

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

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13 **ABSTRACT**

14 Surface concentrations of secondary inorganic particle components over the UK have been
15 analysed for 2001-2010 using the EMEP4UK regional atmospheric chemistry transport model
16 and evaluated against measurements. Although gas/particle partitioning in the EMEP4UK
17 model used a bulk approach, which may lead to uncertainties in simulated secondary
18 inorganic aerosol, the EMEP4UK model simulations in this work were able to accurately
19 represent both the long-term decadal surface concentrations of particle sulphate and nitrate
20 and an episode in early 2003 of substantially elevated nitrate measured across the UK by the
21 AGANet network. The latter was identified as consisting of three separate episodes, each of
22 less than 1 month duration, in February, March and April. The primary cause of the elevated
23 nitrate levels across the UK was meteorological: a persistent high pressure system, whose
24 varying location impacted the relative importance of transboundary versus domestic
25 emissions. Whilst long-range transport dominated the elevated nitrate in February, in contrast
26 it was domestic emissions that mainly contributed to the March episode, and for the April
27 episode both domestic emissions and long-range transport contributed. A prolonged episode
28 such as the one in early 2003 can have substantial impact on annual average concentrations.

29 The episode led to annual concentration differences at the regional scale of similar magnitude
30 to those driven by long-term changes in precursor emissions over the full decade investigated
31 here. The results demonstrate that a substantial part of the UK, particularly the south and
32 south-east, may be close to or exceeding annual mean limit values because of import of
33 inorganic aerosol components from continental Europe under specific conditions. The results
34 reinforce the importance of employing multiple year simulations in the assessment of
35 emissions reduction scenarios on PM concentrations and the need for international
36 agreements to address the transboundary component of air pollution.

37

38 **1 Introduction**

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

48 The complexity of ambient PM composition and formation, combined with the influence of
49 meteorology on chemistry, dispersion and deposition, considerably complicates pinpointing
50 the contributions of different chemical pollutant emission sources to ambient PM at specific
51 locations (USEPA, 2009; AQEG, 2012). Consequently, it is a complicated process to
52 formulate cost-effective policy action to reduce harm caused by PM. The inorganic chemical
53 components of PM, ammonium (NH_4^+), sulphate (SO_4^{2-}) and nitrate (NO_3^-), constitute a
54 major fraction of PM_{2.5} (Putaud et al., 2010). The anthropogenic emissions of the gaseous
55 precursors of inorganic PM – ammonia (NH_3), sulphur dioxide (SO_2) and nitrogen oxides
56 (NO_x) – are also subject to various legislation that seeks to limit and reduce either a country's
57 total emissions or the emissions from individual sources or source sectors (Heal et al.,
58 2012; Reis et al., 2012). For SO_2 and NO_x in particular, emissions reductions have been very
59 effective over the past few decades and this is reflected in reductions in ambient

60 concentrations of the gases (RoTAP, 2012). Despite this, PM₁₀ concentrations across much of
61 western Europe have not fallen significantly since the year 2000 (Harrison et al., 2008).

62 The longer lifetime of secondary PM components compared with their gaseous precursors
63 means that transboundary transport from Europe and meteorology are important drivers.
64 Previous studies suggest transatlantic transport of these secondary inorganic aerosol (SIA)
65 species has a small effect on EU surface SIA concentrations and deposition (Sanderson et al.
66 2008; Simpson et al. 2014), hence “transboundary” hereafter refers to Europe. This is of
67 particular relevance for the design of air quality policies seeking to reduce PM concentrations,
68 especially as some limit values may be sensitive to a small number of high concentration
69 episodes rather than long-term average concentrations. This is particularly important for the
70 nitrate component which has shown to be the dominant component on days when PM₁₀
71 exceeds 50 µg m⁻³ (Yin and Harrison, 2008).

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

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

87

88 2 Methods

89 2.1 Model description and set-up

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

94 The EMEP4UK model is driven by the Weather Research Forecast (WRF) model version
95 3.1.1 (www.wrf-model.org). The model horizontal resolution scales down from 50 km × 50
96 km in the main EMEP ‘Greater European’ domain to 5 km × 5 km for the domain covering
97 the British Isles (Fig. 1). The boundary conditions for the inner domain are derived from the
98 results of the European domain in a one-way nested setup. The EmChem09 chemical scheme
99 was chosen for the present study, as it has been extensively validated at the European scale
100 (Simpson et al. (2012), www.emep.int). The EMEP mode is based on Berge and Jakobsen
101 (1998), but extended with photo-oxidant chemistry (Andersson-Skold and Simpson,
102 1999;Simpson et al., 1995). The EmChem09 mechanism used for this work has 72 species
103 and 137 reactions. Full details of the chemical scheme are given by Simpson et al. (2012).
104 Gas/aerosol partitioning used the EQSAM formulation (Metzger et al., 2002a;Metzger et al.,
105 2002b). The calculated nitrate is then split into coarse and fine mode using a parameterised
106 approach dependent on relative humidity, as described by Simpson et al. (2012). In this
107 version of the EMEP model, nitrate is the only secondary inorganic component present in
108 PM_{coarse} (the difference between PM_{10} and $PM_{2.5}$). This split between $PM_{2.5}$ and $PM_{2.5-10}$ for
109 nitrate is rather uncertain as discussed in Aas et al. (2012); a more explicit aerosol scheme is
110 under development. The EQSAM scheme used here is equivalent to the EQSAM2 scheme
111 used in the global model TM5 (Karl et al., 2009;Huijnen et al., 2010).

112 Anthropogenic emissions of NO_x , NH_3 , SO_2 , primary $PM_{2.5}$, primary PM_{coarse} , CO, and non-
113 methane volatile organic compounds (NMVOC) are included. PM_{10} is the size fraction of
114 particles with an aerodynamic diameter $\leq 10 \mu m$. For the UK, emissions values are taken
115 from the National Atmospheric Emission Inventory (NAEI, <http://naei.defra.gov.uk>) at 1 km²
116 resolution and aggregated to 5 km × 5 km resolution. The underpinning methods by which
117 these emission inventories have been established are reported by Hellsten et al. (2008) and
118 Dore et al. (2008). For the rest of the outer domain, the model uses the EMEP 50 km × 50 km

119 resolution emission estimates provided by the Centre for Emission Inventories and
120 Projections (CEIP, <http://www.ceip.at/>). Emissions estimates for international shipping
121 (ENTEC, 2010) are aggregated to 5 km × 5 km for those emissions within the inner domain.
122 The EMEP(4UK) model uses a yearly boundary condition for SIA at the edge of the
123 European domain adjusted for each year as describe in Simpson et al. (2012).

124 **2.2 Model experiments**

125 Hourly surface concentrations of several pollutants, including NO₂, SO₂ and NH₃, and particle
126 NO₃⁻, SO₄²⁻ and NH₄⁺, were simulated for the decade 2001-2010. To quantify the influence
127 of long-range (i.e. non-UK, or ‘transboundary’) and short-range (UK, ‘domestic’) emissions
128 on the UK surface concentrations of these components, a perturbation experiment was carried
129 out by setting UK land emissions to zero for the year. This provides an approximate model
130 estimate of the contribution of non-UK emissions to gaseous and particulate matter
131 concentrations in the UK.

132 **2.3 Measurement data**

133 Model surface concentrations were compared with observational data from the UK Acid
134 Gases and Aerosols Network (AGANet), which is one of the four component UK
135 Eutrophying and Acidifying Pollutants monitoring networks (Conolly et al., 2011;Tang et al.,
136 2013). The AGANet monitoring sites were established in 1999 for the long-term simultaneous
137 measurement of the concentrations of SO₂, HNO₃ and NH₃ gases and particle NO₃⁻, SO₄²⁻
138 and NH₄⁺, in relation to changes in European emissions of SO₂, NO_x and NH₃. Measurements
139 are made using DELTA system (DENuder for Long-Term Atmospheric sampling) and have
140 monthly-averaged time resolution (Sutton et al., 2001). The size cut-off of the DELTA
141 sampler has been estimated to be ~4.5 μm (Tang et al., 2009), therefore the measured
142 concentrations are between the PM_{2.5} and PM₁₀ size fractions.

143 The EMEP4UK model assigns all SO₄²⁻ and NH₄⁺ components to PM_{2.5}. Modelled NO₃⁻ is
144 assigned to both PM_{2.5} and PM_{coarse} which leads to potential negative bias in modelled versus
145 measured concentrations for NO₃⁻. Four sites representing different areas of the UK (marked
146 on Fig. 1) have been selected for the comparisons presented here: Strathvaich Dam (north-
147 west Scotland); Bush (central Scotland); Rothamsted (south-east England); and Yarner Wood
148 (south-west England).

149 3 Results

150 The time series of the modelled and observed monthly mean surface concentrations of particle
151 NO_3^- and SO_4^{2-} at the four selected AGANet sites are shown in Fig. 2 and Fig. 3,
152 respectively. The observations span the period 2001-2010, whereas the model values span the
153 period 2001-2010. A peak in 2003 in NO_3^- concentrations can be seen in both observations
154 and the EMEP4UK simulations. Fig. 2 and Fig. 3, show generally good agreement between
155 the two datasets for three of the four sites included here, as illustrated quantitatively by the
156 correlation and linear regression statistics for these particle-phase components and for the gas-
157 phase species HNO_3 and SO_2 (Table 1). The model-measurement comparison at the
158 Strathvaich Dam site is adversely impacted by two extreme measurement values in 2006 and
159 2007 not present in the simulations. No anomaly is present in the meteorology at this location
160 for these two months. From an analysis of the mass balance of the aerosol components, the
161 two anomalous data points appears to be outliers and which may be attributed to sampling or
162 analytical contamination in determination of NO_3^- and SO_4^{2-} . The anomaly could be
163 potentially due to local influence or an unusually high positive artefact on the HNO_3 . Recent
164 investigations indicate that the AGANet HNO_3 observation using the DELTA methodology
165 includes a positive bias from other NO_y chemical species, which could include HONO
166 (heterogeneously oxidised), N_2O_5 and PANs. However, there is nothing to indicate that
167 Strathvaich Dam should be affected more from this than other sites.

168 The spatial pattern across the British Isles and the inter-year variability of modelled annual
169 mean surface concentrations are shown in Fig. 4 for NO_2 , SO_2 and NH_3 and in Fig. 5 for
170 particle NO_3^- , SO_4^{2-} and NH_4^+ . In each case, the top left panel shows the spatial distribution
171 for 2001 and the other 9 panels show the differences in annual mean concentrations for each
172 of years 2002-2010 relative to 2001. The maps for 2001 show highest concentrations of NO_2
173 and SO_2 over central and south east England, related to UK emission sources, and over the
174 English Channel, mostly related to shipping emission sources. The highest concentrations of
175 NO_2 and SO_2 over the UK are in 2003, with the lowest concentrations during 2008-2010. The
176 extended periods of elevated NO_3^- during February to April 2003 were sufficient to enhance
177 the annual average NO_3^- concentration across the whole of the UK in 2003 by between 0.2-
178 0.3 $\mu\text{g N m}^{-3}$ compared with preceding and subsequent years (Fig. 5a), with a even larger
179 enhancement in the annual mean for 2003 of 0.2-0.5 $\mu\text{g N m}^{-3}$ for NH_4^+ (Fig. 5c). In contrast,
180 the somewhat less elevated SO_4^{2-} concentrations during this period led to a modest increase in

181 annual average SO_4^{2-} for 2003 of 0.0-0.1 $\mu\text{g S m}^{-3}$ (Fig. 5b). The spatial distribution of NH_3
182 shows a very different pattern to the other modelled components, with highest modelled
183 concentrations in Brittany and north-west France and north-west England, reflecting the
184 distribution of modelled NH_3 emissions which mainly arise from agricultural sources.

185 The concentrations of the particle components NO_3^- , SO_4^{2-} and NH_4^+ are spatially smoother
186 across the UK than the gaseous precursors (Fig. 4 and Fig. 5). The modelled annual surface
187 concentrations of NO_2 and SO_2 (Fig. 4a and Fig. 4b) show that the concentrations of these
188 gaseous components decline during 2001-2010 by substantially more than the decline in NO_3^-
189 and SO_4^{2-} . Over much of the UK (particularly England), declines in modelled NO_2 and SO_2
190 between 2001 and 2010 exceed 1 $\mu\text{g N/S m}^{-3}$ in 2010 compared with the 0.1-0.2 $\mu\text{g N m}^{-3}$
191 decline in NO_3^- , and the 0.1-0.3 $\mu\text{g S m}^{-3}$ decline in SO_4^{2-} (up to 0.4 $\mu\text{g S m}^{-3}$ decline in
192 eastern England). On the other hand the model shows concentrations of NH_3 hardly changing
193 over the decade; in fact increasing slightly, up to $\sim 0.2 \mu\text{g N m}^{-3}$ over England, especially for
194 2009 and 2010 (Fig. 4c), whereas, with the exception of 2003, the modelled concentration of
195 NH_4^+ in PM decreases from 2001-2010. Of note also, is a decrease of SO_2 annual surface
196 concentration over the North Sea from 2007 onwards (Fig. 4b).

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

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

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

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

225 The monthly modelled concentrations for the simulation with zero UK emissions are also
226 shown in Fig. 8 (green line). The modelled monthly NO_3^- concentrations (blue line) were
227 enhanced by $2.6 \mu\text{g m}^{-3}$ by UK emissions in February, but by $5.0 \mu\text{g m}^{-3}$ in March and by 2.6
228 $\mu\text{g m}^{-3}$ in April as compared with the model simulation with no-UK emissions (green line).
229 The daily mean model NO_3^- concentrations highlight substantial temporal variability within
230 this February-April period. The daily average surface concentrations (orange line of Fig. 8)
231 show three separate episodes; the first approximately matches the period 12-28th of February
232 (F), the second 10-27th March (M) and the third 1-30th April (A).

233 The characteristic differences between these three periods are illustrated in Fig. 9. Here the
234 12:00 wind vector is superimposed to the mean modelled surface concentration of PM NO_3^-
235 for selected days during the three component episodes. It is seen that 12-15th Feb (episode F)
236 and 17-20th Mar (episode M) were associate with stagnant air masses allowing NO_3^- PM
237 concentrations to build up, while the period 11-14th Apr (episode A) was associated with a
238 highlight polluted airmass arriving from the East.

239 The UK February episode was associated with an easterly light wind advecting PM NO_3^-
240 produced in the area of the north of France, Holland, north of Germany, and Denmark, where
241 the centre of the high pressure was located (Fig. 9). During the March episode, the centre of

242 the high pressure was over the UK with an associated light wind, clear sky, and cooler
243 conditions leading to the accumulation of NO_3^- from UK emissions with little import of NO_3^-
244 or its precursors from outside the UK. The April episode was a mixture of conditions
245 described for February and March.

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

254 Based on the simulations it is possible to estimate the annual contribution of non-UK
255 emissions to the different components of PM_{10} at the four study sites. This is summarized in
256 Fig. 11 for the year 2003, also including the contribution of primary particulate matter
257 (emitted PM). Pollution import for $\text{PM}_{2.5}$ from non-UK sources ranges from an estimated 41%
258 for Bush 1, up to 63% for Yarner Wood, highlighting the importance of transboundary
259 pollution import on UK $\text{PM}_{2.5}$ concentrations. The same model results for 2003 can be
260 expressed in terms of the contribution of non-UK emissions to the current European
261 Commission (EC, 2013) limit value for $\text{PM}_{2.5}$ and to the World Health Organisation (WHO,
262 2005) guideline value for $\text{PM}_{2.5}$ at each of the four sites (Table 2). For these example sites, up
263 to 18% and 45% of the limit and guideline values, respectively, is provided by non-UK
264 emissions.

265

266 **4 Discussion**

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

272 Two inorganic aerosol schemes were available for the EMEP and EMEP4UK model: the
273 EQSAM (used in this work) and the MARS scheme (Simpson et al., 2012). As discussed in
274 section 2.1, both schemes use a bulk approach for particle formation. The EQSAM aerosol
275 scheme was used here as it has demonstrated good performance in the TM5 atmospheric
276 chemistry transport model (Karl et al., 2009;Huijnen et al., 2010). However the bulk approach
277 may lead to uncertainties in the simulated SIA, as shown in Hu et al. (2008), as the particle
278 sizes are not explicitly resolved in the model. The current aerosols scheme and size
279 partitioning in the EMEP model has been validated and compared with observations across
280 Europe as shown in Fagerli and Aas (2008) and in Simpson et al. (2006). In addition, in a
281 recent model intercomparison (Carslaw, 2011b, a) SIA and its gaseous precursors simulated
282 by EMEP4UK showed good agreement with observations.

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

290 The highest modelled concentrations over this period are in 2003, particularly for PM NO_3^-
291 and NH_4^+ , and to a lesser extent for SO_4^{2-} , whilst lowest concentrations for each of these
292 components are in 2008-2010. The notably high PM NO_3^- concentrations in February to April
293 2003 were observed at AGANet stations across the UK and could be well reproduced by the
294 model (Fig. 2, Table 1). Concentrations of PM SO_4^{2-} were also elevated during this period,
295 although by a smaller amount, and were also well captured by the model (Fig. 3, Table 1).
296 The magnitude of this elevation in annual average PM NO_3^- concentration in 2003 is greater
297 than the decline in annual average concentration across the whole decade to 2010 of 0.1-0.2
298 $\mu\text{g N m}^{-3}$ (Fig. 5). The August 2003 heatwave (Vieno et al., 2010) was not associated with
299 high nitrate as the higher temperature limits the partitioning to the condensed phase.
300 However, a secondary peak in sulphate is noted during summer 2003, which is directly
301 attributed to the 2003 August heatwave, whereby elevated temperatures lead to faster SO_2
302 oxidation to sulphate (Dawson et al., 2007;Jacob and Winner, 2009).

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

320 The geographic origins of the PM episodes have been investigated in the model perturbation
321 experiment. The monthly average surface concentrations for the zero UK emissions
322 experiment show that surface concentrations of SO_2 and NO_2 are mainly driven by UK
323 emissions (Fig. 6) and by similar proportions of UK emissions throughout the period of high
324 surface concentrations of NO_3^- . However, the proportions of the NO_3^- that are derived from
325 UK and non-UK emissions changes between months (Fig. 7). The model results show that for
326 February 2003 trans-boundary emissions had a small influence on NO_3^- , whereas for March
327 and April the trans-boundary transport of NO_3^- and/or its precursors was substantial.
328 Abdalmogith et al. (2006) suggest that the annual average import of NO_3^- aerosol to the UK
329 from Europe (as an average of 2002 and 2003) is between 35-65% of the UK total NO_3^-
330 concentration. Our study has found that, for 2003 (Fig. 7), the import to the UK from Europe
331 was in the range 20-60% of UK total NO_3^- concentrations, with this proportion varying
332 between the three episodes (labelled F, M and A in Fig. 8). Abdalmogith et al. (2006)
333 concluded that the 2003 NO_3^- spring event was not well represented by their model, and the
334 low emissions resolution (10 km \times 10 km grid) was suggested as a possible cause. In the

335 present study the elevated NO_3^- concentrations are well represented by the EMEP4UK model
336 at 5 km x 5 km resolution. However, we find that simulation at 50 km \times 50 km horizontal
337 spatial resolution of the EMEP4UK model outer domain also represented these features
338 (results not included here), indicating that transport and dispersion were the main drivers of
339 the pollution events. As shown in Fig 10, over the full 10-year period there was a substantial
340 variation (10% to 80%) in the contribution of UK emissions to SIA concentrations in the UK.

341 The simulated changes in the gaseous precursors for 2001-2010 follow the reductions in UK
342 emissions over that period especially for NO_2 and SO_2 (MacCarthy et al., 2012). The change
343 of SO_2 annual surface concentration especially after 2007 over the North Sea (Fig. 4b) is a
344 direct response to the introduction of a sulphur emission control area (SECA) in the North
345 Sea, including the English Channel, by the 2007 MARPOL convention on marine pollution
346 (Dore et al., 2007). Under the convention the sulphur content of bunker fuel was restricted to
347 1.5 % by mass in 2007 (and will be further reduced to 0.1% in SECAs by 2020). This has
348 resulted in a substantial reduction of emissions of SO_2 from the shipping sector.

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

362 The modelled annual average NH_4^+ shows a change between 2001 and 2010 over the UK
363 which is intermediate between that of NO_3^- and SO_4^{2-} (Fig. 5c). By 2010, NH_4^+
364 concentrations decreased by 0.3-0.4 $\mu\text{g N m}^{-3}$ over most of England, but, as was the case for
365 NO_3^- concentrations, annual average NH_4^+ concentrations in 2003 were elevated by 0.2-0.3

366 $\mu\text{g N m}^{-3}$ compared with preceding and subsequent years. This confirms that the episodes of
367 elevated NO_3^- in 2003 were driven by ammonium nitrate specifically. The modelled decrease
368 in PM NH_4^+ concentrations as compared with minimal decrease (and some increase) in NH_3
369 concentrations over the period 2001-2010 is consistent with the conclusions of Bleeker et al.
370 (2009) and Horvath et al. (2009) for other parts of Europe that reducing SO_2 emissions have
371 contributed to maintaining or even increasing gaseous NH_3 concentrations.

372

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

384 Table 2 expresses the non-UK contribution to modelled annual mean $\text{PM}_{2.5}$ relative to the EC
385 limit value and WHO guideline value for $\text{PM}_{2.5}$ (for the protection of human health). The non-
386 UK contribution ranges from 5% at Strathvaich to 18% at Rothamsted for the limit value at 25
387 $\mu\text{g m}^{-3}$ (or 14% to 45% for the same sites with respect to the guideline value of $10 \mu\text{g m}^{-3}$).
388 This indicates a clear gradient of non-UK contribution from greatest in the south-east and
389 least in the north; this is likewise visible in Fig. 5.

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

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

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

406 **5 Conclusions**

407 For the first time the EMEP4UK model has been operated at high resolution for a multi-year
408 period (2001-2010) and simulated secondary inorganic component concentrations compared
409 with observations from the AGANet network. The drivers of three remarkably high secondary
410 inorganic aerosol episodes across the UK have been investigated in detail, revealing
411 contrasting causes for different periods. Whilst it has been documented that the bulk
412 gas/particle partitioning approach used in these simulations (EQSAM formulation) may lead
413 to uncertainties in simulated secondary inorganic aerosol, the EMEP4UK model was able to
414 accurately represent both the long-term decadal (2001-2010) surface concentrations of
415 particulate matter (PM) and specific episodes of elevated PM NO_3^- in 2003. The latter was
416 identified as consisting of three separate episodes, each of less than 1 month duration, in
417 February, March and April. The primary cause of the elevated nitrate levels across the UK
418 was meteorological, related to a persistent high pressure system, with the contribution of
419 imported pollution differing markedly between these events.

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

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

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433 Meteorological Institute (Met.No) and the European Union projects NitroEurope IP and
434 ÉCLAIRE.

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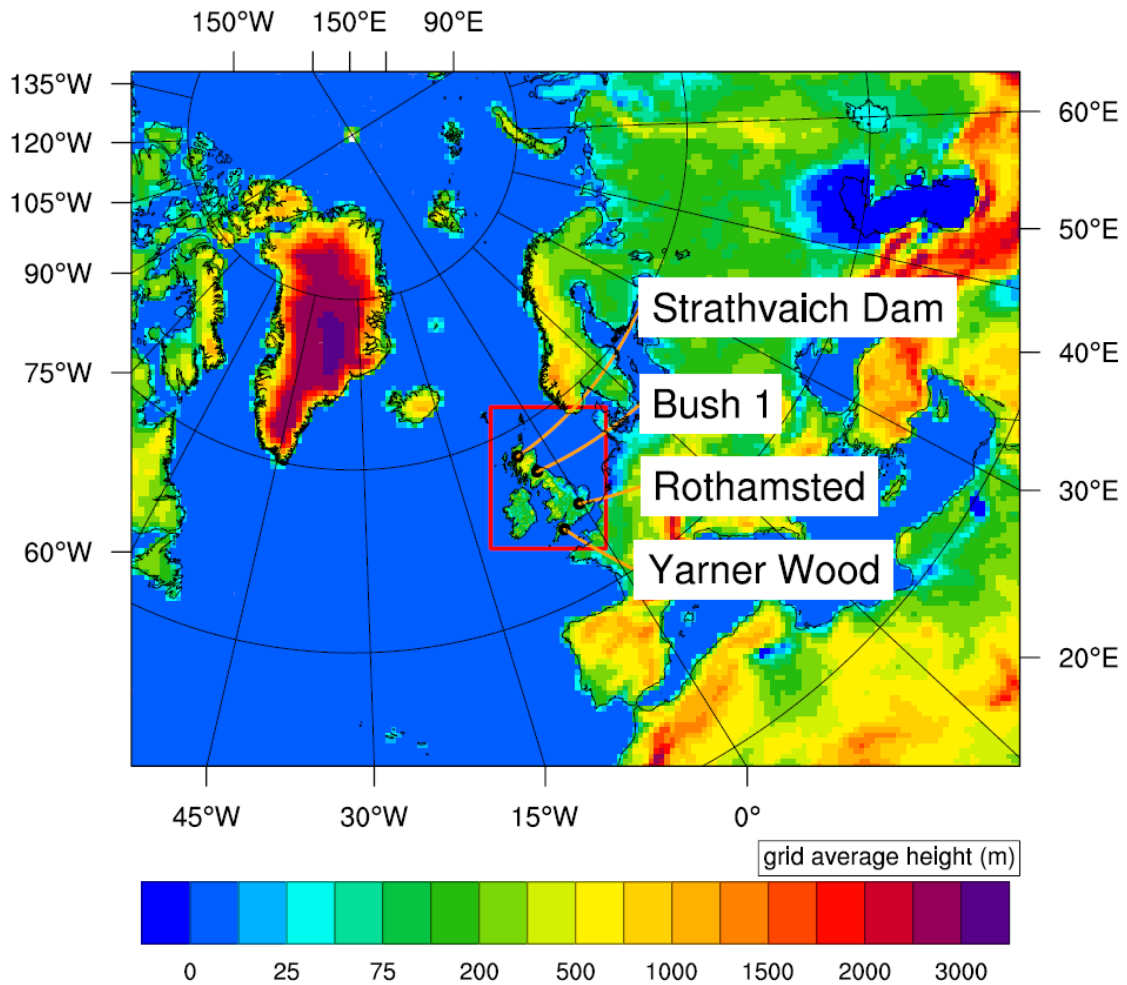
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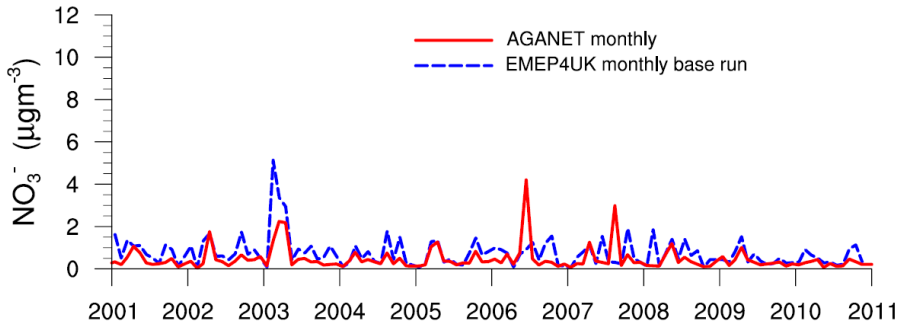
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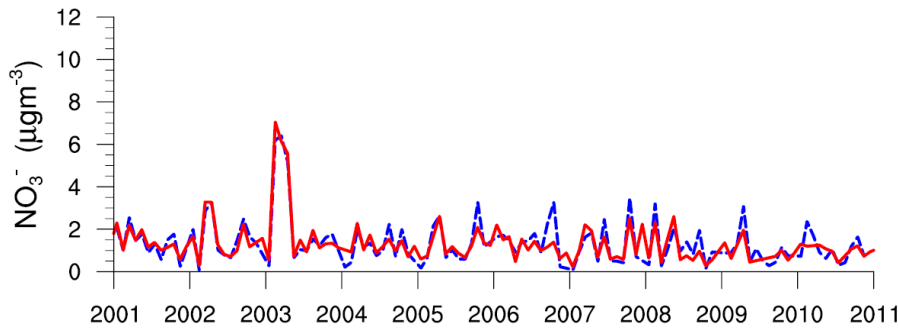
598 Fig. 1: The EMEP4UK Greater European domain, modelled at 50 km × 50 km horizontal
599 resolution and, outlined in red, the nested British Isles domain, modelled at 5 km × 5 km
600 horizontal resolution. The colour scale indicates grid-average altitude. The four UK AGANet
601 measurement sites used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

Strathvaich Dam



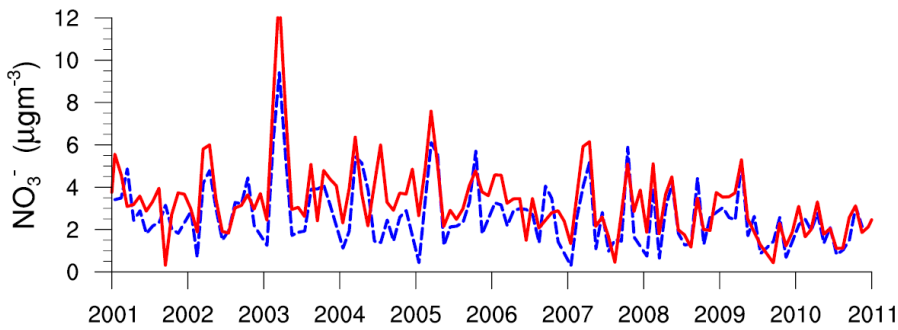
602 a)

Bush 1



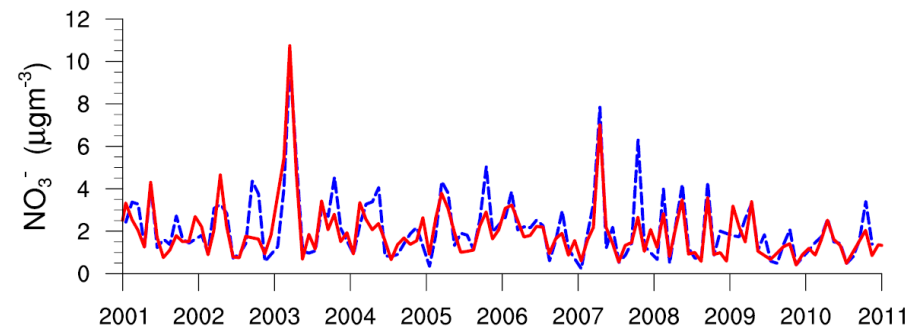
603 b)

Rothamsted



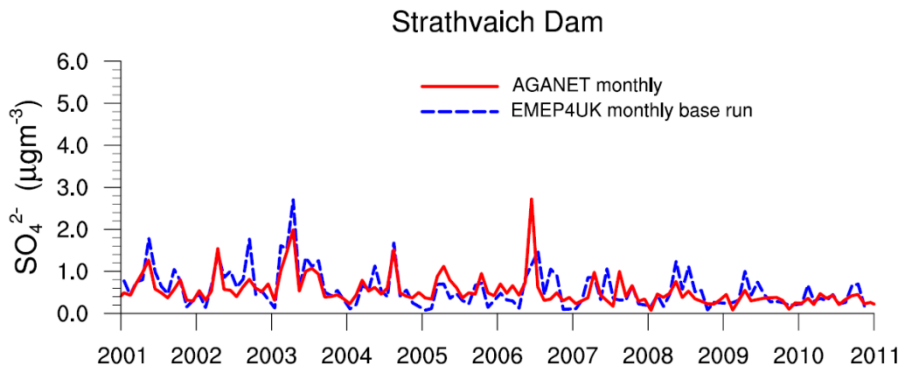
604 c)

Yarner Wood

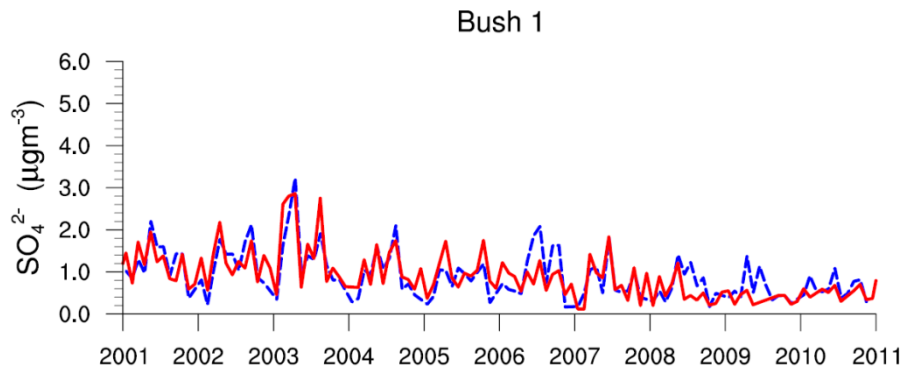


605 d)

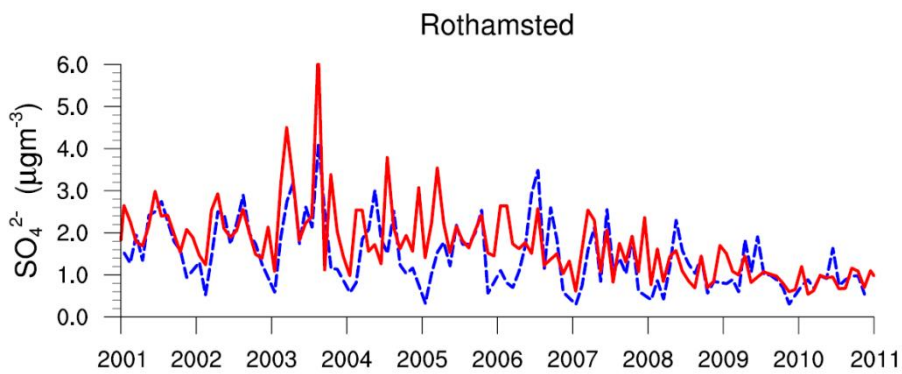
606 Fig. 2: Monthly average surface concentrations of particulate matter nitrate, observed (RED)
607 and modelled (BLUE), for 2001-2010 at four sites of the AGANet network: Strathvaich Dam
608 (north-west Scotland), Bush (central Scotland), Rothamsted (south-east England), and Yarner
609 Wood (south-west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



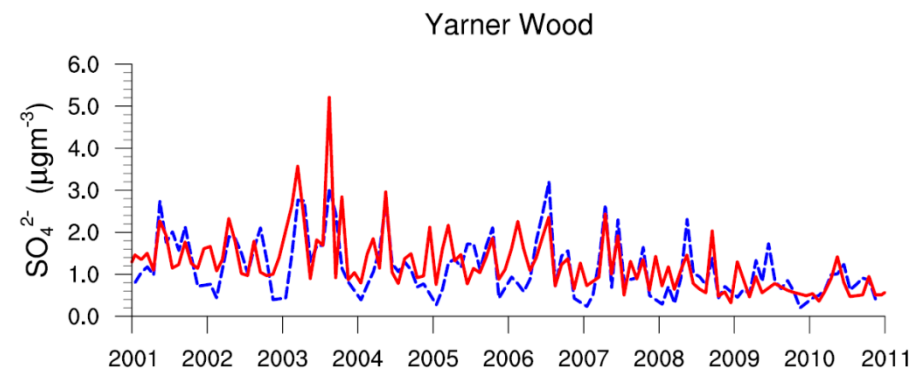
610 a)



611 b)



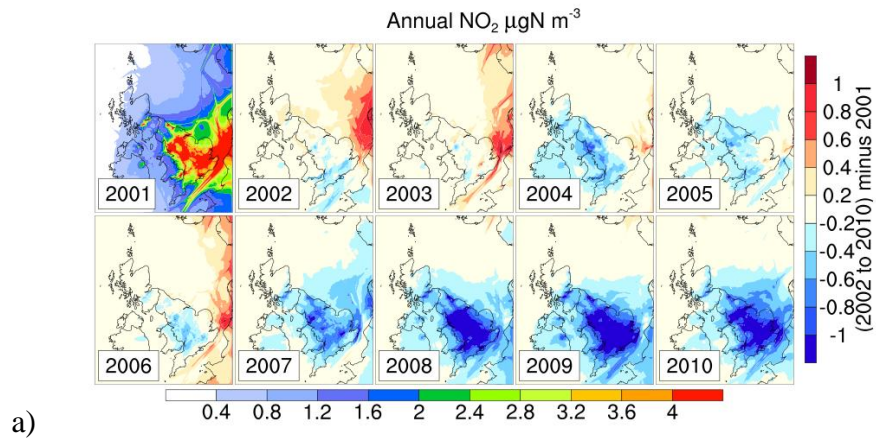
612 c)



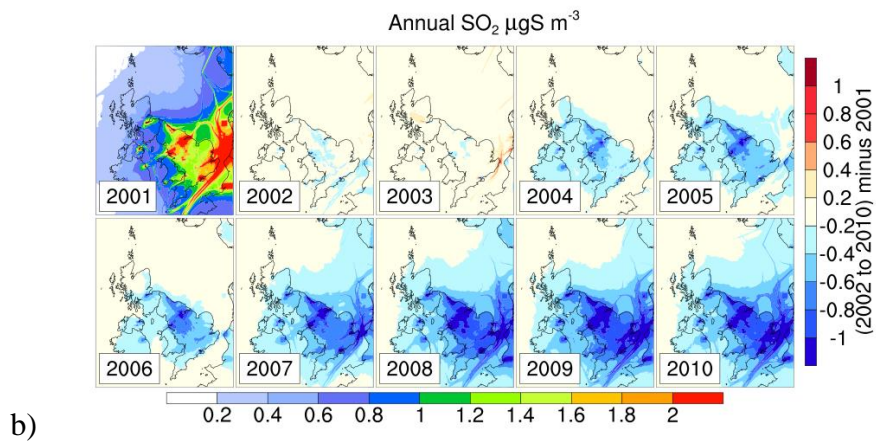
613 d)

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

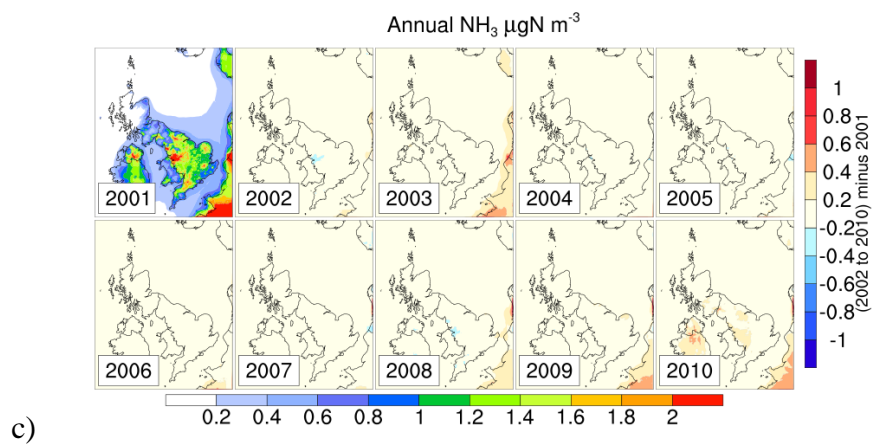
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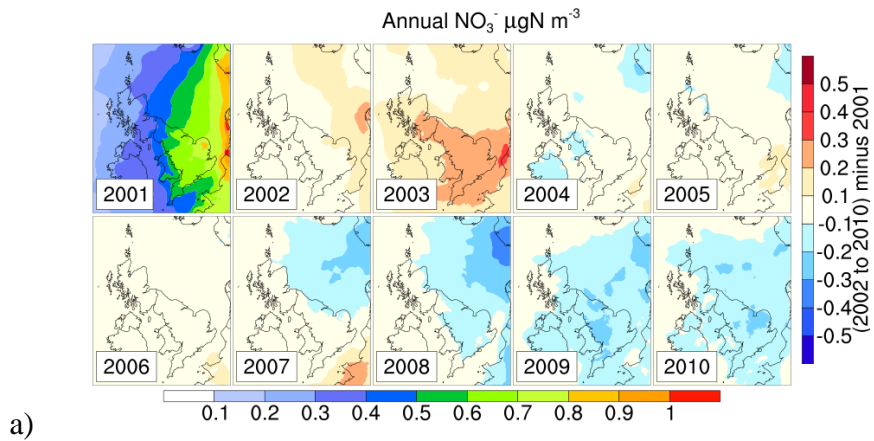


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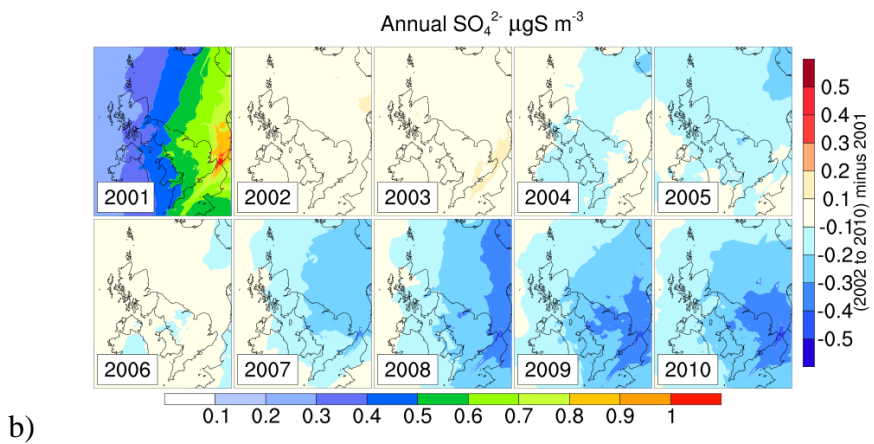


621 Fig. 4: Modelled annual average surface concentrations of (a) NO₂, (b) SO₂ and (c) NH₃. The
622 top left panel of each figure shows the concentrations in 2001 (horizontal scales in µg N m⁻³
623 or µg S m⁻³, as relevant). The remaining panels illustrate the difference in surface
624 concentrations in each of years 2002 to 2010 compared with 2001 (vertical scales in µg N m⁻³
625 or µg S m⁻³, as relevant).

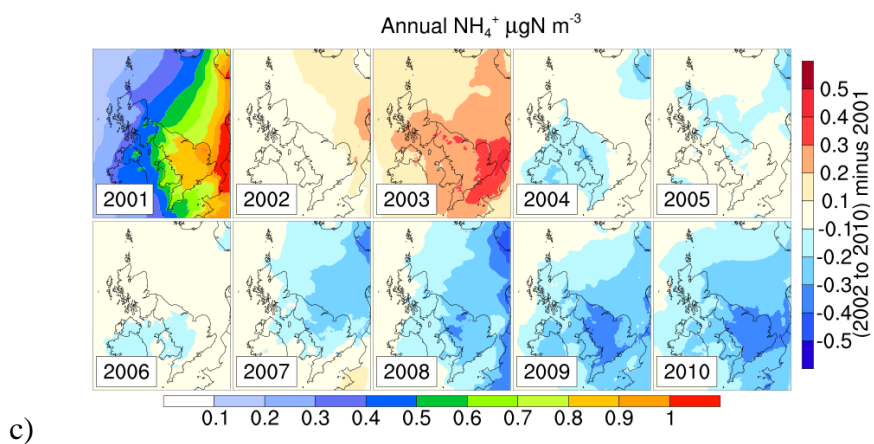
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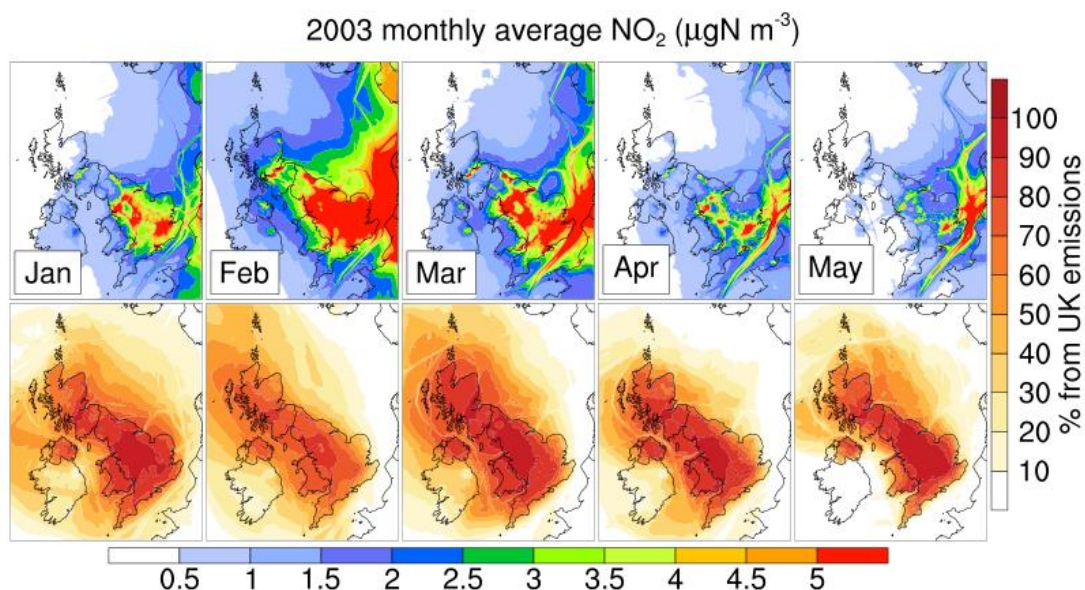
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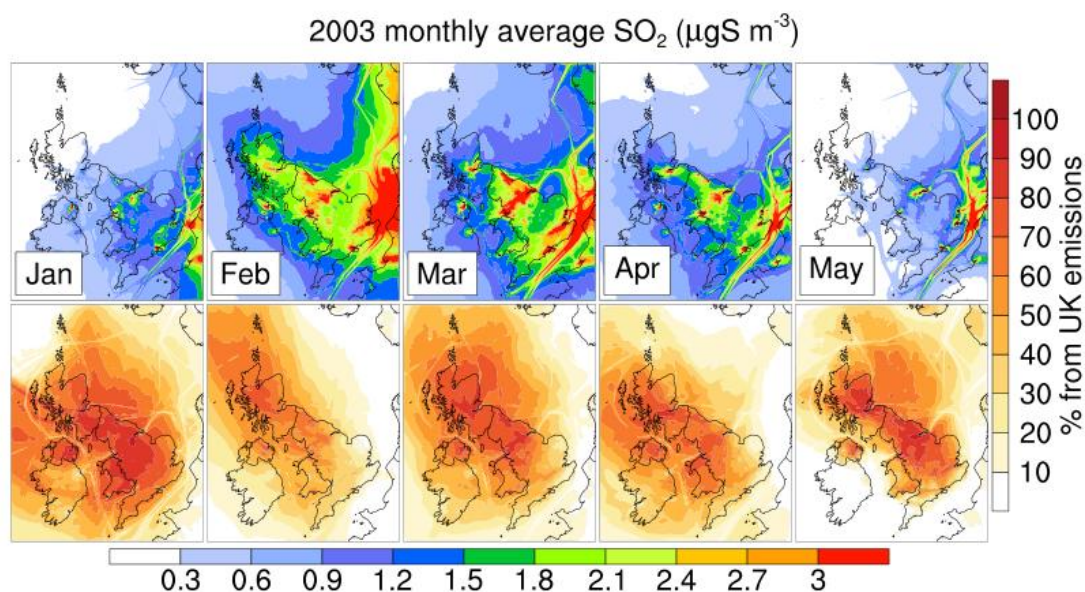
628



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

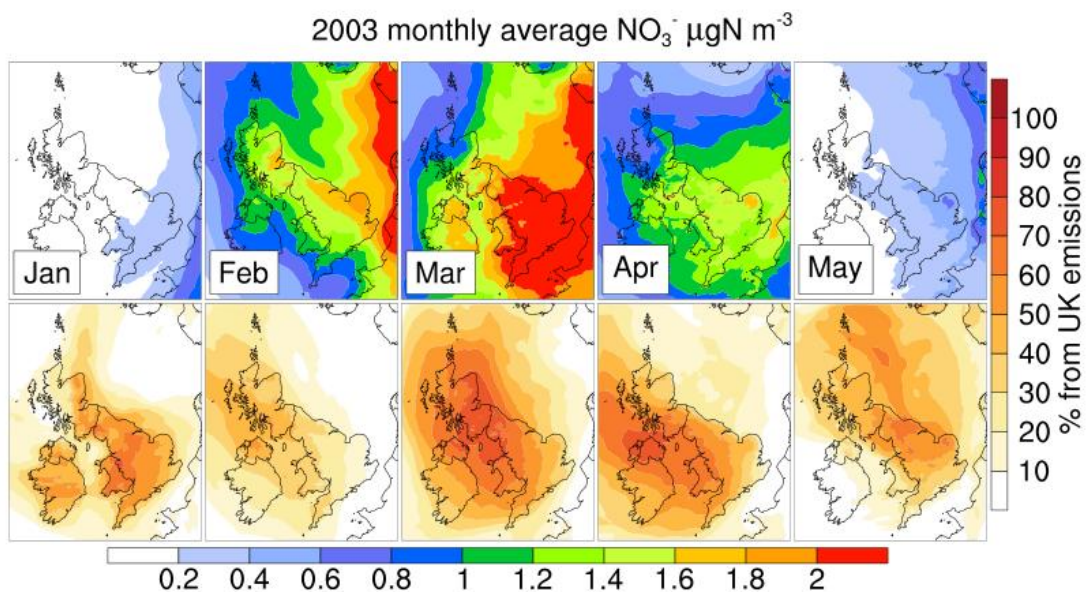


634 a)

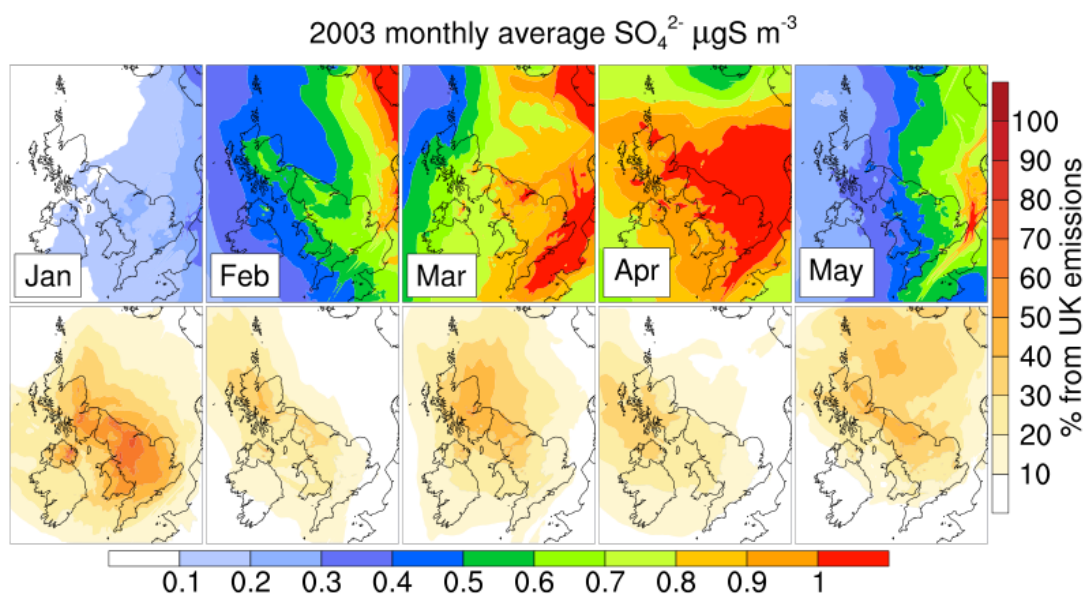


635 b)

636 Fig. 6: Modelled monthly average surface concentrations and UK contributions for a) NO₂
 637 and b) SO₂ through January to May 2003. In each case the upper panel shows the mean
 638 concentrations (µg N m⁻³ or µg S m⁻³), while the lower panel shows the percentage
 639 contribution from UK emissions (calculated as $[100 \times (\text{Base} - \text{no UK emi})/\text{Base}]$ between the
 640 base simulation and the simulation with zero UK emissions).



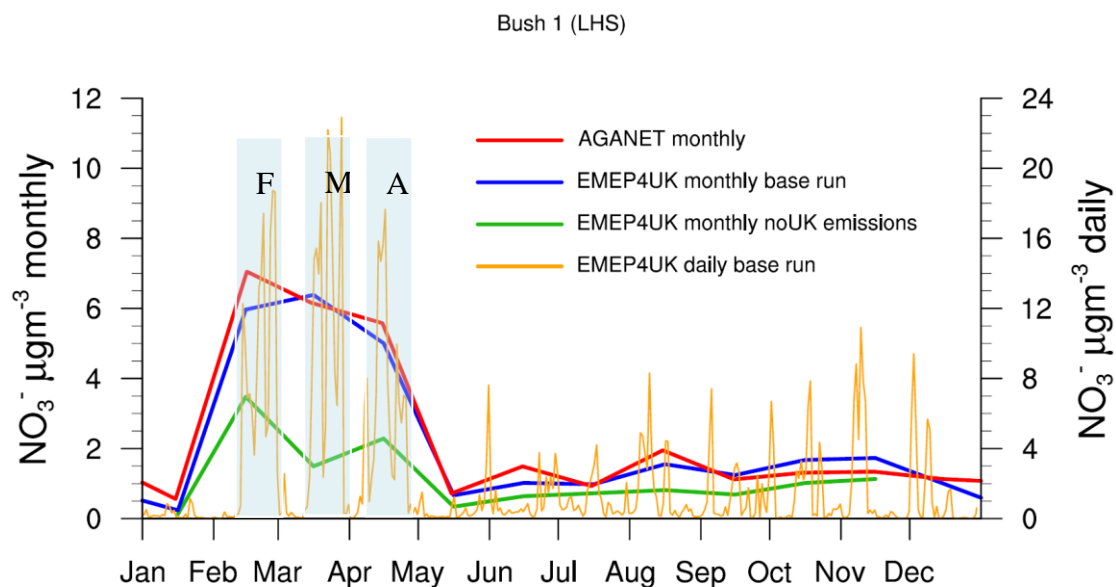
641 a)



642 b)

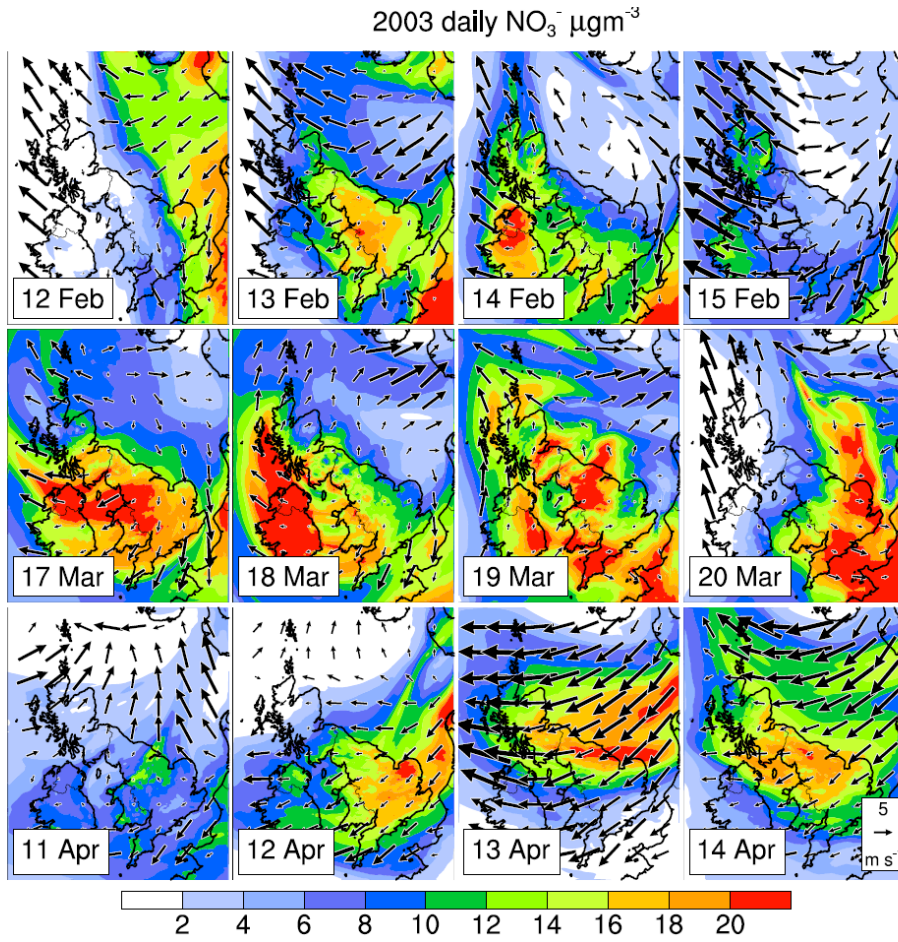
643 Fig. 7: Modelled monthly average surface concentrations and UK contributions for a) NO_3^-
 644 and b) SO_4^{2-} through January to May 2003. In each case the upper panel shows the mean
 645 concentrations ($\mu\text{g N m}^{-3}$ or $\mu\text{g S m}^{-3}$), while the lower panel shows the percentage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

648



649

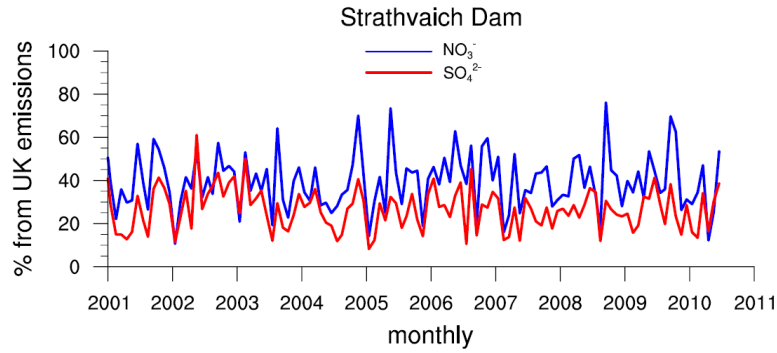
650 Fig. 8: Modelled and observed monthly mean (left axis) and daily mean (right axis) surface
 651 concentrations of NO_3^- at the Bush site (Scotland) for the year 2003. The red line is the
 652 measured monthly values from the AGANet network, the blue line is the modelled monthly
 653 means for the base run, the green line is the modelled monthly means for the experiment with
 654 no UK emissions, and the orange line is the modelled daily means for the base run. (All
 655 model values are averages of hourly data). The blue shadows highlight the three episodes
 656 labelled F, M and A.
 657



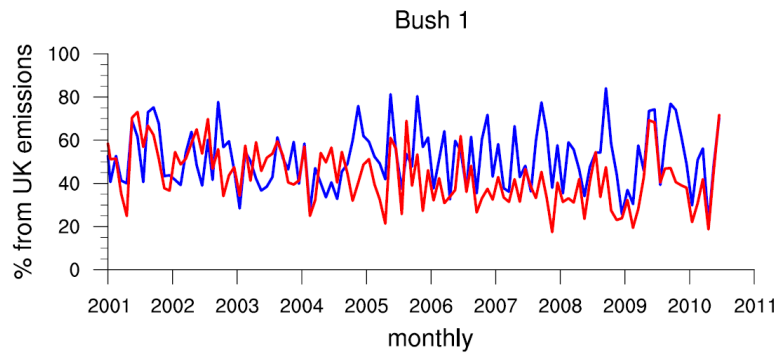
659

660 Fig. 9: Modelled daily mean surface concentration of NO_3^- and the 12:00 wind vector for 12-
 661 15th Feb (episode F), 17-20th Mar (episode M) and 11-14th Apr (episode A).
 662

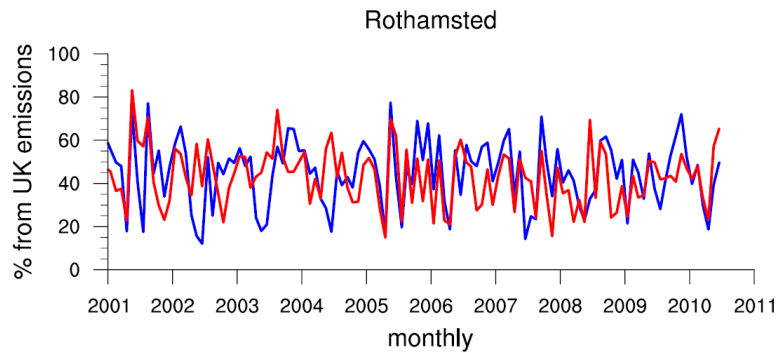
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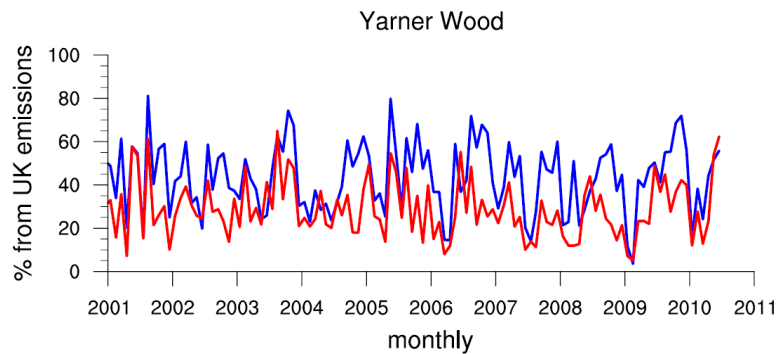
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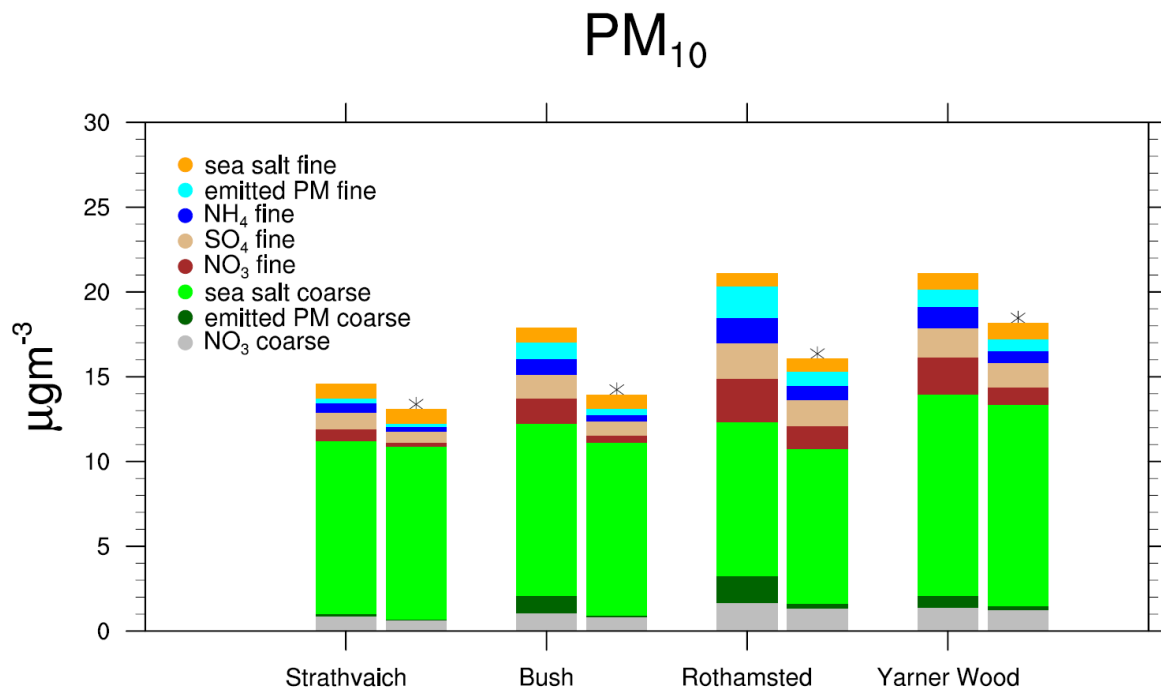


666



667

668 Fig 10: Modelled monthly average proportions of NO_3^- (blue line) and SO_4^{2-} (red line) derived
669 from UK precursor emissions, for 4 sites in the UK for the decade 2001-2010 (calculated as
670 $[100 \times (\text{Base} - \text{no UK emi}) / \text{Base}]$ between the base simulation and the simulation with zero
671 UK emissions).
672



673

674 Fig. 11: Mean composition of PM₁₀ components as estimated by the EMEP4UK model for
 675 four sites across the UK, averaged for the whole of 2003. The model base run (including all
 676 national and international emissions) is compared with the results from a simulation excluding
 677 UK emissions (*). The difference in magnitudes between the pairs of adjacent bars indicates
 678 the PM derived from emissions within the UK. As well as the SIA components, the total
 679 modelled PM₁₀ includes the contribution from emitted primary fine PM (PM_{2.5}) and primary
 680 PM_{coarse} (i.e. PM_{2.5-10}), and fine and coarse sea salt.

681 **Tables**

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

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

688

689 Table 2: Model simulated contributions of Continental European PM_{2.5} import to the current
 690 European Commission limit value (EC, 2013) and to the World Health Organisation guideline
 691 value (WHO, 2005) at each of the four sites for the EMEP4UK model simulations for the year
 692 2003.

Continental European contribution	Strathvaich Dam	Bush 1	Rothamsted	Yarner Wood
EC limit value of 25 µg m ⁻³	5%	8%	18%	15%
WHO guideline of 10 µg m ⁻³	14%	20%	45%	38%

693