Response to Reviews of Paper:
The role of long-range transport and domestic emissions in determining atmospheric secondary inorganic particle concentrations across the UK, by Vieno et al.

We thank the reviewers for their time spent reviewing our manuscript and for the comments raised. Below we respond to each comment in turn and indicate the revisions we have made to our paper. The original comments from the referees are in plain text and our responses are *in italic.* References given in our responses are included at the end

Reviewer #1
This study focuses on intercomparisons of surface measurements of inorganic particulate species concentrations with model predictions. The study focuses on the UK between 2001-2010. The paper concludes that its key findings are that the model and measurements agree for the most part, and that high nitrate episodes encountered were a result of imported pollution from other regions. The overall topic of inorganic aerosol composition (including identifying sources, transformations, sinks) is of relevance to ACP. The paper is generally well-written and the methods used are described well and seem fine. The title reflects the contents of the paper and the abstract provides a concise summary of the paper.

The key issue that requires much more attention is that this reviewer did not identify new insight provided by this manuscript that can help advance the community's knowledge of inorganic aerosol formation. The paper seemed like an intercomparison exercise between measurements and model predictions, with very general results.

> *We thank the reviewer for their points raised. The overall scope of the paper was to investigate the variability in composition of secondary inorganic aerosol (SIA) and the drivers of episodes of elevated secondary inorganic PM. We focus on the simulation of episodes as they have important consequences for policy and human health. Indeed, there are a number of new features and insights to this work. 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 entire UK for a multi-year period. This is also the first time that the EMEP(4UK) model simulations have been compared with the UK-wide AGANet monitoring network, providing a model validation for a decade of simulated hourly atmospheric inorganic species data (necessarily averaged to monthly means for comparison with the measurements). Hence this research represents a novel model comparison with observations. Furthermore, for the first time this paper diagnoses the key processes driving high SIA pollution episodes across the UK, and reveals contrasting causes for different periods, e.g. recirculation events building up UK emissions versus long-range transport. We now clarify the focus of the paper, its novelty (as highlighted above) and highlight the relevance of this work to the wider community.*
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> *In addition, in response to comments also from Reviewer #3 we have now undertaken and included further evaluation of the domestic/import drivers for UK SIA (see further description below) which further enhances the scientific insight gained. Further text to emphasise these new results and insights have been added to the revised paper, (abstract, introduction and particularly to the in the discussion (section 4) and conclusions sections.*

More depth is required in the analysis to contribute something to our knowledge of secondary formation of key species such as sulfate and nitrate. It would be recommended also to generate sufficient depth such that the results have broader geophysical implications for other parts of the globe too.

> *The full EMEP model domain used here already covers a significant global region - an area greater than Europe. Our focus is on understanding the origin of SIA in the UK, but to do this necessarily requires the context of emissions, transport and chemistry of NO_x, SO_x and NH_3 at the wider regional European scale, in order to assess the local vs. regional influences.*

The authors should consider addressing the sensitivity of nitrate, ammonium, and sulphate formation to various meteorological and thermodynamic conditions and the importance of formation pathways in fine versus coarse aerosol.

> *As noted above, in response to comments from Reviewer #3 our paper now includes further model validation and further evaluation of the domestic/import drivers for UK SIA. The additional work includes: more species included in the model vs. measurement comparisons; partitioning of nitrate between fine and coarse PM; a discussion of the effect of temperature on SIA formation where relevant, and a 10 year time series of the percentage contribution from UK emissions to UK SIA. These additional analysis and accompanying text are in the revised paper (sections 3, 4 and 5).*

Another topic that should be discussed in greater detail is how much of the aerosol mass is accounted for by the species investigated in this work for the study region.

> *The focus of this study was specifically on the role of long-range transport versus domestic emissions in determining atmospheric secondary inorganic particle concentrations in the UK, particularly during periods of very high SIA, not an investigation of model-simulated mass balance of all components of PM. In the Introduction we cite literature which has shown that instances of high PM in the UK generally have proportionally high SIA composition, particularly nitrate (Yin and Harrison, 2008;Putaud et al., 2010). However, we agree with the reviewer that the contribution of SIA to total PM is important, hence we have now re-plotted Figure 11 to include the total simulated PM_{10} showing the relative contribution of fine and coarse nitrate to the total PM, but draw attention that in the model version used for this work the modelled PM_{10} was equal to the sum of primary PM, SIA and sea salt only.*

More intercomparison of the results of this study with other regions is warranted to at least try to put these results in greater perspective. The focus right now is too narrow for publication in ACP. Due to the issues above, I cannot support publication of this work in its present form.

> *We disagree that the focus is too narrow; especially with our further analyses and discussion that address Reviewer #3's comments. We have also added further text and references to section 4 that highlights other studies where long-range transport of PM is analysed globally (Sanderson et al., 2008), for China (Zhang et al., 2014;Wang et al., 2014) and for the USA (Mwaniki et al., 2014) to place this work in a more general context.*

Reviewer #2

This paper uses a model to evaluate the contribution of continental Europe to secondary inorganic aerosols in the UK. Although national emissions have a dominant role in gas phase concentrations, it is found that long range transport has an important role for secondary species. The paper shows that there have been declines in pollution levels, but cautions that health limits may be exceeded due to long range transport. On a separate note, the results show that meteorological variability from year to year can lead to big changes in average pollutant levels on an annual timescale such that multi-year time periods should be considered for more robust evaluation. The paper is clearly written and the methodology is sound. Publication is recommended in ACP.

Minor Comments: There is no consideration of intercontinental transport (i.e. from North America) - could a brief description be added to the introduction about what is known about this and the magnitude of this compared with continental Europe?

> *The trans-Atlantic transport of SIA to the UK is small compared with the European import. The EMEP(4UK) model uses a yearly boundary condition for SIA at the edge of the European domain adjusted for each year. The cross Atlantic transport of SIA has a small effect on the EU surface SIA concentration and deposition as has been demonstrated by Simpson et al. (2014) and Sanderson et al. (2008). A brief note about this has now been added to the introduction.*

Page 33439, Line 4-5: The 2006 peak at Strathvaich is curious. Is this just an anomaly, or could something be said about it from the meteorology at the time? A couple of lines in the discussion would be appreciated.

> *We have not found any anomaly in the meteorology during this period. Both measured nitrate and sulphate were high for this month, but not chloride. We can only speculate that the anomaly is due to undetected measurement issues or related to very local influences, and have added this suggestion to the text in section 3.*

Page 33440, Line 20: Presumably a large factor in the greater contribution of non-UK emissions to UK secondary particles is the formation lifetime of the aerosols. Could this be added in the discussion?

> *Yes. The lifetime up to a few days for oxidation of* NO_x *and* SO_2 *to* HNO_3 *and* H_2SO_4 *is 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. This text has been added to the discussion (section 4).*

Page 33443, line 23-26: The wording is confusing: SO4 is less sensitive than NO3 which is itself insensitive?

> *We have shortened this sentence to avoid confusion. The text now reads: "This is consistent with Redington et al. (2009) whose modelling showed that* SO_4 *formation in the UK was less sensitive to a 30% NH3 emissions reduction than* NO_3 *formation."*

Page 33444, line 23-25: The discussion of spring 2003 is split up over several paragraphs in combination with other things. It could benefit from re-organization. Are there differences in emissions in the model for this episode? The model gets the peak correctly, is this just due to meteorology? Also, would it be worth saying something about the 2003 heat wave? I cannot tell from the figures if it associated with the high sulphate values.

> *We have now re-organised the text on episodes in 2003, into several consecutive paragraphs in the discussion.*
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> *There are no differences in emissions for the spring of 2003 (other than proportional changes to the annual total each year) since the model applies fixed monthly, weekly and diurnal profiles to the national annual totals of emissions for each component from each source sector (different profiles for the different source sectors).*
>
> *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 peak in sulphate was captured by the model and observations in the south of England (Rothamsted - shown in figure A below but not included in the paper). As the reviewer suggests we believe this peak was associated with high temperatures, since sulphate*

concentrations increase with temperature due to faster SO_2 oxidation (Dawson et al., 2007;Jacob and Winner, 2009) We have added text to this effect in the discussion section.

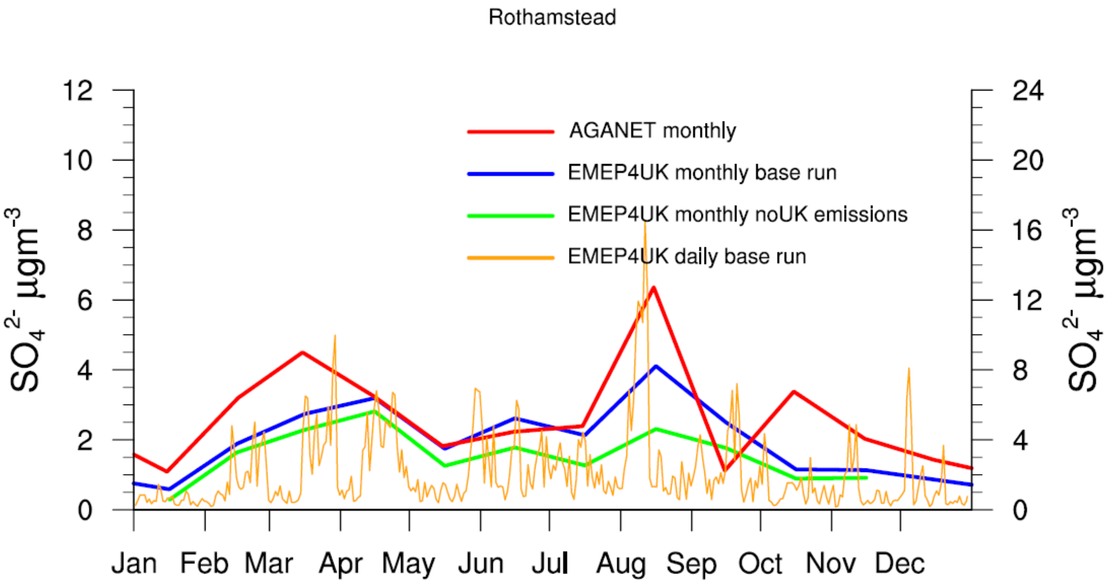

Fig. A. Modelled and observed monthly mean (left axis) and daily mean (right axis) surface concentrations of SO_4^{2-} at the Rothamsted site (England) for the year 2003. The red line is the measured monthly values from the AGANet network, the blue line is the modelled monthly means for the base run, 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.

PPM2.5 seems like a clumsy acronym given the prevalence of parts per million – could something else be found?

We have changed "PPM2.5" to "emitted PM2.5" throughout to avoid any confusion.

Reviewer #3

This paper applies the EMEP4UK regional atmospheric chemistry transport model to evaluate the roles of long-range transport and domestic emissions during the 2001-2010 decade in determining the secondary inorganic particle concentrations across the UK. Modeled surface concentrations are evaluated with the long-term observational data from four representative sites of the UK AGANet monitoring network, which provided simultaneous measurements of SO2, NOx, NH3 gases and particulate NO3-, SO4=, and NH4+. Modeled monthly average particulate concentrations are in general agreement with the observed values for the decade. Model analysis of 2003 suggested that 40-60% of the monthly average total inorganic particulate mass at the UK sites was due to long-range transport from continental Europe. The paper is generally well written, but the analysis seems a bit hurried and lacks the depth necessary to figure out the roles of different mechanisms that govern the inorganic aerosol concentrations. The manuscript can be recommended for publication in ACP after the following issues are carefully addressed.

Specific Comments:

1) Authors refer to Simpson et al (2012) for the description of the EMEP model and state that the gas-particle partitioning is done by EQSAM formulation (Metzger et al., 2002a,b). After reading these two papers, I find that EMEP simulates aerosols with two size modes (designed to calculate PM10 and PM2.5) while EQSAM is essentially a bulk aerosol equilibrium solver that does not treat size-dependent gas-particle partitioning. This is a gross

oversimplification that is prone to large errors, especially in the modeled long range transport of semi-volatile species such as NO3-, Cl-, and NH4+ as they interact with sea-salt during transit from continental Europe to the UK. It has been shown that a fully dynamic mass transfer treatment is needed to accurately perform gas-particle partitioning to fine and coarse mode particles (Hu et al., 2008) and a considerable amount of effort has been put into developing such schemes (e.g., Jacobson, 2005; Zhang and Wexler, 2006; Zaveri et al., 2008). Also, the fundamental basis of the EQSAM thermodynamics model formulation itself appears to be fraught with serious issues (e.g., see interactive discussions for Metzger and Lelieveld, 2007; Xu et al., 2009; Metzger et al., 2010). The authors therefore need to clearly defend their choice of thermodynamic model as well as the bulk equilibrium approach, especially since the focus of this paper is on the role of long-range transport vs. domestic sources of inorganic aerosols, of which NO3- and NH4+ are shown to be major components based on observations.

At the time of this work (and currently) two aerosol schemes are available for the EMEP and EMEP4UK model: the EQSAM scheme (used in this work) and the MARS scheme as in Simpson et al. (2012). Both schemes use a bulk approach for particle formation. We have tested model output using both schemes against observations and they gave similar performance. We chose the EQSAM aerosol scheme over the MARS scheme as EQSAM is the scheme used in the TM5 global model (Karl et al., 2009;Huijnen et al., 2010) which gave us reassurance of our choice of gas/particle scheme. However, we agree that the reviewer highlights valid issues and we now include in the methods the relevant suggested references and in the discussion a clear statement of potential model limitations for SIA. The EMEP and EMEP4UK model calculates SIA in the two size ranges, $PM_{2.5}$ *and PMcoarse, using a parameterised approach as described in Simpson et al. 2012. We have extended the description of the model on these points in the methods section 2.1. We also not here that the EQSAM version used here is EQSAM2 whereas the parameterisation discussed in the Metzger et al. (2010) work is EQSAM3.*

2) Model predictions for both gas and particle phase observations of the three inorganic species (sulfate, nitrate, and ammonium) should be evaluated to ascertain the accuracy of the simulation.

We have now added extra rows to Table 1 that provides statistics summarising the model comparison against AGANet data for the available gas-phase (SO_2 *and* HNO_3*) inorganic precursor species, and accompanying text to section 3. In addition, we have add two citations in section 4 where the EMEP4UK model has also been validated against an extensive observational dataset in a model inter-comparison exercise organised by the UK Department for Environment, Food and Rural Affairs (Carslaw, 2011a, b).*

3) Since EMEP simulates two size modes, it would be very useful to show the relative importance of the modeled inorganic species in the two modes (broken down by aerosol types - primary dust, primary sea-salt, and secondary) to the overall contribution.

We have amended Figure 11 to show the relative contribution to PM_{10} *(i.e.* $PM_{2.5}$ *and PMcoarse) from the various SIA components, and added text to section 3 to describe the results. The large contribution from sea-salt to PM 10 is clearly shown. See also our responses to reviewer 1.*

4) The model perturbation study (turning off UK emissions) should be expanded to the entire decade to examine the variability in the relative contributions from domestic and long-range transport sources of inorganic aerosol.

We have now undertaken the full 10 years of model simulations as suggested by the reviewer and have calculated the monthly contribution of UK domestic emissions to SIA.

We have added a new figure (Figure 10) and further discussion to sections 3 and 4 to present and interpret these new results.

References cited in our responses:

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