC/EC measurements at four Number and Composition network sites that can be used for POT-based estimates (Harwell, Auchencorth, Marylebone Road and North Kensington) but with the exception of the AURN monitoring station at North Kensington, the UK does not have any direct long term SOA monitoring capability

compatible with PMF-AMS. After a DEFRA funded project (which ran in tandem with the NERC funded CLEARFLO project), where an Aerodyne C-ToF-AMS was deployed for the calendar year 2012, the site is now equipped with an ASCM for long term monitoring of the non-refractory aerosol, from which SIA and SOA can be derived. The data from the C-ToF-AMS provides the first year long data for the UK. Prior to this, the only source of information from direct measurements of SOA is gleaned from University and NERC centre (CEH) lead research projects. To date, there are 6 published data sets from 4 UK cities which have analysed AMS data using the PMF method described in section B2.2. This have been intensive campaigns of a relatively short (less than 2months) duration.

In winter, there is an increase in emission of POA, especially the biomass burning aerosol from domestic space heating demands, and reduction of boundary layer height, which inhibits mixing. In warmer months, there is increase in biological and photochemical activity that increases SOA production. Table B.5 summaries these ratio for the published datasets in the UK and unpublished datasets held at Manchester University that have been ratified to the same standard as published data.

Harrison and Yin, 2008, provide a different picture of the SOA seasonal variability. Using the primary organic tracer methods described in section B2.4, they found that the fraction of OC attributable to SOA had a weak seasonal variation, with peaks in spring and lower in summer. The trend followed more the trends in nitrate. There are two possible explanations for this difference. The first is that during the Harrison and Yin study, the processes affecting the SOA fraction were different e.g that spring 2005 experienced a polluted event.. The second is that the methodology for apportioning the OC fractions has attributed some of the POA to the SOA, causing the shift in seasonal variation. Harrison and Yin suggest there is evidence to support the former, reaffirming the influence of long range transport on SOA.

The UK is currently lacking in extensive data on SOA and efforts to better quantify and improve scientific understanding and predictive capability will be improved if more routine measurements of organic aerosols at more sites, ideally using high resolution measurements so as to capture episodic events better. Because the SOA fraction must be inferred through data analysis rather than explicitly measured, these measurements would benefit from being made alongside measurements that can be used as tracers for POA, so as to better inform the subtraction of POA. Note that the measurements of SOA should not be seen as limited to the rural sites; as it is known that SOA can form on rapid timescales in polluted environments (Volkamer et al., 2006), attention should be paid to SOA at urban background sites (e.g. North Kensington) as well.

Recommendation – More measurement sites are equipped with semicontinuous OC/EC analysers or ACSMs.

Recommendation – Routine measurements of organic aerosols should be accompanied by measurements of primary tracers, ideally CO, NO_x, BC, levoglucosan and potassium.

B3.4 Case study - London 2012

This section details data from a yearlong DEFRA-supported study in London where a C-ToF-AMS was deployed at the AURN North Kensington site. This provided both the SIA and SOA fractions, alongside the FDMS (PM 2.5) and URG monitors. Note that this site now houses an ACSM, so further data will be available in the future, albeit with a lower signal-to-noise.

Figure B.6 shows the first PMFAMS analysis for the UK of the annual trends in the SOA: total OM fractions and SOA:total PM$_{2.5}$ from the year long C-ToF-AMS. The data has not yet been published, but has been ratified to the same standard as other data collected by The University of Manchester. Both trends clearly shows an increases in the ratio during the warmer summer months where photochemistry is most prevalent. Whilst this is extremely insightful it also highlights a gap in the knowledge regarding long term SOA measurements in the UK. This data (and the data from the published intensive field campaigns) are all from the urban to urban back ground. Currently there is only one analysed dataset from a rural site and no spatially distributed, representative sample of the UK been taken.
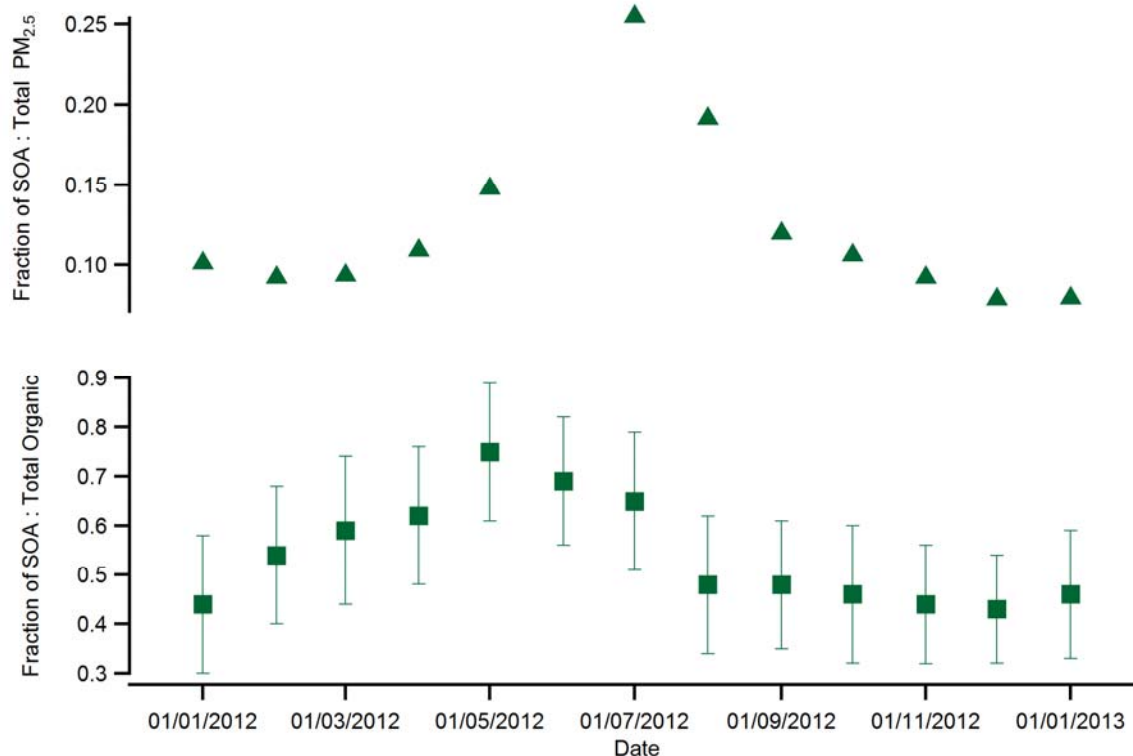
Figure B.6. Average monthly SOA:Total OM from North Kensington, London, UK from Jan 2012 – Jan 2013. Error bars are standard deviations.

The annual variation in SIA can be seen in figure B.7 below. This shows that the total SIA is always higher than the total SOA, and the ratio between the two is higher in the cooler months. This increase is seen to be a result of the dominance of NO$_3$ in the spring months, which can lead to almost 50% of the total PM$_{2.5}$ mass being SIA.
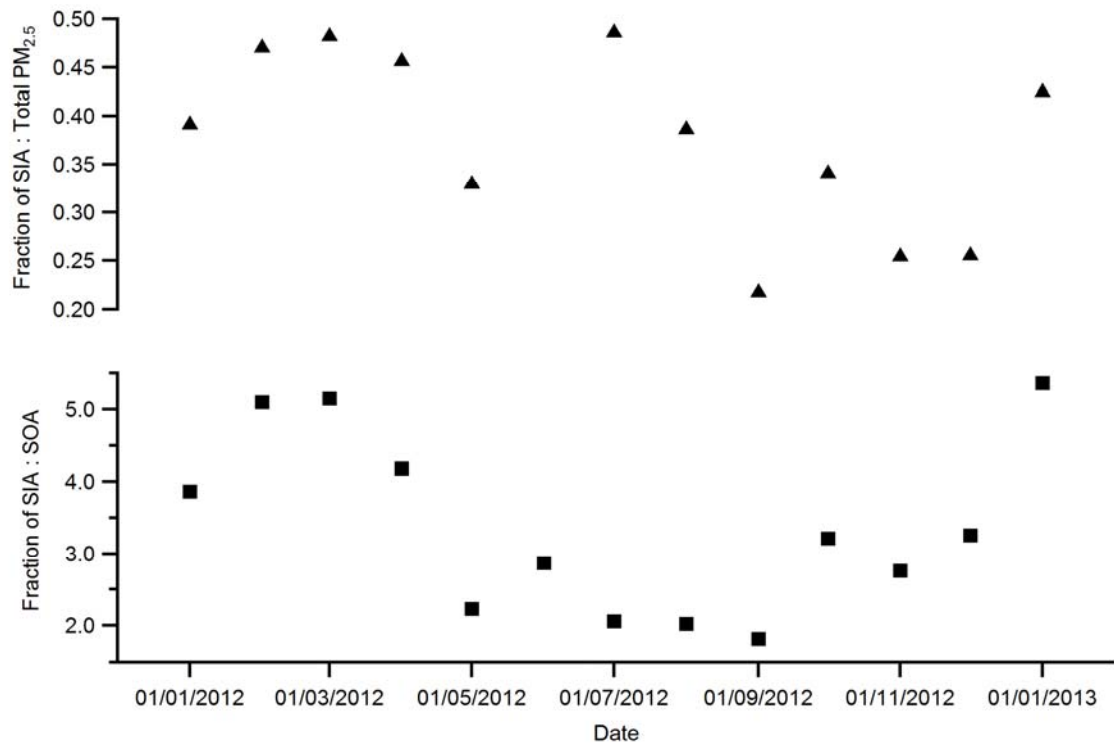
Figure B.8 below combines the SIA and SOA data, and also shows the relative fraction to the total AMS mass with the POA aerosol included. The increases in NO_3 during the spring months can be seen along with the SOA increase in summer. What is also evident is the increase is SO_4 during the summer months. The increase in SO_4 is often associated with long range transport from polluted areas, such as continental Europe.

B3.4.1 Comparison with AGANet - limitations of monthly means

As discussed previously, AGANet reports the monthly mean values of the major SIA components, but not strictly $PM_{2.5}$. Plotted below are the monthly means from 3 sites around London and the South East (Cromwell Road, Rothamsted and Delting, Tang et al., 2013) along with the C-ToF-AMS data for NO_3 aerosol. The C-ToF-AMS data is displayed in the raw, 5 minute format and also averaged up to a monthly mean.
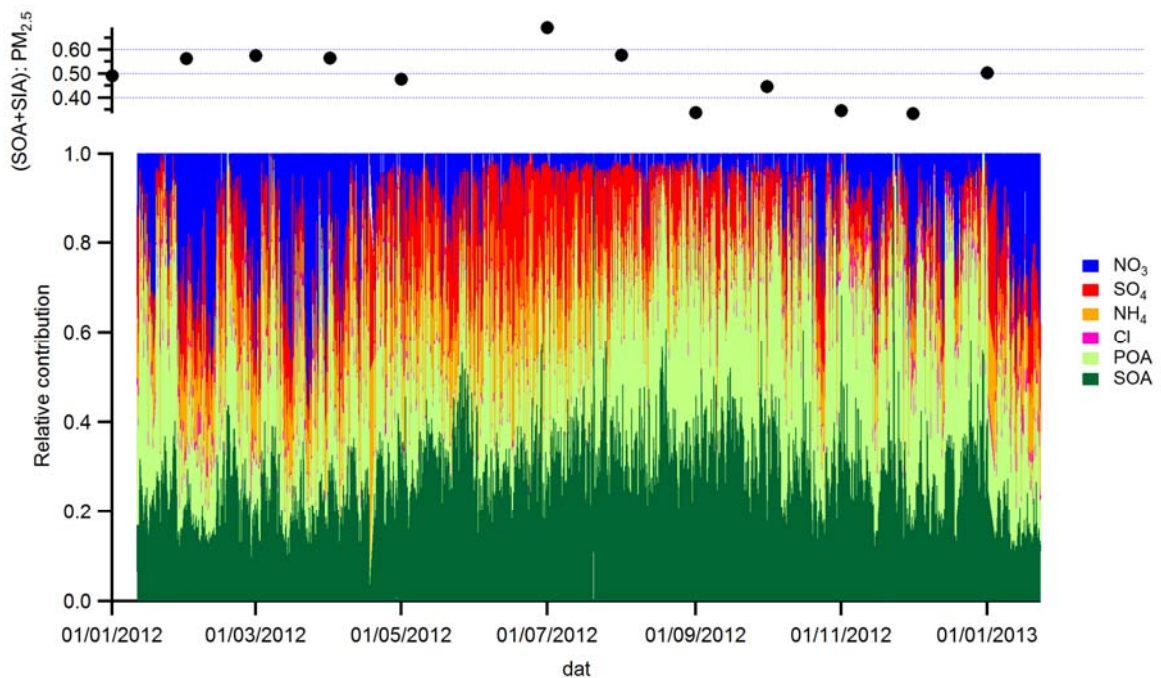
The monthly means exhibit similar trends over the year, although the absolute values are different, which is not unexpected. However, what is clear is that these means are masking the large episodic events in NO_3 and also the total SA. The 24 period beginning at 0000 23/03/2013 has an average NO_3 of ~34 µg m^{-3}, and a average total SA (SIA +SOA) of ~55 µg m^{-3}, which violates the EU directive on daily mean exposure levels. The monthly mean for March 2012 from the C-ToF-AMS reports a value of 9.3µg m^{-3}.
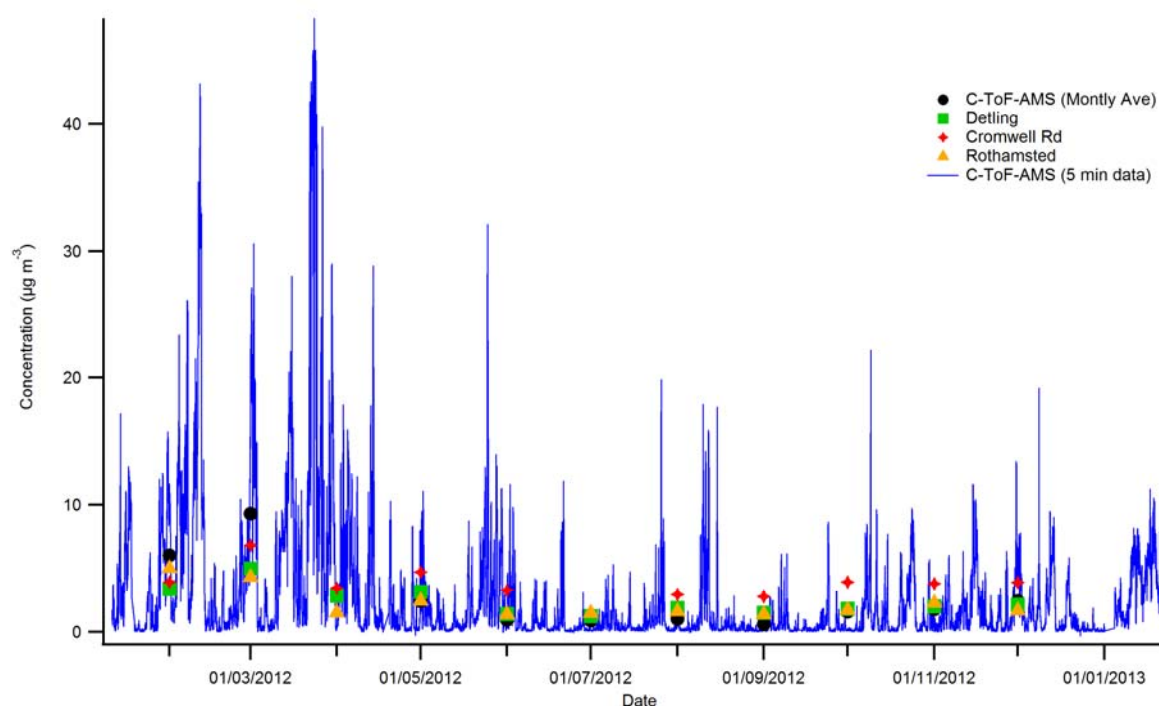
Recommendation: It will benefit the move to UK compliance with EU directives on daily PM exposure levels to commit to long-term monitoring of the major secondary contributors to $PM_{2.5}$ on time scales that capture episodic events, resolving the contributors using appropriate numerical techniques. This will better inform policy makers where any future regulation is needed to reduce the total $PM_{2.5}$. This requires the use of semicontinuous analysers (both inorganic and OC/EC) or ACSMs at more sites according to EU Report EUR 22779 EN (2007) and directive 2008/50/EC.

Technical Annex C - Secondary Aerosol Modelling

Large-scale models use a range of assumptions to model production of $PM_{2.5}$ SIA and SOA, from equilibrium bulk schemes to size dependent dynamic mass transfer (see Annex A). Additional empirical and semi-empirical approaches include reliance on interpolated data from measurement sites or the use of pre-calculated source receptor relationships. Combinations of model scales and dynamical framework are important for air quality predictions. In relation to domain size and resolution, there is a practical trade-off between ability to account for detailed local dispersion versus ability to incorporate more sources and transformation mechanisms between local dispersion models and larger scale Eulerian models. Too coarse a resolution has been noted to hinder ability to resolve concentrations of pollutants and limit the ability to perform accurate exposure assessments. While little attention has been paid to the affects of spatial resolution on SOA predictions, increased process resolution requires an increased resolution of gridded emissions. Similarly, vertical resolution requires further detailed investigation. Particular focus is required on the representation of boundary layer processes, since unreasonable boundary layer depths will bias predictions of both primary and secondary pollutants with additional sensitivity to unresolved topography and vertical emissions. The decisions relating to sub-grid boundary layer and cumulus cloud parameterisation is further compounded in the consideration of offline (uncoupled meteorology and chemistry) versus online models (coupled meteorology and chemistry). There are advantages of both Eulerian and Lagrangian models. Studies are starting to reveal substantial interactions between meterology on chemistry in online models. The lack of online coupling with NWP models in Lagrangian frameworks could be very important. Recent studies are highlighting the effect of temperature increases on air quality planned abatement strategies and reviews summarise the affected model parameters pertinent to SOA and SIA formation that include temperature affects on reactions rates, aerosol dynamics, gas/particle partitioning and boundary layer effects. Evaluating model structural and parametric uncertainties is important when evaluating effectiveness of control strategies for $PM_{2.5}$. Traditional brute force sensitivity analyses have been used to investigate the impact of emission abatements, in the UK typically using trajectory models. The 'one at a time' approach can be accurate in regimes where output is linearly related to inputs or a more qualitative overview of potential nonlinear effects between model components is required. Recent developments include approaches where sensitivity diagnostics are embedded within the model framework and solved at the same time to extract complex source-apportionment relationships and enabling parametric sensitivity analyses. In comparison, the quantification of structural model uncertainties is more challenging and often reliant on model intercomparison exercises. As the state of the science currently indentifies a large number of uncertainties associated with the complex mechanisms leading to the production of SOA (Annex A), some means of accessing structural sensitivities appears necessary and well-constrained model intercomparisons are likely required to give confidence in the effectiveness of control strategies. Diagnostic analysis of model outputs is now facilitated using the opensource tool Openair alongside traditional methods such as Taylor plots.

The response of SIA $PM_{2.5}$ in the UK to perturbations in precursor emissions has been investigated using a range of models. In order to have confidence in future emission scenario responses, it is necessary to have confidence in capturing a number of non-linear interactions (section C1). There is apparently contradictory evidence relating to the sensitivity of SIA to emission perturbations. UK PTM studies have indicated that NH_3 emission reduction can have the largest effect in reducing levels of SIA $PM_{2.5}$ through combined impact on $(NH_4)_2SO_4$ and NH_4NO_3 with marked seasonal differences. However, sulphate mass loadings in one Eulerian study have been found to respond to reductions in SO_2 to have the largest effects on reducing total UK PM SIA, again with strong seasonal variability. Nitrate was shown to respond non-linearly to SO_2 abatement with subsequent

reduced sensitivity to NO_x reductions as NH_4NO_3 formation becomes favourable and is predicted to dominate under episodic conditions. Contributions from transboundary sources are not insignificant. In European studies, it has been suggested that EU regulatory strategies should focus on reductions in NO_x rather than NH_3 as, unlike the UK, continental SIA is thought to be NO_x limited for nitrate formation. UK studies are largely focused on a limited number of measurement sites for model validation. While speciated SIA data for model constraint and comparison is becoming increasingly available, there is relatively patchy coverage and a number of remaining uncertainties associated with existing measurements (Annex B).

Predicting the effects of VOC abatement strategies on SOA $PM_{2.5}$ is extremely difficult. In contrast to SIA, these processes are highly uncertain (see Annex A) leading to correspondingly large uncertainties in their simplifications included in large-scale models. Such primitive process representation suggests that conclusions should be drawn on existing studies only with caution. While mechanistic models perform poorly with regards to total mass, they should offer the ability to better constrain composition dependencies should speciated SOA data become available (Annex B). Semi-empirical SOA models that are tuned to chamber simulations can better predict observed SOA mass, though have better skill for biogenically rather than anthropogenically dominated conditions (see Annex A). There is an implicit assumption that the yields extracted from the chamber simulations are representative of atmospheric conditions. With either mechanistic or semi-empirical model, quality of emission inventory needs improvement. While precursor emission regulations generally only target anthropogenic emissions, it is essential to understand how effects of biogenic emissions affect air quality standards via their interactions with anthropogenic species. Mechanisms through which the interaction occurs are noted to include the impact on oxidant levels (O_3, OH, NO_3) thus impacting production of semi-volatile products in the gas phase. European studies have predicted that most of the SOA mass is biogenic in origin and elimination of the biogenic sources would therefore have the largest effect in reducing SOA mass by over ~80%. Through effects on oxidant levels and pre-existing absorbing mass however, elimination of anthropogenic emissions would reduce SOA by less than~20%.

C1: Current Modelling Capabilities

Introduction

C1.1: Dynamical Framework, Scale and Resolution

C1.2: Representations of Aerosol Size Distribution and Microphysics

C1.3: Secondary Aerosol Treatments

C1.4: Available models used at the regional scale suitable for UK application

C1.4.1: ADMS

C1.4.2: NAME

C1.4.3: FRAME

C1.4.4: UKIAM

C1.4.5: CMAQ

C1.4.6: WRF-CHEM

C1.4.7: AQUM

C1.4.8: EMEP4UK

C1.4.9: PCM

C1.4.10: PTM

C.1.5: Other models (non-UK)

C2 Modelling Interpretation Capabilities

Introduction

C2.1: Source apportionment from measurement data and statistical methods

C2.2: Source apportionment from model sensitivity analysis

C2.3: Model uncertainty

C2.4: Diagnostic analysis of model outputs

C3 State of knowledge

Introduction

C3.1: Eulerian versus Lagrangian

C3.2: 'Online' and 'offline' approaches

C3.3: Scales

C3.4: Effects of gas phase representation on secondary aerosol prediction

C3.5: $PM_{2.5}$ Modelling studies

C3.5.1: Secondary Inorganic Aerosol

C3.5.2: Secondary Organic Aerosol

C1: Current Modelling Capabilities

Introduction

This section reviews currently available models used to predict the inorganic and organic contribution to secondary $PM_{2.5}$ (secondary inorganic aerosol; SIA; secondary organic aerosol; SOA). There are a number of models for predicting air quality in the UK. They are based on different methodologies, have different domain sizes, use different inputs and outputs and have varying levels of flexibility for future development. For example, table C.1, taken from the the sixth draft (version 6.2) of the guidance on the use of models for the European air quality Directive, an activity of Working Group 1 of FAIRMODE (http://fairmode.ew.eea.europa.eu/), summarises typical features used in the wide range of AQ models (Denby et al 2010). Because of the widely varying frameworks used, each model has advantages and disadvantages. Historically, Europe has not adopted a community approach to modelling and this has led to a large number of model development programmes, usually working almost independently, thereby yielding results tailored for specific applications. The models differ considerably in the number of interactions and the level of details of the process representations (Baklanov et al 2013). This also holds for models used for UK predictions. These details are important when resolving the predictive capability of existing models when judged against current state of the knowledge of key factors that determine the production and evolution of SIA and SOA (Annex A).

A brief introduction is given to the range of model 'types' used for predicting SIA and SOA. In section C3 the same aspects are revisited through discussions of known advantages and disadvantages taken from UK studies where possible and more broadly where necessary.

C1.1: Dynamical Framework, Scale and Resolution

Each of the models described is broadly classed as either Eulerian or Lagrangian, although some models employ various combinations of both or can be thought of as sub-types within these two groups. The Eulerian models work from a grid that is fixed at the earth's surface. The Lagrangian models follow a pollutant trajectory, where the pollutant is modelled as a well-mixed parcel (or box) of air moving through the trajectory. Most of the earlier photochemical models follow the Lagrangian approach, while the latest generation of photochemical models is largely Eulerian (www.epa.gov).

There is a wide diversity of spatial scales covered by the available models. Of the available models used in the UK, the scale for which the model was designed determines the coordinate framework used, its emission dependencies and the chemical complexity included. For regional models, ROTAP (2009) distinguish between 'simple' (e.g. HARM) and 'complex' (e.g. CMAQ / WRF-Chem) regional models. Fast simulation time is one advantage often sold with the simple models that allows them to be used more easily for uncertainty analysis, which might otherwise take a long time, and for source-receptor relationship determination. These models also tend to be used at finer resolutions, such as the ADMS model for predicting kerbside concentrations. Examples of complex Eulerian models include EMEP4UK, CMAQ and WRF-Chem. In these models emissions cover a much wider domain than the likes of ADMS, with sources often aggregated. Transboundary sources can also be considered. For model applied at smaller scales, sources outside of the domain are derived from empirical databases or from large-scale models such as CMAQ (e.g. CMAQ-Urban). Emission sources in such models are normally from specific point sources and cover smaller scales such as empirical roadside emissions. At smaller scales, or 'local' scales, Gaussian equations are often used to describe the dispersion of specific sources. For example, the ADMS dispersion model on its own is reliant on background concentrations provided empirically or from a regional model (e.g. CMAQ-Urban). Conversely, the PCM model, a GIS (Geographical Information System) based semi-empirical model driven by the NAEI,

was designed to provide roadside concentrations for an effective distance of 4m from the kerb using an empirical approach (Williams, 2011). Background concentrations across the UK are placed on a 1x1km grid using measured interpolated data. Near sources within 15km are then modelled explicitly using the ADMS 4 model. Roadside concentrations are for a nominal 4 m from the kerb.

Table C.1: Typical features of a range of AQ models (Denby et al. 2010).

Online 'integrated systems' modelling approaches are receiving increased attention since as meteorology and chemistry feedbacks are increasingly recognised as important for air quality forecasting. For example, Action ES1004 (EuMetChem) in the European Cooperation in Science and Technology (COST) Framework was launched in February 2011 to develop a European strategy for online integrated air quality and meteorology modelling. The action is not aimed at determining or designing one best model, but to identify and review the main processes and to specify optimal modular structures for integrated Meteorology-Chemistry (MetChem) models to simulate specific phenomena. The COST Action will develop recommendations for efficient interfacing and integration of new modules, keeping in mind

Description	Area of assessment		
	local/hotspot	Urban	Regional
Model type	Gaussian and non-Gaussian parameterised models	Gaussian and non-Gaussian parameterised models	Eularian chemical transport models
	Statistical models	Eularian chemical transport models	Lagrangian chemical models
	Obstacle resolving fluid dynamical models	Lagrangian particle models	
	Lagrangian particle models		
Meteorology	Local measurements	Mesoscale meteorological models	Synoptic/mesoscale meteorological models
	Obstacle resolving fluid dynamical models	Localised meteorological measurements	
	Diagnostic wind field models	Diagnostic wind field models	
Chemistry	Parameterised or none	Ranging from none to comprehensive depending on application	Comprehensive
Emission modell	Bottom up traffic emissions	Bottom up and/or top down emission modelling	Top down emission modelling
	Source specific emissions		Emission process models
		Emission process models	
PM2.5	No/Few chemical processes	SIA formation	SIA formation
		SOA formation	SOA formation
NO2	Simple photo-oxidant chemist	Limited photo-oxidant chemistry	Desposition
	Statistical/empirical relations	Photo-stationary scheme	Full photo-oxidant chemistry
		Statistical/empirical relations	
		Deposition	
NOx	No chemical processes	No chemical processes	Full photo-oxidant chemistry
		Full photo-oxidant chemistry for larger scales	
O3	As in NO2	As in NO2	As in NO2
SO2	No chemical processes	Deposition	Deposition
		SIA formation	SIA formation
			Full photo-oxidant chemistry

that there is no one best model, but that an ensemble of models is likely to provide the most skillful forecasts (Baklanov et al 2013). The Cost model inventory (http://www.mi.uni-

hamburg.de/index.php?id=539) includes a list of model designed for microscale, makroscale and meso scale air-pollution and dispersion applications. Some models applied for UK air quality purposes are listed in that database (ADMS-Urban, AQUM, CMAQ, EMEP, NAME, WRF-CHEM).

C1.2: Representations of Aerosol Size Distribution and Microphysics

Representations of aerosol size are accounted for using sectional or model representations in large-scale models. Alternatively, only particulate mass is accounted for not accounting for size dependent processes. Mann et al (2012) summarise the different approaches used. In a sectional representation, the particle size range is divided into a finite number of sections and all particles within a given size section are represented with the same composition. While computational and measurement capabilities place constraints on the maximum number of sections, in principle only the number of sections used limits resolution of a sectional representation (Lu 2005). Noted disadvantages of the fixed sectional method are the numerical diffusion that occurs when simulating condensational growth. Condensation enables particles to grow to a larger size, but if its size is set as exactly the same as all the other particles in that bin this leads to a numerical diffusion of the size distribution. The moving sectional and moving centre sectional method (Gelbard 1990; Jacobson 1997b, a) have been developed to address this. In the former, the boundaries of sections are no longer fixed but its usage in air quality models is limited (Lu 2005). In the moving center sectional method, the boundaries of sections are still fixed, but the diameter of particles is not limited to the middle of size range, varying within the size bin. With similar accuracy as the moving sectional method this method has been widely used in many air quality models (Pilinis et al. 2000; Jacobson 2001; Zhang et al. 2004), yet, numerical errors may still be produced for condensation process. Whitby (1981) developed the computationally cheaper "modal" approach, whereby the continuous General Dynamic Equation is given in terms of integral moments of the size distribution within lognormal modes covering different parts of the particle size range. A single modal representation of the aerosol size distribution assumes all particles within a given mode have the same composition. Different modes, however, may have different compositions so particles of the same size may belong to different modes and have different compositions. The modal method has much faster simulation speed and less computational requirements than the sectional method. However, as particle populations with different composition are treated separately, the number of modes required will increase. Often within modal approaches the size distribution are assumed to remain fixed. However, Zhang et al (1999) state that for condensational growth the modal approach provides more accurate results when the standard deviations of the modes are allowed to vary than it does when they are fixed. A variation on these approaches is to apply the method of moments (e.g., McGraw, 1997) that does not require any assumption about distribution function within each bin/mode. There are more complex representations of both modal and section approaches (e.g. Spracklen et al 2008; Kokkola et al 2008; Luo and Yu 2011;Vignati et al 2010; Pringle et al 2010) with model approaches often favoured over sectional schemes, particularly in large-scale models, because of lower computational costs (Mann et al 2012). Finally, in mass based models, only the mass is advected and, for size dependencies, a fixed distribution must be assumed.

At one extreme each aerosol component can be assumed to be physically separated from the other components creating an external mixture of chemically pure modes. At the other extreme the aerosols can be assumed to be internally mixed as a homogeneous material reflecting the chemical and physical average of all the contributing components. The real mixed state can be expected to lie somewhere in between these two extremes (Lesins et al 2002). By assuming an entirely internal mixture, whether represented by a modal or sectional method, there is only one aerosol size distribution in these models, and the compositional differences between particles of the same size, but from various sources, is neglected. The ability to account for externally mixed particle distributions in air quality

models can decrease the errors resulting from assuming an internal mixture (Lu 2005; Jacobson 2002; Mysliwiec and Kleeman 2002; Held et al. 2004), such as inability to account for biomodel features of observed size distributions (Kleeman et al. 1997; Kleeman et al. 1999; Kleeman and Cass 2001; Bhave et al. 2002).

C1.3: Secondary Aerosol Treatments

The mechanisms used for predicting SIA and SOA vary in complexity. It is widely recognised that aerosol models include only a fraction of the important processes (Lee et al 2011). A substantial fraction of secondary aerosol is unlikely to be involatile as discussed in Annex A. There are two general approaches currently used to model the partitioning of semi-volatile species between gas and particle phases. The first assumes equilibrium, the other accounts for dynamic mass transfer.

i) Under thermodynamic equilibrium assumptions, where particles across all sizes are treated as a bulk aerosol phase, it is assumed that gas and aerosol phases are always in equilibrium. For SIA, available thermodynamic models used in UK air quality schemes include the ISORROPIA model (versions 1 and 2) (Fountoukis and Nenes 2007; Nenes et al 1998) and EQSAM model (Metzger et al 2002a,b). In both of these methods, inorganic ions, in a single-phase aqueous mixture, are combined using pre-defined composition domains to prescribe the concentration of solids (where appropriate), dissociated ions, water and gases in equilibrium. Other techniques use a less rigorous approach and assume all sulphate, nitrate and ammonium ions combine to form ammonium sulphate and ammonium nitrate depending on the concentrations of ammonia (NH_3), nitric acid (HNO_3) and sulphuric acid (H_2SO_4) and temperature dependent partitioning coefficients. For SOA, models based on absorptive partitioning theory (Pankow 1994; Odum et al 1996) predicting equilibrium partitioning between the gas and particle phase uses either purely theoretical or empirically constrained approaches. For the former, detailed gas phase mechanisms used to model the degradation of precursor VOCs are combined with temperature dependent partitioning coefficients derived from a range of possible estimation methods (Barley and McFiggans 2009). For the latter approach, discrete volatility bins represent the secondary organic fraction and partitioning coefficients are constrained to chamber simulations. Commonly used frameworks include the two-product model and the volatility basis set (Donahue et al 2006; 2009).

ii) In the fully dynamic mass transfer method, where particles in each section are treated separately, equations are solved to determine mass transfer between gas and aerosol in each section. For SIA, the same thermodynamic models used to define a 'complete' equilibrium condition can be used to prescribe equilibrium concentrations of solids and ions in an aqueous phase and equilibrium vapour pressures for solving disequilibrium mass transfer.

A hybrid partitioning approach based on these two methods is also employed, where the equilibrium of small particles (Dp<1 µm) with gas phase is based on thermodynamic equilibrium, while the partitioning between large particles and gas phase is calculated by fully dynamic mass transfer method (Jacobson 1997; Capaldo et al. 2000). For SOA, dynamic methods are much less developed than for the SIA fraction.

In additional to physically based bottom-up treatments of gas to particle mass transfer, other empirical approaches include: a) using pre-calculated source-receptor relationships calculated for each emission (e.g. UKIAM); b) calibration directly using interpolated monitoring data (e.g. PCM).

At present, SIA and SOA modules used for UK applications do not 'interact' through condensed phase processes, but perturbations to gas phase oxidants, for example, can impact both SIA and SOA precursors. In the following section the available models used at

the regional scale suitable for the UK are presented. Main focus is given to models currently used in the UK, after which other models are briefly listed. Initially the provenance of each model is discussed before focus is given to methods used for predicting SIA and SOA respectively. The details provided for each model vary with application and source.

C1.4: Available models used at the regional scale suitable for UK application

Here the available models that include treatments of secondary aerosol processes are outlined, with particular emphasis on those that have been employed for prediction of UK air quality, briefly summarising each model then detailing the SIA and SOA treatment.

C1.4.1: ADMS

(CERC – Cambridge Environmental Research Consultants [www.cerc.co.uk]).

The Atmospheric Dispersion Modelling System, ADMS, was developed for modeling the dispersion of common pollutants in multiple urban environments. The current version '5' is described as a new generation 3D Gaussian plume air dispersion model. It has been developed in the UK by CERC. As noted by Williams et al (2011), it covers dispersion from point, area, volume and line sources with a straight-line plume trajectory from source to receptor or grid point. Numerous versions are available, designed for specific purposes. These include: ADMS-Urban, ADMS-Roads, ADMS-Airport and ADMS-Screen. For predictions of $PM_{2.5}$ it requires detailed emission inventories (Mohan et al 2011). Generally, available models for dispersion and transport of pollutants in urban areas (such as ADMS Urban) cannot adequately take into account particle size distributions and the size dependence of aerosol processes (Clarke et al 2004). Gaussian dispersion models are often nested within larger scale Lagrangian and Eulerian models for regulatory purposes (Holmes and Morawska 2006). For UK purposes, the ADMS model has been nested within the CMAQ framework (e.g. Stocker et al 2012). Dry deposition is modelled as a function of gravitational settling and deposition velocity with respect to aerodynamic, sub-layer and surface resistances. Wet deposition is approximated using a washout coefficient derived from the precipitation rate (Holmes and Morawska 2006).

Summary: Prediction of $PM_{2.5}$ **requires detailed emission inventories and can be nested within large-scale models such as CMAQ.**

C1.4.2: NAME

(Met Office: Numerical Atmospheric-dispersion Modelling)

NAME is a Lagrangian dispersion model that simulates the dispersion and deposition processes occurring in the atmosphere and parameterizes the key chemical processes involved in sulphate and nitrate formation (Redlington et al 2009). Pollutant emissions are represented by releasing hundreds of thousands of air parcels, each able to represent the released mass of many different species. The air parcels are carried passively by the three-dimensional wind field obtained from the Met Office's Unified Model (UM) (Davies et al., 2005). According to Fournier et al (2004), dry deposition for SO_2, NO_2, NH_3, SO_4^{2-}, NO_3^-, HNO_3, PAN and H_2O_2 is treated by assigning a deposition velocity to each chemical species. Some species have a specified average value. However, for SO_2 and NO_2, the values have been derived from a dry deposition model (Smith et al., 2000). Fournier et al (2004) describes the wet deposition scheme. Briefly, wet deposition is dependent on prescribed scavenging, concentration and rainfall rates. The wet deposition flux to the surface is the sum of wet removal from all volume elements aloft, assuming that the scavenged material comes down as precipitation. In the model, no differentiation is made between in-cloud and below-cloud processes and an averaged value of a scavenging ratio is used to represent the overall effect.

SIA: Redlington et al (2002) summarised the developments of the inorganic gas phase chemistry scheme included in NAME. The ammonia and nitric acid equilibria with ammonium nitrate are based on the scheme presented in Ackermann et al. (1995). Ammonia is combined with available aerosol sulphate to form ammonium sulphate. Any ammonia that remains will form a thermodynamic equilibrium with nitric acid and ammonium nitrate (Meng and Seinfeld, 1996) that is dependent on temperature and relative humidity. Aqueous phase oxidation of sulphur dioxide by hydrogen peroxide is also accounted for using Met Office UM model cloud fraction predictions. The aqueous phase mechanism used in the NAME model is based on that used in the Met Office global chemistry model, STOCHEM (Collins et al., 1997). The gaseous species dissolved into the cloud are nitric acid (HNO_3), ozone (O_3), carbon dioxide (CO_2), hydrogen peroxide (H_2O_2), ammonia (NH_3) and sulphur dioxide (SO_2). Sulphate aerosol in the cloud is assumed to be completely dissolved.

SOA: Redlington and Derwent (2013) describe the inclusion of SOA in NAME. The parameterisations describing SOA formation that have been employed in NAME were constructed using the PTM model. The SOA formation from 123 emitted VOCs was described using the CRIv2 mechanism. The 123 VOCs include isoprene and the monoterpenes, together with aliphatic, olefinic, aromatic and oxygenated hydrocarbons with carbon numbers C ≤ 12. The model, as described by Redlington and Derwent (2013) is heavily tuned to measurements carried out by by Harrison and Yin (2008) at the Churchill Pumping Station site, near Birmingham. Tuning factors include man-made VOC emissions scaled by a factor of 5, the authors both noting that it is likely that the NAME model predictions based on these parameterisations are highly uncertain, that is to say they have a predicted SOA uncertainty which is at least ± an order of magnitude. The SOA mechanism is a bulk mechanism with no consideration of the dynamics of mass transfer or of the aerosol size distribution evolution.

Summary: Bulk equilibrium partitioning assumed for both SIA and SOA. Tuning factors are used for the SOA model based on ambient measurements.

C1.4.3: FRAME

(Fine Resolution Atmospheric Multi-pollutant Exchange, CEH)

FRAME is a Lagrangian model that simulates an air column moving along trajectories over the UK. The domain of FRAME covers the British Isles with a grid resolution of 5 km or 1 km. Input gas and aerosol concentrations at the edge of the UK FRAME domain are calculated using FRAME-EUROPE, a larger scale European simulation which runs over the entirety of Europe on the EMEP grid with a 50 km scale resolution (Dore et al 2009). Whilst described as Lagrangian, the calculated diffusion between vertical layers (using the finite volume approach) is effectively Eulerian in nature. Dry deposition of SO_x, NO_x and NH_x is calculated individually to five different land cover categories (forest, grassland, moor-land, urban and arable) (Kryza et al 2011). Wet deposition of chemical species is calculated using scavenging coefficients based on those used in the EMEP model (Kryza et al 2011). An enhanced washout rate is assumed over mountainous areas due to the scavenging of cloud droplets by the seeder-feeder effect to calculate local scale orographic enhancement of precipitation and concentration (Dore 2009).

SIA: Dore (2009) notes that the chemical scheme in FRAME is similar to that employed in the EMEP Lagrangian model where the prognostic chemical variables calculated are: NH_3, NO, NO_2, HNO_3, PAN, SO_2, H_2SO_4, as well as NH_4^+, NO_3^- and SO_4^{2-} aerosol. NH_4NO_3 aerosol is formed by the dry equilibrium reaction between HNO_3 and NH_3. A second category of large nitrate aerosol is present and simulates the deposition of nitric acid on to soil dust or marine aerosol. The formation of H_2SO_4 by gas phase oxidation of SO_2 is represented by a predefined oxidation rate. H_2SO_4 then reacts with NH_3 to form ammonium

sulphate aerosol. The aqueous phase reactions considered in the model include the oxidation of S(IV) by O_3, H_2O_2 and the metal catalysed reaction with O_2.

SOA: It is unclear from the literature whether or how FRAME deals with SOA.

Summary: Following the EMEP model description, all sulphate and ammonium is prescribed to $PM_{2.5}$ assuming equilibrium; nitrate can be present in both $PM_{2.5}$ and PM'coarse'.

C1.4.4: UKIAM

(UK Integrated Assessment Model, Imperial College Centre for Environmental Policy. [http://www3.imperial.ac.uk/environmentalpolicy/research/environmentalquality/iau/iam/ukiam])

The UKIAM was developed at Imperial College to investigate emissions control strategies in the UK from the ASAM model (Abatement Strategies Assessment Model) at the European scale. Described by Oxley (2011), the modelling of pollutant concentrations and deposition by UKIAM relies on the use of pre-calculated source-receptor relationships calculated for each source with a more comprehensive model such as FRAME or the EMEP model. Nested within ASAM, UKIAM operates at a 5x5km resolution, refined to a 1x 1 km grid for London and other major cities through development of the BRUTAL (Oxley et al., 2009) sub-model for road transport and urban air quality. Emissions from road transport are calculated separately on a road-by-road basis across the UK within BRUTAL using ADMS-Urban for different types of road and traffic mix. Initially the BRUTAL and UKIAM models were developed to treat PM_{10} only. Accounting for $PM_{2.5}$ emissions has been carried out by prescribing 'appropriate' fractions of PM_{10} for each source in the inventory, and hence deriving an emissions inventory for the primary $PM_{2.5}$ emissions. Shipping emissions on a 5x5 km grid for the sea areas surrounding the UK have been compiled by ENTEC and incorporated in UKIAM. Specific treatment of SOA is not reported.

SIA: Secondary Inorganic aerosol, in the form of SO_4, NO_3 and NH_4 are either i) derived from the FRAME model (see above), using source-receptor relationships for each UK source to estimate adjusted concentrations of each component on a 5x5 km grid, and imported contributions from FRAME-Europe OR ii) derived from the EMEP model, using source receptor relationships on a 50x50 km grid to adjust concentrations of each component. $PM_{2.5}$ emissions are derived as sub-fractions of the existing PM_{10} emissions. The secondary inorganic aerosols require adjustment to the nitrate to allow for a fraction (~15%) being coarser particulate rather than the finer ammonium nitrate.

SOA: Contribution from SOA within the PM_{10} fraction is based on the HARM (Hull Acid Rain Model) model. Described by Metcalfe et al (2005), it is unclear how SOA is incorporated. Whyatt et al (2007) describe the coupling with the ELMO model noting it has a 'more complete chemical scheme' which allows modelling of SOA. In that paper the authors note inclusion of SOA through photo-oxidation of terpenes (represented by α-pinene) (Hoffmann et al., 1997), and anthropogenic SOA through photo-oxidation of toluene. The model does not account for re-partitioning of SOA back into the gas phase. ELMO is used to model secondary organic aerosol through the implementation of a condensed version of the α-pinene photo-oxidation scheme taken from the STOCHEM model (Derwent et al. 2003: http://www.geos.ed.ac.uk/~dstevens/publications/derwent_jac03.pdf)

Summary: $PM_{2.5}$ predictions are based on pre-calculated source-receptor relationships from either FRAME , EMEP, HARM or ELMO.

C1.4.5: CMAQ

(The Community Multiscale Air Quality (CMAQ) modelling system/ WRF/CMAQ, CMAQ-Urban / Kings College London, University of Hertfordsire, Ricardo-AEA[www.airqualityengland.co.uk])

The Community Multiscale Air Quality (CMAQ) modelling system (Byun and Schere, 2006) has been developed by USEPA and is a multiscale Eularian model. The CMAQ aerosol component was derived from the Regional Particulate Model (RPM) (Binkowski and Shankar , 1995), which is an extension of the Regional Acid Deposition Model (RADM) (Stockwell et al. ,1990). The following is taken from Mebust et al (2003): Particle size distributions within CMAQ are represented as the superposition of three lognormal sub distributions, or modes. Two different modes, the Aitken and accumulation modes, each having variable standard deviations, represent $PM_{2.5}$ particles in the CMAQ aerosol component. Fine mode species considered within the CMAQ aerosol component include sulfate, nitrate, ammonium, water, primary organic aerosols, secondary organic aerosols of anthropogenic and biogenic origin, elemental carbon, and primary aerosol material not otherwise specified. The coarse particle mode within CMAQ, representing particles having aerodynamic diameters between 2.5 and 10 μm, consists of wind-blown dust and other large particles. Further details on the aerosol module are given by Binkowski and Roselle (2003). Meteorological models are not built in the CMAQ model, requiring coupling the meteorological models like the Fifth-Generation Pennsylvania State University-National Center for Atmospheric Research Model (MM5) or Weather Research and Forecasting (WRF) (Skamarock et al., 2008). Traditionally there is no chemistry feedback to meteorology in the offline version. The latest version CMAQ 5.0 (Released February 2012, http://www.cmaq-model.org/cmaqwiki/), which hasn't been included in UK studies to our knowledge, includes an option to run the model in a 2-way coupled (online) mode with the WRFv3.3 model. It also includes a new aerosol module AERO6. CMAQ and the Atmospheric Dispersion Modelling System (ADMS) Roads model (version 3) have been coupled to create CMAQ-urban. WRF provides the meteorological input to this KCL CMAQ model that provides air quality predictions starting at a European scale and through a series of model nests which reduce in size, finally to focus on Greater London (AQEG, 2012). Ricardo-AEA (www.airqualityengland.co.uk/) employ the CMAQ model to provide 48-Hour forecasts for PM_{10} and $PM_{2.5}$ for Defra (AQEG, 2012). Similarly, the CMAQ model is used by the Centre for Atmospheric and Instrumentation Research (CAIR), University of Hertfordshire. The CMAQv4.7 operational document (http://www.cmascenter.org/help/model_docs/cmaq/4.7.1/CMAQ_4.7.1_OGD_28june10.pdf) notes the cloud module in CMAQ performs several functions related to cloud physics and chemistry. Three types of clouds are modelled in CMAQ: sub-grid convective precipitating clouds, sub-grid nonprecipitating clouds, and grid-resolved clouds. The meteorological model provides information about grid-resolved clouds, with no additional cloud dynamics considered in CMAQ. For the two types of sub-grid clouds, the cloud module in CCTM vertically redistributes pollutants, calculates in-cloud and precipitation scavenging, performs aqueous chemistry calculations, and accumulates wet deposition amounts.

SIA: The use of CMAQ for air-quality predictions in the UK have been based on v4.6 and 4.7 in CMAQ/Urban. CMAQ 4.6 is described by Beevers et al (2012). This includes ISORROPIA v1.7 which includes corrections in activity coefficients for temperatures other than 298K (CMAQ manual) and upper limit RH of 95%. It includes H^+, Na^+, NH_4^+, Cl^-, SO_4^{2-}, HSO_4^-, NO_3^- in a single aqueous phase. ISORROPIA calculates concentrations in the gas and aerosol phase at chemical equilibrium. Carlton et al (2010) describe the extension for v4.7. As in previous CMAQ model versions, the fine particle modes are assumed to reach equilibrium with the gas phase instantaneously. In contrast, dynamic mass transfer is simulated for the coarse mode because large particles are often out of equilibrium with the gas phase (Meng and Seinfeld, 1996). CMAQ version 5.0 became available from Feb 2012, though it currently has not been referenced as being used for UK studies. The

representation of gas/particle partitioning of inorganic species was improved through the incorporation of ISORROPIA version 2.0. Many of the numerical instabilities associated with the previous version of ISORROPIA have been eliminated/moderated in this new version. An additional advancement in ISORROPIAv2.0 is the treatment of Ca^{2+}, K^+, and Mg^{2+}, species abundant in sea-salt and soil dust.

SOA: Beevers et al (2012) report the use of CMAQ version 4.6 with gas phase chemistry simulated using the CB05 mechanism with initial and boundary conditions from the UK Meteorological Office chemistry-transport model, STOCHEM, which provides 14 pollutant species including CO, NH_3, NO_x, O_3, HNO_3 and VOC's (Beevers et al 2012). SOA treatment in v4.6 is described by Carlton et al (2010). Partitioning of SOA is calculated by assuming absorptive partitioning (Zhang et al 2007) using 8 classes of condensable semivolatile organic compounds resulting from five classes of parent VOCs. Six classes of the condensable SVOCs arise from anthropogenic precursor VOCs (from 3 classes of aromatics including xylene, toluene, and cresol, and 1 class of higher alkanes) and two classes from biogenic monoterpenes. Partitioning coefficients are fixed to chamber data, the study of Zhang et al (2007) relaint on the data of Kroll et al (2006). In versions 4.7, the SOA module was updated to include new NO_x-dependent aromatic SOA yields along with new empirical measurements of the enthalpies of vaporization for each condensing component. In CMAQv4.7, SOA is produced from an expanded list of precursors and can be formed via both gas- and aqueous-phase oxidation processes, as well as aerosol-phase reactions. Isoprene SOA is formed exclusively via oxidation by OH. Its yield and partitioning behavior are modeled according to the two-product parameterisation, based on the low-NO_x laboratory experiments of Kroll et al (2006). As in previous versions of CMAQ, SOA parameters for monoterpenes are based on the daylight experiments of Griffin et al. (1999).

Summary: Modal representations of the Aitken and Accumulation modes, each having variable standard deviations, represent $PM_{2.5}$ particles; Equilibrium is assumed for SIA $PM_{2.5}$ and calculated using ISORROPIA. SOA mass predicted assuming equilibrium absortive partitioning; Partitioning coefficients calculated from chamber studies

C1.4.6: WRF-CHEM

(University of Manchester, University of Hertfordshire)

The Weather Research and Forecast (WRF; http://www.wrf-model.org/) model coupled with Chemistry (WRF-Chem; Grell et al., 2005: Fast et al., 2006). The development is lead by NOAA/ESRL with contributions from National Center for Atmospheric Research (NCAR), Pacific Northwest National Laboratory (PNNL), EPA, and university scientists (http://www.wrf-model.org/WG11). WRF-Chem is an online model. Standard gas phase chemistry options of WRF-Chem include the RADM2 and the CBMZ mechanism; additional chemistry options are available with a preprocessing tool based on KPP. The Manchester model incorporates the CRI-MECH mechanism. For the aerosol it offers the choice between bulk (GOCART: Chin et al (2000)), modal (MADE-SORGAM; Schell et al (2001))), and sectional (MOSAIC; Zaveri et al 2008) schemes. In both the modal and sectional model, gas-particle partitioning is treated as a dynamic process. The Volatility Basis Set (VBS) approach is also available for the modal and sectional aerosol approaches to treat Secondary Organic Aerosol formation. WRF-Chem is used for research applications or for forecasting of air quality (e.g. http://verde.lma.fi.upm.es/wrfchem_eu), volcanic ash dispersion, and weather. Current aerosol modules assume internally mixed modes and bins.

SIA: In both the modal (MADE-SORGAM; Schell et al (2001))), and sectional (MOSAIC; Zaveri et al 2008) schemes, the production of secondary inorganic material is treated as a dynamic process as described by Ackermann et al (1995) and Zaveri et al (2008). [which compounds] For the MADE-SORGAM model, the mean of the lognormal distributions are

assumed fixed, split between the aitken, accumulation and coarse model. For the former, inorganic thermodynamics are treated using the Bromley method (Bromley 1973) and the MTEM method (Zaveri et al 2005a). The equilibrium vapor pressure of each condensate is treated using ISORROPIA (Nenes et al 1998) and MESA (Zaveri et al 2005b) respectively. Thermodynamic equilibrium is prescribed within the condensed phase, that is, any solid precipitation is based on results of the equilibrium models ISORROPIA and MESA. Aqueous phase oxidation of SO_2 by H_2O_2 and O_3 is included. Aerosol number determines cloud droplet number with account for aqueous chemistry and wet removal. The CMU aqueous chemistry (Fahey and pandis 2001) only accounts for stratocumulus clouds whereas the EPA aqueous chemistry scheme (Walcek and Taylor, 1986) deals with both stratocumulus and cumulous clouds. Wet removal accounts for activated aerosol and dissolved gas phase species.

SOA: The standard scheme used with the modal MADE scheme, (Ackermann et al.,1998) in WRF-Chem is SORGAM (Schell et al. (2001)). SORGAM assumes that SOA compounds interact and form a quasi-ideal solution. The gas/particle partitioning of SOA compounds is parameterised according to Odum et al. (1996) with all activity coefficients assumed unity. SORGAM treats anthropogenic and biogenic precursors separately, and may be used with each of the chemical mechanism in WRF-Chem. As standard, the sectional MOSAIC scheme is not coupled to a SOA module and simply carries primary organic material as "OC". Implementation of the VBS in the WRF-Chem MOSAIC treatment has been described in Shrivastava et al. (2011). A 9-species VBS approach coupled with SAPRC-99 gas-phase mechanism represents gas-particle partitioning and multiple generations of gas-phase oxidation of organic vapours. Predictions were evaluated against MILAGRO 2006 Mexico City organic aerosol data. An alternative VBS implementation in the modal WRF-Chem MADE aerosol treatment, coupled to the RACM mechanism, was validated and evaluated against TEXAQS-2006 data in the southern US is given in Ahmadov et al (2012). This parameterisation does not include the treatment of "unconventional" SOA precursors treated in PMCAMx in, for example, Donahue et al., (2006). None of these schemes has been applied to the UK at the present time. A new scheme has recently been developed and implemented. Coupled to the CRI-Mech gas phase scheme, 13 of the intermediates are allowed to partition between the gas phase and the evolving particle size sections in MOSAIC. Two additional compounds, currently assumed involatile, representing POA and "aged" components are also carried. Activity coefficients are calculated using the PD-FiTE methodology (Topping at al., 2012). This new scheme has been detailed in Lowe et al. (2013).

Summary: Bulk, modal and sectional aerosol model options; Partitioning treated using equilibrium or dynamic mass transferwith separate models treating condensed phase thermodynamics and equilibrium phase state. SOA model treatment includes options for explicit gas phase mechanism or empirically tuned volatility basis set approach.

C1.4.7: AQUM

(Air quality modelling in the Met Office Unified Model)

AQUM is used as regional forecasting using the UM enabled through development of atmospheric chemistry model already in the UM, the UKCA The Met Office Unified Model (MetUM) (Davies et al, 2005). It uses the bulk aerosol scheme CLASSIC (Bellouin et al, 2011) that previously was applied in climate and air quality configurations. The chemistry scheme is the UKCA scheme. A two-moment modal aerosol scheme, UKCA-GLOMAP-mode, has also been developed for use with the MetUM ported from the offline model TOMCAT (Mann et al., 2010). The model is two-way coupled with the direct radiative effects of gases/aerosols and the indirect effects of aerosols capable of being treated. It has been designed to predict operationally running forcasts of O_3, NO_x, CO and SO_2 and PM (2.5 and

10). AQUM works on a domian size of 12x12km covering UK and Ireland with 38 vertical levels but can be used across a very wide range of spatial and temporal scales from short range weather forecasting at 1.5 km resolution to multi–decadal simulations in an earth system model configuration (Collins et al., 2011).

SIA: AQUM uses the Coupled Large-Scale Aerosol Simulator for Studies in Climate (CLASSIC) aerosol module as decribed by Belluoin et al (2011). CLASSIC contains six prognostic tropospheric aerosol types: ammonium sulphate, mineral dust, fossil fuel black carbon (FFBC), fossil fuel organic carbon (FFOC), biomass burning aerosols and ammonium nitrate. It is a bulk aerosol scheme, where the aerosol species are treated as an external mixture. For most species, aerosol mass is distributed across three model tracers associated with the Aitken, accumulation, and dissolved (or in-cloud) modes. Each aerosol type is assumed to have a fixed log-normal size distribution (apart from dust). Sulphate aerosol is represented by Aitken and accumulation modes and an additional tracer for sulphate dissolved in cloud droplets. Sulphate mass is assumed to all be in the form of ammonium sulphate. Ammonia (NH_3) is a transported tracer in the model and is removed from the atmosphere by the formation of ammonium sulphate (as well as by dry and wet deposition); any excess ammonia can react with nitric acid (HNO_3) to form ammonium nitrate aerosol. Thermal decomposition of ammonium nitrate to nitric acid and ammonia is permitted according to the equilibrium model described by Ackermann et al. (1995). Nitric acid concentrations are derived from the RAQ scheme and depleted by nitrate aerosol formation. The mass of nitrate aerosol formed goes into an accumulation mode and cloud formation transforms some of the accumulation mode into the dissolved mode, as with sulphate. Sulphate mass is assumed to be fully in the form of ammonium sulphate (Bellouin et al 2011). The reaction between HNO_3 and NH_3, and the phase of the resulting nitrate aerosol, depend strongly on relative humidity and temperature. In CLASSIC, this dependence is parameterized by computing the dissociation constant.

SOA: The AQUM gas phase chemistry is a further development of the UKCA tropospheric scheme (O'Connor et al 2013), but with new mechanism added for regional air quality modelling (RAQ). The regional air quality (RAQ) chemistry mechanism based on STOCHEM. AQUM uses global chemistry forecasts from GEMS-Global Reactive Gases project (daily T and 72 forecasts) for boundary conditions. Biogenic secondary organic aerosols from the oxidation of terpenes is based on a climatology of monthly three-dimensional mass mixing ratios, taken from the chemistry-transport model STOCHEM (Derwent et al., 2003). The condensable species are then 'scavanged' by the accumulation mode using a globally constant first order reaction in competition with further gas phase conversion reactions that would ultimately have led to the formation of low molecular weight oxidation products such as acetone and carbon moNO$_x$ide (Derwent et al 2003). The scavenging process was given a time constant of the order of a few per cent per hour.

Summary: In the CLASSIC mass based external mixture scheme, sulphate mass is assumed to be fully in the form of ammonium sulphate and nitrate in the form of ammonium nitrate; Aerosol mass is distributed across three model tracers associated with the Aitken, accumulation, and 'dissolved' (or in-cloud) modes. Aerosol size distributions are assumed not to evolve. SOA mass loadings based on STOCHEM mechanism where condensable products are 'lost' to the accumulation mode using a globally constant first order reaction

C1.4.8: EMEP4UK

(Coordinated by CEH in conjunction with the University of Edinburgh).

The EMEP aerosol model is a bulk scheme that assumes 4 size modes: nucleation, Aitken, accumulation and coarse. All particles in the same mode are assumed to have the same size distribution and are internally mixed. The EMEP4UK model increases spacial resolution

from 50km in the european vairant to a 5km scale for UK applications. It was also developed specifically to support UK transboundary air pollution policy evaluation, incorporating the effects of actual meteorology and allowing analysis of future scenarios for different years (CEH ref). It was developed with an eye to improve capabilities over models like FRAME (see above), which while more computationally expensive, are better able to represent atmospheric chemical processes and provide a more reliable simulation of source-receptor relationships. The chemical scheme is identical to the EMEP Unified Model and is based upon the ozone chemistry from the Lagrangian photo-oxidant model (Andersson-Sköld and Simpson, 1999, Simpson at al., 1993), but with additional reactions introduced to extend the model's capabilities to acidification and eutrophication. Two types of emissions are present in the model: anthropogenic and biogenic (Vieno et al 2010). Taken from Veino et al (2010): for the UK, anthropogenic emissions of NO_x, NH_3, SO_2, $PM_{2.5}$, PM_{coarse} (coarse particulate matter), CO, and non-methane VOC (NMVOC) are integrated from the UK National Atmospheric Emissions Inventories (NAEI) 1×1 km^2 emissions to the required 5×5 km^2. Elsewhere and for international shipping, EMEP 50×50 km^2 emissions are used (www.emep.int). NMVOC are speciated into 10 reactive and one unreactive species, using emission-sector specific values as shown in Simpson et al. (2003). Biogenic emissions of isoprene are based on Guenther et al. (1993) and Simpson et al. (1999), driven by EMEP 50×50 km^2 land- use, temperature and light. The EMEP model distinguishes five classes of fine and coarse particles, which for dry-deposition purposes are assigned mass-median diameters, geometric standard deviations, and densities (Simpson et al 2012).

SIA: The three secondary inorganic species (sulphate, nitrate and ammonium) are derived from gas and condensed-phase chemical reactions involving the gaseous precursors sulphur dioxide, nitrogen oxides (i.e. nitric oxide (NO) and nitrogen dioxide (NO_2)) and ammonia. The EMEP models assign all sulphate and ammonium to $PM_{2.5}$ but nitrate can be present in both $PM_{2.5}$ and PM_{coarse} (i.e. particles in the size range between PM_{10} and $PM_{2.5}$). The current EMEP Unified Model includes the EQSAM (Equilibrium Simplified Aerosol Model) gas/aerosol partitioning model detailed by Metzger et al. (2002) for the partitioning of inorganic species between the gas and aerosol phase. The main assumption made in EQSAM is that volatile species in the gas and aerosol phases are in chemical equilibrium. Then, the aerosol activity (or aerosol molality) and hence the chemical composition is governed by the relative humidity. Based on the cation/anion mole ratios ([Na]+[NH]+[NH])/[SO], the entire set of possible aerosol compositions is divided in concentration domains. Each domain represents a certain aerosol type and is further subdivided into several sub-domains, according the the regime of deliquescence relative humidity for the corresponding aerosol composition. Assumption on metastable aqueous aerosols is adopted. The aerosol water content is calculated basen on the semi-empirical so-called ZSR-relation. The chemical composition of aerosol (i.e. aerosol/gas partitioning) is found from aerosol chemical equilibrium, which is determined by a temperature dependent equilibrium coefficient.

SOA: SOA was first introduced into the generalised 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 use of the volatility basis set (VBS) mechanisms in European SOA production (Bergström and Simpson, 2010). Simpson et al (2012) note developments of modules used for predicting SOA in the general EMEP model. In that paper the authors state how a large number of schemes for organic aerosol have also been tested (Simpson et al., 2007; Bergstrom et al., 2012), the default chemical scheme is EmChem09.

Summary: All sulphate and ammonium is prescribed to $PM_{2.5}$ **assuming equilibrium; nitrate can be present in both** $PM_{2.5}$ **and PM'coarse'; EQSAM treats the equilibrium in**

the aqueous-inorganic ion system. Unclear which method for predicting SOA loadings is favoured; Approaches in EMEP include mechanistic models with dynamic mass transfer and a VBS approach.

C1.4.9: PCM

(Pollution Climate Mapping (PCM) model. Ricardo-AEA on behalf of Defra):

The Pollution Climate Mapping (PCM) model is a collection of models designed to fulfill part of the UK's EU Directive (2008/50/EC) requirements to report on the concentrations of particular pollutants in the atmosphere. These models are run by Ricardo-AEA on behalf of Defra. PCM is a GIS (Geographical Information System) based semi-empirical model, driven by the NAEI but consisting of modules which provide concentrations of the different component parts of the PM mix. The basis of the model is the calculation of background concentrations across the UK on a 1 km x 1 km grid using measured data to derive the regional background, with near sources (those within about 15 km) modelled as area sources using a kernel approach based on ADMS 4, and large point sources modelled explicitly using ADMS 4. Roadside concentrations are based on an empirical approach with concentrations defined for an effective distance of 4 m from the kerb. The model produces annual mean concentrations, relying on empirical relationships to derive shorter-period concentrations. There is one model per pollutant (NO_x, NO_2, PM_{10}, $PM_{2.5}$, SO_2, CO, benzene, ozone, As, Cd, Ni, Pb and B[a]p) each with two parts: a base year model and a projections model. The model is calibrated using automatic monitoring data from the AURN where the HARM/ELMO models are used for secondary organic aerosol. Secondary inorganic aerosols are interpolated from SO_4, NO_3 and NH4 measurements.

SIA: Secondary inorganic aerosol concentrations have been derived by interpolation and scaling of measurements of sulphate, nitrate and ammonium. The scaling factors are required to take account of the contribution from bound water, counter ions and to apportion the mass between the fine ($PM_{2.5}$) and coarse ($PM_{10} - PM_{2.5}$) fractions (Stedman et al 2007)

SOA: SOA is estimated from results from the HARM/ELMO model (Stedman et al 2009). HARM (Hull Acid Rain Model) and ELMO (Edinburgh Lancaster Model for Ozone) are both receptor-orientated, Lagrangian statistical models, which track the changing composition of a series of air parcels travelling across both the EMEP and UK areas. The chemical scheme of ELMO includes the generation of natural SOA through photo-oxidation of terpenes (represented by a-pinene) (Hoffmann et al., 1997), and anthropogenic SOA through photo-oxidation of toluene. ELMO contains a description of the photochemical reactions that drive ozone production in the polluted atmospheric boundary layer over North- west Europe (Metcalfe et al 2002). The hydrocarbons accounted for are: methane, ethane, propane, butane, ethylene, propylene, isoprene, toluene and o-xylene. This mechanism is a condensation of the Master Chemical Mechanism and includes 70 model species. The ELMO model makes the simplification that the degradation of the above nine emitted hydrocarbon species can be made to represent the ozone formation from the sum total of the hundreds of hydrocarbons that contribute to ozone formation in the real atmosphere (Metcalfe et al 2002). As noted by Whyatt et al: (www.harmo.org/conferences/Proceedings/_Garmisch/publishedSections/2.13.pdf). ELMO is used to model secondary organic aerosol through the implementation of a condensed version of the α-pinene photo-oxidation scheme taken from the STOCHEM model (Derwent et al. 2003: http://www.geos.ed.ac.uk/~dstevens/publications/derwent_jac03.pdf). The process is represented in STOCHEM by a globally constant first order reaction in competition with further gas phase conversion reactions.

Summary: SIA model is calibrated with measured $PM_{2.5}$ inorganic ions. SOA loadings based on the STOCHEM method of prescribing a globally constant first order reaction in which condensable products from a detail gas phase mechanism are 'lost' to the

accumulation mode.

C1.4.10: PTM

(Photochemical trajectory model; University of Birmingham, Atmospheric Chemistry Services, RDScientific):

The UK-PTM is a boundary-layer trajectory model originally assembled to simulate photochemical ozone production and subsequently used to derive Photochemical Ozone Creation Potentials (Beddows et al 2012). Beddows et al (2012) comprehensively report the recent modifications designed to improve the PTM. Back trajectory calculations are used to describe the meteorological component, the work of Beddows et al (2012) using the NOAA Hybrid Single Particle Lagrangian Integrated Trajectory (HYSPLIT-4) model (Draxler and Hess, 1998) and the archived NCEP/NCAR global data assimilation system data (GDAS). The secondary inorganic aerosol module is ISORROPIA, combined with the Common Reactive Intermediate (CRI) mechanism (version CRI v02) developed by Jenkin et al. (2008) to account for VOC degradation mechanisms. Dry deposition of PM (chloride, nitrate, sulphate) is accounted for using the scheme developed by Smith et al (1993), modifying this to account for land, relative to marine environments.

SIA: Originally, aerosol chemistry was accounted for using a simple thermodynamic equilibrium model. In the current version described by Beddows et al (2012), the thermodynamic model ISORROPIA II is used (Fontoukis and Nenes 2009). In ISORROPIA solid, liquid and gas phase chemistry is modeled for the sulfate, nitrate, ammonium, chloride aerosol system using the internally mixed assumption. In the equilibrium concentration mode, the ISSOROPIA calculates the equilibrium vapor pressure of the semi-volatile components from the known aerosol composition. Beddows et al (2012) also describe the inclusion of aqueous phase oxidation of SO_2 to H_2SO_4 in clouds using a first order process with reaction constant represented using a paraetersaition based on RH and cloud cover according to Schaap et al (2004). Cloud cover, in the Beddows et al (2012) paper, was included as a field within the back trajectory data.

SOA: SOA formation can be represented in terms of the bulk equilibrium partitioning oxidation products between the gas-phase and a particulate phase (Johnson et al 2006). In that study, temperature dependent partitioning coefficients were calculated using a range of predictive techniques. Derwent et al (2009) used a version of the PTM to simulate contributions to observed PM in relation to UK observations in 2006 at Harwell, UK. The SOA module used was very basic, having two components involving the oxidation of biogenic- derived a-pinene by hydroxyl OH, nitrate NO_3 and ozone and the oxidation of man-made aromatic compounds by OH. For linkage with the CRI mechanism, Beddows et al (2012) did not report predictions of any SOA.

Summary: SIA bulk mass loadings calculated using the latest version of the ISSOROPIA model. SOA bulk mass loadings predicted using equilibrium absorptive partitioning theory and products derived from choice of MCM or CRI mechanism.

C1.5: Other models (non-UK)

Backlanov et al (2013) list and describe additional coupled chemistry-climate models used across Europe covering scales from 1km to 20km : BOLCHEM [Italy: http://bolchem.isac.cnr.it], COSMO-ART [Germany, Eulerian, http://www.imk-tro.kit.edu/3509.php], COSMO-MUSCAT [Germany, Eulerian, : http://projects.tropos.de/cosmo muscat], Enviro-NIRLAM [Denmark http://hirlam.org/chemical], GEM-AQ [Poland, http://ecoforecast.eu], IFS-MOZART [MACC/ECMWF, http://www.gmes-atmosphere.eu], MCCM [Germany, http://www.imk-ifu.kit.edu/829.php], MEMO/MARS [Greece, Eulerian http://pandora.meng.auth.gr/mds/

showlong.php?id=19], Meso-NH [France, Eulerian, http://mesonh.aero.obs-mip.fr/mesonh], M-SYS [Germany, http://www.mi.uni-hamburg.de/SYSTEM-M-SYS.651.0.html], NMMB/BSC-CTM (BSC-CNS) [Spain, http://www.bsc.es/earth-sciences/mineral-], RACMO2/LOTUS-EUROS (KNMI, TNO) [Netherlands, http://www.knmi.nl/research/regional climate/models/racmo.html http://www.lotos-euros.nl] RAMS/ICLAMS [Greece, http://forecast.uoa.gr/ICLAMS/index.php], RegCM-Chem4 [Italy, http://users.ictp.it/RegCNET/model.html], REMO-HAM/REMOTE [Germany, http://www.remo-rcm.de/The-REMO- model.1190.0.html]. Additional models not listed in that study include CHIMERE [France, Eulerian: http://euler.lmd.polytechnique.fr/chimere/], EURAD [Germany, Eulerian: http://www.eurad.uni-koeln.de], CAMx [US, Eulerian, http://www.camx.com/].

C2 Modelling Interpretation Capabilities

Introduction

This section describes the available methods for model interpretation, evaluation of sensitivities, uncertainties and diagnostics relevant to this review aiming to address considerations such as the impacts of reductions in precursor emissions on secondary $PM_{2.5}$ loadings and secondary aerosol source-receptor relationships. As UK specific studies have not exploited all of the currently available methods, we incorporate developments internationally as, in some cases, inorganic/organic aerosol modules used within the same frameworks employed in the UK have been extended to account for this additional analysis or are in current development. At the end of the sections available tools for model intercomparisons and uncertainty analyses are briefly reviewed.

The terms 'receptor modelling' and 'source apportionment' are often used interchangeably. In this document techniques are split into the direct use of measured $PM_{2.5}$ data or from sensitivity studies using existing lagrangian or eularian frameworks. In the UK, and Europe in general, effort tends to focus on the former, whereas the US, for example, are developing numerical methods to target the latter.

C2.1: Source apportionment from measurement data and statistical methods:

Watson et al (2002) summarise the main type of receptor modelling techniques based on measurement datasets, clearly recognising their complementarity with the source models that estimate concentrations from emissions inventories and transport meteorology. Available techniques include enrichment factor, chemical mass balance, multiple linear regression, eigenvector, edge detection, and neural network methods. The steps for using receptor models to elucidate on air quality problems are also summarised by Watson et al (2002): (1) formulating a conceptual model; (2) identifying potential sources;(3) characterising source emissions;(4) obtaining and analyzing ambient PM samples for major components and source markers; (5) confirming source types with multivariate receptor models; (6) quantifying source contributions with the chemical mass balance; (7) estimating profile changes and the limiting precursor gases for secondary aerosols; and (8) reconciling receptor modeling results with source models, emissions inventories, and receptor data analyses. Viana et al (2008) summarise the main techniques used in Europe. In that report, Principal Component Analysis (PCA) was the most frequently used model up to 2005 (30% of the studies), followed by the Lenschow approach (11%) and back-trajectory analysis (11%). Other models commonly used were Positive Matrix Factorisation PMF (8%) and chemical Mass balance CMB (7%). PCA-back trajectory analysis is almost a hybrid of the two categories mentioned earlier and has been employed in the UK. The AQEG (2012) report notes that the PCM model is also a hybrid of the two approaches in that it uses measured concentrations as the basis for estimating source contributions from different types of particles and dipersion modelling to estimate the contribution from primary sources.

This only seems applicable to SIA however, the scheme used for predicting SOA based on a rudimentary uptake model linked to a gas phase mechanism.

For SOA in the UK, the CMB method has been used with measurement data of varying levels of complexity. Harrison and Yin (2008) calculated separate concentrations associated with primary and secondary sources based on the elemental carbon tracer method which is based 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 (AQEG, 2012). A more detailed analysis is the search for specific marker compounds, which are assumed representative of specific sources. Again, as noted by the AQEG (2012) report, numerous trace element species compiled by (Harrison and Yin, 2010) and Yin et al. (2010) enabled the latter study to disaggregate the measured organic carbon into specific sources including: wood smoke, particles from diesel engines etc. As discussed in section C2.2, there is difficulty in prescribing source relationships to secondary material important for $PM_{2.5}$ where non-linear interactions play an important role. For SIA, this has been confirmed in numerous UK and EU sites (Jones and Harrison 2011). Furthermore, the AQEG (2012) report notes that the CMB method 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 from which the chemical profile information is derived may not be wholly applicable to the UK (e.g. if the profile was deririved from a US based study). This is important since the relationships between concentrations of SIA or SOA in $PM_{2.5}$ and emissions of key precurors help dictate any abatement strategies

C2.2: Source apportionment from model sensitivity analysis:

Attributing climate or air quality degradation to sources is challenging with sensitivity analysis techniques based on standard model output (Capps et al 2012). Yarwood et al (2007) broadly classifies two types of approach for determining source apportionment of particulate matter with techniques nested in the host models: Sensitivity analysis and reactive tracers. It is useful to distinguish between sensitivity analysis methods and uncertainty methods following Rao (2005), as the two terms are often used interchangeably. Sensitivity analysis is the systematic study of the behavior of a model over ranges in variation of inputs and parameters. Uncertainty analysis is the quantitative assessment of how the uncertainties in model physics and input data, as well as the random variability in input parameters, propagate through the model to give a single measure of uncertainty in the model results. Determining the importance of uncertainties in model components and model inputs to predictions of $PM_{2.5}$ is very important when evaluating effectiveness of control strategies. Historically, multiple air quality model simulations using different sets of emissions have been used to evaluate the expected benefit of different strategies. This approach is resource-intensive (Zhang et al 2013) leading to the development of new uncertainty analysis methods discussed briefly in this section.

The more complex the model, the more challanging the analysis becomes. For example, Fine et al (2003) note that many model sensitivity evaluations have been conducted using trajectory models because of their computational and input simplicity advantages, though recent efforts in the US have used Eulerian models. It is easier to work with trajectory models, but their simplifying assumptions are violated more readily (Fine et al 2003).

The simplest and most frequently used sensitivity analysis is the perturbative approach. Often referred to as the brute force method (BFM), a parameter value is perturbed, the model is rerun, and the change in observables is calculated to determine sensitivity coefficients (Fine at al 2003). The brute force method estimates first-order sensitivity coefficients (e.g., dSO_4/dSO_x) by making a small input change (dSO_x) and measuring the change in model output (dSO_4). This method is simple and can be applied to any model, but

is inefficient because a complete model run is required for each sensitivity (Yarwood et al 2007). There have been few, if any, UK regional modelling studies that have not followed the 'one parameter at a time' (OAT) sensitivity analysis method. Rao (2005) notes that these sensitivity analyses will be fairly accurate in a weak response regime where the output is linearly related to the inputs for a base case with a specific value for each input variable (Rao 2005). The difficulty with OAT methods is inability to capture the true effect of non-linear dependencies among the input parameters. While Monte Carlo techniques propagate probability distributions through a large number of model simulations, the applicability of such techniques are largely limited to models with the lowest computational burden such as the Gaussian plume trajectory models which tend to lack the process level descriptions key to $PM_{2.5}$ formation. Lee et al (2011) note that the Met Office Hadley Centre quantifying uncertainty in model predictions (QUMP) project has resulted in several sensitivity studies undertaken using climate models attempting to improve on the OAT approach (Murphy et al., 2004)

Rao (2005) describes the use of uncertainty analysis in atmospheric dispersion modeling. They have also been applied to box-model simulations (e.g. Milford et al 1992; Derwent and Hov, 1988). As Yarwood et al (2007) state however, source apportionment for primary PM is relatively simple to obtain from any air pollution model because source-receptor relationships are essentially linear for primary pollutants. The Gaussian and Lagrangian approaches work for primary PM because the models can assume that emissions from separate sources do not interact. This assumption breaks down for secondary $PM_{2.5}$ pollutants (e.g., sulfate, nitrate, ammonium, secondary organic aerosol) and so puff models may dramatically simplify the chemistry (to eliminate interactions between sources) so that they can be applied to secondary PM. ApSimon and Oxley (2010) note that, for example, using the UKIAM lagrangian dispersion model care, has to be taken where there are non-linear chemical interactions between pollutants. For example, reducing ammonia emissions can have a large effect in reducing nitrate aerosol concentrations as well as ammonium ions, because of its role in the formation of ammonium nitrate. This is important because it magnifies the importance of ammonia in reducing secondary particulate concentrations (ApSimon and Oxley 2010).

Whilst Eulerian grid models are noted to be better suited to modeling secondary pollutants they do not naturally provide source apportionment because the impact of all sources has been combined in the total pollutant concentration (Yarwood et al 2007). This has lead to the development of numerical methods that are employed within the host model. On that basis there are a number of approaches in which sensitivity differential equations are derived from the original parent equations and solved at the same time (Zhang et al 2013). The equations can be derived analytically, as in the decoupled direct method (DDM). Most DDM applications focused on first-order sensitivity equations. A separate set of equations has to be derived for higher-order sensitivity coefficients. (Fine et al 2003). The DDM provides the same type of sensitivity information as the brute force method but using a computational method that is directly implemented in the host model (Dunker, 1981). This method operates integrally within a chemical transport model and simultaneously computes local sensitivities of pollutant concentrations to perturbations in input parameters. Zhang et al (2013) describe the development of the high-order decoupled direct method in three dimensions for particulate matter (HDDM-3D/PM) to enable advanced sensitivity analysis of ISORROPIA, the inorganic aerosol module of CMAQ (specifically the authors implement this in CMAQ v4.5). They state that although nonlinear effects of aerosol precursors on aerosol concentrations have been of concern in the past decade (Ansari and Pandis, 1998; West et al., 1999), developing HDDM for PM has not yet been undertaken due to the discontinuous, highly nonlinear solution surface of the inorganic aerosol thermodynamics. At the present time, there appears to be no extension to account for any SOA mechanism.

The adjoint method is related to an approach known as Green functions method (GFM) (Fine

et al 2003). Capps et al (2012) state that adjoint-based sensitivity analysis enhances the ability to assess the relative influence of aerosol precursor emissions on air quality metrics as well as providing a means of refining emissions estimates with observations in an inverse modeling framework. Moreover, the authors state that the adjoint method complements forward sensitivity approaches by efficiently elucidating the relationship of model output (e.g., specified concentrations, air quality metrics) to the field of model parameters, or input, (e.g., emissions, initial conditions) without perturbing model inputs. Computational requirements for calculation of these receptor-oriented sensitivities are insensitive to the number of model parameters investigated. Of the modules incorporated in models used in the UK, again developments have been limited to the inorganic thermodynamic model ISORROPIA, as implemented in CMAQ and the PTM. The adjoint version, ANISORROPIA (the AdjoiNt of ISORROPIA, an aerosol thermodynamic model), was developed by Capps et al (2012) to determine the sensitivity of fine mode aerosol concentrations to inorganic aerosol precursor concentrations. In the adjoint of a chemical transport model, it can be used to assess the relative contributions of emissions from different sources at various times and places. At present, there is only evidence of incorporation of ANISORROPIA into the adjoint models of GEOS-CHEM (e.g. SIA sensitivity by Henze et al 2009) and CMAQ for non-UK use. There is however evidence of use for the adjoint in determining source contributions to ozone, an important oxidant and determinant of SOA. Zhang et al (2009) used the GEOS-Chem adjoint to quantify source contributions to ozone pollution at two adjacent sites on the U.S. west coast.

C2.3: Model uncertainty

There is a range of potential uncertainties that impact on predicted $PM_{2.5}$. For example, uncertainties in emission databases as well as secondary material process descriptions. In addition, uncertainties associated with model formulation may be due to erroneous or incomplete representations, numerical solution techniques, and choice of modeling domain and grid structure (Fine et al 2003). Defining structural model uncertainties, rather than parametric uncertainties, is challenging and often relies on model intercomparison exercises. As Fine et al (2003) note, as improved representations of processes are developed and incorporated into air quality models, structural sensitivity studies will provide a means for describing how the improvements may alter the outcome of previous regulatory modeling assessments. This is also where less computationally expensive models might be used to get a 'feel' for any improvements in more complex schemes.

As mentioned in the previous section, while Monte Carlo type techniques propagate probability distributions through a large number of model simulations, the applicability of such techniques are largely limited to models with the lowest computational burden such as the Gaussian plume trajectory models. The techniques described in section C2.2 apply equally for deriving model uncertainty so are not repeated here.

With the same computational costs associated with existing techniques in mind, new statistical models have been applied to identify the major source of uncertainty with respect to specific outputs of complex large-scale models. Whilst aimed at studying the predictions of cloud condensation nuclei, they are worthwhile briefly mentioning. As the state of the science currently indentifies a large number of uncertainties associated with the complex mechanisms leading to the production of SOA, these methods might be considered in future studies for evaluating effectiveness of control strategies. Emulation is the process by which the computer model is replaced by a statistical surrogate model that can be run more efficiently. Lee et al (2011) present a cost-effective application of variance-based sensitivity analysis to quantify the sensitivity of a 3-D global aerosol model to uncertain parameters. In that study, they use a Gaussian process emulator to estimate the model output across multi-dimensional parameter space, using information from a small number of model runs using the 'full' model at points chosen using a Latin hypercube space-filling design. Gaussian

process emulation is a Bayesian approach that uses information from the model runs along with some prior assumptions about the model behaviour to predict model output everywhere in the uncertainty space. It must be made clear however, that such analyses are dependent on the robustness of the host model. In this respect, as with other statistical sensitivity methods, prioritising uncertainties with regards to production of SIA and SOA would have to be combined with expert elicitation and inclusion of important processes within the host model.

C2.4: Diagnostic analysis of model outputs

Validation of model outputs is fundamentally carried out through comparison with measurement data discussed in section B. Examples of this are discussed in section C(iii). A selection of the above models is designed to specifically predict loadings of $PM_{2.5}$ from both SIA and SOA. Other models derive this information from the appropriate size distribution and composition representations. There are now modelling tools designed for collating existing meaurement data in a format that can be compared with model outputs. The openair project is a Natural Environment Research Council (NERC) knowledge exchange project that aims to provide a collection of open-source tools for the analysis of air pollution data (http://www.openair-project.org/). Openair is an Open source package written in the language 'R', commonly used for new statistical applications (Carslaw et al 2012; Carslaw 2013). As described in the software manual, the software arose from an initiative to develop and make available a consistent set of tools for analysing and understanding air pollution data in a free, open-source environment. The rationale was based on the substantial and increasing amount of monitoring data that is only briefly analysed with several barriers that prevent the more effective analysis of air pollution data.

Additional statistical techniques for comparison with measurement data include Taylor plots. These simultaneously show error, standard deviation and Pearson Correlation Coefficient (PCC). They summarise that the observed field is represented by a point at a distance from the origin along the abscissa that is equal to the variance. All other points on the plot area represent values for the simulated fields and are positioned such that the variance of the modelled fields is the radial distance from the origin. In practical terms, the closer a model point is to an observed point, the better the model performance.

Non-UK exemplar tools for assessing model performance in predicting particulate matter impacts include the Aerosol Modelling Testbed developed by PNNL (http://www.pnl.gov/atmospheric/research/aci/amt/). As noted on the website, the Aerosol Modeling Testbed consists of the WRF-Chem model that simulates meteorology, chemistry, and aerosols interactively, a series of testbed cases, and a suite of tools called the Analysis Toolkit that documents the evaluation of aerosol process modules. The Aerosol Modeling Testbed uses a wide range of measurements to address uncertainties in the predictions of aerosol properties. The Analysis Toolkit is a suite of software programs that extract WRF variables corresponding to observations in the testbed dataset, plot observed and simulated quantities, and calculate various statistical measures, similar to the openair project described previously.

C3 State of knowledge

Introduction:

This section combines international and UK-specific studies to distill a state-of-the-science review of SIA and SOA predictive capability. It is difficult to quantify predictive capabilities for SIA and SOA based on disparate comparisons with field measurements alone. The reason for this is the non-linear contributions from the aerosol modules themselves and other model components (for example the representation of meteorology in online or offline approaches). This section therefore necessarily considers influences of aspects of the

models not directly related to the secondary aerosol representations, such as model resolution, domains and Eulerian versus Lagrangian approaches. To capture the state of knowledge on SIA and SOA predictive capabity, case studies from both the US and EU are also used where appropriate. In all, evaluations on the predictive capability of models to capture SOA $PM_{2.5}$ are much less abundant than similar studies focusing on SIA. In a summary of the AQMEII initiative over the EU and North America, Sollazo et al (2012) note that model skill in estimating some of the major chemical components of $PM_{2.5}$ (i.e., SO_4, NO_3, NH_4 and EC) was found to be more homogenous than for total $PM_{2.5}$ mass. From this it was implied that the evaluated Eulerian models performed relatively well for the inorganic aerosol species with large uncertainty remaining in the simulation of other $PM_{2.5}$ components (SOA and unspeciated $PM_{2.5}$).The main findings of this section are:

C3.1: Eulerian versus Lagrangian.

Historically, Lagrangian modeling was mostly performed in Europe whereas Eulerian grid modeling was predominantly applied in the US (Daly and Zannetti 2007). Eulerian models include both single box models and multidimensional grid-based air quality models (Russell and Dennis 2000). Eulerian air quality modeling started in the early 1970s from the extension of the photochemical box model where the chemistry mechanisms used were mostly intended to simulate daytime urban ozone evolution (Byuan and Schere 2006). The decreased computational cost of box models has given opportunity to investigate the usually computationally demanding aerosol dynamic processes with a higher level of detail than possible in large scale regional or global models (Tunved et al 2010). Box models still enjoy some use for studying atmospheric chemistry but can lack physical realism (e.g., horizontal and vertical transport, spatial variation, etc.) according to Russell and Dennis (2000). Grid models are potentially the most powerful (Liu and Seinfeld, 1975; Hansen et al., 1994; Dennis et al., 1996), but are also the most computationally intensive (Russell and Dennis 2000). There are advantages and disadvantages noted with each approach. The review of Manning et al (2006) states that for some air-quality applications, the Lagrangian off-line approach to dispersion modelling is the most appropriate approach. The authors state that the approach has many advantages, such as a good representation of near source effects which would be sub-grid in an Eulerian model, a lack of numerical diffusion, the ability to use quite sophisticated turbulent dispersion schemes to account for the detailed structure of boundary layer turbulence (e.g. skew distribution of vertical velocities in convective conditions), and the ability to treat buoyant plume rise. A further strength of the approach is the ability to run the model in reasonable computational times on PCs. Early photochemical modeling of urban ozone and long-range transport was conducted using Lagrangian trajectory models (e.g., Eliassen et al., 1982; Eliassen, 1980), in part because of the more limited computational requirements (e.g., memory) resulting from following an air parcel versus a large number of computational cells (Russell and Dennis 2000). Liu and Seinfeld (1975) quite early on noted that advantages of using Lagrangian approaches are offset by significant limitations. Russell and Dennis (2000) suggest while Lagrangian trajectory models do have some advantages over Eulerian models, (e.g., the ability to more easily isolate process impacts and are computationally faster), their formulation and trajectory error may bring into question their suitability for quantitatively assessing the response of a region to emissions controls and for source apportionment. They further state that it is not apparent that the modifications made in some of the trajectory models (e.g., including some effective horizontal diffusion) adequately overcome the limitation in the formulation. Conversely, Wen et al (2012) note that grid-averaged concentrations prognosed by gridded models are difficult to compare with point observations. Gaussian models such as ADMS are noted to be appropriate for some short-range applications where a very fast response is needed (Manning et al 2006). Williams et al (2011) report that the earlier DEFRA review of ozone models carried out by Monks et al (2007) weighed carefully the advantages and disadvantages of an Eulerian versus a Lagrangian approach and that, while both had their merits, they concluded that Eulerian models were, on balance, to be favoured. Moreover,

they recommended that Defra should consider moving its ozone modelling capability to a Eulerian basis (Williams et al 2011). Although the earlier review focussed only on ozone models, the reasons for preferring Eulerian to Lagrangian models apply equally well to other pollutants (Williams te al 2011), Monks et al (2007) also noted that the USEPA concluded that their future modelling should be based on an Eulerian approach. For example, Monks et al (2007) use the example of SO_4^{2-} transport occuring above the boundary layer but brought down by wet scavenging. The authors note that this is more natural in a 3D framework, and while there are some complex 3D lagragian frameworks, the extra processing required diminishes the advantage over Eulerian models that is typically reduced computational cost. Manning et al (2006) similarly note advantages of Eularian over Lagrangian approaches: the lack of close integration with the NWP models in Lagrangian schemes and the lack of access to meteorology with time-step resolution; the lack of feedback on the meteorology from active tracers such as dust or ozone and the difficulty of reducing the statistical noise inherent in the approach for problems involving chemicals like ozone that are present throughout the atmosphere and not just in discrete plumes. With regards to treating influxes of boundary level concentrations of domain edges, Redington et al (2009) note the non-trivial task of achieving this in a Lagragian framework due to the vast numbers of additional air parcels created.

C3.2: 'Online' and 'offline' approaches.

Zhang et al (2012) note that online-coupled models that simulate feedbacks between meteorological variables and chemical species may provide more accurate representations of the real atmosphere for regulatory applications and can be more accurately applied to simulate chemistry-climate feedbacks over a longer period of time. Tuccella et al (2012) similarly note that decoupling between the meteorological and chemical model leads to a loss of information, because of the physical and chemical processes occurring on a time scale smaller than the output time step of the meteorological model (typically 1 hour). In addition, Grell et al. (2004) showed that most of the model variability in vertical velocity is attributable to higher frequency motions (period less than 10 minutes), yielding to much larger errors in vertical mass distribution in offline models with respect to "online" models [figure 3a of that paper]. Examples of this interaction also include consideration of temperature increases in future emission profile scenarios.

Table C.2, taken from Backlanov et al (2013), illustrates the feedbacks between particulate matter, 'chemistry' and meteorological effects in online models.

Meteorological effects on chemistry		
Meteorological parameter	**Effect on**	**Model variables**
temperature	reaction rates	T, rate coefficients
	biogenic emissions	BVOC emission rates
	aerosol dynamics	Aerosol number size distribution, Scattering and absorption coefficients PM mass and composition
temperature and humidity	aerosol formation gas/aerosol partitioning	gas phase SO2, HNO3, NH3, particulate NO3, SO4, NH4, VOCs, SOA
	aerosol water uptake aerosol solid/liquid phase transition	PM size distributions, extinction coefficient Aerosol water content
Shortwave radiation	Photolysis rates	JNO2, JO1D, etc
Photosynthetic active radiation	Biogenic emissions	SW radiation BVOC emissions
Cloud liquid water and precipitation	Wet scavenging of gases and particulates	Wet deposition (HSO3, SO4, NO3, NH4, Hg) precipitation (rain/total precip) cloud liq water
	Wet phase chemistry, e.g. sulphate production	SO2, H2SO4, SO4 in cloud and rainwater
	Aerosol dynamics (activation, coagulation) Aerosol cloud processing	aerosol mass and number size distributions
Wind speed	transport of gases and aerosols vs offline coupling interval, transport in mesoscale flows	U, V (W)
	emissions of dust, salt salt and pollen	U, V dust, sea salt and pollen emission rates
boundary layer parameters	turbulent and convective mixing of gases and aerosols, intrusion from free troposphere, dry deposition at surface	T, Q, TKE, surface fluxes (latent/sensible heat, SW and LW radiation) deposition velocities, dry deposition flux (O3, HNO3, NH3)
water vapour	OH radicals	Q, OH, HO2, O3

Table C.2 - Adapted from Baklanov et al (2013), a list of meterological effects on chemistry within the air-quality framework. Associated model vriables are also listed.
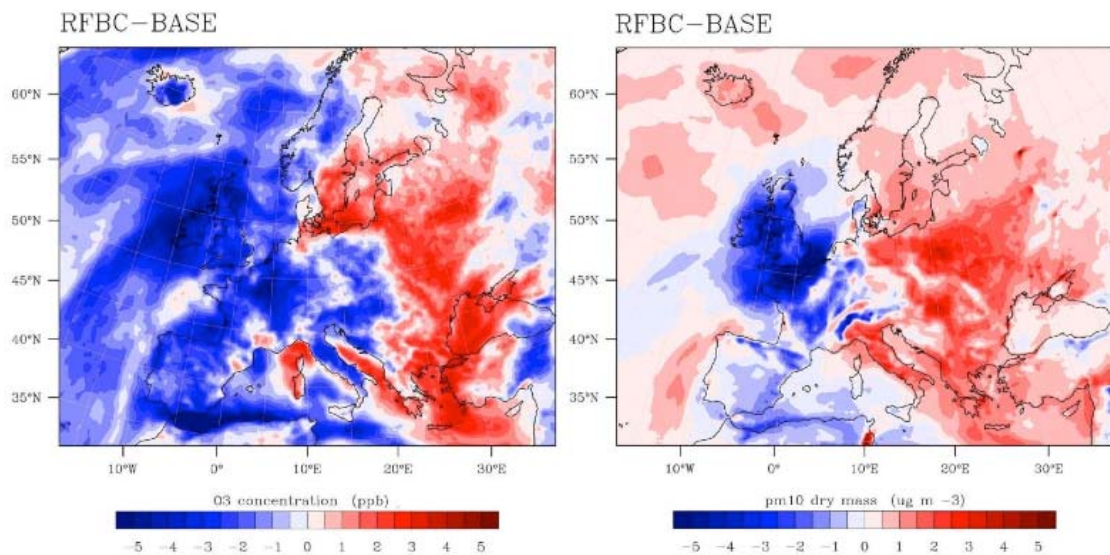
Figure C.1. Differences in Ozone (left) and PM$_{10}$ (right) concentrations in July 2006 between two WRF-CHEM simulations. The BASE simulation does not consider interactions between aerosols and meteorology, whereas the other does. Copied from Forkel et al (2012).

C3.3: Scales

Grid resolution has been viewed as a model uncertainty that is limited by the availability of computational resources (Garcia-Menendez and Odman 2011). Dispersion models on the local scale can be designed for specific applications (e.g. ADMS-Airport, ADMS-Road) but

often account for detailed chemical or physical processes leading to $PM_{2.5}$ formation. Determining source contributions then becomes dependent on the quality of the input boundary conditions or measurement network to which it is applied. As Williams et al (2011) reports, for the important process of assessing policy options to achieve future compliance or to attain other policy targets, reliance on a calibrated model must be considered scientifically questionable and open to criticism, as it introduces potentially significant uncertainties into future projections. The same authors then also go on to state that the use of deterministic models with full (or as full as practicable) descriptions of physics and chemistry would add confidence to the future projections. Advantages of local models are noted to be that they consider more detailed local dispersion (e.g. ADMS), allowing concentrations at individual receptor locations to be predicted. However, as regional models can incorporate more sources and transformation mechanisms than is the case with urban or local models, the results from regional models are often used to initialize urban or local models (e.g. PCM used on local scales, ADMS).

Savage et al (2013) showed that, based on comparisons with yearly data, the AQUm model at 12km resolution tends to under predict NO_2 with a mean negative bias of $-6/1$ µg m^{-3}, though potential for overestimation by the measurement technique (chemiluminescence) is also noted as a factor. The authors note that AQUM does not adequately resolve the sources of primary NO and NO2 emission (typically dominated by road trans-port and combustion at point sources) and the pattern of over-estimation of NO_x at rural sites and under-estimation at urban ones is consistent with the model resolution being too coarse to properly resolve sources of NO_x. Supplementing the discussion in section C3.1, Savage et al (2013) note that in an Eulerian model, primary emissions are instantaneously spread over an entire grid box, thus giving apparently lower concentrations close to source regions than occur in reality.

Some general non-UK based studies have also attempted to identify the resolution required to assess predictive capability of existing air-quality models. Whilst the above text discusses the benefits of more complex models, typically Eularian based with coarser grid sizes, Garcia-Menendez and Odman (2011) state that a large grid size can lead to unacceptable errors for many pollutants formed via nonlinear chemical reactions. Furthermore the same authors state that insufficient grid resolution limits the ability to perform accurate exposure assessments. Some studies have noted that gas-phase chemistry can be affected by model resolution, since chemical reactions in subgrid- scale plumes are unlikely to be accurately represented (Stroud et al 2011). This dependence has led to the development of a number of plume-in-grid approaches to represent chemistry in subgrid-scale plumes (e.g., Kumar and Russell, 1996; Karamchandani et al., 2006). For example, Cohan et al. (2006) suggested that to predict regional ozone patterns, the grid spacing used should be on the order of 12 km or less to represent ozone production and loss processes accurately with subsequent impacts on the formation of SIA (Karamchandani et al. (2002, 2006). Stroud et al (2011) found that accurate simulation of OA in urban and large industrial plumes requires the use of a high-resolution model (2.5 km nested grid) in order to represent urban primary organic aerosol emissions, urban VOC emissions, and the secondary organic aerosol production rates properly. They note that the positive feedback between the secondary organic aerosol production rate and existing organic mass concentration is also represented more accurately with the highest-resolution model and suggest that not being able to capture these finer-scale features may partly explain the consistent negative bias reported in the literature when urban-scale organic aerosol evaluations are made using coarser-scale chemical transport models. Pay et al (2012) note that higher horizontal resolution and the detailed disaggregation techniques of the CALIOPE-EU system (based on EMEP emissions inventory and coupled WRF-CMAQ model) may be responsible for the better scores obtained in 'primary' SIA precursor gasses compared with other EU studies (SO_2, HNO_3 and NH_3). They note that horizontal resolution may impact urban and industrial areas at a higher degree than rural areas and that the higher horizontal resolution of the CALIOPE-EU system

may be responsible for the better comparisons obtained for NO_2 and SO_2. They also note that it is reasonable to think that a detailed emission inventory at a finer horizontal resolution could further improve the air quality model performances. Similarly, the AQEG (2012) report notes a spatial grid resolution of 18 km x 18 km was not optimum for simulating pollutants generated on smaller, local scales when comparing CMAQ [Hertfordshire] predictions of $PM_{2.5}$ with observations at Harwell and London. Pay et al (2012) note that another relevant issue that arises from model comparisons is the impact of vertical resolution. Models presented in that evaluation ranged from 3 to 20 vertical layers.

Wainright et al (2012) note how little attention has been paid to the effects of model spatial resolution on SOA predictions. Using a two product SOA formation model in the GEOS-CHEM framework, they found that predictions of organic aerosol concentrations at Whistler were greatly dependent on the resolution during the 'Whistler Aerosol and Cloud Study' (WACS 2010). They note that the increase in SOA with resolution is largely due to sub-grid variability of organic aerosol (OA) that leads to an increase in the partitioning of secondary organic matter to the aerosol phase at higher resolutions, whilst still under-predicting relative to measurements. In addition, they found that SOA concentrations were further increased because the shift of secondary organic gases to SOA at higher resolutions increased the lifetime of secondary organic matter (secondary organic gases have a shorter deposition lifetime than SOA in the model). Similarly, Stroud et al. (2011), using a nested version of Environment Canada's AURAMS model (42- to- 15- to- 2.5-km nested grid spacing), explored the effects of spatial resolution on SOA predictions in a regional model of a populated area in southern Ontario, Canada. They found that when higher spatial resolutions were used, the predicted SOA production rates and subsequent temporal correlation were found to be more accurate.

Niemeier and Zheng (2004) notes the ability to model air quality dispersion at increasingly smaller resolutions requires a concomitant improvement in the resolution of the gridded source emissions used as input to these models. Power et al. (1998) used a 1 × 1 km resolution to estimate emissions over the large industrial areas of North Cheshire, Merseyside, and Greater Manchester in the U.K. They found that very fine resolution was important because of the presence of strong localized emission sources and rapid variation in the meteorological conditions in some parts of the modeling domain.

Pay et al (2012) also note that it is expected that models with higher vertical resolution covering the planetary boundary layer are able to simulate the vertical mixing better, especially for NH_3 which can have very large vertical gradients close to the ground, both decreasing and increasing with height (Schaap et al., 2004a). Walker et al (2012) compared predicted $PM_{2.5}$ using GEOS-CHEM, using the size independent ISOROPIA model, with a network of measured inorganic species over the US at 2 x 2.5° resolution with 47 vertical layers. They found that the offline GEOS-5 meteorological fields displayed unrealistic low mixed layer depths at night, causing the GEO5 GEOS-CHEM simulations to predict an artificially large build up of aerosols at night and corresponding high biases in predicted daily and monthly averages. They also further state that nitrate aerosols are particularly sensitive to mixed layer depths, owing to the gas-particle equilibrium, resulting in a sensitivity of predicted SIA to unresolved topography.

Techniques using multiple grid sizes are called nested grid or multiscale modeling techniques. Of the models listed above using this technique, CMAQ-Urban is one. Similarly, Isakov et al (2009) presented a methodology to demonstrate the linkage of regional- and local-scale air quality models (in that case CMAQ and AEROMOD for US based studies) with human exposure models. In that study the authors note that a hybrid approach is the most computationally efficient way to combine regional-scale photochemical grid and local-scale plume dispersion models to provide the total ambient air pollutant concentrations from nearby and distant sources (Isakov et al 2009). Because dispersion models are less

resource intensive than regional models, a hybrid methodology can be used to study the sensitivity of local concentration to changes in model parameters. This constitutes a clear advantage of the hybrid approach, because the estimation of local concentration variability using a photochemical grid model at higher resolution would be a computationally resource-intensive task, especially when annual concentrations over larger urban areas are needed (Isakov et al 2009). A different approach to achieve local resolution involves using dynamic adaptive grids (Garcia-Menendez and Odman 2011). Recently, some of these techniques have been applied to existing air quality models (Lagzi et al 2009) including CMAQ (Srivastava et al 2000).

C3.4: Effects of gas phase representation on secondary aerosol prediction

In the following section a selection of studies evaluating the performance of gas phase mechanisms often employed in the range of models are dicussed. Whilst not exhaustive, it reinforces the need for evaluating gas phase model performance on $PM_{2.5}$ predictive capability.

Pay et al (2012) note that the different performance of models in reproducing SIA and gaseous precursors over Europe are related with the chemical mechanism used and the assumption of thermodynamic equilibrium between the gaseous and condensed phase. For example, they state that many of the European models used the CB-IV mechanism that was updated to the CB05 mechanism, Yu et al (2010) noting the latter performing better for predictions of HNO_3 and SO_2. As Pay et al (2012) note, since NO_3 formation tends to be HNO_3 limited over continental Europe rather than NH_3 limited, this is important. The same authors note that modeled NH_3 did not compare well with observations, underestimating by roughly 100% in the summer. Similarly, Kim et al (2011) found that differences in predicted SIA mass loadings result from differences in the oxidant concentrations of OH, O_3 and NO_3.

Zhang et al (2012) used WRF-Chem MADRID to assess the impact of choosing one of three gas phase mechanisms (CBM-Z, CB05 and SAPRC-99) on predicted gas phase oxidant and $PM_{2.5}$ levels (both SIA and SOA). Different gas-phase mechanisms lead to different predictions of mass concentrations of O_3 (up to 5 ppb), $PM_{2.5}$ (up to 0.5 μgm^{-3}), secondary inorganic $PM_{2.5}$ species (up to 1.1 μgm^{-3}) and organic PM (up to 1.8 μgm^{-3}). They note this illustrates the important impact of gas-phase mechanisms on chemical and aerosol predictions, their subsequent effects on meteorological predictions, and a need for an accurate representation of such feedbacks through various atmospheric processes in the model. Other interesting observations from that study include a more important role of organic chemistry in dictating the nitrogen budget in SAPRC-99 and CB05 than in CBM-Z. The differences in HNO_3 predictions were found to be largely due to a different reaction rate for conversions of NO_2 and N_2O_5 to HNO_3 used in these mechanisms. Tuccella et al (2012) note that the simulated SOA to total organic PM has values of 5-40% using WRF-CHEM compared with 50-80% observed. They suggest that one of the most probable reasons for the underestimation is that the RADM2 chemical mechanism is 'outdated' in the treatment of SOA because it does not include the oxidation of biogenic monoterpenes and has a limited treatment of anthropogenic VOC oxidation.

Derwent et al (2009) found that the CBM gas phase model, coupled with the PTM model, consistently underestimated NH_3 and NO_x observations based at the rural site of Harwell UK. The authors did however attribute some of this discrepancy from the inability of representing surface observations using a boundary layer-averaged model. For example, the observed mean monthly NO_x concentration was 5.3 ppb, compared with the model value of 3.3 ppb. For NH_3, the annual mean model NH_3 concentration was 0.4ppb compared with 2.4 ppb from observations. The available observations showed a clear summertime maximum that was not evident in the model results. The model underestimation was greatest during March and April when it approached a factor of 11 and was least during November and January when it was about a factor of 3.

C3.5: PM$_{2.5}$ Modelling studies

This section addresses the performance of available models for predicting PM$_{2.5}$ in the UK, supplementing existing Defra reports with additional international and UK studies..

In a summary of the AQMEII initiative over Europe and North America, Sollazo et al (2012) note how although PM$_{2.5}$ was found to be much better estimated by the models than PM$_{10}$, no model was found to consistently match the observations for all locations throughout the entire year. Of the models used for UK purposes, both WRF-CHEM (using the MADE inorganic model; SORGAM for the organic) and WRF-CMAQ [v4.7] (ISORROPIA for inorganic; organic model described by Foley et al 2010) were employed. PM$_{2.5}$ and PM$_{10}$ were collected by the AirBase (European AQ database; see http://acm.eionet.europa.eu/databases/airbase/) network and the EMEP (European Monitoring and Evaluation Programme; see http://www.emep.int/) network. A total of 863 stations with valid data for 2006 were made available in the ENSEMBLE database for Europe, which includes urban, sub-urban and rural stations. They found model skill in estimating some of the major chemical components of PM$_{2.5}$ (i.e., SO$_4$, NO$_3$, NH$_4$ and EC) was found to be more homogenous than for total PM$_{2.5}$ mass. This trend was used to suggest that while the models do relatively well in simulating the inorganic aerosol species, large uncertainty remains in the simulation of other components of PM$_{2.5}$ (e.g., secondary organic aerosols (Annex A) and unspeciated PM$_{2.5}$). As the AQEG (2012) report notes, there remain many challenges involved in evaluating models that predict PM$_{2.5}$, the summary of the AQMEII inititiave mentioned earlier a recent thorough intercomparison. An important contribution to this are availability of large datasets from which an evaluation can take place (Galmarini and Rao, 2011) (see Annex B). An indication of the effect of future changes in emissions on UK concentrations can be derived from perturbation studies of the emissions of both SIA and SOA precursors. UK studies are supplemented by non-UK ones to address aspects absent from the former. For SIA, relatively well-known responses of the aerosol thermodynamic frameworks can be used to verify the sensitivity studies performed. For example, Lovblad et al. (2004) investigated trends of the emissions of sulfur dioxide, nitrogen oxides and ammonia in Europe and the corresponding response of the major inorganic fine particulate components over the past 2 decades. They observed that between 1980 and 2000, SO$_2$ emissions decreased approximately 70 % while sulfate concentrations decreased around 50 %. Emissions of nitrogen oxides and ammonia also decreased 25 % and 20 % respectively with a non-linear response of ammonium nitrate. The more complex models also account for changes in oxidant levels occurring from both SIA and SOA precursors emissions.

As noted by Owen et al (2000), the family of ADMS models have been evaluated using a number of studies. Bennet and Hunter (1997) assessed the ability to predict dispersion of aerosol generated from a power station using Lidar backscatter measurements. Whilst the measurements could not give an absolute concentration measure, the measured profile of particulate dispersion was found to be good, with high sensitivities to the meteorological data used. The AQEG (2012) report on the performance of ADMS-Urban taken as part of the model intercomparison exercise study described by Carslaw et al (2011) for London 2008. For roadside emissions, the London Atmospheric Emission Inventory was used, other sources attributed to specific fractions of PM$_{10}$ emissions (AQEG 2005). Comparisons with data at background and roadside locations show that whilst some comparisons were reasonable, model loadings often underpredicted by ~5 μgm^{-3}for high monitored values (> 15 μgm^{-3}).

C3.5.1: Secondary Inorganic Aerosol:

Beddows et al (2012) compared predictions from an enhanced version of the UK-PTM for speciated inorganic PM$_{10}$. They found that the model tends to correct for previous under-

predictions of sulphate and nitrate. In general the model predicted sulphate and nitrate loadings within the 1:2 and 2:1 boundary. The 'improved' model decreased discrepancies between modelled and measured PM_{10} nitrate and sulphate from 56% to within 1.5% and 3.3% respectively. Predictions for particulate chloride were not as good, although multiple factors were used to explain this discrepancy including uncertainties in trajectory values of higher wind speeds.

Savage et al (2013) note the performance of AQUM in predicting speciated $PM_{2.5}$. Without a detailed analysis the authors compare measured speciated data of SIA at the Harwell site between 13-27 of April 2011. The model seems to replicate the measured trend well though there are periods of over and under estimations. However, the authors do note that the CLASSIC aerosol scheme treats the sulphur chemistry in a separate module to the rest of the gas phase chemistry which makes it difficult to assess from the emissions perspective and introduces the potential for inconsistencies in the chemical mechanism. The authors reference future use of the more consistent UKCA-GLOMAP-mode scheme in which the sulphur chemistry is an intrinsic part of the chemical mechanism and emissions of all gases and aerosols are dealt with in the same framework. The analysis of global model simulations using both schemes shows that UKCA-GLOMAP-mode compares better than CLASSIC against a global aerosol reanalysis and aerosol ground-based observations (Bellouin et al., 2013).

The AQEG (2012) report evaluations of WRF-CMAQ predictions for 2008 at two rural, six suburban and 21 urban background sites. They note that the model generally underestimates hourly $PM_{2.5}$ mass. Looking at speciated data, model results were found to be quite good for $PM_{2.5}$ particulate nitrate when compared with measurements at North Kensington, whilst underestimating PM_{10} nitrate by an order of magnitude. Speciated predictions were also compared against measurements from the AURN and London Air Quality Network using CMAQ 4.7. In that study two nesting levels from 81km grid over Europe to 9km grid over the UK was used, emissions from the EMEP, NAEI and EPER register processed and coupled with the CB05 chemical mechanism. Whilst focusing mainly on PM_{10}, results show that the model underestimated coarse levels of NO_3 and Cl^-, the latter improving at coastal sites. For daily SO_4^{2-} PM_{10} predictions in North Kensington, the model predicted 'non episodic' concentrations of the observations well at both Harwell and North Kensington, whereas some spikes were undrepredicted by ~8 μgm^{-3}. This discrepancy was attributed to potential errors in the shipping emission inventories, which can differ by a factor of two between the TNO and EMEP databases.

Zhang et al (2010) showed that WRF-CHEM exhibits a bias in $PM_{2.5}$ over continental US regions of -7% to +30% in January and 8-30% in July when coupling the MOSAIC aerosol model with the CBM-Z gas-phase mechanism. Tuccella et al (2012) reviewed the capability of WRF-CHEM to replicate $PM_{2.5}$ over Europe using the MADE/SORGAM aerosol model and the RADM2 gas phase mechanism comparing with the EMEP surface stations in February 2007. They note that sulphate is underestimated by a factor of 2, while nitrate and ammonia are both overestimated by a factor of 2, the latter linked to performance of the former through simple particulate thermodynamic considerations. Sensitivity analysis indicated that the main reason for the under-estimation of sulphate was the missing aqueous-phase oxidation of SO_2 by H_2O_2 and O_3. Results however were comparable with other models reviewed by Loon et al (2007). In addition to the main identified process that could account for the predicted discrepancy, they also discuss potential effects of boundary layer dynamics with shallow mixing at night, with most sources of SOx above the night-time PBL (Tuccella et al 2012). In addition, as 30km grid scales was used, additional errors could be attributable to resolution effects on both meterological and chemical processes as discussed in section C3.3. The effect of aqueous phase processing and emission (vertical) resolution has been noted elsewhere. Aan de Brugh et al (2011) estimated that 45% of SO_2 aqueous oxidation to sulphate over Europe happens within the boundary layer and may thus have an important

impact on surface concentrations. Tuccella et al (2012) prescribed 5% of SO_2 emissions in WRF-CHEM go straight to sulphate aerosol. In that study they didn't have cloud processing in their model as MADE/SORGAM doesn't include it so they had to use a 5% fractionation of emissions, and then assessed the sensitivity of parameterisations for simulating cloud processing. Similarly, as documented in the 2002 simulation report for GEOS-CHEM (http://www.gaepd.org/Files_PDF/plans/sip/Appendix_I.1_GEOSchem_evaluation.pdf), anthropogenic sulphur is emitted as SO_2 except for a small fraction as sulphate, 5% in Europe and 3% elsewhere. For CMAQ, Yu et al (2003) (http://www.ecd.bnl.gov/steve/pubs/MomentSulfateEasternUS.jgr.pdf) note that the emission of gas phase SO_2 and aerosol sulphate are prescribed based on the 1990 National Emissions Trends (NET90) Inventory where 1.2% of SO_2 is assumed to partition straight to sulphate. It is unclear whether this is used in the UK applications of CMAQ.

C3.5.1.1: Emission scenario studies:

In the AQEG (2012) report, both the PCM and UKIAM models were used to predict future concentrations calculated for the year 2020. Both models show the same general patterns of higher $PM_{2.5}$ towards the southeast. Predictions from both the PCM and UKIAM show same general pattern of higher $PM_{2.5}$ SIA towards the southeast influenced by transboundary contributions from continental Europe and shipping in the North Sea, decreasing towards Scotland. The UKIAM model however generally predicted lower concentrations that the PCM model. This was attributed to the fact that UKIAM scenarios used emissions from countries outside the UK in 2020 whilst also allowing for the MARPOL convention leading to reductions of the order of 85% in SO_2 emissions from the North Sea. The reductions in $PM_{2.5}$ SIA from the UKIAM model were calculated to be 33% compared with 15% from the PCM model. They also note that NO_3 is the biggest component and will dominate in the future with decreasing SO_2 emissions. As noted in section C1.4.9 the PCM model uses an empirical approach to SIA and interpolates between measurements. It is therefore subject to uncertainties surrounding inter-annual variations in measurements influenced by meteorology in different years, causing problems in future projections (AQEG, 2012). UKIAM, while using output from more complex models to derive source-receptor relationships, relies on assumed linear relationships between pollutants and predicted $PM_{2.5}$. However, numerous studies in the literature have highlighted the non-linear relationship between $PM_{2.5}$ SIA and precursor emissions. The NAME model was used by Redington et al (2009) to study the sensitivity of SIA to changes in ammonia emissions. They used $PM_{2.5}$ data taken from the rural observation site at Harwell UK from April 2003 and increased/decreased ammonia emissions by 30%. They found that ammonium concentrations required big change in ammonia emissions in order to be reduced significantly. A 30% reduction in ammonia emissions resulted in very little change of nitrate aerosol as did a 30% increase. Dividing the ammonia emissions by a factor of ten did produce a dramatic reduction, with the production of ammonium nitrate being limited by availability of ammonia. Conversely multiplying the ammonia emissions by ten did not have such a significant effect. Once ammonia is in excess, increasing its concentration does not result in production of more nitrate aerosol. Sulphate aerosol production was found to be very dependent on ammonia due to its role in balancing acidity in the aqueous phase in cloud simulations. They found that correct prediction of the acidity is limited firstly by the set of species modelled in the chemistry scheme and secondly by the accuracy of their modelled atmospheric concentrations. In all, they found that a 30% increase or decrease in ammonia could lead to change in particulate sulphate of over 1 $\mu g.m^{-3}$. Derwent et al (2009) ran a series of sensitivity tests using the PTM by reducing VOC, NO_x, NH_3, CO and SO_2, by 30% across-the-board, relative to the base case emissions. They found that sulphate mass concentrations responded linearly with SO_2 emissions and increased slightly as NO_x emissions decrease. The authors attribute this to a rise in OH radical concentrations as NO_x levels are reduced, increasing the homogeneous oxidation rate of SO_2 to sulphate. They also found that sulphate decreases as VOC emissions decrease because decreasing VOC

emissions inhibit the formation of photochemical oxidants, thereby inhibiting the photochemical conversion of SO_2 to sulphate. Conversely, they found a non-linear relationship between NO_3^- and NO_x emissions because as NO_x emissions decrease, OH radical concentrations increase, increasing the conversion rate of NO_x to gaseous nitric acid and partially counteracting for the decrease in NO_x concentrations. In contrast, the fine nitrate is linear in NH_3 emissions (Derwent et al 2009). When comparing contributions from both the UK and EU, in this study the authors attribute a larger sensitivity of $PM_{2.5}$ NO_3 to EU emissions reductions in NO_x and NH_3 emissions.

The AQEG (2012) report reported the use of the AEA version of WRF-CMAQ at 12km resolution to investigate sensitivity of PM to a reduction in SO_2, NO_x and NH_3 for four months in 2006. Focusing on SIA $PM_{2.5}$ (NO_3^-, SO_4^{2-}, Cl^-, Na^+), the study found a reduction in SO_2 emissions has the largest overall effect on PM loadings with the response non-linear and varying with season and location. In this study, reducing NO_x and NH_3 had the smallest effects on PM loadings. In apparent contradiction, using the PTM model, Derwent et al (2009) found that, for a 30% reduction in precursor emissions, the reduction in NH_3 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, VOC and CO emissions). In that study, the 'one parameter at a time' sensitivity method discussed in section C2 was used. Obviously, non-linearities and interactions between parameter reductions could not be evaluated, but no consistent conclusions could be drawn from the two studies. Harrison et al (2013) used the enhanced PTM model, described by Beddows et al (2012) to further study the effect of reducing primary SIA precursors on SIA mass loadings. They found that abatement in SO_2 emissions increased the contribution from particulate nitrate and that a projected reduction in SO_2, NO_x and NH_3 of 64%, 75% and 96% led to a reduction of 2 μgm^{-3} of SIA. They noted the non-linear interactions between a reduced fall in particulate nitrate from reduced NO_x emissions caused by an abatement in SO_2 emissions. The authors conclude that despite substantial reductions in both NO_x and SO_2 (by 25% and 36% respectively), the reduction in SIA is almost wholly due to a fall in the sulphate concentration. Nitrate, which already exceeds sulphate in the southern UK, and becomes dominant under episodic conditions (Yin and Harrison, 2008), responded little to the reduction in NO_x, reflecting the low sensitivity of nitrate to NO_x emission reductions and the effect of decreasing SO_2 emissions in increasing nitrate. This is reflected in the very small changes in nitrate in the UK in recent years, despite substantial reduction in NO_x emissions (Harrison et al 2013). There are noted modelled influences from transboundary sources. For example, The UKIAM model, which uses both the EMEP (covering EU) and NAME (covering UK) to derive source-receptor relationships, produced a 20% lower population-weighted mean concentration of SIA when just using the NAME relationships (AQEG 2012).

Outside of the UK, Pay et al (2012) attempted to characterize SIA formation regimes and probe the sensitivity of SIA to gaseous precursors using the CALIOPE air quality modelling system (a combination of WRF-ARW, and CMAQ v4.5) and the EMEP European database for the year 2004. They note that continental European SIA tend to be NO_x limited for nitrate formation, suggesting regulatory strategies should focus on reductions in NO_x rather than NH_3. Some general trends are noted in that study based on model-measurement comparisons: (1) The high levels of SO_4^{2-} in eastern Europe depletes the available gas-phase NH_3 so that little NH_4NO_3 can form in this region due to the low NH_3 levels; (2) the higher ambient temperature in the south favors the gas phase prevalence of 3; and (3) the high humidity conditions in the north which stabilize NH_4NO_3 even during the summer. It is clear that such conditions will not generally apply to the UK atmosphere and therefore unclear that conclusions drawn from this study are directly applicable to UK conditions. Megaritis et al (2013) used the PMCAMx-2008 model to quantify the changes in predicted $PM_{2.5}$ over Europe in response to different emission reductions as well as a temperature increase. They found that a reduction of 50% in NH_3 emissions seems to be the most effective control strategy for reducing $PM_{2.5}$, in both periods, resulting in a decrease of $PM_{2.5}$ up to 5.1 $\mu g\ m^{-3}$

and 1.8 µg m^{-3} (5.5% and 4% on average) during summer and winter respectively, mainly due to reduction of ammonium nitrate (NH$_4$NO$_3$)(20% on average in both periods). The reduction of SO$_2$ emissions by 50% significantly decreases PM$_{2.5}$ in both periods. The reduction of NO$_x$ emissions by 50% reduced PM$_{2.5}$ (up to 3.4 µg m^{-3}) during the summer period, due to a decrease of NH$_4$NO$_3$. Interestingly, the 50% reduction in NO$_x$ lead to an increase in PM$_{2.5}$ during the winter period as more oxidants become available to react with SO$_2$ and VOCs. An investigation into an increase in temperature of 5K decreased the levels of PM$_{2.5}$ mainly due to a decrease in NH$_4$NO$_3$ of 18% during the summer.

C3.5.2: Secondary Organic Aerosol:

As already noted in section A, there are a large number of processes that can affect mass loadings, and subsequent composition, of SOA. It is widely known that accurately predicting the atmospheric concentration of SOA remains a significant challenge. A number of comparisons between models and ambient measurements have shown that mechanistic models systematically underpredict, often by orders of magnitude, the measured loading of SOA. For example, this includes including polluted urban air (Volkamer et al., 2006), the outflow of pollution sources (de Gouw et al., 2005; Johnson et al., 2006). The study of Johnson et al (2006) used the PTM to simulate measured concentrations of SOA during the TORCH 2003 campaign. They found that the partitioning coefficients had to be scaled by a factor of 500 or so, and include a persistent background of organic aerosol, to match measured levels of organic PM during the TORCH campaign 2003. The AQEG (2012) report notes that the CMAQ model (KCL) failed to predict SOA by a large margin at the North Kensington site. Using a prescribed ratio of primary to secondary contributions using an EC tracer approach (Jones and harrison 2006), the modelled and measured averages were 0.04 and 1.3 µg m^{-3} respectively. Without a detailed analysis or sensitivity study it is difficult to ascertain what this could be attributable too (see section C2).

Derwent et al (2009) used a version of the PTM to simulate contributions to observed PM in relation to UK observations in 2006 at Harwell, UK. The SOA module used was very basic, having two components involving the oxidation of biogenic- derived a-pinene by hydroxyl OH, nitrate NO$_3$ and ozone and the oxidation of man-made aromatic compounds by OH. The organic carbonaceous (OC) observations from the EMEP EC- OC Campaign (Yttri et al., 2007) were used to examine PTM model performance with regards to total predicted OA mass. Observations were converted from an (OC) to an organic matter (OM) basis using a factor of 1.5 based on Jones and Harrison (2005), giving a wintertime OM concentration of 2.5 µg m^{-3} and a summertime average of 2.1 µg m^{-3}. In comparison, the model indicated winter- time and summertime mean concentrations of 2.0 and 3.2 µg m^{-3}, respectively. Whilst the authors note a lack of adequate observations precluded a satisfactory evaluation of model performance, the model results appear to be of a similar order of magnitude to the observations, particularly during wintertime. It is not possible to extract the overall capability for predicting SOA in such studies.

Bergstrom et al (2012) used a 4 bin volatility basis set representation for SOA formation in the EMEP model over Europe. Mass yields for high and low NO$_x$ cases were constrained to alkanes, alkenes, aromatics, isoprene and terpene from chamber studies. Assuming all of the secondary material partitions to the PM$_{2.5}$ fraction, four versions of the model was setup for use with the VBS scheme, all assuming a background concentration of 1.0 µg m^{-3}. The four schemes changed assumptions regarding the partitioning and aging of both primary and secondary organic material. Temperature dependencies were accounted for by prescribing a constant enthalpy of vaporisation across all volatility bins, despite the variability with volatility described by Epstein et al (2010). Model simulations were run over 2002-2007. Some general observations include the result that simple SVBS based models can give reasonably good results for summer OA but no model permutation could produce observed levels of OA in winter in Europe. There was large variability between sites and much less

data for $PM_{2.5}$ than PM_{10} made conclusions difficult. They also found that the volatility of primary emissions was an important issues, as was the parameterised aging of organic aerosol. For example, when the primary organic matter was considered involatile and no aging was accounted for, the predicted $PM_{2.5}$ concentrations were a factor of 3 lower than AMS measurements in Switzerland. Including volatile primary emissions and aging improved predictions to lower than 27% than the AMS results. The authors conclude that major model uncertainties are related to assumed biogenic emission profiles in the summer and further work is required to constrain particulate volatility and background concentrations. They found it difficult to chose a 'best model' from the permutations listed and that improvements in emissions inventories are needed. Additional studies have assessed the applicability of the VBS representation over the US. Fountoukis et al (2011) also demonstrated the use of the VBS approach over Europe using the PMCAMx-2008 model and focusing on PM1. In that study the VBS approached used was based on the assumption that both primary and secondary material was semivolatile. They found that the model produced more than 94% of the dialy average data and 87% of the hourly averaged data within a factor of 2 for PM1 OA when compared with ground and airborne AMS measurements. Baek et al (2011) used CMAQ and added aged aerosol formation from the biogenic and anthropogenic precursors as a new SOA formation mechanism coupled with a VBS approach. Overall the modified SOA mechanism significantly improved OC simulation performance in summer in the historic episodes modeled, as well as the total and organic $PM_{2.5}$ predictions in an operational forecasting system. Aerosol yields with aged aerosol were closely in line with measurements supporting that increases due to aged aerosol is feasible. They noted that comparison of results with CAMQ version 4.7 simulations indicated that a significant source of organic aerosol is still missing and that the mechanism for organic aerosol production from multigenerational oxidations of SVOCs could fill the gap. Other possibilities include the potential for missing intermediate VOC, and aging as well as increased oxidation, recondensation and emissions of primary organic aerosols.

Comparing predictions from the WRF-Chem SAPRC-99-VBS-MOSAIC model, Shrivastava et al. (2011) found reasonable comparison with both ground and aircraft measurements using 9-species and a simplified 2-species VBS predictions, with mass of total, primary, secondary and biomass burning OA fractions all comparable in magnitude. Oxygen-to-carbon (O:C) ratio predictions from both approaches agree within 25%. Model sensitivity to amount of anthropogenic semi-volatile and intermediate volatility (S/IVOC) precursor emissions was examined by doubling the default emissions. Both the emission cases significantly underpredict primary organic aerosols in the city center and along aircraft flight transects. Secondary organic aerosols are predicted reasonably well along flight tracks surrounding the city, but were consistently overpredicted downwind of the city. Also, O:C ratio predictions were significantly improved compared to prior studies by adding 15% oxygen mass per generation of oxidation; however, all modelling cases still underpredict these ratios downwind in comparison to measurements, suggesting a need to further improve SOA formation parameterisation.

Predictions by Ahmadov et al. (2012) from an alternative modal implementation in WRF-Chem RACM-MADE-VBS were carried out for August–September 2006 and OA concentrations were compared against ground and aircraft data from the TexAQS-2006 in the southern US. Again, the VBS was shown to significantly improve OA prediction over an explicit scheme in that it substantially increased OA mass, improving both correlations and bias. Addition of the multigenerational VOC oxidation drastically improves model performance. Several key uncertainties were identified in perturbation simulations (dry deposition of VOC oxidation products). Biogenic SOA was found to be the dominant OA component for much of the nonurban US. As in noted in Ahmadov et al. (2012), the standard WRF-Chem with MADE-SORGAM aerosol module predicts OA almost entirely as POA due to very little SOA formation from the Schell et al. (2001) formulation. This default model configuration without inclusion of an empirical SOA treatment (VBS) severely

underestimates the OC concentrations in the southeastern US throughout the day regardless the model resolution or the PBL scheme. This is entirely consistent with the prevailing picture of underprediction using "bottom-up" SOA schemes. Similarly, the WRF-Chem CRIMech-PD-FiTE-MOSAIC configuration predicts little SOA, with too little carbon flux from the gaseous intermediates to the condensed phase. A CRIMech-VBS-MOSAIC is under construction to circumvent this.

C3.5.2.1: Emission scenario studies:

Because precursor emission regulations generally only target anthropogenic emissions, high biogenic emissions are not controllable and it is essential to understand how they may increase difficulties in meeting air quality standards via their interactions with anthropogenic species (Startlet et al 2012). Hoyle et al. (2011) detailed the mechanisms through which the anthropogenic emissions enhance the formation of biogenic SOA: anthropogenic emissions impact the concentration of oxidants (O_3, OH, NO_3), which oxidize BVOC to form semi-volatile species, and anthropogenic primary organic aerosols may serve as an absorbing medium favoring their condensation.

For UK studies, Utembe et al (2009) used the PTM coupled with the CRI-Mech mechanism and an 'optimised' SOA module based on the earlier study of Johnson et al (2006) to assess the effect of reducing anthropogenic VOC emissions. Simulating mass concentrations of SOA for the conditions of the TORCH-2003 campaign in the south-east UK in late July and August 2003, the authors found that detailed composition of the simulated SOA depends on the relative contributions of species derived from anthropogenic and biogenic precursors, with the degradation of the latter (predominantly a- and b-pinene) found to generate a progressively more condensable distribution of product species (containing increasing contributions from multifunctional hydroperoxides and acids) as the level of NO_x decreases. The resultant concentration of biogenic SOA generated in the lowest anthropogenic pollution scenario was found to be a factor of three greater than the base case scenario. Looking at different scenarios however, in some cases, reducing anthropogenic emissions by a factor of 100, for example, decreased total SOA mass from roughly 1 to 0.1 µg m^{-3}, whereas in other cases the mass increased to roughly 30. They also conclude that the anthropogenic component of the predicted SOA is generally more significant than reported for locations in central and southern Europe. Derwent et al (2010) used a rudimentary SOA model coupled with the MCM gas phase model, based on the optimisation applied by Johnson et al (2006), to estimate the relative contributions from different human activities to predicted SOA. They concluded that after road transport and the chemical industry, SOA formation is dominated by the solvents sector that contributes 28% of the total UK weighted man-made mass emission. Redlington and Derwent (2002) used the NAME model to simulate SOA formation relative to UK observations at the rural Harwell site. They assessed the sensitivity of the modelled SOA components to a 30% reduction of all NO_x sources and a 30% reduction of all man-made NMVOCs. Whilst noting high uncertainties in the SOA model (see Annex A), the authors note that the anthropogenic SOA component shows the greatest response to 30% reductions in man-made emissions of NO_x and VOC, with the biogenic component remaining largely unchanged. The response to NO_x in particular is highly non-linear with anthropogenic SOA increasing in some regions as NO_x emissions decrease.

Simpson et al. (2007) predicted using the EMEP model that the contribution of biogenic SOA far exceeds that of anthropogenic SOA while the relative contribution of biogenic SOA compared to POA varies significantly across Europe and at different times of the year. Bessagnet et al. (2008) compared predictions of the CHIMERE CTM with filter measurements during 2003, emphasizing the importance of isoprene chemistry on SOA formation. Startlet et al (2012) studied the effect of reducing biogenic emissions on ozone and particulate matter as part of the Air Quality Model Evaluation International Initiative (AQMEII) study. They used the Polyphemus air quality model combined with the RACM

chemical mechanism for Europe and CB05 for North America, where SOA is mostly formed from isoprene (20-23%) and terpenes (62-67%) in the model. Noting that most of secondary organic aerosols (SOA) formed at the continental scale over Europe and NA are therefore biogenic in origin, they found that eliminating biogenic emissions reduces SOA by 72 to 88% over Europe and by 90% over North America. However, they also note that biogenic SOA are not only impacted by biogenic but also by anthropogenic emissions. Thus they found that eliminating all anthropogenic emissions affects oxidant levels and the absorbing carbon mass, reducing the formation of SOA by 15 to 16% over Europe and by about 10% over North America;. In addition, they found that, locally, the reduction may be as large as 50%, especially over large urban centers in Europe. Similarly, Carlton et al. (2010) estimated that more than 50% of biogenic SOA in the eastern U.S. can be controlled via the influence of anthropogenic emissions on biogenic SOA.

Megaritis et al (2013) used the PMCAMx-2008 model to quantify the changes in predicted $PM_{2.5}$ over Europe in response to different emission reductions as well as a temperature increase. Using a summer and winter period systematic reductions of 50% were applied to SO_2, NH_3, NO_x, anthropogenic VOCs and anthropogenic primary VOCs. The reduction in anthropogenic primary material reduced total OA by 15 % during the modeled winter period and 8 % in the summer period. The reduction of total OA is higher in urban areas close to its emissions sources. A slight decrease of OA (8 % in the modeled summer period and 4 % in the modeled win- ter period) is also predicted after a 50 % reduction of VOCs emissions due to the decrease of anthropogenic SOA. Increasing the temperature of 5K significantly increased the predicted OA due to an increase in biogenic VOC emissions, indicating the importance of climate interactions. The authors note that the substantial reduction in $PM_{2.5}$, both from SIA and SOA, due to emissions reductions of their precurosrs outlines the importance of emissions for improving air quality, combined with the sensitivity to changes in temperature indicating climate interactions are important.

Other studies have focused on the effect of role of climate change on the concentrations of ozone, particulate matter and other pollutants and the impact of various climate change scenarios on air quality over Europe (Tuovinen et al., 2002; Langner et al., 2005; Ordonez et al., 2005; Szopa et al., 2006; Forkel and Knoche, 2007; Giorgi and Meleux, 2007; Jacob and Winner, 2009). Forkel and Knoche (2006) used an online regional coupled atmospheric–chemistry model in order to investigate possible effects of global climate change on the near-surface concentrations of photochemical compounds in Southern Germany. They showed a 10 % increase on average daily maximum ozone concentrations during summer mainly due to an increase of temperature and biogenic emissions along with a decrease of cloud water and ice. A regional CTM was used by Meleux et al. (2007) to investigate the effects of climate change on summer ozone levels over the European region, under different IPCC emissions scenarios (IPCC, 2007). Their study showed a substantial increase of ozone concentrations during summer in future climate conditions, mostly due to higher temperatures and reduced cloud and precipitation. They also addressed the importance of temperature-driven increase in biogenic emissions on ozone production. In a global study by Heald et al. (2008), the authors used a global atmosphere-land model to investigate the sensitivity of secondary organic aerosol (SOA) concentration to changes in climate and emissions under the year 2100 IPCC A1B scenario. They predicted increases of SOA levels in the future climate, mainly due to increase of biogenic SOA, which were estimated to rise around 35 % in Europe.

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