The contributions to long-term health-relevant particulate matter at the UK EMEP supersites between 2010 and 2013: Quantifying the mitigation challenge

Christopher S. Malley a,b,⁎, Mathew R. Heal b, Christine F. Braban a, John Kentisbeer a, Sarah R. Leeson a, Heath Malcolm a, Justin J.N. Lingard c, Stuart Ritchie c, Richard Maggs d, Sonya Beccaceci e, Paul Quincey e, Richard J.C. Brown e, Marsahild M. Twigg a

a NERC Centre for Ecology & Hydrology, Bush Estate, Penicuik EH26 0QR, UK
b School of Chemistry, University of Edinburgh, David Brewster Road, Edinburgh EH9 3JF, UK
c Ricardo Energy & Environment, The Gemini Building, Fermi Avenue, Harwell, Didcot OX11 0QR, UK
d Bureau Veritas, Fifth Floor, 66 Prescot Street, London, E1 8HG, UK
e Environment Division, National Physical Laboratory, Hampton Road, Teddington, Middlesex TW11 0LW, UK

⁎ Corresponding author at: Stockholm Environment Institute, Environment Department, University of York, York YO10 5NG, UK. E-mail address: chris.malley@york.ac.uk (C.S. Malley).

Article info
Received 12 April 2016
Received in revised form 12 August 2016
Accepted 16 August 2016
Available online 21 August 2016

Keywords:
Particulate matter
Long-term human health
Chemical climatology
Air mass back trajectories
PM composition

Abstract
Human health burdens associated with long-term exposure to particulate matter (PM) are substantial. The metrics currently recommended by the World Health Organization for quantification of long-term health-relevant PM are the annual average PM10 and PM2.5 mass concentrations, with no low concentration threshold. However, within an annual average, there is substantial variation in the composition of PM associated with different sources. To inform effective mitigation strategies, therefore, it is necessary to quantify the conditions that contribute to annual average PM10 and PM2.5 (rather than just short-term episodic concentrations), PM10, PM2.5, and speciated water-soluble inorganic, carbonaceous, heavy metal and polycyclic aromatic hydrocarbon components are concurrently measured at the two UK European Monitoring and Evaluation Programme (EMEP) ‘supersites’ at Harwell (SE England) and Auchencorth Moss (SE Scotland). In this work, statistical analyses of these measurements are integrated with air-mass back trajectory data to characterise the ‘chemical climate’ associated with the long-term health-relevant PM metrics at these sites. Specifically, the contributions from different PM concentrations, months, components and geographic regions are detailed. The analyses at these sites provide policy-relevant conclusions on mitigation of (i) long-term health-relevant PM in the spatial domain for which these sites are representative, and (ii) the contribution of regional background PM to long-term health-relevant PM.

At Harwell the mean (±1 sd) 2010–2013 annual average concentrations were PM10 = 16.4 ± 1.4 μg m⁻³ and PM2.5 = 11.9 ± 1.1 μg m⁻³ and at Auchencorth PM10 = 7.4 ± 0.4 μg m⁻³ and PM2.5 = 4.1 ± 0.2 μg m⁻³. The chemical climate state at each site showed that frequent, moderate hourly PM10 and PM2.5 concentrations (defined as approximately 5–15 μg m⁻³ for PM10, and 3–10 μg m⁻³ for PM2.5) determined the magnitude of annual average PM10 and PM2.5 to a greater extent than the relatively infrequent high, episodic PM10 and PM2.5 concentrations. These moderate PM10 and PM2.5 concentrations were derived across the range of chemical components, seasons and air-mass pathways, in contrast to the highest PM concentrations which tended to associate with specific conditions. For example, the largest contribution to moderate PM10 and PM2.5 concentrations – the secondary inorganic aerosol components, specifically NO3⁻ – were accumulated during the arrival of trajectories traversing the spectrum of marine, UK, and continental Europe areas. Mitigation of the long-term health-relevant PM impact in the regions characterised by these two sites requires multilateral action, across species (and hence source sectors), both nationally and internationally; there is no dominant determinants of the long-term PM metrics to target.

© 2016 The Authors. Published by Elsevier Ltd. This is an open access article under the CC BY license (http://creativecommons.org/licenses/by/4.0/).

1. Introduction

Particulate matter (PM) is an atmospheric component associated with premature mortality and morbidity. The World Health Organization (WHO) Review of the Health Aspects of Air Pollution (REVIHAAP, 2013) concludes that the long-term health effects are not simply the sum of those from exposures to high concentration episodes of PM.
Instead, risk estimates for health effects have been found to be substantially higher from long-term exposure to PM. These assessments are generally based on quantification of PM as the total mass concentration of all particles with aerodynamic diameter <2.5 μm (PM2.5) or <10 μm (PM10); but PM is comprised of a variety of chemical components and particle sizes (Heal et al., 2012). At present, however, the WHO, and the UK Committee on the Medical Effects of Air Pollution (COMEAP), conclude that there is insufficient evidence to differentiate the components of PM that are more closely associated with different health effects (COMEAP, 2015; REVIHAAP, 2013). Consequently, REVIHAAP recommends that long-term human health-relevant PM is quantified through annual average concentrations of both PM2.5 and PM10. The recommended concentration-response function (CRF) to quantify premature mortality associated with long-term exposure to ambient PM in Europe is also defined using the annual average PM2.5 concentration (HRAPIE, 2013), as are the CRFs used in the Global Burden of Disease project (Forouzanfar et al., 2015). Importantly, REVIHAAP (2013) also conclude that mortality outcomes extend to PM2.5 concentrations ‘well below’ the current WHO air quality guideline for PM2.5 of 25 μg m⁻³, and that health benefits would result from any reduction in annual average PM2.5 or PM10 concentrations.

In order to identify how reductions in annual average PM2.5 and PM10 concentrations might be achieved, it is necessary to determine the conditions which contribute in different locations. In the UK context, the Automatic Urban and Rural Network (AURN) (Eaton, 2013) records hourly measurements of both PM2.5 and PM10 at approximately 70 sites, ranging from urban traffic to rural background classifications (http://uk-air.defra.gov.uk/). Based on these measurements, Harrison et al. (2012) showed that, in 2009, the highest PM2.5 concentrations were found in winter and were associated with easterly winds transporting air masses from mainland European emission sources, demonstrating the substantial regional contribution to PM2.5 concentrations in the UK. The UK Air Quality Expert Group (AQEG, 2012) showed that, in 2010, winter made the largest seasonal contribution to annual average PM2.5 concentrations. Both wintertime and summertime high PM2.5 episodes, produced by build-up of local emissions during stagnant conditions, and the transport of secondary PM from continental Europe, respectively, also made important contributions to annual average PM2.5 (AQEG, 2012).

Two rural UK AURN sites at Harwell (SE England) and Auchencorth (SE Scotland) are also European Monitoring and Evaluation Programme (EMEP) supersites (Torseth et al., 2012). Insight into the conditions contributing to the annual average PM2.5 and PM10 concentrations at these sites is considerably enhanced by measurements of a large suite of PM components (summarised in Table 1), including 8 inorganic ions, organic and elemental carbon, heavy metals and polycyclic aromatic hydrocarbons (PAHs). These additional measurements allow investigation of the variation in PM components and source attributions that underpin variation in PM10 and PM2.5. The 8 inorganic ions include the secondary inorganic aerosol (SIA) components nitrate (NO₃⁻), ammonium (NH₄⁺) and sulphate (SO₄²⁻), which are formed by the chemical transformation of gaseous NOₓ, NH₃ and SO₂ emissions (Vieno et al., 2014). The other measured inorganic ions are chloride (Cl⁻), sodium (Na⁺) and magnesium (Mg²⁺), which are components of sea salt, calcium (Ca²⁺) which derives from dust emissions, and potassium (K⁺) which is emitted from biomass burning and as a component of dust emissions (Pio et al., 2008; Viana et al., 2008). The carbonaceous components are elemental carbon (EC), which is emitted during the incomplete combustion of fossil fuels and biomass burning, and organic carbon (OC) which derives from both primary emission and secondary formation from volatile (and semi-volatile) organic compound emissions (Harrison and Yin, 2008). The measured heavy metals and PAHs have a diverse range of sources and analysis of their concentrations has been used for source apportionment (Galarneau, 2008; Querol et al., 2007). Twigg et al. (2015) previously interpreted measurements of inorganic ions at Auchencorth between 2006 and 2012 and showed that PM10 during high concentration

<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>PM10</td>
<td>Hourly</td>
<td>77%</td>
<td>80%</td>
<td>97%</td>
<td>53%</td>
<td>69%</td>
<td>80%</td>
<td>92%</td>
<td>59%</td>
</tr>
<tr>
<td>PM2.5</td>
<td>Hourly</td>
<td>99%</td>
<td>94%</td>
<td>97%</td>
<td>57%</td>
<td>70%</td>
<td>99%</td>
<td>93%</td>
<td>61%</td>
</tr>
<tr>
<td>Nitrate (NO₃⁻) in PM10</td>
<td>Hourly</td>
<td>N.D.</td>
<td>N.D.</td>
<td>41%</td>
<td>87%</td>
<td>N.D.</td>
<td>N.D.</td>
<td>61%</td>
<td>83%</td>
</tr>
<tr>
<td>Sulphate (SO₄²⁻) in PM10</td>
<td>Hourly</td>
<td>N.D.</td>
<td>N.D.</td>
<td>47%</td>
<td>85%</td>
<td>N.D.</td>
<td>N.D.</td>
<td>61%</td>
<td>83%</td>
</tr>
<tr>
<td>Ammonium (NH₄⁺) in PM10</td>
<td>Hourly</td>
<td>N.D.</td>
<td>N.D.</td>
<td>68%</td>
<td>87%</td>
<td>N.D.</td>
<td>N.D.</td>
<td>67%</td>
<td>83%</td>
</tr>
<tr>
<td>Chloride (Cl⁻) in PM10</td>
<td>Hourly</td>
<td>N.D.</td>
<td>N.D.</td>
<td>50%</td>
<td>95%</td>
<td>N.D.</td>
<td>N.D.</td>
<td>56%</td>
<td>83%</td>
</tr>
<tr>
<td>Sodium (Na⁺) in PM10</td>
<td>Hourly</td>
<td>N.D.</td>
<td>N.D.</td>
<td>68%</td>
<td>93%</td>
<td>N.D.</td>
<td>N.D.</td>
<td>68%</td>
<td>79%</td>
</tr>
<tr>
<td>Calcium (Ca²⁺) in PM10</td>
<td>Hourly</td>
<td>N.D.</td>
<td>N.D.</td>
<td>68%</td>
<td>93%</td>
<td>N.D.</td>
<td>N.D.</td>
<td>70%</td>
<td>82%</td>
</tr>
<tr>
<td>Magnesium (Mg²⁺) in PM10</td>
<td>Hourly</td>
<td>N.D.</td>
<td>N.D.</td>
<td>68%</td>
<td>93%</td>
<td>N.D.</td>
<td>N.D.</td>
<td>70%</td>
<td>86%</td>
</tr>
<tr>
<td>Potassium (K⁺) in PM10</td>
<td>Hourly</td>
<td>N.D.</td>
<td>N.D.</td>
<td>67%</td>
<td>93%</td>
<td>N.D.</td>
<td>N.D.</td>
<td>70%</td>
<td>86%</td>
</tr>
<tr>
<td>Nitrate (NO₃⁻) in PM2.5</td>
<td>Hourly</td>
<td>N.D.</td>
<td>N.D.</td>
<td>41%</td>
<td>89%</td>
<td>N.D.</td>
<td>N.D.</td>
<td>59%</td>
<td>82%</td>
</tr>
<tr>
<td>Sulphate (SO₄²⁻) in PM2.5</td>
<td>Hourly</td>
<td>N.D.</td>
<td>N.D.</td>
<td>47%</td>
<td>86%</td>
<td>N.D.</td>
<td>N.D.</td>
<td>59%</td>
<td>82%</td>
</tr>
<tr>
<td>Ammonium (NH₄⁺) in PM2.5</td>
<td>Hourly</td>
<td>N.D.</td>
<td>N.D.</td>
<td>67%</td>
<td>89%</td>
<td>N.D.</td>
<td>N.D.</td>
<td>64%</td>
<td>79%</td>
</tr>
<tr>
<td>Chloride (Cl⁻) in PM2.5</td>
<td>Hourly</td>
<td>N.D.</td>
<td>N.D.</td>
<td>49%</td>
<td>96%</td>
<td>N.D.</td>
<td>N.D.</td>
<td>54%</td>
<td>84%</td>
</tr>
<tr>
<td>Sodium (Na⁺) in PM2.5</td>
<td>Hourly</td>
<td>N.D.</td>
<td>N.D.</td>
<td>66%</td>
<td>95%</td>
<td>N.D.</td>
<td>N.D.</td>
<td>65%</td>
<td>79%</td>
</tr>
<tr>
<td>Calcium (Ca²⁺) in PM2.5</td>
<td>Hourly</td>
<td>N.D.</td>
<td>N.D.</td>
<td>66%</td>
<td>95%</td>
<td>N.D.</td>
<td>N.D.</td>
<td>67%</td>
<td>81%</td>
</tr>
<tr>
<td>Magnesium (Mg²⁺) in PM2.5</td>
<td>Hourly</td>
<td>N.D.</td>
<td>N.D.</td>
<td>67%</td>
<td>95%</td>
<td>N.D.</td>
<td>N.D.</td>
<td>67%</td>
<td>81%</td>
</tr>
<tr>
<td>Potassium (K⁺) in PM2.5</td>
<td>Hourly</td>
<td>N.D.</td>
<td>N.D.</td>
<td>66%</td>
<td>95%</td>
<td>N.D.</td>
<td>N.D.</td>
<td>67%</td>
<td>80%</td>
</tr>
<tr>
<td>Elemental carbon (EC) in PM10</td>
<td>Daily</td>
<td>N.M.</td>
<td>86%</td>
<td>84%</td>
<td>87%</td>
<td>N.M.</td>
<td>N.M.</td>
<td>N.M.</td>
<td>N.M.</td>
</tr>
<tr>
<td>Organic carbon (OC) in PM10</td>
<td>Daily</td>
<td>N.M.</td>
<td>86%</td>
<td>84%</td>
<td>87%</td>
<td>N.M.</td>
<td>N.M.</td>
<td>N.M.</td>
<td>N.M.</td>
</tr>
<tr>
<td>Elemental carbon (EC) in PM2.5</td>
<td>Weekly</td>
<td>N.M.</td>
<td>N.M.</td>
<td>98%</td>
<td>88%</td>
<td>N.M.</td>
<td>N.M.</td>
<td>94%</td>
<td>90%</td>
</tr>
<tr>
<td>Organic carbon (OC) in PM2.5</td>
<td>Weekly</td>
<td>N.M.</td>
<td>N.M.</td>
<td>98%</td>
<td>88%</td>
<td>N.M.</td>
<td>N.M.</td>
<td>94%</td>
<td>90%</td>
</tr>
<tr>
<td>25 heavy metals in PM10</td>
<td>Weekly</td>
<td>100%</td>
<td>93%</td>
<td>98%</td>
<td>100%</td>
<td>100%</td>
<td>98%</td>
<td>100%</td>
<td>92%</td>
</tr>
<tr>
<td>25 polycyclic aromatic hydrocarbons (PAHs)</td>
<td>Monthly</td>
<td>100%</td>
<td>100%</td>
<td>100%</td>
<td>100%</td>
<td>100%</td>
<td>100%</td>
<td>100%</td>
<td>100%</td>
</tr>
</tbody>
</table>
episodes was comprised predominantly of SIA components, whereas lower PM$_{10}$ concentrations had a substantially larger relative contribution from sea salt.

The aim of this work is to integrate the measurements of total PM$_{10}$ and PM$_{2.5}$ with the suite of PM component measurements to understand the contributions producing long-term human-relevant PM concentrations, i.e., the factors contributing to annual average PM$_{10}$ and PM$_{2.5}$. AQEG has emphasised that PM chemical component measurements as part of the UK’s air quality compliance network can lead to an improved ability to quantify the contributions from individual sources to overall PM loading (AQEG, 2015). The UK EMEP supersites are particularly suited to achieving the additional benefits from concurrent measurements of PM$_{10}$, PM$_{2.5}$ and components identified by AQEG, as a greater number of components are measured at these sites than at any other UK monitoring site. Previous studies in the UK, and Europe, have characterised spatial and temporal variation in PM$_{2.5}$, PM$_{10}$ and components (AQEG, 2012; Harrison et al., 2012; Putaud et al., 2010). The novelty of this study is to focus data interpretation of PM$_{10}$, PM$_{2.5}$ and component measurement datasets, along with air-mass back-trajectory analysis in order to specifically identify the determinants of annual average PM$_{2.5}$ and PM$_{10}$ at these sites. The term ‘long-term health-relevant PM’ is used to refer to annual average PM$_{10}$ and PM$_{2.5}$ concentrations in this work because these metrics were useful to characterise long-term exposure to PM in synthesis reports by WHO (REVIIHAAP, 2013). The novelty of this study is to focus data interpretation of PM$_{10}$, PM$_{2.5}$ and component measurement datasets, along with air-mass back-trajectory analysis in order to specifically identify the determinants of annual average PM$_{2.5}$ and PM$_{10}$ at these sites.

The aim of this work is to integrate the measurements of total PM$_{10}$ and PM$_{2.5}$ with the suite of PM component measurements to understand the contributions producing long-term human-relevant PM concentrations, i.e., the factors contributing to annual average PM$_{10}$ and PM$_{2.5}$. AQEG has emphasised that PM chemical component measurements as part of the UK’s air quality compliance network can lead to an improved ability to quantify the contributions from individual sources to overall PM loading (AQEG, 2015). The UK EMEP supersites are particularly suited to achieving the additional benefits from concurrent measurements of PM$_{10}$, PM$_{2.5}$ and components identified by AQEG, as a greater number of components are measured at these sites than at any other UK monitoring site. Previous studies in the UK, and Europe, have characterised spatial and temporal variation in PM$_{2.5}$, PM$_{10}$ and components (AQEG, 2012; Harrison et al., 2012; Putaud et al., 2010). The novelty of this study is to focus data interpretation of PM$_{10}$, PM$_{2.5}$ and component measurement datasets, along with air-mass back-trajectory analysis in order to specifically identify the determinants of annual average PM$_{2.5}$ and PM$_{10}$ at these sites. The term ‘long-term health-relevant PM’ is used to refer to annual average PM$_{10}$ and PM$_{2.5}$ concentrations in this work because these metrics were useful to characterise long-term exposure to PM in synthesis reports by WHO (REVIIHAAP, 2013). The novelty of this study is to focus data interpretation of PM$_{10}$, PM$_{2.5}$ and component measurement datasets, along with air-mass back-trajectory analysis in order to specifically identify the determinants of annual average PM$_{2.5}$ and PM$_{10}$ at these sites.

The application of the previously-defined ‘chemical climatology’ framework is used to achieve this goal (Malley et al., 2014a). This framework has three components, the ‘impact’ of atmospheric composition (in this case long-term health-relevant PM quantified by annual average PM$_{2.5}$ and PM$_{10}$), the ‘state’ of atmospheric composition variation which produces this impact, and the causal ‘drivers’ of this ‘state’. In deriving complete ‘chemical climates’ in this work, the aim is to target analysis of atmospheric composition data to identify the conditions producing the long-term health-relevant PM metrics. In order to establish both the ‘state’ and ‘drivers’ producing long-term health-relevant PM, a set of standard statistics were calculated during each year at each UK EMEP supersite. The ‘state’ statistics used here are the contributions to the impact metrics from 1 µg m$^{-3}$ PM$_{10}$ and PM$_{2.5}$ concentration bins, as well as the monthly contribution and composition to each bin, in order to understand the relative importance of infrequent/high concentrations vs frequent/moderate concentrations in determining the long-term health-relevant PM metric. The ‘drivers’ of this chemical climate ‘state’ are investigated using 4-day air-mass back trajectories to quantify differences in the number of hours spent over different geographic regions. Principal component analysis (PCA) is used to assess the contribution of short vs long-range transport in determining the contribution of the major PM components. Characterising these ‘chemical climates’ allows identification of the variety of determinants of long-term health-relevant PM at these sites, and therefore the options available to achieve the reductions in annual average PM$_{10}$ and PM$_{2.5}$ which, as identified by the WHO, would result in benefits to human health.

The analyses for these two rural UK sites provides policy-relevant conclusions on mitigation of i) long-term health-relevant PM in the spatial domain for which these sites are representative (approximately 17% of England and Scotland’s populations live in rural areas, equivalent to over 10 million people (Defra, 2015; National Records of Scotland, 2015)), and ii) the contribution of regional background PM to long-term health-relevant PM, which has been shown to be a substantial fraction of total PM in urban areas across the UK (Harrison et al., 2012). Harwell and Auchenborogh have low local emissions of primary PM and secondary PM precursors, and therefore PM concentrations at these sites are largely determined by regional background contributions (although the location of Harwell is closer to larger emissions sources such as the megacity of London and continental Europe). Harwell and Auchenborogh were previously shown to be representative of rural UK conditions based on analysis of ozone measurements across European monitoring sites (Malley et al., 2014b). The future application of this methodology across regional monitoring networks could provide the common basis for assessment of impact severity and the spatial efficacy of different mitigation strategies across larger, transboundary spatial domains.

### 2. Methods

The ‘impact’, ‘state’ and ‘drivers’ framework of the chemical climatology methodology provides a consistent method for the quantification of impact severity and the conditions producing it (Malley et al., 2014a). The following sections first describe the raw measurement data, then the statistics used to characterise each of the impact, state, and drivers. The statistics used are summarised in Table 2.

#### 2.1. Measurement data

The PM$_{10}$, PM$_{2.5}$ and component datasets were obtained from the UK Department for Environment, Food and Rural Affairs (Defra) UK-Air (http://uk-air.defra.gov.uk/) and the Norwegian Institute for Air Research (NILU) EBAS (ebas.nilu.no) data repositories. The measurement and data quality procedures are detailed in Braban et al. (2012); Brown et al. (2013b); Sarantaridis et al. (2013); Beccaceci et al. (2015); Eaton (2013), and Twigg et al. (2015). The ‘chemical climate’

<table>
<thead>
<tr>
<th>Chemical climate component</th>
<th>Statistic</th>
<th>Further description</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Impact</strong></td>
<td>Annual average PM$_{10}$ ($\mu g$ m$^{-3}$)</td>
<td>WHO REVIHAAP (2013) recommends quantification of long-term PM health impact using both PM$<em>{10}$ and PM$</em>{2.5}$ size fractions due to distinct observed health impacts of fine and coarse PM</td>
</tr>
<tr>
<td></td>
<td>Annual average PM$_{2.5}$ ($\mu g$ m$^{-3}$)</td>
<td></td>
</tr>
<tr>
<td><strong>State</strong></td>
<td>Contribution to PM$<em>{10}$, PM$</em>{2.5}$ from 1 µg m$^{-3}$ concentration bins</td>
<td>Monthly contribution to PM concentrations in 1 µg m$^{-3}$ concentration bins</td>
</tr>
<tr>
<td></td>
<td>Monthly contribution to PM concentrations in 1 µg m$^{-3}$ concentration bins</td>
<td>Average PM composition for PM concentrations in 1 µg m$^{-3}$ concentration bins</td>
</tr>
<tr>
<td><strong>Drivers</strong></td>
<td>Contribution from geographic regions to PM concentrations in 1 µg m$^{-3}$ concentration bins</td>
<td>Calculated using cluster analysis of 4-day back trajectories based on the number of hours each trajectory spent in Marine, UK, Ireland, Iceland, Eastern, Western, Northern, Southern Europe and Other regions.</td>
</tr>
</tbody>
</table>

*‘Contribution distribution’: Contribution of 1 µg m$^{-3}$ PM$_{10}$ and PM$_{2.5}$ concentration bins to annual average PM component concentrations. Contribution from each concentration bin separated by geographic region clusters. Principal component analysis of inorganic ions*
statistics which form the basis of the analysis were calculated on measurements, where available and of sufficient data capture, between 2010 and 2013. The data capture for the measurements of PM$_{10}$ and PM$_{2.5}$ components used in this analysis are listed in Table 1. A greater proportion of concurrent measurements were available for 2012 and 2013, and these years were consequently the main focus. At Harwell, there was low data capture for the inorganic ions in 2012, especially NO$_3^-$ (41% (PM$_{2.5}$)), and for PM$_{10}$ (50%) and PM$_{2.5}$ (48%) in 2013. Effective investigation of the conditions producing long-term health-relevant PM required concurrent measurements of PM$_{10}$ and PM$_{2.5}$, and the inorganic ions, since the latter comprise the largest contribution to PM$_{10}$ and PM$_{2.5}$. Therefore proxy PM$_{10}$ and PM$_{2.5}$ datasets were constructed for Harwell for 2013 using data from a nearby urban background site in Reading, approximately 20 km from Harwell, at which the PM$_{10}$ and PM$_{2.5}$ data captures were 92% and 90% respectively. The relatively close proximity of the sites means regional background concentrations of PM$_{10}$ and PM$_{2.5}$ are similar, but the Reading site is located in a cemetery, 100 m from the nearest road in an urban residential area. Therefore local primary PM, and secondary PM precursor emissions may be higher compared with Harwell. Nevertheless, the linear regression between the Reading and Harwell data was statistically highly significant for both PM$_{10}$ and PM$_{2.5}$ (Fig. S1) and the equations were used to adjust the Reading dataset to estimate PM$_{10}$ and PM$_{2.5}$ at Harwell in 2013. At Auchencorth, PM$_{10}$ and PM$_{2.5}$ data capture was substantially higher in 2012 than 2013, while the data capture of the inorganic ions was higher in 2013. In the absence of a suitable proxy site, 2012 was used as the example year at Auchencorth.

2.2. Impact metric

The long-term health-relevant PM metrics were the annual average PM$_{10}$ and PM$_{2.5}$ concentrations, abbreviated here to PM$_{10}$AA and PM$_{2.5}$AA respectively. PM$_{10}$ and PM$_{2.5}$ were measured by a TEOM-FDMS instrument, which calculates the non-volatile and volatile PM components separately. Quantification of volatile PM$_{10}$ and PM$_{2.5}$ is based on the mass lost from a filter sample during a 6-min cycle. However, mass can also be adsorbed to the sample during that period, and at low PM$_{10}$ and PM$_{2.5}$ concentrations this can exceed the volatile PM$_{10}$ or PM$_{2.5}$ lost and result in a negative concentration (AQEG, 2012). This was most limiting for PM$_{2.5}$ measurements at Auchencorth (11% of measurements in 2012, as highlighted by Twigg et al. (2015)). The negative values were included in the calculation of the annual mean due to uncertainties (i.e. shifting the concentration distribution) introduced by either excluding the negative values or setting them to zero.

2.3. State

The overall aim of the ‘state’ statistics is to characterise relevant atmospheric composition variation to link the chemical climate impact to its causal drivers. Hence the statistics selected in this analysis were chosen to determine the contribution to annual average PM$_{10}$ and PM$_{2.5}$ across the PM$_{10}$ and PM$_{2.5}$ concentration distribution, during different months of the year, and from different PM$_{10}$ and PM$_{2.5}$ components. Identification of these contributions, and the different determinants of these contributions (see Section 2.4 for the corresponding drivers statistics outline), therefore derives a ‘chemical climate’ which links the impacts to the conditions producing it, and the potential options for reducing long-term health-relevant PM.

2.3.1. Total PM mass

The state statistics for PM$_{10}$ and PM$_{2.5}$ measurements were calculated using the hourly data, as well as daily averages and weekly averages for comparison with measurements of EC and OC. The contributions of 1 μg m$^{-3}$ concentration bins to PM$_{10}$AA and PM$_{2.5}$AA were calculated to investigate the accumulation of the annual average across different PM$_{10}$ and PM$_{2.5}$ concentrations. The proportions of each concentration bin derived from each month of the year were also calculated.

2.3.2. PM$_{10}$ and PM$_{2.5}$ composition

For each PM$_{10}$ and PM$_{2.5}$ component (Table 1), the annual mean and contribution to PM$_{10}$AA or PM$_{2.5}$AA was calculated. At each hour, the fraction of SO$_4^{2-}$ derived from sea salt (sss-SO$_4^{2-}$) was calculated using Equation 1 (Seinfeld and Pandis, 2006), while the non-sea salt salt SO$_4^{2-}$ (nss-SO$_4^{2-}$) fraction was taken as the difference between the measured SO$_4^{2-}$ concentration and the sss-SO$_4^{2-}$ concentration.

\[
\text{[sSO}_4^{2-} = 0.252 \times [\text{Na}^+] 
\]

A substantial number of the PM$_{10}$ and PM$_{2.5}$ component concentrations were reported as below their respective limit of detection (LOD). The Kaplan–Meier (KM) method was used to estimate the distribution of component concentrations within a year, accounting for values below LOD (She, 1997). The KM method was used to calculate the annual mean, as well as the average concentration for each component for each 1 μg m$^{-3}$ PM$_{10}$ and PM$_{2.5}$ concentration bin. At low concentrations (typically below 5 μg m$^{-3}$), the percentage of total mass PM$_{10}$ or PM$_{2.5}$ accounted for by the sum of the inorganic ions frequently exceeded 100%, exacerbated by the negative PM$_{10}$ and PM$_{2.5}$ measurements recorded by the TEOM-FDMS instrument, i.e. an underestimate of the volatile PM component as described previously by AQEG (2012) and Twigg et al. (2015). At higher mass concentrations, the sum of the inorganic components was less than the PM$_{10}$ or PM$_{2.5}$ concentration. However, it is noted that underestimation of the volatile PM component by the TEOM-FDMS instrument (AQEG, 2012) limits estimation of the accuracy of the unresolved fraction across the distribution of PM$_{10}$ and PM$_{2.5}$ concentrations. Therefore, for PM$_{10}$ and PM$_{2.5}$ concentrations in each 1 μg m$^{-3}$ concentration bin, the contribution of each inorganic ion to the sum of all inorganic ions was calculated to evaluate how the contribution of each inorganic ion to PM$_{10}$AA and PM$_{2.5}$AA was derived across the PM$_{10}$ and PM$_{2.5}$ Concentration distribution. Similarly, the contributions of elemental and organic carbon to total carbon for each 1 μg m$^{-3}$ PM$_{10}$ and PM$_{2.5}$ concentration bin were calculated.

2.4. Drivers

The aim of the drivers statistics is to determine the factors which produce the state statistics (Section 2.3), i.e. to calculate how the contributions to annual average PM$_{10}$ and PM$_{2.5}$ from across the PM$_{10}$ and PM$_{2.5}$ distribution, and from the different PM$_{10}$ and PM$_{2.5}$ components arise. Hence, the geographic drivers were investigated using 4-day HYSPLIT air-mass back trajectories (Draxler and Rolph, 2013). The choice of 4-day back trajectories was considered long enough to capture the geographic regions that air masses traversed on the regional scale prior to arrival at the site, but was sufficiently short that, computationally, trajectories could be calculated at hourly time steps and statistically analysed. For each site, trajectories at hourly intervals were calculated using the R statistical software package Openair (Carslaw and Ropkins, 2012; R Core Team, 2014), and using as input the NCEP-NCAR Reanalysis meteorological data (Kistler et al., 2001). Many studies have used cluster analysis to group trajectories based on the similarity of the trajectory pathway prior to arrival at the site (as reviewed by Fleming et al., 2012). However, small variation in the trajectory pathway can influence the quantification of the source regions traversed (Mareckova et al., 2014). In this study, cluster analysis was used to group air mass back trajectories according to the number of hours spent over different geographic regions, rather than the coordinates of points along the trajectory pathway. For each trajectory (at each site), the number of hours spent above marine locations, the UK, Ireland, Iceland, Northern Europe, Eastern Europe, Southern Europe, Western Europe and Other (generally North America) was determined. The countries belonging to each
region of Europe were defined using the United Nations Statistics Division groupings (http://unstats.un.org/unsd/methods/m49/m49regin.htm), except that Ireland, Iceland and the UK were separated into their own geographic regions.

For each year at each site, Ward’s method hierarchical cluster analysis was used to group trajectories based on the similarity of the time spent over each geographic source region (Mangiameli et al., 1996; Ward, 1963). Trajectory separation was defined using the Euclidean distance (Kaufman and Rousseeuw, 1990). The aim of the clustering was to identify groups of trajectories which spent a distinctive number of hours within each geographic region compared to trajectories belonging to other clusters.

The clustering revealed five major (but different) groupings of trajectories arriving at each site. The number of hours (out of 96) spent in the different regions for each ‘trajectory cluster’ at Harwell in 2013 and at Auchencorth in 2012 are summarised in Fig. 1. The five clusters of trajectories arriving at Harwell in 2013 were named ‘Marine’, ‘Marine-UK’, ‘Western Europe’, ‘UK’ and ‘Northern Europe’. The five clusters of trajectories arriving at Auchencorth in 2012 were named ‘Marine’, ‘Marine-Other’, ‘UK’, ‘Western/Eastern Europe’ and ‘Northern Europe’. While the cluster names identify the distinctive geographic region traversed by air-mass trajectories within that cluster, Fig. 1 show that some of the clusters spent time over multiple regions. For example, at Harwell trajectories belonging to the ‘Western Europe’ cluster also spend an average of 10 h over the UK (Fig. 1).

The contribution of each trajectory cluster for PM$_{10}$ and PM$_{2.5}$ concentrations in each 1 $\mu$g m$^{-3}$ concentration bin was calculated. Additionally, for each PM$_{10}$ and PM$_{2.5}$ component, the contribution to the component annual average from each PM$_{10}$ or PM$_{2.5}$ 1 $\mu$g m$^{-3}$ concentration bin was calculated. The contributions to annual average PM$_{10}$ or PM$_{2.5}$ component from each 1 $\mu$g m$^{-3}$ were divided into the proportion derived during the arrival of trajectories assigned to each trajectory cluster at each site.

Principal component analysis (PCA) was applied to the dataset of 9 inorganic ions (taking ss-SO$_{4}^{2-}$ and nss-SO$_{4}^{2-}$ as separate components). The aim of PCA is to reduce the dimensionality of the dataset and to encapsulate variance in the dataset in as few variables (the Principal Components, PCs) as possible (e.g. Bro and Smilde, 2014). Firstly, the time series of PM$_{10}$ and PM$_{2.5}$ component concentrations were standardised so that an equal proportion of the variance in the dataset was encapsulated in each variable (component). Since the datasets were positively skewed they were natural-log transformed so that the mean was 0 and the variance 1. The output of the PCA (using R software (R Core Team, 2014)) comprised a set of 9 PCs, and time series of the value for each of the PCs and the loading of each PC for each PM component. The value of each PC determines the contribution of that PC to component concentrations at that time step. The relative loading of the PM components determines the level of correlation (and anti-correlation) between components for that PC. For example, a large value for a PC at a given time step will result in higher percentile concentrations for all those components with high loadings for that PC. The first PC (PC1) explains the most variance, the second PC (PC2) explains the most variance not explained by PC1 etc.

Harwell was the focus of the PCA analysis due to higher data capture of the inorganic ions in the example year (Table 1), and because Harwell, with its closer proximity to continental Europe than

![Fig. 1. Number of hours spent in different geographic regions for each of the air-mass back trajectory clusters arriving at a) Harwell in 2013, and b) Auchencorth in 2012. Note the different air masses arriving at each site resulting in a different cluster set at each site, hence the names of the clusters at each site differ.](image-url)
Auchencorth, experiences a wider range of air mass origins. The majority of the variability in the data was explained by PC1 and PC2. The loadings indicated that PC1 quantified the contribution to SIA from short-range transport, and PC2 from long-range transport (this is further discussed in Section 3.3). To investigate the contribution of short and long-range transport during different trajectory clusters, the values of PC1 and PC2 at each time step were apportioned in 20 × 5-percentile bins (percentiles were calculated based on all values of PC1 and PC2 in a given year). The proportion of values from each percentile bin for PC1 and PC2 during each trajectory cluster was calculated.

3. Results

3.1. Impact: Long-term health-relevant PM

The average (±1 std. dev.) PM$_{10AA}$ and PM$_{2.5AA}$ between 2010 and 2013 was 16.4 ± 1.4 μg m$^{-3}$ and 11.9 ± 1.1 μg m$^{-3}$ respectively at Harwell and 7.4 ± 0.4 μg m$^{-3}$ and 4.1 ± 0.2 μg m$^{-3}$ at Auchencorth (Table 3). As described in Section 2, PM values at Harwell for 2013 were derived from adjusted PM concentrations from the nearby Reading monitoring site. The averages for Auchencorth include years where data capture was below 75% (Table 1). While the inclusion of data from Auchencorth in 2012 (Table 3). As described in Section 2, PM values at Harwell for 2013 were derived from adjusted PM concentrations from the nearby Reading monitoring site. The averages for Auchencorth include years where data capture was below 75% (Table 1). While the inclusion of data from Auchencorth in 2012 introduces uncertainty, given the small number of years these years introduces uncertainty, given the small number of years available their inclusion was necessary to provide an indication of the variability in PM$_{10AA}$ and PM$_{2.5AA}$. In comparison with measurements at 60 sites across Europe, the annual averages for Harwell were similar to other ‘rural background’ sites, while those at Auchencorth were closer to ‘natural background’ sites in Scandinavia (Putaud et al., 2010). Although the annual average PM$_{10AA}$ and PM$_{2.5AA}$ concentrations at both sites were within current European AQ limits, the PM is still presumed to be having effects on human health (REVHAAP, 2013). This is discussed further in Section 4.

3.2. State: total mass and PM composition variation

3.2.1. PM$_{10}$ and PM$_{2.5}$ concentrations

At both Auchencorth and Harwell, moderate PM concentrations (approximately between the 25th and 75th percentiles of hourly average values) made the largest contribution to PM$_{10AA}$ and PM$_{2.5AA}$ (Fig. 2). For example, at Harwell, concentrations below 20 μg m$^{-3}$ contributed 53–73% of PM$_{2.5AA}$ at Harwell between 2010 and 2013, while concentrations above 40 μg m$^{-3}$ contributed 6–16% to PM$_{2.5AA}$. At Auchencorth, the contribution to PM$_{2.5AA}$ below 20 μg m$^{-3}$ was 82–90%, and below 10 μg m$^{-3}$ 56–66%. The largest contribution from a single concentration bin varied between years (2010–2013) from 11–12 to 14–15 μg m$^{-3}$ for PM$_{10AA}$ and 6–7 to 9–10 μg m$^{-3}$ for PM$_{2.5AA}$ at Harwell. At Auchencorth, the largest contribution varied between the 5–6 and 8–9 μg m$^{-3}$ bins for PM$_{10AA}$ and between 2–3 to 3–4 μg m$^{-3}$ for PM$_{2.5AA}$.

Figs. 3 and S2 summarise the ‘state’ of this chemical climate in 2013 at Harwell for PM$_{2.5AA}$ and PM$_{10AA}$ respectively, and Fig. 4 for PM$_{10AA}$ at Auchencorth in 2012. Figs. 3b, S2b and 4b show the contribution by month to each 1 μg m$^{-3}$ concentration bin for PM$_{2.5AA}$ or PM$_{10AA}$. The average seasonal contribution to moderate concentrations was not dominated by one season. For example, the seasonal contribution to the five concentration bins with largest contribution to PM$_{2.5AA}$ at Harwell were 21%, 30%, 27% and 21% for spring (Mar, Apr., May), summer (Jun., Jul., Aug), autumn (Sep, Oct., Nov) and winter (Jan, Feb., Dec) respectively (Fig. 3b), and for PM$_{10AA}$ at Auchencorth it was 18%, 31%, 29% and 22% respectively (Fig. 4b). The contributions from spring and winter increased with increasing concentration such that the majority of the highest PM$_{2.5}$ and PM$_{2.5}$ concentrations (95th percentile) occurred in these seasons. Harrison et al. (2012) previously attributed highest monthly-averaged PM$_{2.5}$ concentrations in winter and spring to a higher heating load increasing emissions of primary PM and secondary PM precursor, and reduced dispersion of these emissions locally.

### Table 3

<table>
<thead>
<tr>
<th>Year</th>
<th>PM$_{10}$</th>
<th>PM$_{2.5}$</th>
<th>PM$_{10}$</th>
<th>PM$_{2.5}$</th>
<th>PM$_{10}$</th>
<th>PM$_{2.5}$</th>
<th>PM$_{10}$</th>
<th>PM$_{2.5}$</th>
<th>PM$_{10}$</th>
<th>PM$_{2.5}$</th>
<th>PM$_{10}$</th>
<th>PM$_{2.5}$</th>
<th>PM$_{10}$</th>
<th>PM$_{2.5}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Harwell PM$_{10}$</td>
<td>16.0</td>
<td>1.6</td>
<td>0.0012</td>
<td>1.0%</td>
<td>1.0%</td>
<td>0.01%</td>
<td>2.63</td>
<td>0.22</td>
<td>0.0008</td>
<td>14.5%</td>
<td>1.2%</td>
<td>0.0055</td>
<td>2.14</td>
<td>0.16</td>
</tr>
<tr>
<td>2012</td>
<td>16.6</td>
<td>16.7%</td>
<td>1.1%</td>
<td>9.1%</td>
<td>7.0%</td>
<td>5.0%</td>
<td>3.9%</td>
<td>1.3%</td>
<td>1.3%</td>
<td>1.0%</td>
<td>12.9%</td>
<td>0.9%</td>
<td>0.01%</td>
<td></td>
</tr>
<tr>
<td>2013</td>
<td>14.7</td>
<td>25.3%</td>
<td>12.2%</td>
<td>10.7%</td>
<td>8.0%</td>
<td>7.8%</td>
<td>2.6%</td>
<td>2.0%</td>
<td>1.6%</td>
<td>0.5%</td>
<td>15.5%</td>
<td>1.2%</td>
<td>0.01%</td>
<td></td>
</tr>
<tr>
<td>Harwell PM$_{2.5}$</td>
<td>10.3</td>
<td>11.9</td>
<td>0.09</td>
<td>0.004</td>
<td>1.29%</td>
<td>0.01%</td>
<td>2.67</td>
<td>0.08</td>
<td>0.003</td>
<td>1.17%</td>
<td>0.004%</td>
<td>0.07</td>
<td>0.0012</td>
<td>0.12</td>
</tr>
<tr>
<td>2012</td>
<td>12.8</td>
<td>15.7%</td>
<td>11.8%</td>
<td>8.1%</td>
<td>3.9%</td>
<td>3.2%</td>
<td>3.0%</td>
<td>0.8%</td>
<td>0.9%</td>
<td>0.1%</td>
<td>10.8%</td>
<td>0.01%</td>
<td></td>
<td></td>
</tr>
<tr>
<td>2013</td>
<td>12.5</td>
<td>26.7%</td>
<td>14.7%</td>
<td>12.5%</td>
<td>4.8%</td>
<td>4.8%</td>
<td>1.7%</td>
<td>1.2%</td>
<td>1.1%</td>
<td>0.5%</td>
<td>11.9%</td>
<td>0.01%</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Auchencorth PM$_{10}$</td>
<td>7.12</td>
<td>0.09</td>
<td>0.0004</td>
<td>1.29%</td>
<td>0.01%</td>
<td>2.67</td>
<td>0.08</td>
<td>0.003</td>
<td>1.17%</td>
<td>0.004%</td>
<td>0.07</td>
<td>0.0012</td>
<td>0.12</td>
<td>0.0008</td>
</tr>
<tr>
<td>2012</td>
<td>7.35</td>
<td>25.3%</td>
<td>16.6%</td>
<td>13.3%</td>
<td>15.1%</td>
<td>11.5%</td>
<td>0.9%</td>
<td>2.9%</td>
<td>0.8%</td>
<td>0.9%</td>
<td>0.9%</td>
<td>0.02%</td>
<td></td>
<td></td>
</tr>
<tr>
<td>2013</td>
<td>7.94</td>
<td>16.2%</td>
<td>12.3%</td>
<td>9.3%</td>
<td>14.4%</td>
<td>9.2%</td>
<td>0.8%</td>
<td>2.3%</td>
<td>1.0%</td>
<td>0.8%</td>
<td>1.6%</td>
<td>0.01%</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Auchencorth PM$_{2.5}$</td>
<td>4.03</td>
<td>4.01</td>
<td>0.38</td>
<td>1.09</td>
<td>0.89</td>
<td>0.61</td>
<td>0.48</td>
<td>0.05</td>
<td>0.12</td>
<td>0.04</td>
<td>0.05</td>
<td>0.66</td>
<td></td>
<td></td>
</tr>
<tr>
<td>2012</td>
<td>4.40</td>
<td>40.3%</td>
<td>28.5%</td>
<td>23.3%</td>
<td>16.0%</td>
<td>12.6%</td>
<td>1.2%</td>
<td>3.1%</td>
<td>1.0%</td>
<td>1.2%</td>
<td>17.4%</td>
<td>0.01%</td>
<td></td>
<td></td>
</tr>
<tr>
<td>2013</td>
<td>24.3%</td>
<td>21.4%</td>
<td>14.8%</td>
<td>15.2%</td>
<td>10.0%</td>
<td>1.1%</td>
<td>2.5%</td>
<td>1.1%</td>
<td>1.0%</td>
<td>15.0%</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
3.2.2. PM10 and PM2.5 composition

This section describes (i) the contribution of the different PM10 and PM2.5 components to long-term health-relevant PM (PM10AA and PM2.5AA) and (ii) how these contributions arise based on component variation across the range of PM10 and PM2.5 concentrations measured at Harwell and Auchencorth. At Harwell and Auchencorth, 2013 and 2012 are respectively used as example years, due to the greater data capture of component measurements compared with other measurement periods (Table 1).

The SIA components, NO3−, nss-SO42− and NH4+ comprised the largest fraction of PM10AA and PM2.5AA at both Harwell and Auchencorth (Table 3). For example, the annual average sum of the SIA components accounted for 48% of PM10AA and 54% of PM2.5AA at Harwell in 2013, and 55% of PM10AA concentrations at Auchencorth in 2012. For PM2.5 at Auchencorth, the SIA components accounted for 92% of PM2.5AA. The sum of all measured components was substantially greater than PM2.5AA, including when negative measurements were omitted. At Auchencorth, analysis of contributions of components of PM therefore focussed on PM10, as the higher PM10 concentrations were less affected by limitations of the TEOM-FDMS instrument at low concentrations.

The components of sea salt (Cl−, Na+, ss-SO42− and Mg2+) were, together, the second largest contributor to PM10AA and PM2.5AA at both Harwell and Auchencorth (Table 3). For example, the annual average sum of the sea salt components accounted for 48% of PM10AA and 54% of PM2.5AA at Harwell in 2013, and 55% of PM10AA concentrations at Auchencorth in 2012. For PM2.5 at Auchencorth, the sea-salt components accounted for 92% of PM2.5AA. The sum of all measured components was substantially greater than PM2.5AA, including when negative measurements were omitted. At Auchencorth, analysis of contributions of components of PM therefore focussed on PM10, as the higher PM10 concentrations were less affected by limitations of the TEOM-FDMS instrument at low concentrations.

The components of sea salt (Cl−, Na+, ss-SO42− and Mg2+) were, together, the second largest contributor to PM10AA and PM2.5AA (Table 3). For example, the annual average sum of the sea salt components comprised 19.4% of PM10AA and 11.9% of PM2.5AA at Harwell in 2013, and 30.3% of PM10AA was accounted for by sea salt. These values are higher than those calculated at other rural sites in north-west Europe, where the contribution from sea salt to PM10AA was on average 12% (Putaud et al., 2010). This is likely due to the closer proximity of marine environments along all trajectory pathways at the UK sites compared to European sites. For example, for both Harwell and Auchencorth on average at least 20 h were spent traversing marine environments for all trajectory clusters (Figs. 2 and 3).

Total carbon (TC, the sum of EC and OC) was the next largest component, and also accounted for a larger fraction in PM10AA (15.5% in 2013 at Harwell) compared to PM2.5AA (11.9%). These values are substantially smaller than calculated at an urban background site in the UK, where TC accounted for 37% of PM2.5 (Yin and Harrison, 2008). Overall, the three sets of components, SIA, sea-salt and TC, comprised the major mass fraction of both PM10AA and PM2.5AA, so assessment of the conditions giving rise to their contributions is most useful for consideration of reduction of PM10AA and PM2.5AA, the recommended metrics to quantify long-term health-relevant PM.

The 25 heavy metals measured at Harwell and Auchencorth (listed here: Brown et al., 2013a) contributed approximately 1% of PM10AA at both sites. The most abundant metals in declining contribution were iron (on average 54 ± 4% of the sum of the 25 annual average heavy metals in PM10 at Harwell between 2010 and 2013, 47 ± 8% at Auchencorth), aluminium (23 ± 4% at Harwell, 34 ± 12% at Auchencorth), zinc (6 ± 0.7% at Harwell, 8 ± 2% at Auchencorth) and barium (5 ± 2% at Harwell, 1 ± 0.3% at Auchencorth). The PAHs made a considerably smaller contribution to PM10AA, generally approximately 0.01%. Though not the focus for PM10AA or PM2.5AA, there is motivation for reduction in concentration of PAHs and heavy metals because of their individual specific impacts (health or otherwise). For example,
various PAHs have been shown to be carcinogenic (Kim et al., 2013). Similarly, individual heavy metals such as lead and aluminium are neurotoxins, whereas other metals such as zinc and copper are essential trace elements which can cause toxic effects in high concentrations (Jaishankar et al., 2014). These impacts are not addressed here.

The contribution of each inorganic ion to long-term health-relevant PM is summarised in Table 3. However, the contribution of each inorganic ion to PM$_{10}$ and PM$_{2.5}$ concentrations varies across the PM$_{10}$ and PM$_{2.5}$ concentration distribution. Hence the contribution of each inorganic ion to the total inorganic fraction to each $1 \mu g m^{-3}$ concentration bin is shown in Figs. 3c, 5c, and 4c for PM$_{2.5}$ and PM$_{10}$ at Harwell and PM$_{10}$ at Auchencorth, respectively. At Harwell and Auchencorth, increasing PM$_{10}$ and PM$_{2.5}$ concentrations were associated with an increasing contribution from SIA, and a decreasing contribution from sea salt. Hence for the moderate PM$_{10}$ and PM$_{2.5}$ concentrations, which make the largest contribution to PM$_{10AA}$ and PM$_{2.5AA}$, there were substantial contributions from both SIA and sea salt components. For example, for PM$_{2.5AA}$ at Harwell in 2013 (Fig. 3c), the contributions from NO$_3^-$, nss-SO$_4^{2-}$ and NH$_4^+$ to total inorganic ions were 29%, 22% and 14% respectively, on average, for the five PM$_{2.5}$ concentration bins with the largest contribution to PM$_{10AA}$ and PM$_{2.5AA}$ (6–10 and 11–12 $\mu g m^{-3}$). For Cl$^-$ and Na$^+$, the corresponding contributions were 14% and 9%. At the 95th percentile concentration for PM$_{2.5}$ at Harwell, NO$_3^-$, nss-SO$_4^{2-}$ and NH$_4^+$ respectively comprised 51%, 18% and 21% of the inorganic fraction of PM$_{2.5}$ (Fig. 3c). In contrast to the SIA components, Cl$^-$ and Na$^+$ comprised 2% and 3% of the inorganic fraction of PM$_{2.5}$ at the 95th percentile PM$_{2.5}$ concentration. The contribution of nss-SO$_4^{2-}$ therefore remained relatively constant for moderate and high concentrations, while contributions from NO$_3^-$ and NH$_4^+$ were larger at the high concentrations. Similar results were calculated for PM$_{10}$ at Harwell in 2012 (Fig. S2c). At Auchencorth, when compared with Harwell, during the moderate concentrations with the largest contribution to PM$_{10AA}$, the contribution of sea salt to the total inorganic fraction was greater, and the contribution of the SIA components was smaller (Fig. 4c).

Total carbon (TC) accounted for 16% of PM$_{10AA}$ at Harwell in 2013 (Table 3). At all PM$_{10}$ concentrations, OC was the major TC fraction, but the contribution of EC to TC increased at higher TC (see Fig. S3 for details). The increase in the contribution of EC to TC at elevated PM$_{10}$ concentrations is consistent with measurements detailed in Harrison and Yin (2008) for three UK sites (rural and urban).

3.3. Drivers

3.3.1. Air-mass back trajectories

The average proportion of hours during which trajectories belonging to the clusters ‘Marine’, ‘Marine-UK’, ‘Western Europe’, ‘UK’ and ‘Northern Europe’ (Fig. 1) arrived at Harwell in 2013 for each $1 \mu g m^{-3}$
concentration bin is shown in Fig. 3d for PM$_{2.5}$ and Fig. S2d for PM$_{10}$. For both PM$_{10}$ and PM$_{2.5}$ there was a contrast between the majority of trajectories assigned to ‘Marine’ clusters arriving during hours with low PM$_{10}$ or PM$_{2.5}$ concentrations to a majority of trajectories assigned to the three ‘terrestrial’ clusters arriving during hours with concentrations in high concentration bins. For example, for the PM$_{2.5}$ concentration bins <5 μg m$^{-3}$, the average proportion of hours when ‘Marine’ and ‘Marine-UK’ trajectories arrived at Harwell in 2013 was 64% and 26% respectively. In contrast, for the 95th percentile PM$_{2.5}$ concentration, ‘Western Europe’ trajectories arrived during 60% of hours. This ‘marine’ to ‘terrestrial’ trajectories transition occurred across the moderate PM$_{2.5}$ concentrations, and consequently, during the high frequency, moderate concentrations with largest contribution to PM$_{2.5AA}$ there was a wide range of different geographic source regions influencing PM at Harwell (Fig. 3d). At extreme concentrations (high and low), fewer sources made substantial contributions.

At Auchencorth in 2012, there was a similar transition (Fig. 4d): 73% of trajectories arriving during PM$_{10}$ concentrations <5 μg m$^{-3}$ were ‘Marine’, whereas a larger proportion of terrestrial trajectories arrived during higher concentrations (note the clusters of trajectories arriving at Auchencorth were named ‘Marine’, ‘Marine-Other’, ‘UK’, ‘Western/Eastern Europe’ and ‘Northern Europe’ (Fig. 1)). However, across all PM$_{10}$ concentrations the proportion of trajectories which traversed continental Europe were substantially lower than at Harwell with the ‘Western/Eastern Europe’ trajectory contributing <13% for PM$_{10}$ concentrations below 20 μg m$^{-3}$ (95th percentile, Fig. 4). Hence for the moderate concentration range which had the largest contribution to PM$_{10AA}$ at Auchencorth, a large proportion of the trajectories arriving were both terrestrial and marine, but the terrestrial trajectories most commonly traversed only the UK.

The grouping of trajectories by geographic region was used to assess the PM$_{10}$ and PM$_{2.5}$ composition during different air-mass pathways at Harwell and Auchencorth. A substantial proportion of annual average PM$_{2.5}$ NO$_3^-$ was accumulated during arrival of trajectories assigned to all clusters (Figs. S4 and 5), despite large variation in the frequency with which different types of trajectories arrived (see Fig. 1). For example, 35% of annual average NO$_3^-$ was accumulated during ‘Marine’ or ‘Marine-UK’ trajectories (which account for 68% of hours in 2013). A similar proportion was accumulated during ‘Western Europe’ trajectories (36%), but these trajectories were much less frequent (13% of hours in 2013).

However, the proportion of annual average PM$_{2.5}$ NO$_3^-$ was accumulated differently across the total PM$_{2.5}$ 1 μg m$^{-3}$ concentration bins for each trajectory cluster. A larger proportion of the annual average PM$_{2.5}$ NO$_3^-$ that accumulated during marine-dominated trajectories was accumulated at relatively low concentrations, e.g. 57% of the annual average PM$_{2.5}$ NO$_3^-$ was accumulated during PM$_{2.5}$ concentration bins below 10 μg m$^{-3}$ under ‘Marine’ conditions at Harwell. Whereas for
trajectory clusters which spent a larger number of hours over terrestrial environments, a higher proportion of the annual average PM$_{2.5}$ NO$_3^-$ was accumulated during higher PM$_{2.5}$ concentrations, e.g. between 17% and 22%, of the annual average PM$_{2.5}$ NO$_3^-$ accumulated during 'Western Europe' trajectories was accumulated during PM$_{2.5}$ concentration bins between 10 and 20 μg m$^{-3}$, 20–30 μg m$^{-3}$, 30–40 μg m$^{-3}$, and 40–50 μg m$^{-3}$ (Fig. S4).

The total proportion of annual average PM$_{2.5}$ NO$_3^-$ accumulated in each PM$_{2.5}$ 1 μg m$^{-3}$ concentration bin across all trajectories arriving at Harwell in 2013 is shown in Fig. 5a. The largest contribution to annual average PM$_{2.5}$ NO$_3^-$ occurred during moderate PM$_{2.5}$ concentrations which also had the largest contribution to PM$_{2.5}$ NO$_3^-$ at Harwell in 2013, compared to OC (21% of annual average OC) (Fig. S7).

The contribution to annual average NO$_3^-$, NH$_4^+$, Cl$^-$, and Ca$^{2+}$ in PM$_{10}$ across 1 μg m$^{-3}$ concentrations bins at Auchencorth in 2012 are shown in Fig. 6. A major difference compared with Harwell was the larger proportion of component annual average determined during ‘UK’-classified trajectories compared to European-influenced trajectories, reflecting the greater distance of Auchencorth from mainland Europe. For SIA, there was a similar transition as at Harwell from i) the majority of the contribution to component annual average derived at low PM$_{10}$ concentrations accumulated during 'Marine' trajectories, to ii) the contribution at high concentrations accumulated mainly during terrestrial-influenced (mainly 'UK') trajectories. Hence at Auchencorth, during moderate PM$_{10}$ concentrations, which made the largest contribution to component annual averages, this contribution was determined during both 'Marine' and 'UK' trajectory clusters, with a smaller contribution from the 'Western/Eastern Europe' cluster. For example, the largest contribution to annual average PM$_{10}$ NO$_3^-$ was derived during PM$_{10}$ concentrations between 5 and 10 μg m$^{-3}$, during which 49%, 34% and 10% of the trajectories arriving were grouped in 'Marine', 'UK' and 'Western/Eastern Europe' clusters respectively. For Cl$^-$ and Ca$^{2+}$, the majority of the component annual average was accumulated during 'Marine' trajectories (63% for Cl$^-$ annual average and 57% for Ca$^{2+}$), and a larger proportion of the annual average was accumulated during 'UK' trajectories for Ca$^{2+}$ (24% (Fig. 6c and d)).
3.3.2. Principal component analysis (PCA)

PCA analysis provides insight into why the accumulation of annual average NO$_3^-$, NH$_4^+$, and nss-SO$_4^{2-}$ during the arrival of trajectories assigned to each cluster, e.g. marine vs terrestrial-influenced trajectories, was derived differently across the range of PM$_{2.5}$ concentrations measured at Harwell in 2013. Fig. 7 shows the loading for the first two PCs (which together explained 79% of variability) resulting from the application of PCA to the PM$_{2.5}$ inorganic ion time series in 2013 at Harwell. Similar magnitude and direction of a loading indicates high correlation between components, while similar magnitude but opposite direction of loading indicates anti-correlation between components. For PC1, the SIA components, NO$_3^-$, NH$_4^+$, and nss-SO$_4^{2-}$ had high correlation, and were anti-correlated with sea-salt components Cl$^-$, Na$^+$, and Mg$^{2+}$. The value of PC1 at an hourly time step therefore distinguishes between a relatively large contribution from SIA, and low contribution from sea salt, and vice versa. There was a correlation between all components for PC2, with the exception of K$^+$ which had a relatively low loading. The value of PC2 therefore determines whether there was a simultaneous increase in almost all inorganic components, both sea salt and SIA, at a given time step. However, because the loadings for Cl$^-$ and Na$^+$ were 29% and 53% smaller, respectively, than the loading for NO$_3^-$, a large value of PC2 indicates a relatively higher percentile NO$_3^-$ and NH$_4^+$ concentration than Cl$^-$ and Na$^+$. In the context of SIA formation and the contribution of SIA to PM$_{2.5}$, the value of PC1 indicates the contribution from short-range transport, as SIA is associated with an anti-correlation with sea salt. This is because time spent traversing over SIA precursor emissions sources (i.e. land) during the final hours of a trajectory means less time spent over marine environments. For long-range transport (indicated by PC2), an air mass will pass over both SIA precursor emissions sources and marine environments. For example the ‘Western Europe’ trajectory conditions the air mass still spends on average 20 h over the sea (Fig. 4), which results in an increase of both SIA and sea-salt components.

The proportion of hours with values of PC1 and PC2 in 20 × 5-percentile bins is shown in Fig. 8 separately for hours assigned to each cluster. ‘Western Europe’ trajectories were generally associated with high percentile values of both PC1 (short-range transport) and PC2 (long-term transport), and were also associated with elevated contributions to annual average SIA compared to other trajectory clusters. The PCA analysis indicates that both elevated short and long-range transport contributed. Vieno et al. (2014) modelled UK and European emission contributions to UK SIA concentrations and calculated that both

Fig. 6. Proportion of annual average a) NO$_3^-$, b) NH$_4^+$, c) Cl$^-$, d) Ca$^{2+}$ in PM$_{10}$ at Auchencorth in 2012 accumulated during hours with PM$_{10}$ concentrations in 1 µg m$^{-3}$ concentration bins (distinct bars along x-axis), and during the arrival of trajectories belonging to each cluster (different colours within each bar).

Fig. 7. Loadings of 9 inorganic ions for the first two principal components (PCs) resulting from application of PCA to the inorganic ion dataset for PM$_{2.5}$ at Harwell in 2013.
continental European and UK emissions sources can have a large contribution to the magnitude of a high SIA episodic concentrations. The trajectories assigned to the ‘UK’ and ‘Northern Europe’ clusters were associated with only high percentile PC1 and PC2 values respectively, indicating that the disproportionately large accumulation of annual average SIA during the arrival of these trajectories was associated with a selective increase in short- (‘UK’ trajectories) and long- (‘Northern Europe’ trajectories) range transport only. The proportion of annual average SIA component accumulated during the arrival of ‘Marine’ trajectories was derived mainly during low PM$_{2.5}$ concentrations (Fig. S4). These trajectories were generally associated with relatively low percentile PC1 and PC2 values, and hence low levels of short and long range transport. These conclusions are also likely to extend to OC, which was previously shown to be correlated with SIA and identified as a regional pollutant (Charron et al., 2013).

4. Implications for long-term health-relevant PM mitigation

The Harwell and Auchencorth EMEP supersites are located in rural areas where local primary PM and secondary PM precursor emission sources are low. These sites have previously been shown to be representative of rural background conditions across the UK in an assessment of ground-level ozone concentrations across rural European sites (Malley et al., 2014b). Hence the derivation of chemical climates focussed on the long-term human health-relevant PM (quantified as annual average PM$_{10}$ and PM$_{2.5}$) at these two sites is relevant for two reasons. Firstly, the derived chemical climates informs on the conditions affecting long-term health-relevant PM in the areas for which the sites are representative (i.e. rural areas in south east England and south east Scotland for Harwell and Auchencorth respectively). Secondly, the absence of substantial local emissions sources means that Harwell and Auchencorth are representative of regional background PM and its component concentrations. Regional background PM has been shown previously to be a major contributor to PM concentrations in urban areas in the UK (Harrison et al., 2012; Vieno et al., 2014). Therefore the long-term health-relevant PM chemical climates for Harwell and Auchencorth provide information about the conditions producing the regional contribution to PM concentrations across the UK and Europe, and hence extends the conclusions to a much larger spatial domain and population than the immediate vicinity of the supersites.

The interpretation of PM$_{10}$ and PM$_{2.5}$ measurements at Harwell and Auchencorth showed that a wide variety of conditions contribute to annual average PM$_{10}$ and PM$_{2.5}$ concentrations, and therefore should be taken into account during the formulation of mitigation strategies. Numerous studies have shown that high-concentration episodes of PM$_{10}$ and PM$_{2.5}$, and of its individual components, across the UK are associated with transport of air pollutants from continental Europe emission sources (Abdalmohith and Harrison, 2005; Harrison et al., 2012; Twigg et al., 2015; Vieno et al., 2014). This study has shown that while high PM$_{10}$ and PM$_{2.5}$ concentrations at Harwell were associated with air masses which traversed continental Europe, highest PM$_{10}$ and PM$_{2.5}$ concentrations at Auchencorth resulted from air masses which spent a larger proportion of time over the UK. The highest PM$_{10}$ and PM$_{2.5}$ concentrations were primarily composed of SIA components, NO$_3^-$, NH$_4^+$, and nss-SO$_4^{2-}$, with a smaller contribution from OC and EC. During the arrival of air masses which traversed Western Europe prior to arrival at Harwell, there was an increase in both short and long-range transport of SIA components. Hence in order to reduce the SIA contribution to high PM concentrations, it is necessary to reduce SIA precursor emissions regionally, and also in closer proximity to the location of interest. This is agreement with EMEP4UK model, which reported a combination of domestic emissions and long-range transport influencing annual average NO$_3^-$ (Vieno et al., 2014).

The reduction of these highest concentrations would not be as effective at reducing long-term health-relevant PM as reduction in moderate concentrations which occur substantially more frequently and therefore have a larger contribution to PM$_{10}$AA and PM$_{2.5}$AA. Formulation of mitigation strategies which focus on reduction of moderate PM$_{10}$ and PM$_{2.5}$ concentrations requires considerations of a wider variety of conditions compared to the highest PM$_{10}$ and PM$_{2.5}$ concentrations. A greater number of months, components and trajectories traversing different geographic regions made substantial contributions to moderate PM$_{10}$ and PM$_{2.5}$ concentrations at both Harwell and Auchencorth. The SIA components, NO$_3^-$, NH$_4^+$ and nss-SO$_4^{2-}$, have the largest contribution.

---

**Fig. 8.** Proportion of hours during the arrival of trajectories in each cluster during which the value of PC1 (indicative of short-range transport) and PC2 (indicative of long-range transport) was within 20 × 5-percentile bins, based on PCA analysis of the times series of 9 inorganic ions in PM$_{2.5}$ at Harwell in 2013. The larger the grey bar, the more hours with a 95−100th percentile value of the principal component during the arrival of trajectories assigned to the particular cluster, and the larger the red bar, the more hours with a 0−5th percentile value of the principal component etc. Larger percentile contributions from higher percentiles for PC1 indicates a larger contribution from short-range transport for trajectories in that cluster compared to other clusters. Larger percentile contributions from higher percentiles for PC2 indicates a larger contribution from long-range transport for trajectories in that cluster compared to other clusters.
to moderate PM$_{10}$ and PM$_{2.5}$ concentrations, but minor inorganic ions such as Ca$^{2+}$ and K$^+$, and the components of sea-salt have larger contributions to moderate concentrations compared to high concentrations. Hence reduction in SIA-related emission sources would result in the largest reduction in these moderate concentrations, but the sources of other components could be targeted and achieve greater benefit than at high PM$_{10}$ and PM$_{2.5}$ concentrations. Additionally, sea-salt components, which are naturally derived, also made a not insubstantial contribution to the highest-contributing concentrations to PM$_{10,AA}$ and PM$_{2.5,AA}$, and therefore affect the relative benefit to long-term health-relevant PM which could result from reduction of the other components.

During moderate PM$_{10}$ and PM$_{2.5}$ concentrations, the back trajectories typically traversed a wide variety of geographic regions compared to during high concentrations. These included trajectories which spent a majority of time over marine environments (and a small number of hours over land), over the UK, and over Western, Eastern and Northern Europe. Reducing emissions from large SIA precursor emission sources which were infrequently traversed (e.g. Western Europe trajectories occurred 13% of the time and contributed 35% of annual average PM$_{10}$ NO$_3^-$ at Harwell in 2013) would result in a reduction in the contribution of SIA to moderate PM concentrations. However, similar benefits could be derived, in terms of reducing the SIA contribution to moderate concentrations, from the reduction of smaller SIA precursor emission sources (e.g. those traversed for a small number of hours during mainly ‘marine’ trajectories) which are substantially more frequently traversed.

5. Conclusions

The chemical climates outlined in this paper provide a set of statistics for the interpretation of PM mass and component data which link long-term health-relevant PM (annual average PM$_{10}$ and PM$_{2.5}$) to the contributing drivers. The UK EMEP supersite measurements are representative of rural concentrations in the UK, and therefore the application of these statistics to these sites has provided policy-relevant conclusions on the conditions producing i) long-term health-relevant PM in rural areas of the UK and ii) the regional background contribution to long-term health-relevant PM across the UK which are a substantial fraction of total PM in urban areas of the UK. At the UK EMEP supersites, annual average PM$_{10}$ and PM$_{2.5}$ concentrations were substantially larger at Harwell (SE England) than at Auchencorth (SE Scotland). The chemical climate state showed that frequent, moderate PM$_{10}$ and PM$_{2.5}$ concentrations determined the magnitude of the annual average PM$_{10}$ and PM$_{2.5}$ to a greater extent than the relatively infrequent high, episodic PM$_{10}$ and PM$_{2.5}$ concentrations. Reduction of these moderate PM$_{10}$ and PM$_{2.5}$ concentrations requires consideration of a wider variety of conditions, due to the larger number of months, air mass pathways and components which contribute. For example, the largest contribution to moderate PM$_{10}$ and PM$_{2.5}$ concentrations were from SIA components, specifically NO$_3^-$. This contribution was accumulated during the arrival of trajectories characterised by time spent traversing marine environments, the UK, as well as continental Europe. Hence to reduce the emission sources which are the drivers of the long term PM health impact at the two sites, mitigation strategies must consider reductions in SIA emissions both domestically and internationally. The future application of this methodology across regional monitoring networks in future studies could provide a common basis for assessment of impact severity and the spatial efficacy of different mitigation strategies across larger, transboundary domains.

Acknowledgements

C. S. Malley acknowledges the University of Edinburgh School of Chemistry, the Natural Environment Research Council Centre for Ecology & Hydrology (NERC-CEH studentship funding project no. NERC4544) and the Department for Environment, Food and Rural Affairs for specific funding (Defra, Grant no. AQQ047) and for provision of the national monitoring networks. Authors acknowledge NERC funding and the field team support for making the measurements at the supersites, specifically Christopher Conolly and Michael Davies (RICardo Energy & Environment) for project management and data provision, respectively. Data obtained from uk-air.defra.gov.uk are subject to Crown copyright, Defra, licenced under the Open Government Licence (OGL).

Appendix A. Supplementary data

Supplementary data to this article can be found online at doi.org/10.1016/j.envint.2016.08.005.

References


