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



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## 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  $PM_{10}$  and  $PM_{2.5}$  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  $PM_{10}$  and  $PM_{2.5}$  (rather than just short-term episodic concentrations).  $PM_{10}$ ,  $PM_{2.5}$ , 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 ( $\pm 1$  sd) 2010–2013 annual average concentrations were  $PM_{10} = 16.4 \pm 1.4 \mu\text{g m}^{-3}$  and  $PM_{2.5} = 11.9 \pm 1.1 \mu\text{g m}^{-3}$  and at Auchencorth  $PM_{10} = 7.4 \pm 0.4 \mu\text{g m}^{-3}$  and  $PM_{2.5} = 4.1 \pm 0.2 \mu\text{g m}^{-3}$ . The chemical climate state at each site showed that frequent, moderate hourly  $PM_{10}$  and  $PM_{2.5}$  concentrations (defined as approximately 5–15  $\mu\text{g m}^{-3}$  for  $PM_{10}$  and  $PM_{2.5}$  at Harwell and 5–10  $\mu\text{g m}^{-3}$  for  $PM_{10}$  at Auchencorth) determined the magnitude of 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. These moderate  $PM_{10}$  and  $PM_{2.5}$  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  $PM_{10}$  and  $PM_{2.5}$  concentrations – the secondary inorganic aerosol components, specifically  $\text{NO}_3^-$  – 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 determinant of the long-term PM metrics to target.

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## 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.

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episodes was comprised predominantly of SIA components, whereas lower PM<sub>10</sub> concentrations had a substantially larger relative contribution from sea salt.

The aim of this work is to integrate the measurements of total PM<sub>10</sub> and PM<sub>2.5</sub> with the suite of PM component measurements to understand the conditions producing long-term human health-relevant PM concentrations, i.e. the factors contributing to annual average PM<sub>10</sub> and PM<sub>2.5</sub>. 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<sub>10</sub>, PM<sub>2.5</sub> 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<sub>2.5</sub>, PM<sub>10</sub> and components (AQEG, 2012; Harrison et al., 2012; Putaud et al., 2010). The novelty of this study is to focus data interpretation of PM<sub>10</sub>, PM<sub>2.5</sub> and component measurement datasets, along with air-mass back-trajectory analysis in order to specifically identify the determinants of annual average PM<sub>2.5</sub> and PM<sub>10</sub> at these sites. The term 'long-term health-relevant PM' is used to refer to annual average PM<sub>10</sub> and PM<sub>2.5</sub> concentrations in this work because these metrics were used to characterise long-term exposure to PM in synthesis reports by WHO (REVIHAAP 2013), and recommended health impact assessment methodologies for quantifying human health impacts resulting from long term exposure to PM (HRAPIE, 2013). It does not relate to the length of the time series analysed at the two sites (in this case 2010–2014, with a focus on 2012–2013).

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<sub>2.5</sub> and PM<sub>10</sub>), 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 supersites. The 'state' statistics used here are the contributions to the impact metrics from 1  $\mu\text{g m}^{-3}$  PM<sub>10</sub> and PM<sub>2.5</sub> 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<sub>10</sub> and PM<sub>2.5</sub> 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 Auchencorth 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 Auchencorth 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<sub>10</sub>, PM<sub>2.5</sub> 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 2**

Statistics derived to quantify the 'impact', 'state' and 'drivers' of the chemical climate specific to the long-term human health impact of PM.

| Chemical climate component | Statistic   | Further description   |
|----------------------------|---|---|
| Impact                     | Annual average PM <sub>10</sub> (PM <sub>10AA</sub> , $\mu\text{g m}^{-3}$ )  | WHO REVIHAAP (2013) recommends quantification of long-term PM health impact using both PM <sub>10</sub> and PM <sub>2.5</sub> size fractions due to distinct observed health impacts of fine and coarse PM      |
|                            | Annual average PM <sub>2.5</sub> (PM <sub>2.5AA</sub> , $\mu\text{g m}^{-3}$ )  |   |
| State                      | Contribution to PM <sub>10AA</sub> and PM <sub>2.5AA</sub> from 1 $\mu\text{g m}^{-3}$ concentration bins   |   |
|                            | Monthly contribution to PM concentrations in 1 $\mu\text{g m}^{-3}$ concentration bins  |   |
|                            | Average PM composition for PM concentrations in 1 $\mu\text{g m}^{-3}$ concentration bins   |   |
| Drivers                    | Contribution from geographic regions to PM concentrations in 1 $\mu\text{g m}^{-3}$ concentration bins  | 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. |
|                            | 'Contribution distribution': Contribution of 1 $\mu\text{g m}^{-3}$ PM <sub>10</sub> and PM <sub>2.5</sub> 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<sub>10</sub> and PM<sub>2.5</sub> 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<sub>3</sub><sup>-</sup> (41% (PM<sub>2.5</sub>)), and for PM<sub>10</sub> (50%) and PM<sub>2.5</sub> (48%) in 2013. Effective investigation of the conditions producing long-term health-relevant PM required concurrent measurements of PM<sub>10</sub> and PM<sub>2.5</sub>, and the inorganic ions, since the latter comprise the largest contribution to PM<sub>10</sub> and PM<sub>2.5</sub>. Therefore proxy PM<sub>10</sub> and PM<sub>2.5</sub> 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<sub>10</sub> and PM<sub>2.5</sub> data captures were 92% and 90% respectively. The relatively close proximity of the sites means regional background concentrations of PM<sub>10</sub> and PM<sub>2.5</sub> 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<sub>10</sub> and PM<sub>2.5</sub> (Fig. S1) and the equations were used to adjust the Reading dataset to estimate PM<sub>10</sub> and PM<sub>2.5</sub> at Harwell in 2013. At Auchencorth, PM<sub>10</sub> and PM<sub>2.5</sub> 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<sub>10</sub> and PM<sub>2.5</sub> concentrations, abbreviated here to PM<sub>10AA</sub> and PM<sub>2.5AA</sub> respectively. PM<sub>10</sub> and PM<sub>2.5</sub> were measured by a TEOM-FDMS instrument, which calculates the non-volatile and volatile PM components separately. Quantification of volatile PM<sub>10</sub> and PM<sub>2.5</sub> 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<sub>10</sub> and PM<sub>2.5</sub> concentrations this can exceed the volatile PM<sub>10</sub> or PM<sub>2.5</sub> lost and result in a negative concentration (AQEG, 2012). This was most limiting for PM<sub>2.5</sub> 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<sub>10</sub> and PM<sub>2.5</sub> across the PM<sub>10</sub> and PM<sub>2.5</sub> concentration distribution, during different months of the year, and from different PM<sub>10</sub> and PM<sub>2.5</sub> 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<sub>10</sub> and PM<sub>2.5</sub> 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<sup>-3</sup> concentration bins to PM<sub>10AA</sub> and PM<sub>2.5AA</sub> were calculated to investigate the accumulation of the annual average across different

PM<sub>10</sub> and PM<sub>2.5</sub> concentrations. The proportions of each concentration bin derived from each month of the year were also calculated.

### 2.3.2. PM<sub>10</sub> and PM<sub>2.5</sub> composition

For each PM<sub>10</sub> and PM<sub>2.5</sub> component (Table 1), the annual mean and contribution to PM<sub>10AA</sub> or PM<sub>2.5AA</sub> was calculated. At each hour, the fraction of SO<sub>4</sub><sup>2-</sup> derived from sea salt (ss-SO<sub>4</sub><sup>2-</sup>) was calculated using Equation 1 (Seinfeld and Pandis, 2006), while the non-sea salt SO<sub>4</sub><sup>2-</sup> (nss-SO<sub>4</sub><sup>2-</sup>) fraction was taken as the difference between the measured SO<sub>4</sub><sup>2-</sup> concentration and the ss-SO<sub>4</sub><sup>2-</sup> concentration.

$$[\text{ssSO}_4^{2-}] = 0.252 \times [\text{Na}^+] \quad (1)$$

A substantial number of the PM<sub>10</sub> and PM<sub>2.5</sub> 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<sup>-3</sup> PM<sub>10</sub> and PM<sub>2.5</sub> concentration bin. At low concentrations (typically below 5 µg m<sup>-3</sup>), the percentage of total mass PM<sub>10</sub> or PM<sub>2.5</sub> accounted for by the sum of the inorganic ions frequently exceeded 100%, exacerbated by the negative PM<sub>10</sub> and PM<sub>2.5</sub> measurements recorded by the TEOM-FDMS instrument, i.e. an underestimation 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<sub>10</sub> or PM<sub>2.5</sub> 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<sub>10</sub> and PM<sub>2.5</sub> concentrations. Therefore, for PM<sub>10</sub> and PM<sub>2.5</sub> concentrations in each 1 µg m<sup>-3</sup> 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<sub>10AA</sub> and PM<sub>2.5AA</sub> was derived across the PM<sub>10</sub> and PM<sub>2.5</sub> concentration distribution. Similarly, the contributions of elemental and organic carbon to total carbon for each 1 µg m<sup>-3</sup> PM<sub>10</sub> and PM<sub>2.5</sub> 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<sub>10</sub> and PM<sub>2.5</sub> from across the PM<sub>10</sub> and PM<sub>2.5</sub> distribution, and from the different PM<sub>10</sub> and PM<sub>2.5</sub> 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 spent an average of 10 h over the UK (Fig. 1).

The contribution of each trajectory cluster for PM<sub>10</sub> and PM<sub>2.5</sub> concentrations in each 1 µg m<sup>-3</sup> concentration bin was calculated. Additionally, for each PM<sub>10</sub> and PM<sub>2.5</sub> component, the contribution to the

component annual average from each PM<sub>10</sub> or PM<sub>2.5</sub> 1 µg m<sup>-3</sup> concentration bin was calculated. The contributions to annual average PM<sub>10</sub> or PM<sub>2.5</sub> component from each 1 µg m<sup>-3</sup> 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<sub>4</sub><sup>2-</sup> and nss-SO<sub>4</sub><sup>2-</sup> 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<sub>10</sub> and PM<sub>2.5</sub> 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

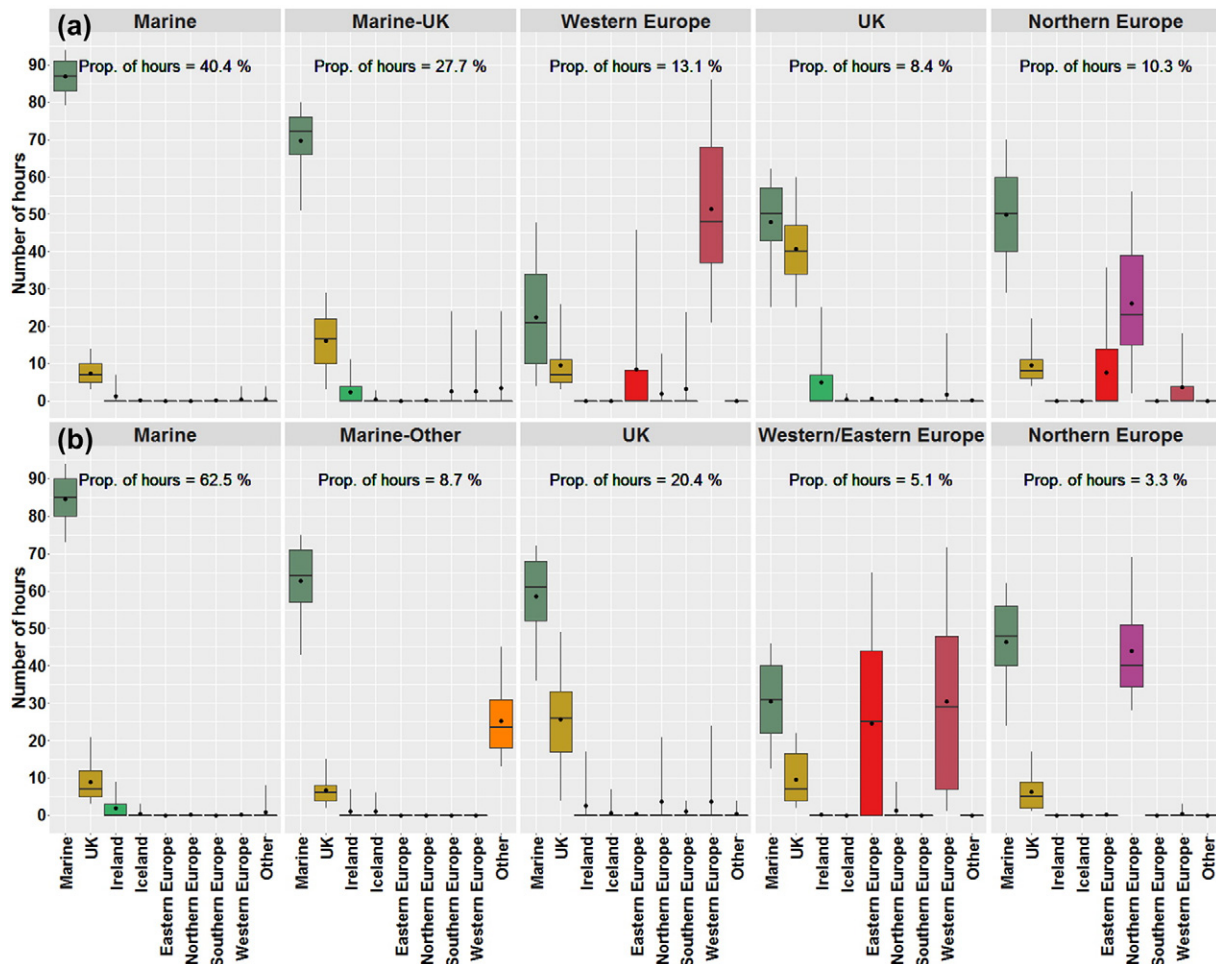


Fig. 1. Number of hours spent in different geographic regions for each of the air-mass back trajectory clusters arriving at a) Harwell in 2013, and b) Auchencorth in 2012. Note the different air masses arriving at each site resulting in a different cluster set at each site, hence the names of the clusters at each site differ.

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  $20 \times 5$ -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 ( $\pm 1$  std. dev.)  $PM_{10AA}$  and  $PM_{2.5AA}$  between 2010 and 2013 was  $16.4 \pm 1.4 \mu\text{g m}^{-3}$  and  $11.9 \pm 1.1 \mu\text{g m}^{-3}$  respectively at Harwell and  $7.4 \pm 0.4 \mu\text{g m}^{-3}$  and  $4.1 \pm 0.2 \mu\text{g m}^{-3}$  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 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  $PM_{10}$  and  $PM_{2.5}$  concentrations at both sites were within current European AQ limits, the PM is still presumed to be having effects on human health (REVIHAAP, 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  $20 \mu\text{g m}^{-3}$  contributed 53–73% of  $PM_{2.5AA}$  at Harwell between 2010 and 2013, while concentrations above  $40 \mu\text{g m}^{-3}$  contributed 6–16% to  $PM_{2.5AA}$ . At Auchencorth, the contribution to  $PM_{2.5AA}$  below  $20 \mu\text{g m}^{-3}$  was 82–90%, and below  $10 \mu\text{g m}^{-3}$  56–66%. The largest contribution from a single concentration bin varied between years (2010–2013) from 11–12 to 14–15  $\mu\text{g m}^{-3}$  for  $PM_{10AA}$  and 6–7 to 9–10  $\mu\text{g m}^{-3}$  for  $PM_{2.5AA}$  at Harwell. At Auchencorth, the largest contribution varied between the 5–6 and 8–9  $\mu\text{g m}^{-3}$  bins for  $PM_{10AA}$  and between 2–3 to 3–4  $\mu\text{g m}^{-3}$  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  $1 \mu\text{g m}^{-3}$  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  $PM_{10}$  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**

Annual average concentrations between 2010 and 2013 at Harwell and Auchencorth for  $PM_{10}$  and  $PM_{2.5}$ , and annual average contribution (mass and percentage) to  $PM_{10}$  and  $PM_{2.5}$  for inorganic ions, total carbon (organic + elemental carbon), the sum of 25 heavy metals and the sum of 25 PAHs.

| Annual average ( $\mu\text{g m}^{-3}$ )<br>contribution to PM average | PM   | $\text{NO}_3^-$ | $\text{nssSO}_4^{2-}$ | $\text{NH}_4^+$ | $\text{Cl}^-$ | $\text{Na}^+$ | $\text{Ca}^{2+}$ | $\text{ssSO}_4^{2-}$ | $\text{Mg}^{2+}$ | $\text{K}^+$ | Total carbon | Heavy metals | PAH    |
|---|------|-----------------|-----------------------|-----------------|---------------|---------------|------------------|----------------------|------------------|--------------|--------------|--------------|--------|
| Harwell $PM_{10}$   |      |                 |                       |                 |               |               |                  |                      |                  |              |              |              |        |
| 2010  | 16.0 |                 |                       |                 |               |               |                  |                      |                  |              |              | 0.16         | 0.0012 |
|   |      |                 |                       |                 |               |               |                  |                      |                  |              |              | 1.0%         | 0.01%  |
| 2011  | 18.1 |                 |                       |                 |               |               |                  |                      |                  |              | 2.63         | 0.22         | 0.0008 |
|   |      |                 |                       |                 |               |               |                  |                      |                  |              | 14.5%        | 1.2%         | 0.005% |
| 2012  | 16.6 | 2.92            | 1.89                  | 1.51            | 1.17          | 0.84          | 0.65             | 0.21                 | 0.22             | 0.02         | 2.14         | 0.16         | 0.0019 |
|   |      | 17.6%           | 11.3%                 | 9.1%            | 7.0%          | 5.0%          | 3.9%             | 1.3%                 | 1.3%             | 0.1%         | 12.9%        | 0.9%         | 0.01%  |
| 2013  | 14.7 | 3.71            | 1.79                  | 1.57            | 1.17          | 1.14          | 0.38             | 0.29                 | 0.24             | 0.08         | 2.28         | 0.17         | 0.0018 |
|   |      | 25.3%           | 12.2%                 | 10.7%           | 8.0%          | 7.8%          | 2.6%             | 2.0%                 | 1.6%             | 0.5%         | 15.5%        | 1.2%         | 0.01%  |
| Harwell $PM_{2.5}$  |      |                 |                       |                 |               |               |                  |                      |                  |              |              |              |        |
| 2010  | 10.3 |                 |                       |                 |               |               |                  |                      |                  |              |              |              |        |
| 2011  | 11.9 |                 |                       |                 |               |               |                  |                      |                  |              |              |              |        |
| 2012  | 12.8 | 2.00            | 1.51                  | 1.04            | 0.50          | 0.41          | 0.38             | 0.10                 | 0.12             | 0.01         | 1.38         |              |        |
|   |      | 15.7%           | 11.8%                 | 8.1%            | 3.9%          | 3.2%          | 3.0%             | 0.8%                 | 0.9%             | 0.1%         | 10.8%        |              |        |
| 2013  | 12.5 | 3.34            | 1.84                  | 1.57            | 0.61          | 0.60          | 0.22             | 0.15                 | 0.14             | 0.06         | 1.49         |              |        |
|   |      | 26.7%           | 14.7%                 | 12.5%           | 4.8%          | 4.8%          | 1.7%             | 1.2%                 | 1.1%             | 0.5%         | 11.9%        |              |        |
| Auchencorth $PM_{10}$   |      |                 |                       |                 |               |               |                  |                      |                  |              |              |              |        |
| 2010  | 7.12 |                 |                       |                 |               |               |                  |                      |                  |              |              | 0.09         | 0.0004 |
|   |      |                 |                       |                 |               |               |                  |                      |                  |              |              | 1.29%        | 0.01%  |
| 2011  | 7.06 |                 |                       |                 |               |               |                  |                      |                  |              |              | 0.08         | 0.0003 |
|   |      |                 |                       |                 |               |               |                  |                      |                  |              |              | 1.17%        | 0.004% |
| 2012  | 7.35 | 1.86            | 1.22                  | 0.98            | 1.11          | 0.85          | 0.06             | 0.21                 | 0.06             | 0.07         |              | 0.07         | 0.0012 |
|   |      | 25.3%           | 16.6%                 | 13.3%           | 15.1%         | 11.5%         | 0.9%             | 2.9%                 | 0.8%             | 0.9%         |              | 0.9%         | 0.02%  |
| 2013  | 7.94 | 1.28            | 0.98                  | 0.74            | 1.15          | 0.73          | 0.06             | 0.18                 | 0.08             | 0.07         |              | 0.12         | 0.0008 |
|   |      | 16.2%           | 12.3%                 | 9.3%            | 14.4%         | 9.2%          | 0.8%             | 2.3%                 | 1.0%             | 0.8%         |              | 1.6%         | 0.01%  |
| Auchencorth $PM_{2.5}$  |      |                 |                       |                 |               |               |                  |                      |                  |              |              |              |        |
| 2010  | 4.03 |                 |                       |                 |               |               |                  |                      |                  |              |              |              |        |
| 2011  | 4.01 |                 |                       |                 |               |               |                  |                      |                  |              |              |              |        |
| 2012  | 3.82 | 1.54            | 1.09                  | 0.89            | 0.61          | 0.48          | 0.05             | 0.12                 | 0.04             | 0.05         | 0.66         |              |        |
|   |      | 40.3%           | 28.5%                 | 23.3%           | 16.0%         | 12.6%         | 1.2%             | 3.1%                 | 1.0%             | 1.2%         | 17.4%        |              |        |
| 2013  | 4.40 | 1.07            | 0.94                  | 0.65            | 0.67          | 0.44          | 0.05             | 0.11                 | 0.05             | 0.04         | 0.66         |              |        |
|   |      | 24.3%           | 21.4%                 | 14.8%           | 15.2%         | 10.0%         | 1.1%             | 2.5%                 | 1.1%             | 1.0%         | 15.0%        |              |        |



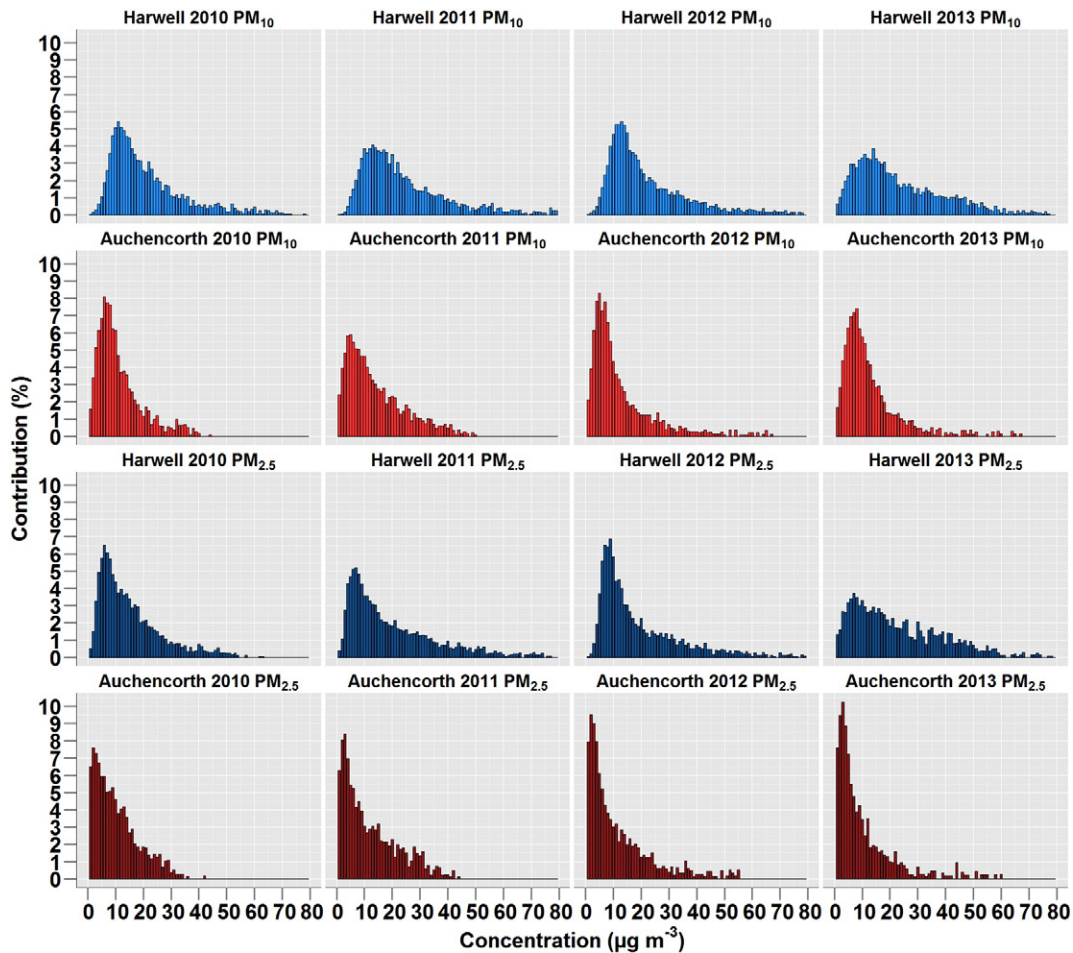


Fig. 2. Contribution of hourly concentrations segmented into  $1 \mu\text{g m}^{-3}$  concentration bins to annual average  $\text{PM}_{10}$  ( $\text{PM}_{10\text{AA}}$ ) and  $\text{PM}_{2.5}$  ( $\text{PM}_{2.5\text{AA}}$ ) at Harwell and Auchencorth for each year between 2010 and 2013.

### 3.2.2. $\text{PM}_{10}$ and $\text{PM}_{2.5}$ composition

This section describes (i) the contribution of the different  $\text{PM}_{10}$  and  $\text{PM}_{2.5}$  components to long-term health-relevant PM ( $\text{PM}_{2.5\text{AA}}$  and  $\text{PM}_{10\text{AA}}$ ) and (ii) how these contributions arise based on component variation across the range of  $\text{PM}_{10}$  and  $\text{PM}_{2.5}$  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).

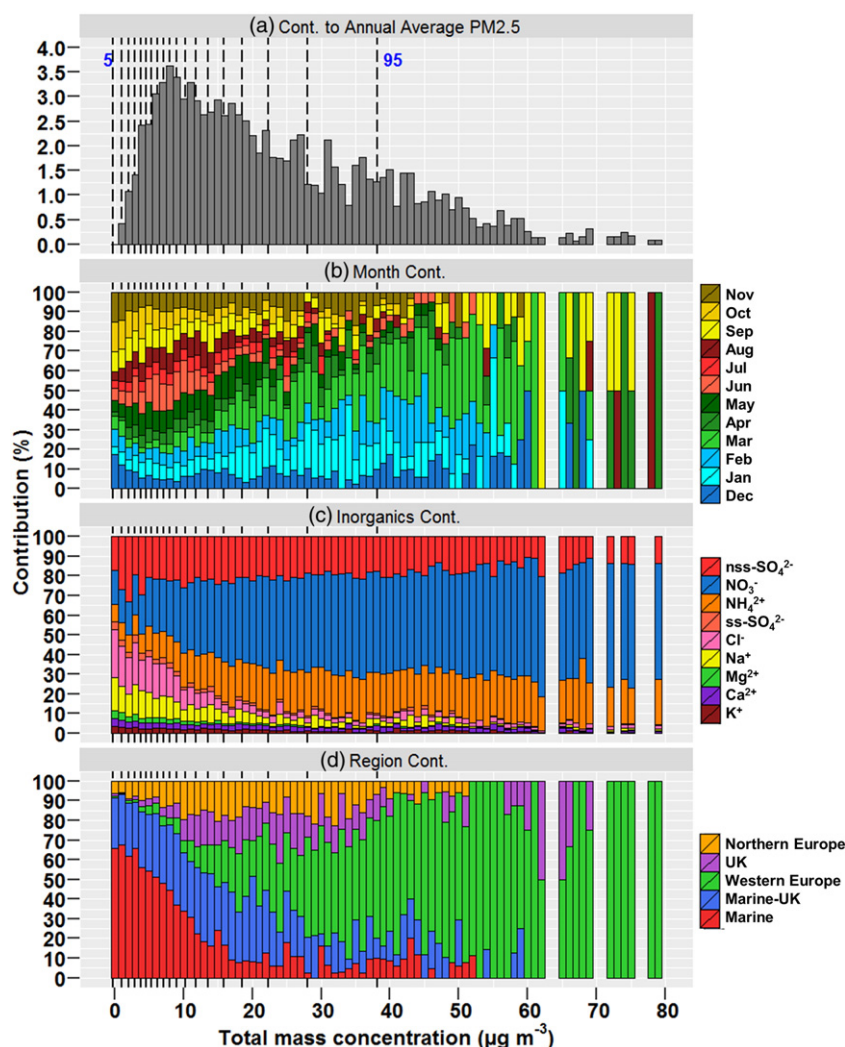
The SIA components,  $\text{NO}_3^-$ ,  $\text{nss-SO}_4^{2-}$  and  $\text{NH}_4^+$  comprised the largest fraction of  $\text{PM}_{10\text{AA}}$  and  $\text{PM}_{2.5\text{AA}}$  at both Harwell and Auchencorth (Table 3). For example, the annual average sum of the SIA components accounted for 48% of  $\text{PM}_{10\text{AA}}$  and 54% of  $\text{PM}_{2.5\text{AA}}$  at Harwell in 2013, and 55% of  $\text{PM}_{10\text{AA}}$  concentrations at Auchencorth in 2012. For  $\text{PM}_{2.5}$  at Auchencorth, the SIA components accounted for 92% of  $\text{PM}_{2.5\text{AA}}$ . The sum of all measured components was substantially greater than  $\text{PM}_{2.5\text{AA}}$ , including when negative measurements were omitted. At Auchencorth, analysis of contributions of components of PM therefore focussed on  $\text{PM}_{10}$ , as the higher  $\text{PM}_{10}$  concentrations were less affected by limitations of the TEOM-FDMS instrument at low concentrations.

The components of sea salt ( $\text{Cl}^-$ ,  $\text{Na}^+$ ,  $\text{ss-SO}_4^{2-}$  and  $\text{Mg}^{2+}$ ) were, together, the second largest contributor to  $\text{PM}_{10\text{AA}}$  and  $\text{PM}_{2.5\text{AA}}$  (Table 3). At Harwell in 2013, sea-salt components comprised 19.4% of  $\text{PM}_{10\text{AA}}$  and 11.9% of  $\text{PM}_{2.5\text{AA}}$ . At Auchencorth in 2012, 30.3% of  $\text{PM}_{10\text{AA}}$  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  $\text{PM}_{10\text{AA}}$  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  $\text{PM}_{10\text{AA}}$  (15.5% in 2013 at Harwell) compared to  $\text{PM}_{2.5\text{AA}}$  (11.9%). These values are substantially smaller than calculated at an urban background site in the UK, where TC accounted for 37% of  $\text{PM}_{2.5}$  (Yin and Harrison, 2008). Overall, the three sets of components, SIA, sea-salt and TC, comprised the major mass fraction of both  $\text{PM}_{10\text{AA}}$  and  $\text{PM}_{2.5\text{AA}}$ , so assessment of the conditions giving rise to their contributions is most useful for consideration of reduction of  $\text{PM}_{10\text{AA}}$  and  $\text{PM}_{2.5\text{AA}}$ , 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  $\text{PM}_{10\text{AA}}$  at both sites. The most abundant metals in declining contribution were iron (on average  $54 \pm 4\%$  of the sum of the 25 annual average heavy metals in  $\text{PM}_{10}$  at Harwell between 2010 and 2013,  $47 \pm 8\%$  at Auchencorth), aluminium ( $23 \pm 4\%$  at Harwell,  $34 \pm 12\%$  at Auchencorth), zinc ( $6 \pm 0.7\%$  at Harwell,  $8 \pm 2\%$  at Auchencorth) and barium ( $5 \pm 2\%$  at Harwell,  $1 \pm 0.3\%$  at Auchencorth). The PAHs made a considerably smaller contribution to  $\text{PM}_{10\text{AA}}$ , generally approximately 0.01%. Though not the focus for  $\text{PM}_{10\text{AA}}$  or  $\text{PM}_{2.5\text{AA}}$ , there is motivation for reduction in concentration of PAHs and heavy metals because of their individual specific impacts (health or otherwise). For example,





**Fig. 3.** (a) Contributions to annual average  $PM_{2.5}$  ( $PM_{2.5AA}$ ) from hourly  $PM_{2.5}$  concentrations segmented into  $1 \mu g m^{-3}$  bins at Harwell in 2013. Also shown are (b) the proportion of hourly  $PM_{2.5}$  concentrations within each bin from the different months of the year, (c) the relative contributions from 9 inorganic ions to total inorganic ion concentrations during hours when  $PM_{2.5}$  concentrations were in each bin and, (d) the proportion of trajectories from each cluster arriving during hours when measured  $PM_{2.5}$  concentrations were in each bin.

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, S2c, 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  $PM_{2.5}$  (38  $\mu g m^{-3}$ ) at Harwell,  $NO_3^-$ ,  $nss-SO_4^{2-}$  and  $NH_4^+$  respectively comprised 51%, 18% and 21% of

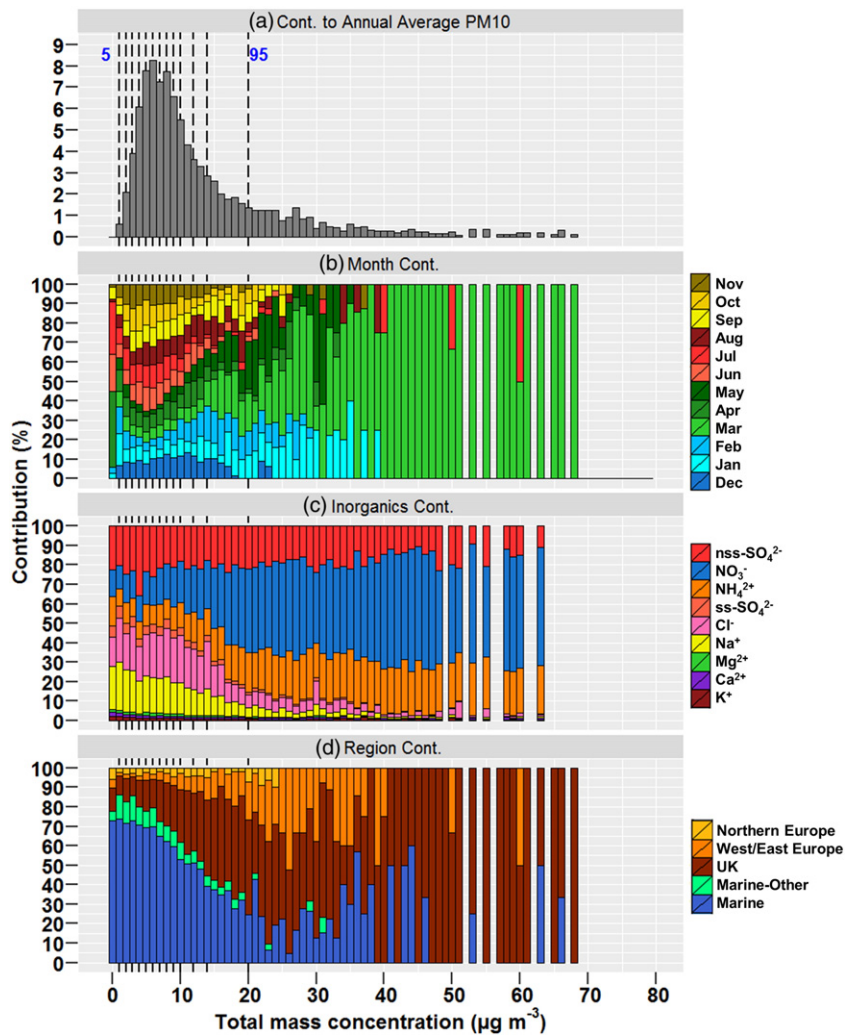
the inorganic fraction of  $PM_{2.5}$  (Fig. 3c). In contrast to the SIA components,  $Cl^-$  and  $Na^+$  comprised 2% and 3% of the inorganic fraction of  $PM_{2.5}$  at the 95th percentile  $PM_{2.5}$  concentration. The contribution of  $nss-SO_4^{2-}$  therefore remained relatively constant for 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  $1 \mu g m^{-3}$



**Fig. 4.** (a) Contributions to annual average PM<sub>10</sub> (PM<sub>10AA</sub>) from hourly PM<sub>10</sub> concentrations segmented into 1 µg m<sup>-3</sup> bins at Auchencorth in 2012. Also shown are (b) the proportion of hourly PM<sub>10</sub> concentrations within each bin from the different months of the year, (c) the relative contributions from 9 inorganic ions to total inorganic ion concentrations during hours when PM<sub>10</sub> concentrations were in each bin and, (d) the proportion of trajectories from each cluster arriving during hours when measured PM<sub>10</sub> concentrations were in each bin.

concentration bin is shown in Fig. 3d for PM<sub>2.5</sub> and Fig. S2d for PM<sub>10</sub>. For both PM<sub>10</sub> and PM<sub>2.5</sub> there was a contrast between the majority of trajectories assigned to 'Marine' clusters arriving during hours with low PM<sub>10</sub> or PM<sub>2.5</sub> 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<sub>2.5</sub> concentration bins <5 µg m<sup>-3</sup>, 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<sub>2.5</sub> concentration, 'Western Europe' trajectories arrived during 60% of hours. This 'marine' to 'terrestrial' trajectories transition occurred across the moderate PM<sub>2.5</sub> concentrations, and consequently, during the high frequency, moderate concentrations with largest contribution to PM<sub>2.5AA</sub>, 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<sub>10</sub> concentrations <5 µg m<sup>-3</sup> 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<sub>10</sub> 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<sub>10</sub> concentrations below 20 µg m<sup>-3</sup> (95th percentile, Fig. 4). Hence for the moderate concentration range which had the largest contribution to PM<sub>10AA</sub> 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<sub>10</sub> and PM<sub>2.5</sub> composition during different air-mass pathways at Harwell and Auchencorth. A substantial proportion of annual average PM<sub>2.5</sub> NO<sub>3</sub><sup>-</sup> 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<sub>3</sub><sup>-</sup> 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<sub>2.5</sub> NO<sub>3</sub><sup>-</sup> was accumulated differently across the total PM<sub>2.5</sub> 1 µg m<sup>-3</sup> concentration bins for each trajectory cluster. A larger proportion of the annual average PM<sub>2.5</sub> NO<sub>3</sub><sup>-</sup> that accumulated during marine-dominated trajectories was accumulated at relatively low concentrations, e.g. 57% of the annual average PM<sub>2.5</sub> NO<sub>3</sub><sup>-</sup> was accumulated during PM<sub>2.5</sub> concentration bins below 10 µg m<sup>-3</sup> 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  $\text{PM}_{2.5} \text{NO}_3^-$  was accumulated during higher  $\text{PM}_{2.5}$  concentrations, e.g. between 17% and 22%, of the annual average  $\text{PM}_{2.5} \text{NO}_3^-$  accumulated during 'Western Europe' trajectories was accumulated during  $\text{PM}_{2.5}$  concentration bins between 10 and 20  $\mu\text{g m}^{-3}$ , 20–30  $\mu\text{g m}^{-3}$ , 30–40  $\mu\text{g m}^{-3}$ , and 40–50  $\mu\text{g m}^{-3}$  (Fig. S4).

The total proportion of annual average  $\text{PM}_{2.5} \text{NO}_3^-$  accumulated in each  $\text{PM}_{2.5}$  1  $\mu\text{g m}^{-3}$  concentration bin across all trajectories arriving at Harwell in 2013 is shown in Fig. 5a. The largest contribution to annual average  $\text{PM}_{2.5} \text{NO}_3^-$  occurred during moderate  $\text{PM}_{2.5}$  concentrations which also had the largest contribution to  $\text{PM}_{2.5\text{AA}}$ . During hours with moderate  $\text{PM}_{2.5}$  concentrations, trajectories belonging to each cluster (marine and terrestrial-influenced) arrived relatively frequently. Hence a wide range of geographic source regions contributed to determining the proportion of  $\text{PM}_{2.5}$  accounted for by a single PM component ( $\text{NO}_3^-$ ). In comparison during relatively low and high  $\text{PM}_{2.5}$  concentrations during which a smaller proportion of annual average  $\text{PM}_{2.5} \text{NO}_3^-$  was accumulated, mainly 'Marine' and 'Marine-UK' trajectories, and 'Western Europe' trajectories arrived (Fig. 5a). This was also the case for  $\text{NH}_4^+$ , reflecting their linked formation pathways as components of SIA (Fig. 5b).

The majority of the annual average  $\text{PM}_{2.5} \text{Cl}^-$  concentration at Harwell in 2013 was derived at relatively low  $\text{PM}_{2.5}$  concentrations, and 68% of annual average  $\text{PM}_{2.5} \text{Cl}^-$  was derived when  $\text{PM}_{2.5}$  concentrations were <10  $\mu\text{g m}^{-3}$  (Fig. 5c). This contribution occurred mostly during the arrival of 'Marine' and 'Marine-UK' trajectory clusters, and similar results were calculated for other sea-salt components such as  $\text{Na}^+$ , and  $\text{Mg}^{2+}$  (Fig. S5). For minor inorganic ions ( $\text{Ca}^{2+}$  and  $\text{K}^+$ ), the accumulation across  $\text{PM}_{2.5}$  concentrations of annual average  $\text{Ca}^{2+}$  and  $\text{K}^+$  occurred to a greater extent during relatively low concentrations (and during 'Marine' and 'Marine-UK' trajectories) compared to SIA

components, and to a greater extent at high concentrations (and 'Western Europe', 'Northern Europe' and 'UK' trajectories) compared to sea-salt components (Fig. 5d). Similar patterns were calculated for the inorganic ion components in  $\text{PM}_{10}$  at Harwell in 2013 (Fig. S6). For EC and OC (derived from daily measurements), a greater proportion of annual average EC was accumulated at higher daily  $\text{PM}_{10}$  concentrations, and hence during 'Western Europe' trajectories (35% of annual average EC at Harwell in 2013), compared to OC (21% of annual average OC) (Fig. S7).

The contribution to annual average  $\text{NO}_3^-$ ,  $\text{NH}_4^+$ ,  $\text{Cl}^-$ , and  $\text{Ca}^{2+}$  in  $\text{PM}_{10}$  across 1  $\mu\text{g m}^{-3}$  concentration 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  $\text{PM}_{10}$  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  $\text{PM}_{10}$  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  $\text{PM}_{10} \text{NO}_3^-$  was derived during  $\text{PM}_{10}$  concentrations between 5 and 10  $\mu\text{g m}^{-3}$ , during which 49%, 34% and 10% of the trajectories arriving were grouped in 'Marine', 'UK' and 'Western/Eastern Europe' clusters respectively. For  $\text{Cl}^-$  and  $\text{Ca}^{2+}$ , the majority of the component annual average was accumulated during 'Marine' trajectories (63% for  $\text{Cl}^-$  annual average and 57% for  $\text{Ca}^{2+}$ ), and a larger proportion of the annual average was accumulated during 'UK' trajectories for  $\text{Ca}^{2+}$  (24% (Fig. 6c and d)).

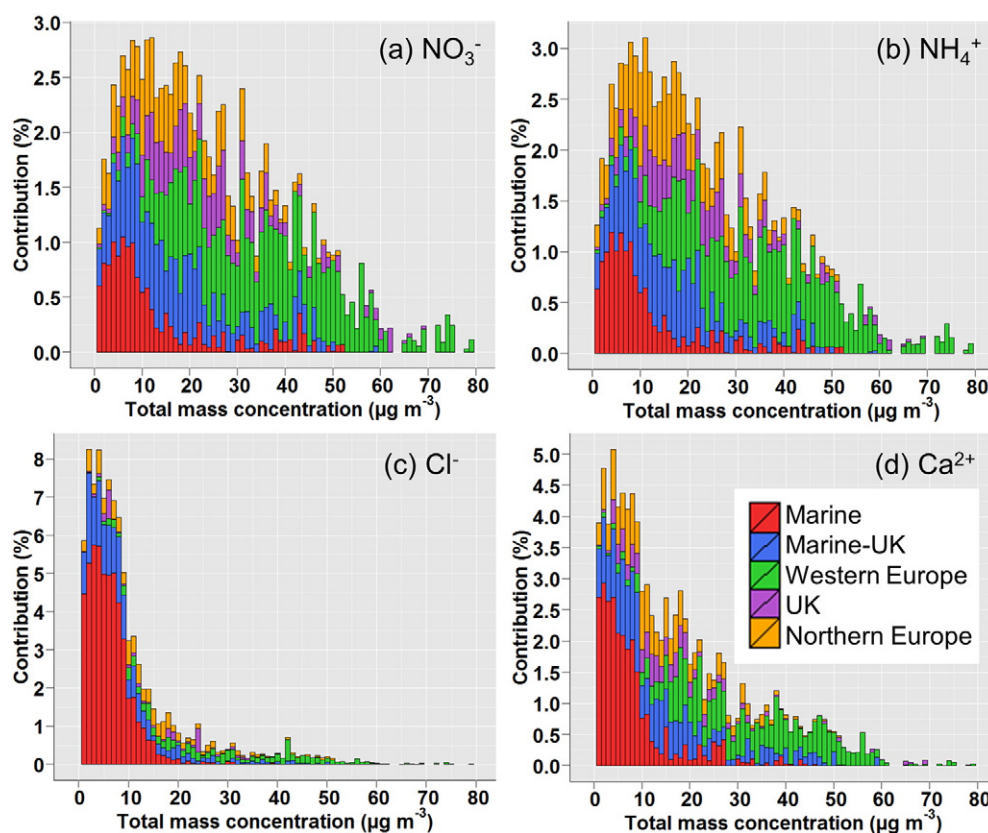
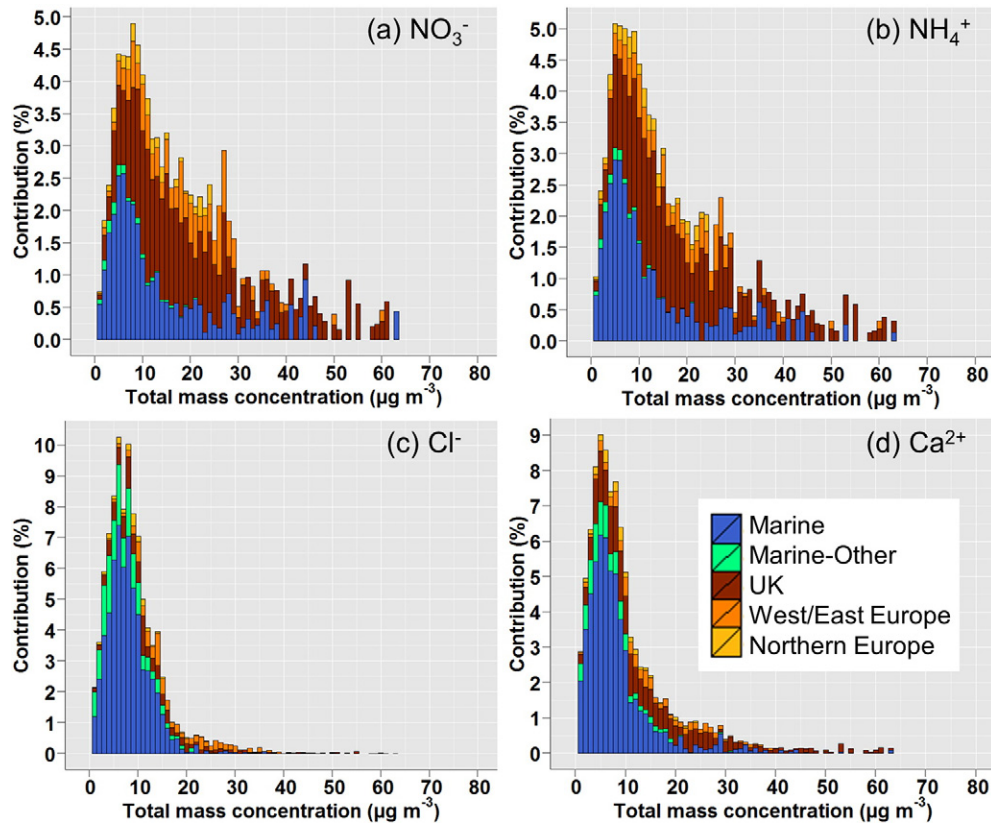


Fig. 5. Proportion of annual average a)  $\text{NO}_3^-$ , b)  $\text{NH}_4^+$ , c)  $\text{Cl}^-$ , d)  $\text{Ca}^{2+}$  in  $\text{PM}_{2.5}$  at Harwell in 2013 accumulated during hours with  $\text{PM}_{2.5}$  concentrations in 1  $\mu\text{g m}^{-3}$  concentration bins (distinct bars along x-axis), and during the arrival of trajectories belonging to each cluster (different colours within each bar).

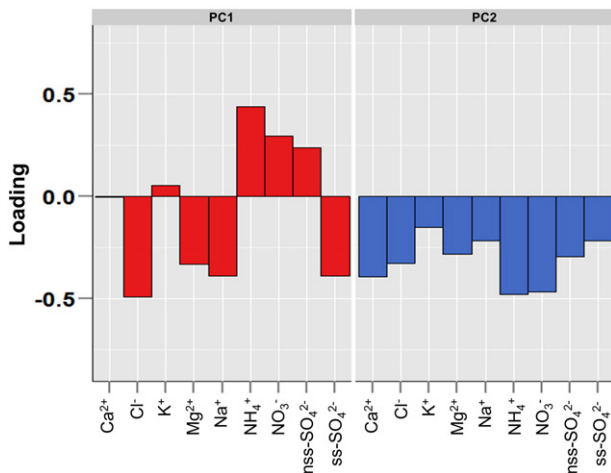




**Fig. 6.** Proportion of annual average a)  $\text{NO}_3^-$ , b)  $\text{NH}_4^+$ , c)  $\text{Cl}^-$ , d)  $\text{Ca}^{2+}$  in  $\text{PM}_{10}$  at Auchincorth in 2012 accumulated during hours with  $\text{PM}_{10}$  concentrations in  $1 \mu\text{g m}^{-3}$  concentration bins (distinct bars along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

### 3.3.2. Principal component analysis (PCA)

PCA analysis provides insight into why the accumulation of annual average  $\text{NO}_3^-$ ,  $\text{NH}_4^+$  and  $\text{nss-SO}_4^{2-}$  during the arrival of trajectories assigned to each cluster, e.g. marine vs terrestrial-influenced trajectories, was derived differently across the range of  $\text{PM}_{2.5}$  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  $\text{PM}_{2.5}$  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

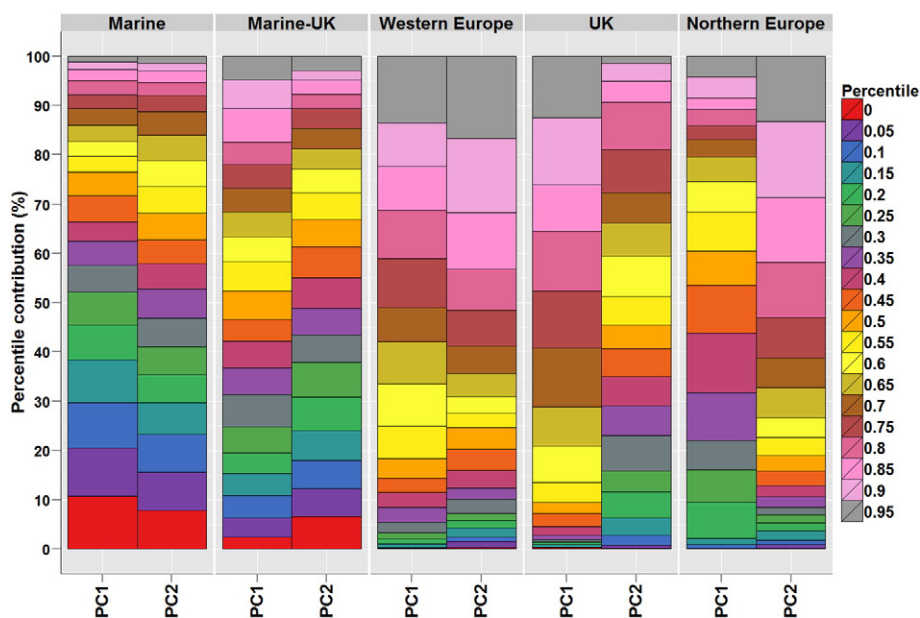


**Fig. 7.** Loadings of 9 inorganic ions for the first two principal components (PCs) resulting from application of PCA to the inorganic ion dataset for  $\text{PM}_{2.5}$  at Harwell in 2013.

direction of loading indicates anti-correlation between components. For PC1, the SIA components,  $\text{NO}_3^-$ ,  $\text{NH}_4^+$  and  $\text{nss-SO}_4^{2-}$  had high correlation, and were anti-correlated with sea-salt components  $\text{Cl}^-$ ,  $\text{Na}^+$  and  $\text{Mg}^{2+}$ . 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  $\text{K}^+$  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  $\text{Cl}^-$  and  $\text{Na}^+$  were 29% and 53% smaller, respectively, than the loading for  $\text{NO}_3^-$ , a large value of PC2 indicates a relatively higher percentile  $\text{NO}_3^-$  and  $\text{NH}_4^+$  concentration than  $\text{Cl}^-$  and  $\text{Na}^+$ . In the context of SIA formation and the contribution of SIA to  $\text{PM}_{2.5}$ , 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  $20 \times 5$ -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. Viena et al. (2014) modelled UK and European emission contributions to UK SIA concentrations and calculated that both





**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  $20 \times 5$ -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.

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 emission 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 (Abdalmogith 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  $PM_{10AA}$  and  $PM_{2.5AA}$ . 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

to moderate PM<sub>10</sub> and PM<sub>2.5</sub> concentrations, but minor inorganic ions such as Ca<sup>2+</sup> and K<sup>+</sup>, 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<sub>10</sub> and PM<sub>2.5</sub> concentrations. Additionally, sea-salt components, which are naturally derived, also made a not insubstantial contribution to the highest-contributing concentrations to PM<sub>10AA</sub> and PM<sub>2.5AA</sub>, and therefore affect the relative benefit to long-term health-relevant PM which could result from reduction of the other components.

During moderate PM<sub>10</sub> and PM<sub>2.5</sub> 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 emissions sources which were infrequently traversed (e.g. Western Europe trajectories occurred 13% of the time and contributed 35% of annual average PM<sub>2.5</sub> NO<sub>3</sub><sup>-</sup> 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 emissions 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<sub>10</sub> and PM<sub>2.5</sub>) 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<sub>10</sub> and PM<sub>2.5</sub> concentrations were substantially larger at Harwell (SE England) than at Auchencorth (SE Scotland). The chemical climate state showed that frequent, moderate PM<sub>10</sub> and PM<sub>2.5</sub> concentrations determined the magnitude of the annual average PM<sub>10</sub> and PM<sub>2.5</sub> to a greater extent than the relatively infrequent high, episodic PM<sub>10</sub> and PM<sub>2.5</sub> concentrations. Reduction of these moderate PM<sub>10</sub> and PM<sub>2.5</sub> 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<sub>10</sub> and PM<sub>2.5</sub> concentrations were from SIA components, specifically NO<sub>3</sub><sup>-</sup>. 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.

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## Appendix A. Supplementary data

Supplementary data to this article can be found online at <http://dx.doi.org/10.1016/j.envint.2016.08.005>.

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