The role of long-range transport and domestic emissions in determining atmospheric secondary inorganic particle concentrations across the UK

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ABSTRACT

Surface concentrations of secondary inorganic particle components over the UK have been analysed for 2001-2010 using the EMEP4UK regional atmospheric chemistry transport model and evaluated against measurements. In early 2003 an episode of substantially elevated surface concentrations of ammonium nitrate was measured across the UK by the AGANet network. The EMEP4UK model was able accurately to represent both the long-term decadal surface concentrations and the episode in 2003. The latter was identified as consisting of three separate episodes, each of less than 1 month duration, in February, March and April. The primary cause of the elevated nitrate levels across the UK was meteorological, a persistent high pressure system, but whose varying location impacted the relative importance of transboundary versus domestic emissions. Whilst long-range transport dominated the elevated nitrate in February, in contrast it was domestic emissions that mainly contributed to the March episode, and for the April episode both domestic emissions and long-range transport contributed. A prolonged episode such as the one in early 2003 can have substantial impact on annual average concentrations. The episode led to annual concentration differences at the regional scale of similar magnitude to those driven by long-term changes in precursor emissions over the full decade investigated here. The results demonstrate that a substantial part of the UK, particularly the south and south-east, may be close to or exceeding annual mean limit values because of import of inorganic aerosol components from continental Europe under specific conditions. The results reinforce the importance of employing multiple year simulations in the assessment of emissions reduction scenarios on PM concentrations and the need for international agreements to address the transboundary component of air pollution.

1 Introduction

Atmospheric particulate matter (PM) concentrations are governed by the transport, transformation and deposition of many chemical species. PM has a range of impacts including on climate through radiative forcing and on human health. Considering the health impacts alone, exposure to $PM_{2.5}$ (the size fraction of particles with an aerodynamic diameter $\leq$ 2.5 µm) has been estimated to contribute to an average loss of life expectancy of around 6-7 months for residents of the UK, with an associated economic cost of some £16 billion per annum (IGCB, 2007). EU legislation sets standards for ambient concentrations of PM, and now includes an obligation on individual member states to reduce population-weighted exposure to $PM_{2.5}$ by a specified percentage between 2010 and 2020 (Heal et al., 2012).

The complexity of ambient PM composition and formation, combined with the influence of meteorology on chemistry, dispersion and deposition, considerably complicates pinpointing the contributions of different chemical pollutant emission sources to ambient PM at specific locations (USEPA, 2009; AQEG, 2012). Consequently, it is a complicated process to formulate cost-effective policy action to reduce harm caused by PM. The inorganic chemical components of PM, ammonium (NH_4^+), sulphate (SO_4^{2-}) and nitrate (NO_3^-), constitute a major fraction of $PM_{2.5}$ (Putaud et al., 2010). The anthropogenic emissions of the gaseous precursors of inorganic PM – ammonia (NH_3), sulphur dioxide (SO_2) and nitrogen oxides (NO_x) – are also subject to various legislation that seeks to limit and reduce either a country's total emissions or the emissions from individual sources or source sectors (Heal et al., 2012;Reis et al., 2012). For SO_2 and NO_x in particular, emissions reductions have been very effective over the past few decades and this is reflected in reductions in ambient concentrations of the gases (RoTAP, 2012). Despite this, PM_{10} concentrations across much of western Europe have not fallen significantly since the year 2000 (Harrison et al., 2008).

The longer lifetime of secondary PM components compared with their gaseous precursors means that transboundary transport from Europe and meteorology are important drivers. Previous studies suggest transatlantic transport of these secondary inorganic aerosol (SIA) species has a small effect on EU surface SIA concentrations and deposition (Sanderson et al. 2008; Simpson et al. 2014), hence "transboundary" hereafter refers to Europe. This is of particular relevance for the design of air quality policies seeking to reduce PM concentrations, especially as some limit values may be sensitive to a small number of high concentration episodes rather than long-term average concentrations. This is particularly important for the nitrate component which has shown to be the dominant component on days when PM_{10} exceeds 50 $\mu g\ m^{-3}$ (Yin and Harrison, 2008).

There remains a gap in understanding the extent to which domestic emissions and transboundary import of secondary inorganic PM contribute inter-annually and to episodes of elevated concentrations in the UK (RoTAP). This was the motivation for this work. Ambient concentrations of the inorganic components have been measured since the 1990s on a monthly average basis, as part of the UK Acid Gas and Aerosol Network (AGANet http://uk-air.defra.gov.uk/networks/network-info?view=aganet, see Tang et al. (2009) for description of the approach), providing a dataset against which to compare model output.

In section 2 the modelling approach using the EMEP4UK Eulerian atmospheric chemistry transport model (ACTM) (Vieno et al., 2010;Vieno et al., 2009) simulations and AGANet measurements are fully described. In section 3, first the model performance is evaluated against these AGANet measurements and then the results of sensitivity simulations to assess the contributions of trans-boundary and domestic emissions to secondary inorganic particle concentrations in the UK and their inter-annual variability are assessed. Section 4 discusses this novel decadal inter-comparison and attribution results and conclusions are presented in section 5.

2 Methods

2.1 Model description and set-up

The EMEP4UK model used for this work is a nested regional ACTM based on version v3.7 of the main EMEP model (Simpson et al., 2012). A detailed description of the EMEP4UK model framework and setup are given in Vieno et al. (2010) and only brief relevant details are presented here.

The EMEP4UK model is driven by the Weather Research Forecast (WRF) model version 3.1.1 (www.wrf-model.org). The model horizontal resolution scales down from 50 km × 50 km in the main EMEP 'Greater European' domain to 5 km × 5 km for the domain covering the British Isles (Fig. 1). The boundary conditions for the inner domain are derived from the results of the European domain in a one-way nested setup. The EmChem09 chemical scheme was chosen for the present study, as it has been extensively validated at the European scale (Simpson et al. (2012), www.emep.int). The EMEP mode is based on Berge and Jakobsen (1998), but extended with photo-oxidant chemistry (Andersson-Skold and Simpson, 1999;Simpson et al., 1995). The EmChem09 mechanism used for this work has 72 species and 137 reactions. Full details of the chemical scheme are given by Simpson et al. (2012). Gas/aerosol partitioning used the EQSAM formulation (Metzger et al., 2002a;Metzger et al., 2002b). The calculated nitrate is then split into coarse and fine mode using a parameterised approach dependent on relative humidity, as described by Simpson et al. (2012). In this version of the EMEP model, nitrate is the only secondary inorganic component present in PM_{coarse} (the difference between PM_{10} and $PM_{2.5}$). This split between $PM_{2.5}$ and $PM_{2.5-10}$ for nitrate is rather uncertain as discussed in Aas et al. (2012); a more explicit aerosol scheme is under development. The EQSAM scheme used here is equivalent to the EQSAM2 scheme used in the global model TM5 (Karl et al., 2009;Huijnen et al., 2010).

Anthropogenic emissions of NO_x, NH_3, SO_2, primary $PM_{2.5}$, primary PM_{coarse}, CO, and non-methane volatile organic compounds (NMVOC) are included. PM_{10} is the size fraction of particles with an aerodynamic diameter $\leq 10\ \mu m$. For the UK, emissions values are taken from the National Atmospheric Emission Inventory (NAEI, http://naei.defra.gov.uk) at 1 km^2 resolution and aggregated to 5 km × 5 km resolution The underpinning methods by which these emission inventories have been established are reported by Hellsten et al. (2008) and Dore et al. (2008). For the rest of the outer domain, the model uses the EMEP 50 km × 50 km resolution emission estimates provided by the Centre for Emission Inventories and Projections (CEIP, http://www.ceip.at/). Emissions estimates for international shipping (ENTEC, 2010) are aggregated to 5 km × 5 km for those emissions within the inner domain. The EMEP(4UK) model uses a yearly boundary condition for SIA at the edge of the European domain adjusted for each year as describe in Simpson et al. (2012).

2.2 Model experiments

Hourly surface concentrations of several pollutants, including NO_2, SO_2 and NH_3, and particle NO_3^-, SO_4^{2-} and NH_4^+, were simulated for the decade 2001-2010. To quantify the influence of long-range (i.e. non-UK, or 'transboundary') and short-range (UK, 'domestic') emissions on the UK surface concentrations of these components, a perturbation experiment was carried out by setting UK land emissions to zero for the year. This provides an approximate model estimate of the contribution of non-UK emissions to gaseous and particulate matter concentrations in the UK.

2.3 Measurement data

Model surface concentrations were compared with observational data from the UK Acid Gases and Aerosols Network (AGANet), which is one of the four component UK Eutrophying and Acidifying Pollutants monitoring networks (Conolly et al., 2011;Tang et al., 2013). The AGANet monitoring sites were established in 1999 for the long-term simultaneous measurement of the concentrations of SO_2, HNO_3 and NH_3 gases and particle NO_3^-, SO_4^{2-} and NH_4^+, in relation to changes in European emissions of SO_2, NO_x and NH_3. Measurements are made using DELTA system (DEnuder for Long-Term Atmospheric sampling) and have monthly-averaged time resolution (Sutton et al., 2001). The size cut-off of the DELTA sampler has been estimated to be ~4.5 μm (Tang et al., 2009), therefore the measured concentrations are between the $PM_{2.5}$ and PM_{10} size fractions.

The EMEP4UK model assigns all SO_4^{2-} and NH_4^+ components to $PM_{2.5}$. Modelled NO_3^- is assigned to both $PM_{2.5}$ and PM_{coarse} which leads to potential negative bias in modelled versus measured concentrations for NO_3^-. Four sites representing different areas of the UK (marked on Fig. 1) have been selected for the comparisons presented here: Strathvaich Dam (north-west Scotland); Bush (central Scotland); Rothamsted (south-east England); and Yarner Wood (south-west England).

3 Results

The time series of the modelled and observed monthly mean surface concentrations of particle NO_3^- and SO_4^{2-} at the four selected AGANet sites are shown in Fig. 2 and Fig. 3, respectively. The observations span the period 2001-2010, whereas the model values span the period 2001-2010. A peak in 2003 in NO_3^- concentrations can be seen in both observations and the EMEP4UK simulations. Fig. 2 and Fig. 3, show generally good agreement between the two datasets for three of the four sites included here, as illustrated quantitatively by the correlation and linear regression statistics for these particle-phase components and for the gas-phase species HNO_3 and SO_2 (Table 1). The model-measurement comparison at the Strathvaich Dam site is adversely impacted by two extreme measurement values in 2006 and 2007 not present in the simulations. No anomaly is present in the meteorology at this location for these two months. From an analysis of the mass balance of the aerosol components, the two anomalous data points appears to be outliers and which may be attributed to sampling or analytical contamination in determination of NO_3^- and SO_4^{2-}. The anomaly could be potentially due to local influence or an unusually high positive artefact on the HNO_3. Recent investigations indicate that the AGANet HNO_3 observation using the DELTA methodology includes a positive bias from other NO_y chemical species, which could include HONO (heterogeneously oxidised), N_2O_5 and PANs. However, there is nothing to indicate that Strathvaich Dam should be affected more from this than other sites.

The spatial pattern across the British Isles and the inter-year variability of modelled annual mean surface concentrations are shown in Fig. 4 for NO_2, SO_2 and NH_3 and in Fig. 5 for particle NO_3^-, SO_4^{2-} and NH_4^+. In each case, the top left panel shows the spatial distribution for 2001 and the other 9 panels show the differences in annual mean concentrations for each of years 2002-2010 relative to 2001. The maps for 2001 show highest concentrations of NO_2 and SO_2 over central and south east England, related to UK emission sources, and over the English Channel, mostly related to shipping emission sources. The highest concentrations of NO_2 and SO_2 over the UK are in 2003, with the lowest concentrations during 2008-2010. The extended periods of elevated NO_3^- during February to April 2003 were sufficient to enhance the annual average NO_3^- concentration across the whole of the UK in 2003 by between 0.2-0.3 $\mu g\ N\ m^{-3}$ compared with preceding and subsequent years (Fig. 5a), with a even larger enhancement in the annual mean for 2003 of 0.2-0.5 $\mu g\ N\ m^{-3}$ for NH_4^+ (Fig. 5c). In contrast, the somewhat less elevated SO_4^{2-} concentrations during this period led to a modest increase in annual average SO_4^{2-} for 2003 of 0.0-0.1 $\mu g\ S\ m^{-3}$ (Fig. 5b). The spatial distribution of NH_3 shows a very different pattern to the other modelled components, with highest modelled concentrations in Brittany and north-west France and north-west England, reflecting the distribution of modelled NH_3 emissions which mainly arise from agricultural sources.

The concentrations of the particle components NO_3^-, SO_4^{2-} and NH_4^+ are spatially smoother across the UK than the gaseous precursors (Fig. 4 and Fig. 5). The modelled annual surface concentrations of NO_2 and SO_2 (Fig. 4a and Fig. 4b) show that the concentrations of these gaseous components decline during 2001-2010 by substantially more than the decline in NO_3^- and SO_4^{2-} . Over much of the UK (particularly England), declines in modelled NO_2 and SO_2 between 2001 and 2010 exceed 1 μg N/S m^{-3} in 2010 compared with the 0.1-0.2 μg N m^{-3} decline in NO_3^-, and the 0.1-0.3 μg S m^{-3} decline in SO_4^{2-} (up to 0.4 μg S m^{-3} decline in eastern England). On the other hand the model shows concentrations of NH_3 hardly changing over the decade; in fact increasing slightly, up to ~0.2 μg N m^{-3} over England, especially for 2009 and 2010 (Fig. 4c), whereas, with the exception of 2003, the modelled concentration of NH_4^+ in PM decreases from 2001-2010. Of note also, is a decrease of SO_2 annual surface concentration over the North Sea from 2007 onwards (Fig. 4b).

Fig. 6a and Fig. 6b (upper panels) show the modelled monthly-mean surface concentrations of NO_2 and SO_2, respectively, for the first 5 months of 2003, which covers the period of high secondary inorganic particle concentrations shown in (Fig. 2 and Fig. 3). To highlight the role of UK sources, the differences between the base simulations and the simulations with zero UK emissions are shown in the lower panels of Fig. 6a and Fig. 6b, with the data expressed as the percentage of the modelled concentrations that are directly attributable to UK domestic emissions (i.e. 100× (Base Run – Experiment)/Base), again as monthly averages. While the lower maps clearly show the dominating contribution of UK domestic sources to NO_2 and SO_2 concentrations over mainland UK, a smaller contribution in the vicinity of major shipping channels reflects the fact that the scenario treated international shipping as part of the non-UK emissions.

Fig. 7a and Fig. 7b show similar model results to Fig. 6 but for surface concentrations of particle NO_3^- and SO_4^{2-}, respectively. For these components, there is a smaller percentage contribution from UK sources than for SO_2 and NO_x concentrations.

The highest concentrations of NO_2 and SO_2 occurred during February and March (Fig. 6), with highest concentrations for NO_3^- and SO_4^{2-} occurring during February, March and April (Fig. 7). Fig. 7 shows that, for February, up to 40% of the monthly average NO_3^- concentrations over the UK are attributable to UK emissions. In March and April, the UK contribution to NO_3^- concentrations rises to up to 80%. The spatial pattern of the UK contribution to these concentrations differs between the months, with February showing the smallest contribution of UK sources to SO_2, NO_2, NO_3^- and SO_4^{2-} concentrations. In contrast, the episodes in March and April 2003 have substantially larger contributions of UK emissions to NO_3^- and SO_4^{2-} concentrations.

A detailed comparison for 2003 between the measured and modelled NO_3^- concentrations at the Bush 1 site (Scotland) is shown in Fig. 8 with the modelled values presented as both monthly and daily means. There is a close agreement between observations (red line) and model (blue line) for these high concentration episodes, with the monthly values broadly agreeing within 10%.

The monthly modelled concentrations for the simulation with zero UK emissions are also shown in Fig. 8 (green line). The modelled monthly NO_3^- concentrations (blue line) were enhanced by 2.6 $\mu g\ m^{-3}$ by UK emissions in February, but by 5.0 $\mu g\ m^{-3}$ in March and by 2.6 $\mu g\ m^{-3}$ in April as compared with the model simulation with no-UK emissions (green line). The daily mean model NO_3^- concentrations highlight substantial temporal variability within this February-April period. The daily average surface concentrations (orange line of Fig. 8) show three separate episodes; the first approximately matches the period 12-28th of February (F), the second 10-27th March (M) and the third 1-30th April (A).

The characteristic differences between these three periods are illustrated in Fig. 9. Here the 12:00 wind vector is superimposed to the mean modelled surface concentration of PM NO_3^- for selected days during the three component episodes. It is seen that 12-15th Feb (episode F) and 17-20th Mar (episode M) were associate with stagnant air masses allowing NO_3^- PM concentrations to build up, while the period 11-14th Apr (episode A) was associated with a highlight polluted airmass arriving from the East.

The UK February episode was associated with an easterly light wind advecting PM NO_3^- produced in the area of the north of France, Holland, north of Germany, and Denmark, where the centre of the high pressure was located (Fig. 9). During the March episode, the centre of the high pressure was over the UK with an associated light wind, clear sky, and cooler conditions leading to the accumulation of NO_3^- from UK emissions with little import of NO_3^- or its precursors from outside the UK. The April episode was a mixture of conditions described for February and March.

The model sensitivity analyses of the proportions of UK nitrate and sulphate derived from UK emissions of anthropogenic precursors was extended over the whole period 2001-2010, and the results for the locations of the four study sites, Strathvaich Dam, Bush, Rothamsted and Yarner Wood (highlighted in Fig. 1) are shown in Fig 10. The 10 years analysed here shows that the monthly-averaged UK emissions contributions to SO_4^{2-} and NO_3^- at these sites ranges from 10% to 80%. Yarner Wood and Strathvaich Dam are closer than the other selected sites to areas of shipping emissions, therefore on average the SO_4^{2-} concentration at this site is less influenced by UK emissions compared with the other two sites.

Based on the simulations it is possible to estimate the annual contribution of non-UK emissions to the different components of PM_{10} at the four study sites. This is summarized in Fig. 11 for the year 2003, also including the contribution of primary particulate matter (emitted PM). Pollution import for $PM_{2.5}$ from non-UK sources ranges from an estimated 41% for Bush 1, up to 63% for Yarner Wood, highlighting the importance of transboundary pollution import on UK $PM_{2.5}$ concentrations. The same model results for 2003 can be expressed in terms of the contribution of non-UK emissions to the current European Commission (EC, 2013) limit value for $PM_{2.5}$ and to the World Health Organisation (WHO, 2005) guideline value for $PM_{2.5}$ at each of the four sites (Table 2). For these example sites, up to 18% and 45% of the limit and guideline values, respectively, is provided by non-UK emissions.

4 Discussion

Inorganic particle components were simulated over the period 2001-2010. This is the first time that high spatial resolution (5 km) and temporal resolution (1 hour) simulations of inorganic atmospheric species have been undertaken across the whole UK for a multi-year period, and the first time that the EMEP(4UK) simulations have been compared with the UK-wide AGANet monitoring network.

Two inorganic aerosol schemes were available for the EMEP and EMEP4UK model: the EQSAM (used in this work) and the MARS scheme (Simpson et. al., 2012). As discussed in section 2.1, both schemes use a bulk approach for particle formation. The EQSAM aerosol scheme was used here as it has demonstrated good performance in the TM5 atmospheric chemistry transport model (Karl et al., 2009;Huijnen et al., 2010). However the bulk approach may lead to uncertainties in the simulated SIA, as shown in Hu et al. (2008), as the particle sizes are not explicitly resolved in the model. The current aerosols scheme and size partitioning in the EMEP model has been validated and compared with observations across

Europe as shown in Fagerli and Aas (2008) and in Simpson et al. (2006). In addition, in a recent model intercomparison (Carslaw, 2011b, a) SIA and its gaseous precursors simulated by EMEP4UK showed good agreement with observations.

The smoother distribution of particle components (Fig. 5 and Fig. 7) as compared with their gaseous precursors (Fig. 4 and Fig. 6) reflects the longer timescales for forming these secondary pollutants, as compared with the emissions-driven patterns for the primary pollutant gases (AQEG, 2012). The lifetime for oxidation of NO_x and SO_2 to HNO_3 and H_2SO_4 is up to a few days and comparable to transnational air-mass transport times. Hence the lifetime of formation plays an important role in determining the influence of non-UK emissions on SIA concentrations in the UK.

The highest modelled concentrations over this period are in 2003, particularly for PM NO_3^- and NH_4^+, and to a lesser extent for SO_4^{2-}, whilst lowest concentrations for each of these components are in 2008-2010.The notably high PM NO_3^- concentrations in February to April 2003 were observed at AGANet stations across the UK and could be well reproduced by the model (Fig. 2, Table 1). Concentrations of PM SO_4^{2-} were also elevated during this period, although by a smaller amount, and were also well captured by the model (Fig. 3, Table 1). The magnitude of this elevation in annual average PM NO_3^- concentration in 2003 is greater than the decline in annual average concentration across the whole decade to 2010 of 0.1-0.2 $\mu g\ N\ m^{-3}$ (Fig. 5). The August 2003 heatwave (Vieno et al., 2010) was not associated with high nitrate as the higher temperature limits the partitioning to the condensed phase. However, a secondary peak in sulphate is noted during summer 2003, which is directly attributed to the 2003 August heatwave, whereby elevated temperatures lead to faster SO_2 oxidation to sulphate (Dawson et al., 2007;Jacob and Winner, 2009).

Although the magnitude of monthly/daily elevated NO_3^- is similar for the three months of February, March and April 2003, each month has a different characteristic. A distinctive meteorological feature for the three months was a persistent high pressure over the UK and Europe (unusual for this season) with an associated relatively cool temperature and little rainfall (not shown). The location and persistency of the high pressure strongly influenced the production and transport of NO_3^-. Although emissions of NO_3^- precursors are controlled, the model analysis shows the substantial influence of meteorology underpinning the high concentrations of NO_3^- observed in the UK during the first part of 2003. Wang et al. (2014) examined the drivers of PM concentrations in the Shanghai region. Similar to our results for the UK they showed that meteorology determined whether the dominant contributor to PM concentrations was local emissions or regional transport. The authors suggest that particular attention should be given to emissions controls in the upwind adjacent provinces, as well as in local areas, for developing effective strategies to reduce $PM_{2.5}$ pollution in Shanghai, again consistent with our conclusions. Zhang et al. (2014) also found that PM concentrations in central China have a clear link with long-range transport. A recent study in the USA by Mwaniki et al. (2014) showed nitrate to have a large variation in winter time, contributing substantially to elevated PM events.

The geographic origins of the PM episodes have been investigated in the model perturbation experiment. The monthly average surface concentrations for the zero UK emissions experiment show that surface concentrations of SO_2 and NO_2 are mainly driven by UK emissions (Fig. 6) and by similar proportions of UK emissions throughout the period of high surface concentrations of NO_3^-. However, the proportions of the NO_3^- that are derived from UK and non-UK emissions changes between months (Fig. 7). The model results show that for February 2003 trans-boundary emissions had a small influence on NO_3^-, whereas for March and April the trans-boundary transport of NO_3^- and/or its precursors was substantial. Abdalmogith et al. (2006) suggest that the annual average import of NO_3^- aerosol to the UK from Europe (as an average of 2002 and 2003) is between 35-65% of the UK total NO_3^- concentration. Our study has found that, for 2003 (Fig. 7), the import to the UK from Europe was in the range 20-60% of UK total NO_3^- concentrations, with this proportion varying between the three episodes (labelled F, M and A in Fig. 8). Abdalmogith et al. (2006) concluded that the 2003 NO_3^- spring event was not well represented by their model, and the low emissions resolution (10 km × 10 km grid) was suggested as a possible cause. In the present study the elevated NO_3^- concentrations are well represented by the EMEP4UK model at 5 km x 5 km resolution. However, we find that simulation at 50 km × 50 km horizontal spatial resolution of the EMEP4UK model outer domain also represented these features (results not included here), indicating that transport and dispersion were the main drivers of the pollution events. As shown in Fig 10, over the full 10-year period there was a substantial variation (10% to 80%) in the contribution of UK emissions to SIA concentrations in the UK.

The simulated changes in the gaseous precursors for 2001-2010 follow the reductions in UK emissions over that period especially for NO_2 and SO_2 (MacCarthy et al., 2012). The change of SO_2 annual surface concentration especially after 2007 over the North Sea (Fig. 4b) is a direct response to the introduction of a sulphur emission control area (SECA) in the North Sea, including the English Channel, by the 2007 MARPOL convention on marine pollution (Dore et al., 2007). Under the convention the sulphur content of bunker fuel was restricted to 1.5 % by mass in 2007 (and will be further reduced to 0.1% in SECAs by 2020). This has resulted in a substantial reduction of emissions of SO_2 from the shipping sector.

The results in Fig. 4 and Fig. 5 illustrate the non-linear relationship between changes over time in SO_2 and NO_2 surface concentrations over the 2001- 2010 decade and changes in the respective PM SO_4^{2-} and NO_3^{-} concentrations. The sensitivity of PM SO_4^{2-} to changes in its precursors is, however, considerably greater than for NO_3^{-}. The small decline in NO_3^{-} and low sensitivity to UK NO_x emission found in this work was supported by the results in (Harrison et al., 2013). The formation of both NO_3^{-} and SO_4^{2-} requires NH_4^{+} as a counter-ion and there appear to be sufficient NH_3 emissions not to be a limiting factor to SO_4^{2-} formation. Conversely, UK NO_x emissions are still relatively high, especially in urban areas, so with an abundance of NO_x available for formation of ammonium nitrate available NH_3 eventually may be consumed. Consequently, in areas of high NO_x emissions, NO_3^{-} formation appears to be more sensitive to NH_3 emissions than is the case for SO_4^{2-} formation. This is consistent with Redington et al. (2009) whose modelling showed that SO_4^{2-} formation in the UK was less sensitive to a 30% NH_3 emissions reduction than NO_3^{-} formation.

The modelled annual average NH_4^{+} shows a change between 2001 and 2010 over the UK which is intermediate between that of NO_3^{-} and SO_4^{2-} (Fig. 5c). By 2010, NH_4^{+} concentrations decreased by 0.3-0.4 μg N m^{-3} over most of England, but, as was the case for NO_3^{-} concentrations, annual average NH_4^{+} concentrations in 2003 were elevated by 0.2-0.3 μg N m^{-3} compared with preceding and subsequent years. This confirms that the episodes of elevated NO_3^{-} in 2003 were driven by ammonium nitrate specifically. The modelled decrease in PM NH_4^{+} concentrations as compared with minimal decrease (and some increase) in NH_3 concentrations over the period 2001-2010 is consistent with the conclusions of Bleeker et al. (2009) and Horvath et al. (2009) for other parts of Europe that reducing SO_2 emissions have contributed to maintaining or even increasing gaseous NH_3 concentrations.

Current EU legislation has established a limit value of 25 μg m^{-3} for annual mean $PM_{2.5}$ for the protection of human health; at the same time, the World Health Organisation (WHO) publishes a guideline value of 10 μg m^{-3} annual mean $PM_{2.5}$ for the protection of human health. As Fig. 11 illustrates, determining the contribution of transboundary and regional transport to local PM concentrations is vital to inform policy development, as local measures can only address the local contribution. For the four sites analysed for 2003, Fig. 11 shows the share of non-UK contribution to modelled $PM_{2.5}$ concentrations ranging from 63% (Yarner Wood) to 41% (Bush 1). It is also clear that PM_{10} at these locations is dominated by sea-salt. As these stations are representative of rural or background levels, it is likely that the relative long-range contribution to $PM_{2.5}$ concentrations at urban hotspots is smaller, but still substantial.

Table 2 expresses the non-UK contribution to modelled annual mean $PM_{2.5}$ relative to the EC limit value and WHO guideline value for $PM_{2.5}$ (for the protection of human health). The non-UK contribution ranges from 5% at Strathvaich to 18% at Rothamsted for the limit value at 25 μg m^{-3} (or 14% to 45% for the same sites with respect to the guideline value of 10 μg m^{-3}). This indicates a clear gradient of non-UK contribution from greatest in the south-east and least in the north; this is likewise visible in Fig. 5.

The results presented here clearly demonstrate the need for international agreements to address the transboundary component of air pollution. If, for instance, an overall limit value of 10 μg m^{-3} were to be established following the WHO guideline, a substantial number of UK monitoring sites (Fig. 2) in particular in the south and south-east of the country may be close to or exceed annual mean limit values due to import of inorganic particle components from continental Europe under specific conditions.

In the view of these results, the rather moderate further reductions agreed by parties to the Convention on Long-range Transboundary Air Pollution in the revision of the Gothenburg Protocol (Reis et al., 2012) for the period between 2010 and 2020 would result in a substantial remaining contribution of transboundary aerosol transport to UK particulate matter concentrations for the next decade.

The results further illustrate how the inter-annual variability of surface concentrations of nitrate for the 2001-2010 decade as a response to changes in meteorological conditions is larger than the effect of changes in anthropogenic emissions. This suggests that for compliance assessment, an average over several years would provide a more robust basis than individual years, where a few short episodes can have a major influence.

5 Conclusion

For the first time the EMEP4UK model has been operated at high resolution for a multi-year period (2001-2010) and simulated secondary inorganic component concentrations compared with observations from the AGANet network. The drivers of three remarkably high secondary inorganic aerosol episodes across the UK have been investigated in detail, revealing contrasting causes for different periods. The EMEP4UK model was able accurately to represent both the long-term decadal (2001-2010) surface concentrations of particulate matter (PM) and specific episodes of elevated PM NO_3^- in 2003. The latter was identified as consisting of three separate episodes, each of less than 1 month duration, in February, March and April. The primary cause of the elevated nitrate levels across the UK was meteorological, related to a persistent high pressure system, with the contribution of imported pollution differing markedly between these events.

The findings emphasise the importance of employing multiple year simulations in the assessment of emissions reduction scenarios on PM concentrations. The inter-annual variability of surface concentrations of nitrate for the 2001-2010 decade as a response to changes in meteorological conditions is larger than the effect of changes in anthropogenic emissions. For instance, up to 60% of NO_3^- may be imported from outside the UK under specific conditions.

Our results highlight how inter-annual variability can profoundly affect the sensitivity to the attainment of limit values for ambient PM concentrations as a result of non-domestic contributions from transboundary air pollution transport.

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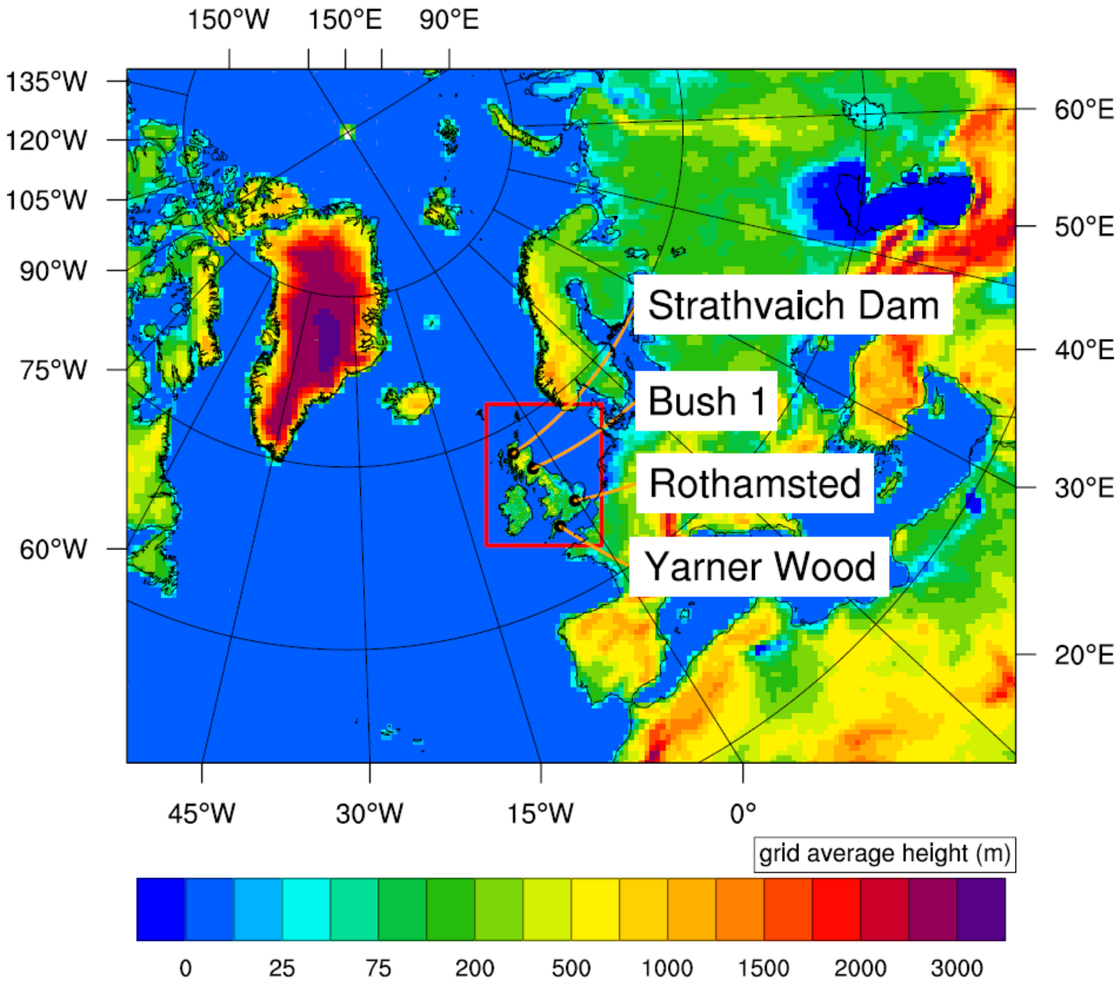


Fig. 1: The EMEP4UK Greater European domain, modelled at 50 km × 50 km horizontal resolution and, outlined in red, the nested British Isles domain, modelled at 5 km × 5 km horizontal resolution. The colour scale indicates grid-average altitude. The four UK AGANet measurement sites used in this study are also shown.

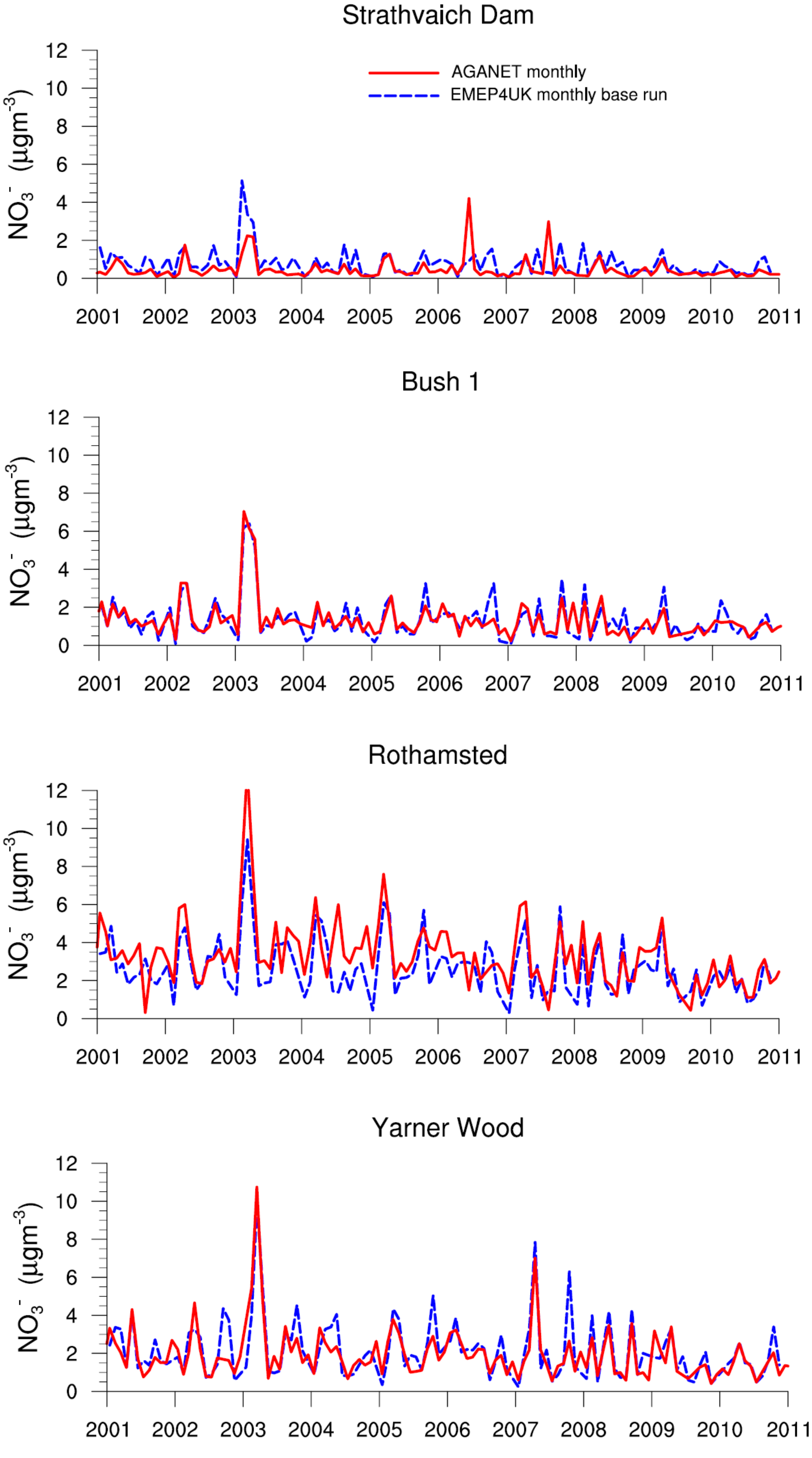


Fig. 2: Monthly average surface concentrations of particulate matter nitrate, observed (RED) and modelled (BLUE), for 2001-2010 at four sites of the AGANet network: Strathvaich Dam (north-west Scotland), Bush (central Scotland), Rothamsted (south-east England), and Yarner Wood (south-west England).

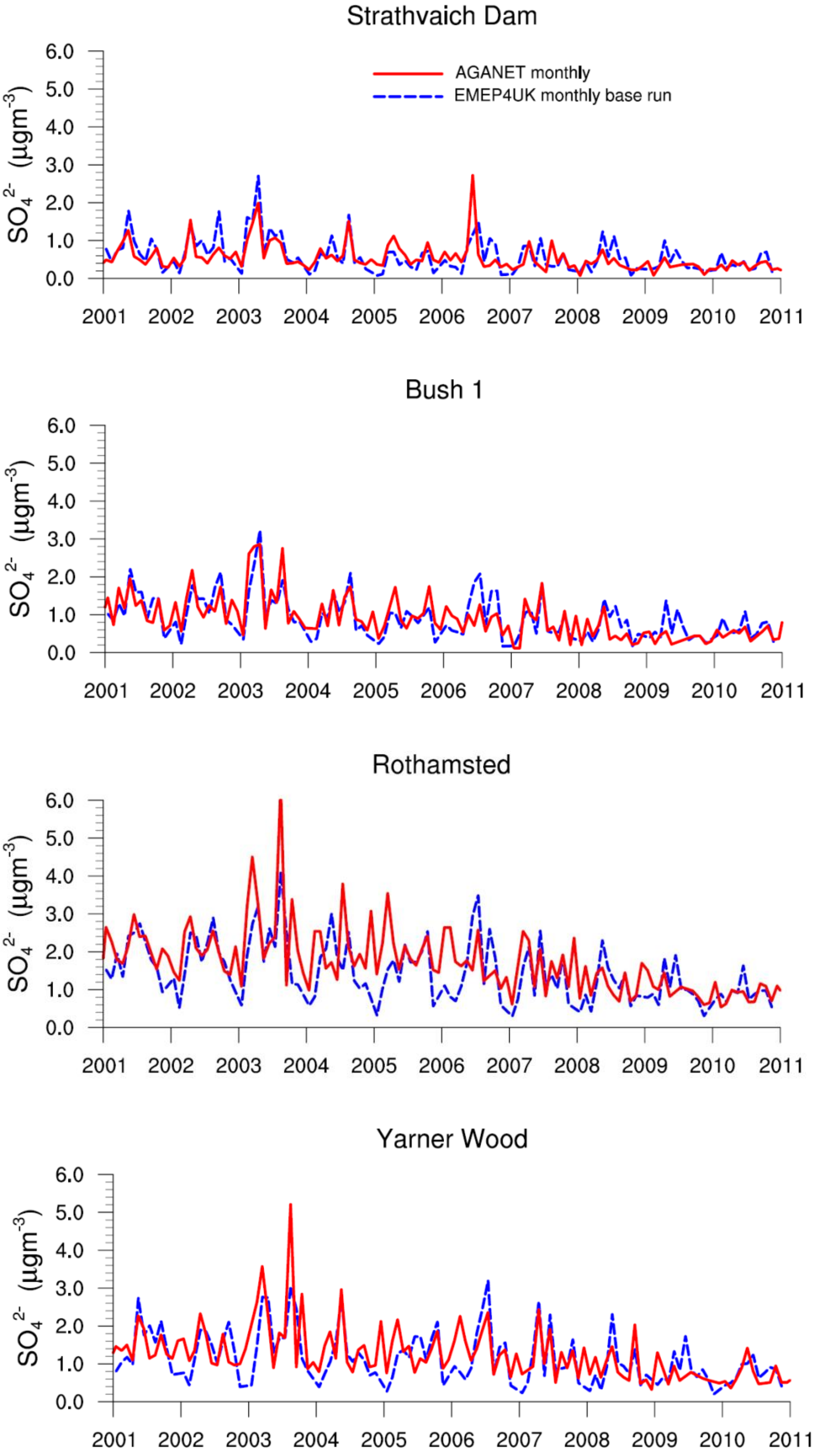
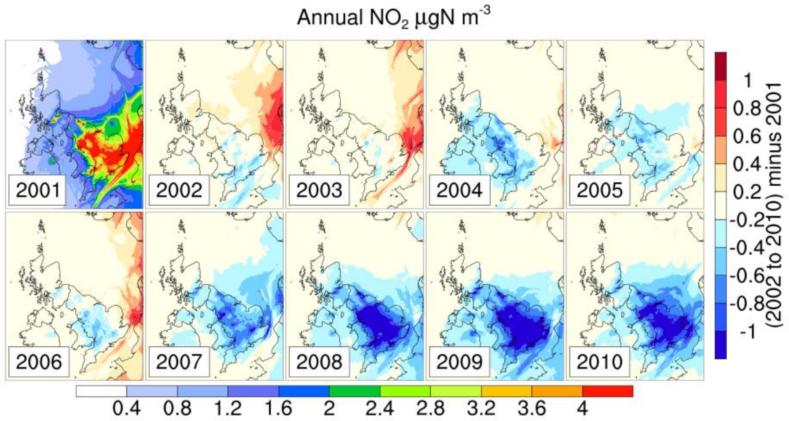


Fig. 3: Monthly average surface concentration of particulate matter sulphate, observed (RED) and modelled (BLUE), for 2001-2010 at four sites of the AGANet network: Strathvaich Dam (north-west Scotland), Bush (central Scotland), Rothamsted (south-east England), and Yarner Wood (south-west England).



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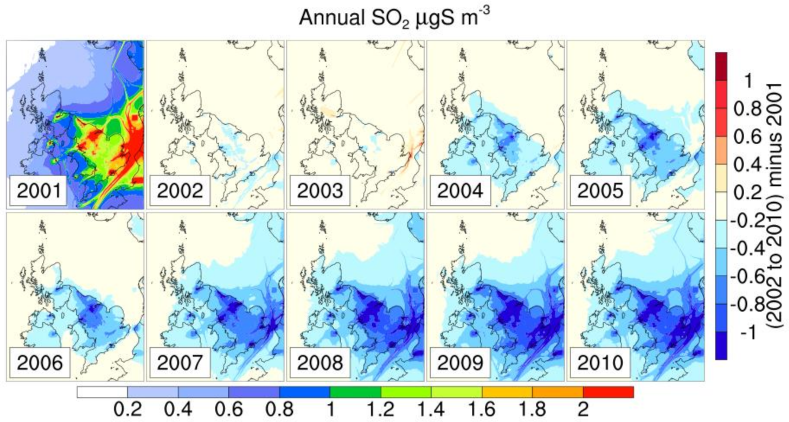
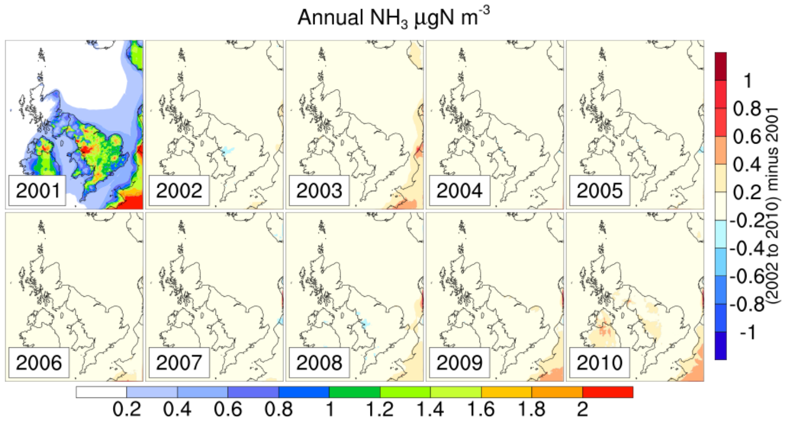
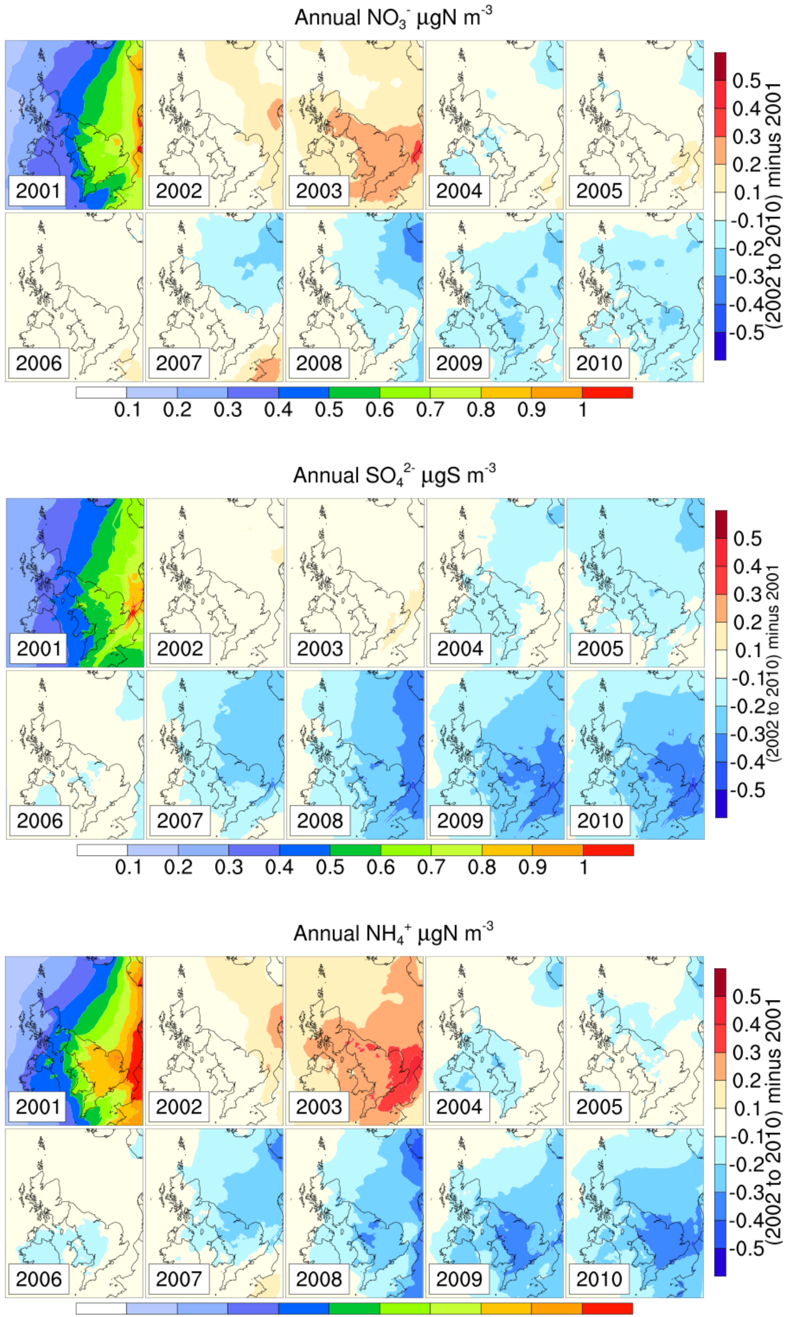


b)



c)

Fig. 4: Modelled annual average surface concentrations of (a) NO$_2$, (b) SO$_2$ and (c) NH$_3$. The top left panel of each figure shows the concentrations in 2001 (horizontal scales in µg N m^{-3} or µg S m^{-3}, as relevant). The remaining panels illustrate the difference in surface concentrations in each of years 2002 to 2010 compared with 2001 (vertical scales in µg N m^{-3} or µg S m^{-3}, as relevant).



a)

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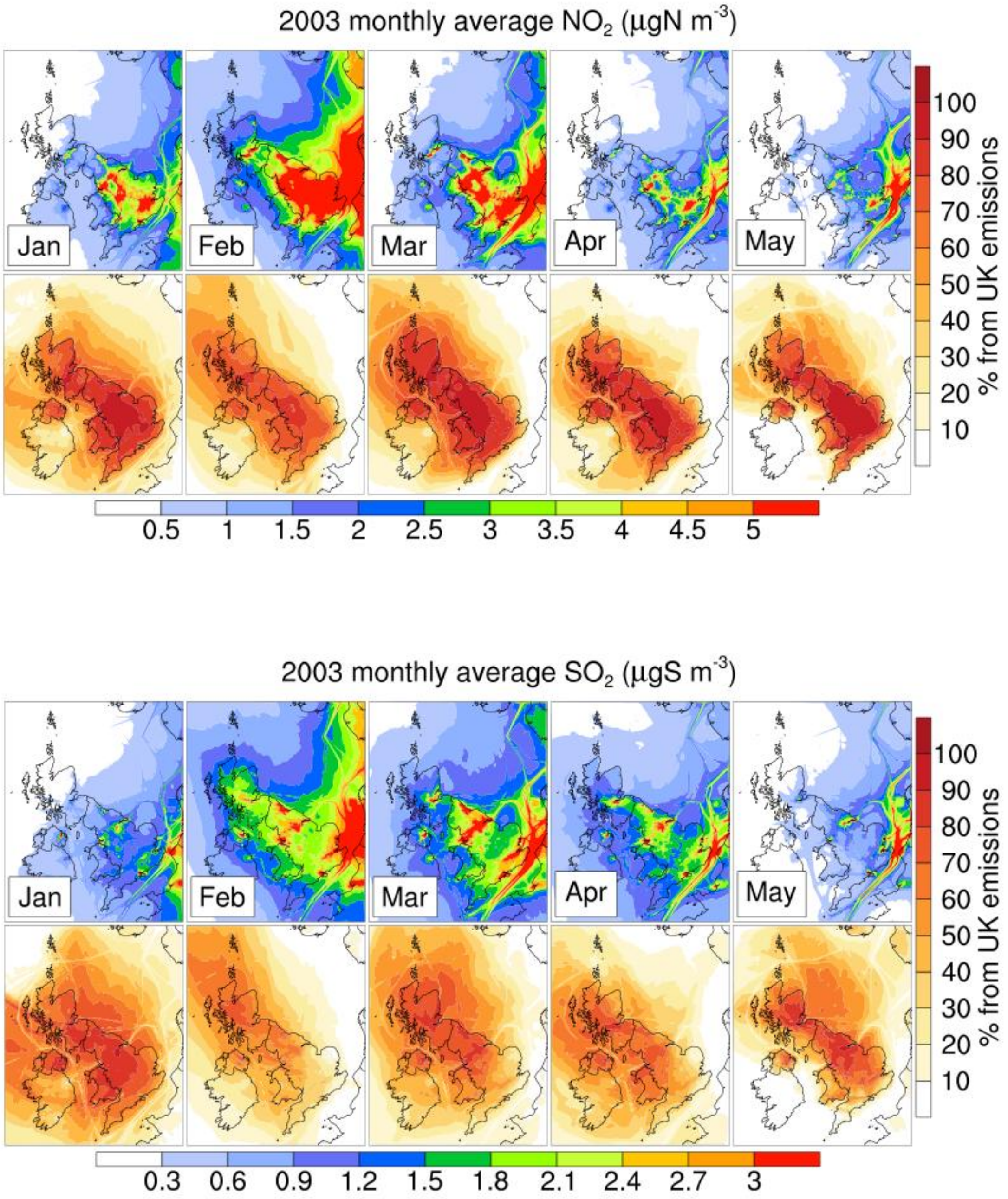
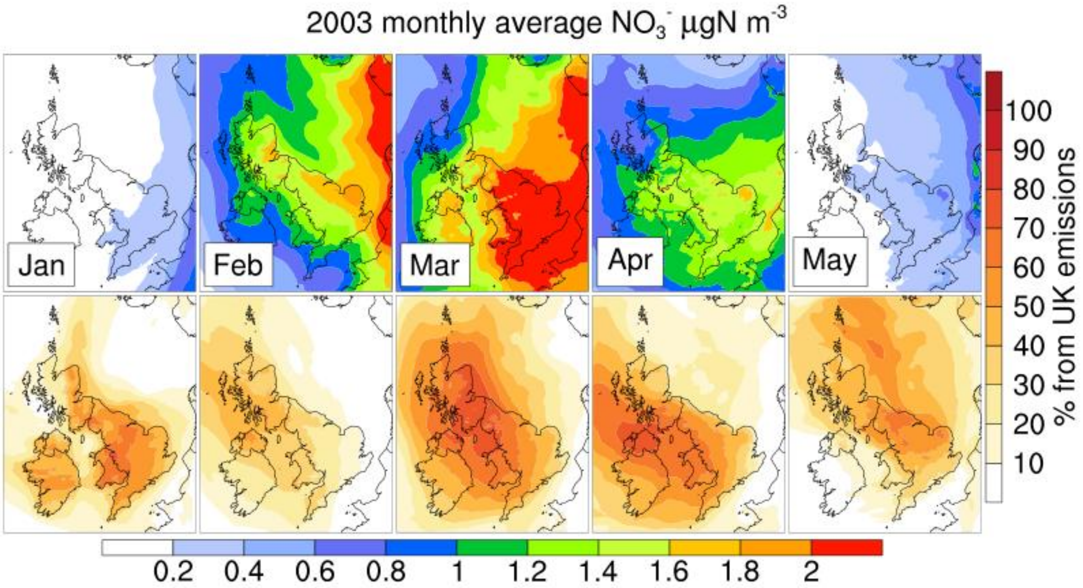
Fig. 5: Modelled annual average surface concentrations of (a) NO_3^-, (b) SO_4^{2-} and (c) NH_4^+. The top left panel of each figure shows the concentrations in 2001 (horizontal scales in µg N m^{-3} or µg S m^{-3}, as relevant). The remaining panels illustrate the difference in surface concentrations in each of years 2002 to 2010 compared with 2001 (vertical scales in µg N m^{-3} or µg S m^{-3}, as relevant).



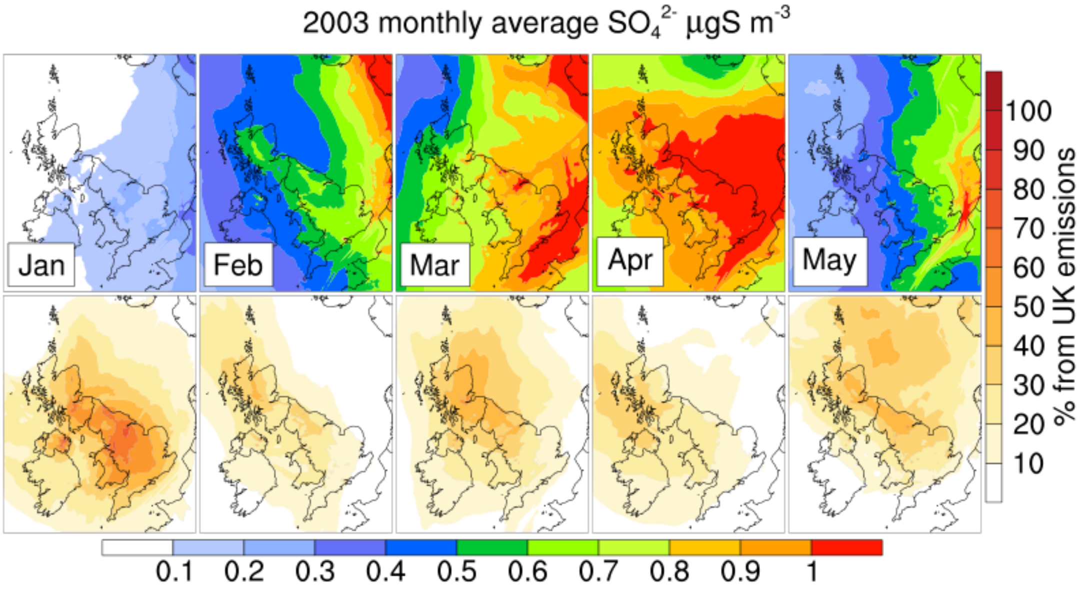
a)

b)

Fig. 6: Modelled monthly average surface concentrations and UK contributions for a) NO$_2$ and b) SO$_2$ through January to May 2003. In each case the upper panel shows the mean concentrations (μg N m^{-3} or μg S m^{-3}), while the lower panel shows the percentage contribution from UK emissions (calculated as [100 × (Base – no UK emi)/Base] between the base simulation and the simulation with zero UK emissions).



a)



b)

Fig. 7: Modelled monthly average surface concentrations and UK contributions for a) NO_3^- and b) SO_4^{2-} through January to May 2003. In each case the upper panel shows the mean concentrations (µg N m^{-3} or µg S m^{-3}), while the lower panel shows the percentage contribution from UK emissions (calculated as [100 ×(Base – no UK emi)/Base] between the base simulation and the simulation with zero UK emissions).

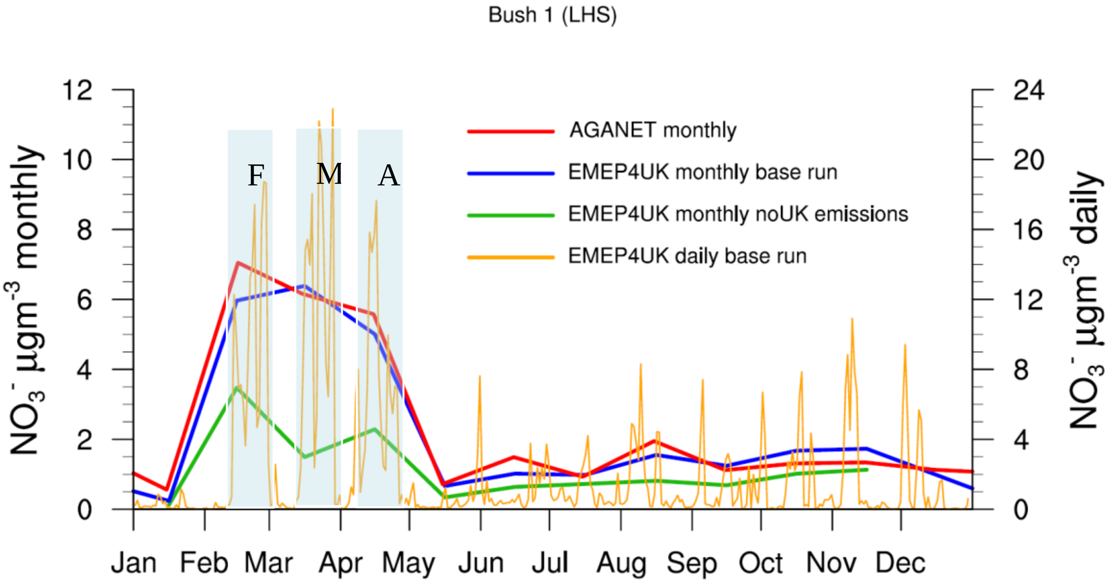


Fig. 8: Modelled and observed monthly mean (left axis) and daily mean (right axis) surface concentrations of NO_3^- at the Bush site (Scotland) for the year 2003. The red line is the measured monthly values from the AGANet network, the blue line is the modelled monthly means for the base run, the green line is the modelled monthly means for the experiment with no UK emissions, and the orange line is the modelled daily means for the base run. (All model values are averages of hourly data). The blue shadows highlight the three episodes labelled F, M and A.

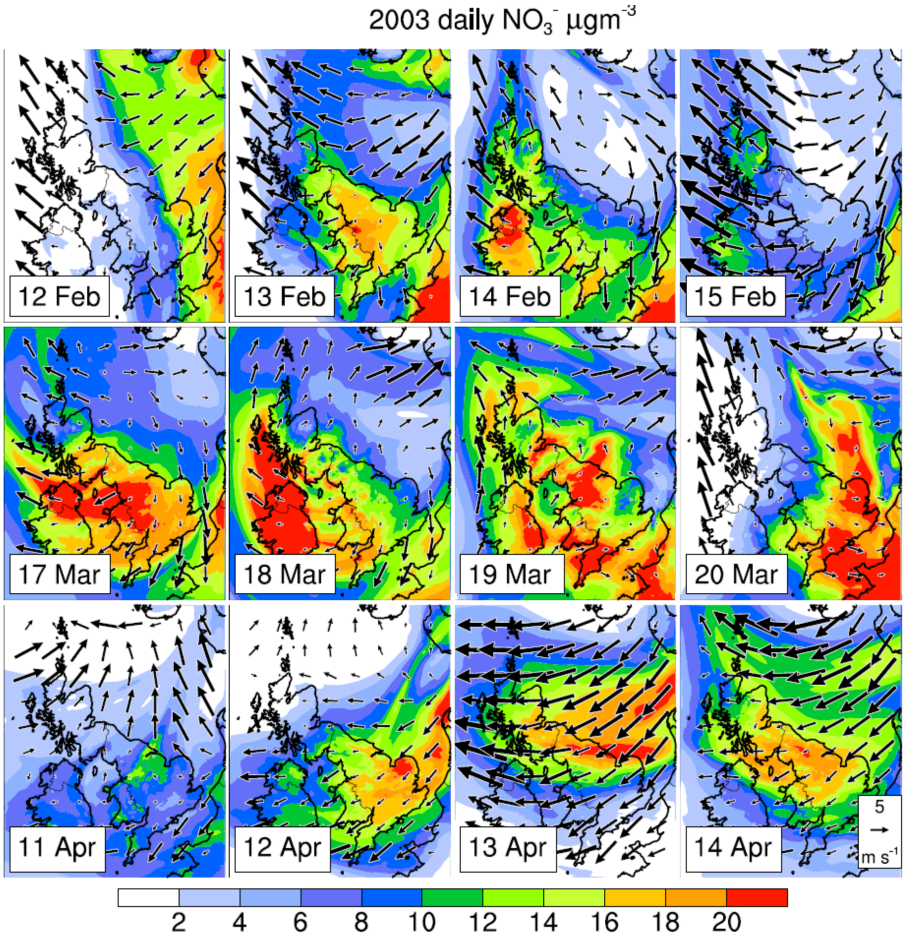


Fig. 9: Modelled daily mean surface concentration of NO_3^- and the 12:00 wind vector for 12-15th Feb (episode F), 17-20th Mar (episode M) and 11-14th Apr (episode A).

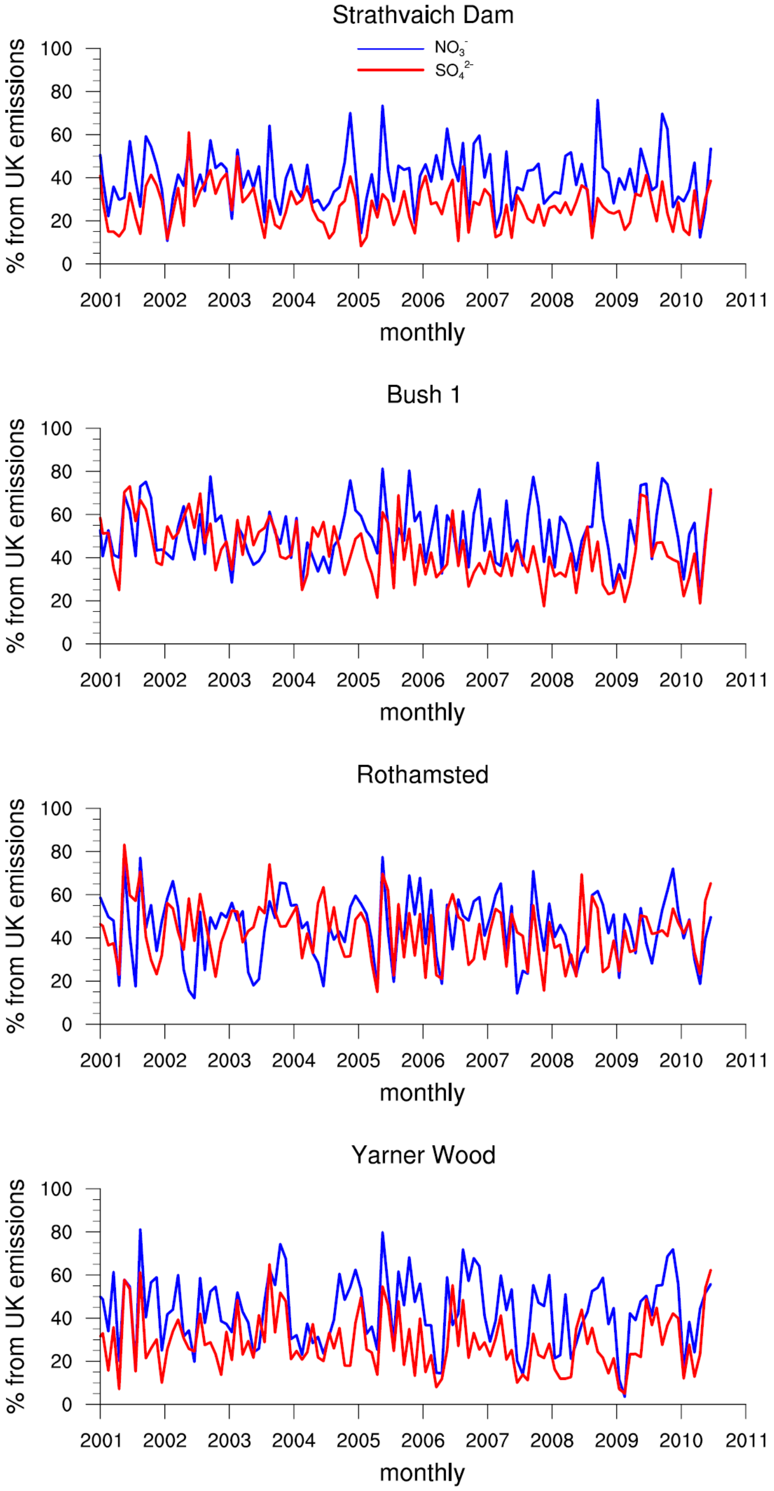


Fig 10: Modelled monthly average proportions of NO_3^- (blue line) and SO_4^{2-} (red line) derived from UK precursor emissions, for 4 sites in the UK for the decade 2001-2010 (calculated as [100 ×(Base – no UK emi)/Base] between the base simulation and the simulation with zero UK emissions).

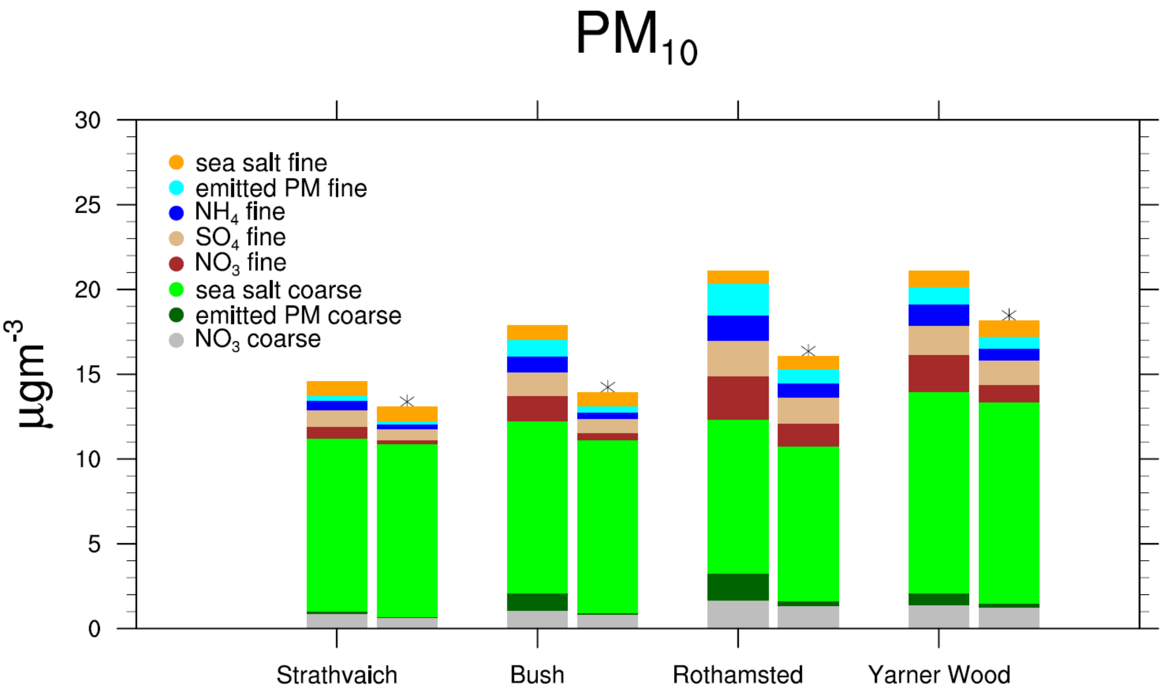


Fig. 11: Mean composition of PM$_{10}$ components as estimated by the EMEP4UK model for four sites across the UK, averaged for the whole of 2003. The model base run (including all national and international emissions) is compared with the results from a simulation excluding UK emissions (*). The difference in magnitudes between the pairs of adjacent bars indicates the PM derived from emissions within the UK. As well as the SIA components, the total modelled PM$_{10}$ includes the contribution from emitted primary fine PM (PM$_{2.5}$) and primary PM$_{coarse}$ (i.e. PM$_{2.5-10}$), and fine and coarse sea salt.

Tables

Table 1: Mean concentrations, and correlation and regression statistics, for monthly-averaged modelled and measured NO_3^- and SO_4^{2-} in particulate matter, and HNO_3 and SO_2 gas for the period 2001-2010 at four sites of the AGANet network: Strathvaich Dam (north-west Scotland), Bush 1 (central Scotland), Rothamsted (south-east England), and Yarner Wood (south-west England). The comparison is based on a linear fit where measurement = slope * model + intercept.

	Particulate NO_3^-			
	Strathvaich Dam	Bush 1	Rothamsted	Yarner Wood
Measurement mean	0.49 μg m^{-3}	1.37 μg m^{-3}	3.35 μg m^{-3}	1.98 μg m^{-3}
Model mean	0.77 μg m^{-3}	1.42 μg m^{-3}	2.73 μg m^{-3}	2.23 μg m^{-3}
R	0.49	0.91	0.81	0.86
Slope	0.59	0.96	0.68	0.95
Intercept	0.48 μg m^{-3}	0.10 μg m^{-3}	0.44 μg m^{-3}	0.34 μg m^{-3}
	Particulate SO_4^{2-}			
	Strathvaich Dam	Bush 1	Rothamsted	Yarner Wood
Measurement mean	0.57 μg m^{-3}	0.94 μg m^{-3}	1.75 μg m^{-3}	1.20 μg m^{-3}
Model mean	0.61 μg m^{-3}	0.95 μg m^{-3}	1.48 μg m^{-3}	1.28 μg m^{-3}
r	0.72	0.79	0.65	0.69
Slope	0.86	0.76	0.56	0.65
Intercept	0.12 μg m^{-3}	0.24 μg m^{-3}	0.50 μg m^{-3}	0.36 μg m^{-3}
	HNO_3			
	Strathvaich Dam	Bush 1	Rothamsted	Yarner Wood
Measurement mean	0.23 μg m^{-3}	0.57 μg m^{-3}	1.89 μg m^{-3}	0.73 μg m^{-3}
Model mean	0.16 μg m^{-3}	0.36 μg m^{-3}	0.96 μg m^{-3}	0.56 μg m^{-3}
r	0.77	0.45	0.35	0.59
Slope	0.59	0.44	0.32	0.65
Intercept	0.03 μg m^{-3}	0.11 μg m^{-3}	0.36 μg m^{-3}	0.09 μg m^{-3}
	SO_2			
	Strathvaich Dam	Bush 1	Rothamsted	Yarner Wood
Measurement mean	0.18 μg m^{-3}	1.28 μg m^{-3}	1.92 μg m^{-3}	0.75 μg m^{-3}
Model mean	0.43 μg m^{-3}	1.43 μg m^{-3}	2.05 μg m^{-3}	1.16 μg m^{-3}
r	0.62	0.60	0.80	0.83
Slope	1.5	0.57	0.71	1.09
Intercept	0.16 μg m^{-3}	0.71 μg m^{-3}	0.68 μg m^{-3}	0.35 μg m^{-3}

Table 2: Model simulated contributions of Continental European $PM_{2.5}$ import to the current European Commission limit value (EC, 2013) and to the World Health Organisation guideline value (WHO, 2005) at each of the four sites for the EMEP4UK model simulations for the year 2003.

Continental European contribution	Strathvaich Dam	Bush 1	Rothamsted	Yarner Wood
EC limit value of 25 $\mu g\ m^{-3}$	5%	8%	18%	15%
WHO guideline of 10 $\mu g\ m^{-3}$	14%	20%	45%	38%