Interactive comment on “Pan-European rural atmospheric monitoring network shows dominance of NH_3 gas and NH_4NO_3 aerosol in inorganic pollution load” by Y. Sim Tang et al.
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RESPONSE TO REVIEWER 1

Martijn Schaap (Referee)

The authors thank Dr. Schaap for his supportive comments for publication and for taking the time to look at all the details described in the manuscript. We have carefully considered all comments. Please refer to the specific responses.

Understanding the budgets of sulfur and nitrogen compounds and how they interact by e.g. inorganic aerosol formation is of key importance. The NEU network provides an outstanding contribution as it provides a comprehensive and quality controlled dataset across many countries. This paper clearly shows the large efforts required to set-up and run such a large monitoring network. Hence, although the dataset is from some time ago, it should be published and I recommend to publish the paper with a number of revisions.

My main concern is that the paper is quite long. I have the feeling that some features which are now presented at different locations could be merged to guide the reader. One of these is the message that ammonium nitrate dominates above ammonium sulfate which is concluded from the correlation between components, ion balance, seasonality, etc. I would appreciate if the authors could try to focus the results section into a more integrative storyline than the stepwise approach chosen now.

Author response

Whilst we acknowledge that our paper brings together and interprets a large body of network measurements, we nevertheless believe that it has a coherent flow that guides the reader through the material that is presented.

- Quality assessment of data: laboratory and field intercomparisons
- Spatial variability – with comparisons against national emissions densities (to demonstrate correlation of concentrations with emissions), according to sites grouped by land-use types and geographical regions of Europe, and which required examination of spatial correlation,
- Seasonal variability - according to sites grouped by land-use types and geographical regions of Europe.
- Absolute and relative concentrations of the different inorganic components are also investigated, as well as their spatial and temporal variations
- Bulk wet deposition composition.
- A comprehensive final section of key conclusions.

Two parts I feel are less important for the paper are the following:

1. *Concentration to Country emission correlation: The short life time of ammonia and NOx cause substantial gradients within larger countries. For that reason I would argue that the correlation between country emissions and averaged concentration levels is not saying a lot. Figure 9 presents these data and is hardly discussed in the paper. The emission density in the surroundings cells to me sounds more appropriate and tells something about the representativeness of the stations for the different pollutants.*

Author response
A similar comment was posted by Reviewer 2 *"Page 15 – Line 34. I am unsure of the point of the comparisons between air concentrations and emissions, which is not motivated by the description of the NitroEurope project or in the description of the specific objectives of the manuscript. I think this analysis could be removed from the paper without any implication for the main points or conclusions. But if it is to remain, the purpose of the analysis should be clearly stated and it should be shortened where possible., e.g. only including the comparisons to gridded emissions".*

Response (as also provided in response to reviewer 2):

Sect. 3.3.3. Comparison with gridded emissions: Deleted and moved to supplementary materials.

Sect 3.3.2. Comparisons with national gas emissions: Retained
Additional supporting text added at the end of section 3.3.2 (see below):

"The comparisons here used national emission totals, where emissions have been summed and averaged across very large and heterogeneous areas in each country. Additional analysis were also undertaken to compare the individual site mean data with i) gridded emissions from individual 0.1° x 0.1° EMEP grids in which the NEU sites are located (Supp. Figure S8, S9), and ii) averaged emissions of an extended number of EMEP grids (4 x grids) closest to the site (Supp. Figure S10). Since results from these analysis were similar to the comparisons with national emission densities, they are not included for further discussions in this paper. The purpose of the ranked emission densities is to compare the pollution climate in terms of primary gas emissions (SO_2, NO_2, NH_3) across the 20 European countries and to see if this is matched by the DELTA measurements. Despite the complex relationship between emissions and concentrations, the pollution gradient in Europe is clearly captured by the present data. At the same time, it also demonstrated the potential application of the DELTA® approach in providing national concentration fields, as evidence to compare against spatial and long-term trends in the national emissions data."

Page 15, lines 38 – 39
The lines below has been deleted, as the details are provided in the Figure 9 caption already.
"The error bars, where shown, is the range (min and max) of annual averaged concentrations of sites in each country"
Page 15, lines 39 – 40
The lines below has been moved to Figure 9 caption
"Where error bars are not visible, this indicates either that the country has measurement from just one site, or the range of concentrations measured are very close to the average."
.

2. *Section 4: This section is hardly connected to the monitoring network results. I would rather see a discussion on the future of this network. Should it be continued? Adapted? Or? The two main findings presented in the conclusions section are not new, and a few references to earlier works could be provided. Content wise, I have the feeling that the role of chloride depletion reactions of sea salt are interpreted as outliers in the interpretation of data, see below. As a modeler I would be very eager to compare our model results to the dataset and hope that the data will be openly available.*

Reviewer 2 posted a couple of similar comments *"Page 29 – Section 4.0. It seems like the material in this section could be greatly condensed and integrated into the Conclusions."* And *"Page 32 – Line 11. Some additional concluding comments, building on this key feature of the analysis, would be* *welcomed. For example, what does this shift from a sulfate dominated to nitrate dominated inorganic aerosol regime suggest for future European monitoring needs in support of ecological and human health protection? What else can be gleaned from the current study, with respect to data quality, methods, and ability to resolve spatial and temporal patterns, that can inform future monitoring efforts?"*

Author Response:
See revised text below which addresses both reviewers' comments:
(Please note Section 4.0 has been removed and integrated into the Conclusions)

The NitroEurope DELTA® network has provided for the first time a comprehensive quality-assured multi-annual dataset on reactive gases (NH_3, HNO_3, SO_2, HCl) and aerosols (NH_4^+, NO_3^-, SO_4^{2-}, Cl^-) across the major gradients of emission densities, ecosystem type and climatic zones of Europe. By sharing the method and protocol with several European laboratories, and developing synergies with established infrastructure (e.g. CarboEurope network and EMEP field sites), it has proven possible to establish a large-scale network within a relatively short time-scale and with low costs. Key elements were a harmonised methodology and the implementation of quality protocols that included regular laboratory and field inter-comparisons to monitor and improve performance.

At the same time, the concurrent measurement of the gas and aerosol components permitted an assessment of the atmospheric composition, spatial and seasonal characteristics in the gas and aerosol phase of these components. The dataset has also been used to develop estimates of site-based N_r dry deposition fluxes across Europe, including supporting the development and validation of long-range transport models. Combined with estimates of wet deposition (from NEU bulk wet deposition network and other networks such as EMEP), an assessment of the interactions between N supply and greenhouse gas exchange was addressed in a separate paper by Flechard et al. (2020), using N_r and CO_2 flux data from the co-location of the NEU DELTA® with CarboEurope Integrated Project sites.

Two key features have emerged in the data. The first is the dominance of NH_3 as the largest single component at the majority of sites, with molar concentrations exceeding that of HNO_3 and SO_2, combined. As expected, the largest NH_3 concentrations were measured at cropland sites, in intensively managed agricultural areas dominated by NH_3 emissions. The smallest concentrations were at remote semi-natural and forest sites, although concentrations in the Netherlands, Italy and Germany were up to 45 times larger than similarly classed sites in Finland, Norway and Sweden (< 0.6 µg NH_3-N m^{-3}), illustrating the high NH_3 concentrations that sensitive habitats are exposed to in intensive agricultural landscapes in Europe. The second key feature is the dominance of NH_4NO_3 over $(NH_4)_2SO_4$, with on average twice as much NO_3^- as SO_4^{2-} (on a molar basis). A change to an atmosphere that is more abundant in NH_4NO_3 will likely increase the atmospheric lifetimes and extend the footprint of the NH_3 and HNO_3 gases, by the re-volatilisation of NH_4NO_3 in warm weather.

Temporally, peak concentrations in NH_3 for crops and grassland sites occurred in spring, reflecting the implementation of the EU Nitrates Directive that prohibits winter manure spreading. The spring agriculture-related peak was seen even at semi-natural and forest sites, highlighting the influence of NH_3 emissions at sites that are more distant from sources. Summer peaks, promoted by increased volatilisation of NH_3, but also by gas-aerosol phase thermodynamics under warmer, drier conditions were seen in all ecosystem groups, except at Forest sites. The seasonality in the NH_3 concentrations thus provided important insights into both the relationship to occurrence of emissions and possible abatement measures to target peak emission periods. Seasonality in the other gas and aerosol components is also driven by changes in emission sources, chemical interactions and by changes in environmental conditions influencing partitioning between the precursor gases (SO_2, HNO_3, NH_3) and secondary aerosols (SO_4^{2-}, NO_3^-, NH_4^+).

Seasonal cycles in SO_2 were mainly driven by emissions (combustion), with concentrations peaking in winter, except in Southern Europe where the peak occurred in summer. HNO_3 concentrations were more complex, as affected by photochemistry, meteorology and by gas-aerosol phase equilibrium. Southern and eastern European regions provided the clearest seasonal cycle for HNO_3, with highest concentrations in summer and smallest in winter, attributed to increased photochemistry in the summer months in hotter climates. In comparison, a weaker seasonal cycle is seen in other regions, with marginally elevated concentrations in late winter, spring and summer and smallest in March and November. Increased ozone in spring is likely to enhance oxidation of NO_x to HNO_3 for forming the semi-volatile NH_4NO_3 by reaction with a surplus of NH_3. Cooler, wetter conditions in spring also favour the formation of NH_4NO_3 and more of the NH_4NO_3 remains in the aerosol or condensed phase. This accounts for the higher concentrations of NH_4^+ and NO_3^- in spring and the absence of a HNO_3 peak at this time of year. Conversely, increased partitioning to the gas phase in summer decreases NH_4NO_3 concentrations relative to gas phase NH_3 and HNO_3. Particulate SO_4^{2-} showed large peaks in concentrations in summer in Southern and also Eastern Europe, contrasting with much smaller peaks occurring in early spring in other regions. The peaks in particulate SO_4^{2-} coincided with peaks in NH_3 concentrations, illustrating the importance of NH_3 in driving the formation of $(NH_4)_2SO_4$. Since NH_4NO_3 is more abundant than $(NH_4)_2SO_4$, the seasonality of NH_4^+ is likely to be influenced more by the temperature and humidity dependence of the semi-volatile NH_4NO_3, than by the stable $(NH_4)_2SO_4$. This is supported by similarity in the the seasonal profiles of NH_4^+ and NO_3^- at all sites, demonstrating temporal, as well as regional correlation between these two components.

Data from the network showed Critical Levels of 1 and 3 $\mu g\ NH_3\ m^{-3}$ for the protection of lichens-bryophytes and vegetation were exceeded at 62 % and 27 % of the sites, respectively. At the same time, NH_3 dry deposition will also contribute to a significant fraction of deposited acidity and total N deposition to sensitive habitats, along with NH_4^+ and HNO_3 dry deposition and wet deposited NH_4^+ and NO_3^-. Although the concentrations of SO_2 have fallen to very low levels at all sites, SO_2 will continue to be important in contributing to the exceedance of acidification in European ecosystems (EEA, 2019), since SO_2 has a higher acidification potential than NO_x (0.70 kg SO_2 = 1 kg eq. NO_2 in acidity) (see Hauschild and Wenzel, 1998). Changes in the relative concentrations of the pollutant gases captured in the data suggests that the deposition rates of SO_2 and NH_3 will increasingly be controlled by the molar ratio of NH_3 to combined acidity (sum of SO_2, HNO_3 and HCl) and deposition models should take these changes into account. Indications from the current and projected trends in emissions of SO_2, NO_x and NH_3 are that NH_3 and NH_4NO_3 will continue to dominate the inorganic pollution load over the next decades, contributing to ecosystem effects through acid and N deposition. The growing relative importance of NH_3 and NH_4^+ to total acidic and total N deposition indicates that strategies to tackle acidification and eutrophication need to include measures to abate emissions of NH_3 (Sutton and Howard, 2018).

There is still a lack of NH_3 and speciated monitoring of the inorganic gas and aerosol composition across the EU. An implementation of the DELTA® approach across Europe would provide cost-efficient monitoring of the gas and aerosol phase pollutants for which reduction commitments are set out in Annex II to the NECD. Monitoring of NH_3 and the interacting acid gases and aerosols are needed to assess contributions of NH_3 to $PM_{2.5}$ and which will provide the baseline and evidence against which any changes and potential recovery in ecosystem response to changes in emissions can be assessed, as required under Article 9 of the NECD. Issues such as human health impacts from fine ammoniums aerosols will also drive policy decisions, since controlling NH_3 should also reduce PM concentrations.

Individual remarks:

3. *Title: I would recommend to move the word "atmospheric" to in "inorganic atmospheric pollution"*

Author Response:

Thank you.

"Pan-European rural atmospheric monitoring network shows dominance of NH_3 gas and NH_4NO_3 aerosol in inorganic pollution load"

Amended to:

"Pan-European rural monitoring network shows dominance of NH_3 gas and NH_4NO_3 aerosol in inorganic atmospheric pollution load"

4. ***4.*** *Line 7: Vieno reference is a bit strange here – not a monitoring work*

Author Response:

The sentence in question copied below:

"The aerosols, formed through neutralisation reactions between the alkaline NH3 gas and acids generated in the atmosphere by the oxidation of SO_2 and NO_x (Huntzicker et al., 1980; AQEG, 2012) are a major component of fine particulate matter ($PM_{2.5}$) (AQEG, 2012; Vieno et al., 2016a) and precipitation (ROTAP, 2012; EMEP, 2019)."

The modelling work by Vieno et al. looked at the sensitivity of annual-average surface concentrations of $PM_{2.5}$ across the UK to reductions in UK terrestrial anthropogenic emissions in primary $PM_{2.5}$, NH_3, NO_x, SO_x and non-methane VOC. The work shows that the reactions between NH_3, SO_x and NO_x are major contributors to $PM_{2.5}$.

We feel it is a relevant and important reference to cite here.

5. *Line 9: the negative impacts . . . should not be a new paragraph. The first two paragraphs contain two sentences now.*

Author Response:

The first two paragraphs have been merged into a single paragraph.

6. *Section 2.2.1 page 7 line 25: Could you indicate the breakthrough estimation is in comparison to ammonium aerosol levels, especially for the agricultural sites.*

Author Response:

Po Valley (IT-PoV) is used as an example agricultural site here:

Ammonia

Mean concentration = 4.5 µg NH_3 m^{-3}, range = 1.6 – 17 µg NH_3 m^{-3}

Denuder capture efficiency: Mean = 87 %, range = 57 – 96 %, N = 44

Ammonium aerosol

Mean concentration = 2.5 µg NH_4^+ m^{-3}, range = 0.4 – 6.2 µg NH_4^+ m^{-3}, N = 44

Correction for breakthrough: Mean = 4.5 %

For example (Feb-09 data):
Den 1 = 123 µg NH_4^+
Den 2 = 12.6 µg NH_4^+
Blank = 0.29 µg NH_4^+
Capture efficiency = 91 %
Volume of air collected = 21.47 m^3 (1.5 month exposure)

$$\chi_a\ (\text{corrected}) = \chi_a\ (\text{Denuder 1}) \times \frac{1}{1 - \left[\frac{\chi_a(\text{Denuder 2})}{\chi_a(\text{Denuder 1})}\right]}$$

NH_3 (µg NH_3 m^{-3}) applying infinite series correction equation above = 6.02

$$\chi_a\ (\text{Denuder 1}) + \chi_a\ (\text{Denuder 2})$$

NH_3 (µg NH_3 m^{-3}) by adding Den 1 + Den 2 = 5.96
The correction amounted to 0.06 µg NH_3 m^{-3} (= 0.06 µg NH_4^+ m^{-3})

Aerosol ammonium = 2.54 µg NH_4^+ m^{-3}
Corrected (by subtracting 0.06 µg NH_4^+ m^{-3} breakthrough from denuders) = 2.48 µg NH_4^+ m^{-3}
Correction = 2.3 %

Nitric acid
Mean concentration = 1.9 µg HNO_3 m^{-3}, range = 0.5 – 4.0 µg HNO_3 m^{-3}
Denuder capture efficiency: Mean = 84 %, range = 58 – 94 %, N = 44

Nitrate aerosol
Mean concentration = 5.2 µg NO_3^- m^{-3}, range = 1.5 – 13.5 µg NO_3^- m^{-3}, N = 44
Correction for breakthrough: Mean = 1.4 %

For example (Feb-09 data):
Den 1 = 41 µg NO_3^-
Den 2 = 5.8 µg NO_3^-
Blank = 0.24 µg NO_3^-
Capture efficiency = 88 %
Volume of air collected = 21.47 m^3 (1.5 month exposure)

$$\chi_a\ (\text{corrected}) = \chi_a\ (\text{Denuder 1}) \times \frac{1}{1 - \left[\frac{\chi_a(\text{Denuder 2})}{\chi_a(\text{Denuder 1})}\right]}$$

HNO_3 (µg HNO_3 m^{-3}) applying infinite series correction equation above = 2.23 µg HNO_3 m^{-3}

$$\chi_a\ (\text{Denuder 1}) + \chi_a\ (\text{Denuder 2})$$

HNO3 (µg HNO_3 m^{-3}) by adding Den 1 + Den 2 = 2.19 µg HNO_3 m^{-3}
The correction amounted to 0.04 ug HNO3 m-3 (= 0.04 µg NO_3^- m^{-3})

Aerosol (µg HNO_3 m^{-3}) = 12.61 µg NO_3^- m^{-3}
Corrected (by subtracting 0.04 µg HNO_3 m^{-3} breakthrough from denuders) = 12.57 µg HNO_3 m^{-3}
Correction = 0.00 %

7. *Page 8, line 13: please refer forward to the results section on the impact of the NaCL denuders.*

Author Response:
Thank you, see added text at end of sentence (highlighted)

"At the French Fougéres parallel site (FR-FgsP), NaCl coated denuders were used to measure HNO_3, to compare with results from K_2CO_3/glycerol coated denuders at the main site (FR-Fgs) (see Sect. **Error! Reference source not found.** for methodology and Sect. 3.3.1 for data intercomparison results).

8. *Section 2.6: Some countries may have large shipping contributions to NOx and SO2, how did you treat these in the indicator used here? Why did you choose 4 grids around a station and not the nine around and including the grid cell with the station?*

Author Response to the first part of the comment:
"Some countries may have large shipping contributions to NOx and SO2, how did you treat these in the indicator used here?
The comparisons made used the EMEP emissions totals, as reported in each of the grid squares. In the UK, estimates for domestic shipping emissions, based on a database of ship movements are included in the emissions inventory, reported to the EC and EMEP. We have not looked at the breakdown of emission sources in the EMEP database, so we can't say whether shipping emissions are also included in the reporting from countries that have contributions from shipping.

As the reviewer indicated, it would be interesting to address the question of shipping emissions in a future measurement-model paper with data from this study. It could include scenarios modelling with and without shipping emissions (e.g. update methodology for estimating emissions using individual ship tracking data) and assess contribution/sensitivities to the gas and aerosol pollution load. Of course, it would also be nice to have a monitoring network across Europe with sufficient spatial coverage and providing speciated gas and aerosol measurements to test the models.

Author Response to the second part of the comment:
"Why did you choose 4 grids around a station and not the nine around and including the grid cell with the station?"
Section 2.6: Line 39 – 40: "Extract gas emissions for groups of 4 grids (each = 0.1° x 0.1°) that surrounds a NEU site and derive grid-averaged emissions"

To confirm, the 4 grids selected included a grid cell containing the NEU site.
One grid contains the NEU site, and the other three are the closest in proximity to the grid containing the NEU site, i.e. a block of 4 grids containing and surrounding the NEU site.

To make it clearer, it has been reworded:
"Extract gas emissions for blocks of 4 grids (each = 0.1° x 0.1°) and derive grid-averaged emissions. One grid contains the NEU site and the other three in the block are the closest in proximity to grid containing the NEU site"
(note that in response to comments from both reviewers, this section has now been moved to supplementary materials)

We can expect there to exist a stronger correlation between emissions (NH_3, NO_x, SO_2) and the concentrations of the primary pollutants (NH_3, NO_x, SO_2) at the local scale (single grid square), since these reactive gases have relatively short atmospheric lifetimes.

For NH_3, which is a diffuse source, emitted mainly at ground level from agriculture, there was good correlation comparing national averages, single grid squares or 4 x grid square average.

In the case of SO_2, the analysis indicates that a single gridded EMEP square (0.1° x 0.1°) may be too local a spatial scale for an emissions-concentration comparison. Likely reasons are that SO_2 emissions are highly localised, from a very small number of large point sources at an elevated height.

Secondary pollutants (HNO_3, NH_4^+, NO_3^-) vary on regional scales, since it takes time for chemical transformation (gas to aerosols) and transport (longer atmospheric lifetimes). Emissions from one grid square could lead to secondary aerosols appearing in adjacent grid squares.

We therefore chose blocks of 4 grids (each = 0.1° x 0.1°) as the footprint to compare emissions and concentrations. This is approx. 17 x 22 km for sites that are at latitude 40°. As the reviewer suggests, we could have extended the footprint to include the 8 grid cells around the grid containing the station, to see if this improved the correlation. The comparison against the sum of emissions from an extended number of EMEP grids is more or less what is done with comparison with national emissions density (for the smaller countries at least), with similar results in the correlation. We feel that it will not add anything further to the data interpretation by choosing 9 instead of 4 grid squares.

As some useful, interesting features did emerge in comparisons of concentrations with gridded emissions, according to ecosystem types, we have retained this discussion but have moved it to supplementary materials, together with the associated figures and tables.

Please note that in response to both reviewers' comments concerning comparisons made between emissions and concentrations, we have deleted "Sect. 3.3.3. Comparison with gridded emissions" and moved it to supplementary materials, which also helped to reduce the length of the paper.

9. *Section 3.3.1 page 14 Line 1-3 details on the dry deposition schemes seem out of place here.*

Author Response:
On re-reading, we agree that the details on the dry deposition schemes does seem out of place and we have deleted the text (see below).

"In some models such as the Concentration Based Estimates of Deposition (CBED) model (Smith et al., 2000; Flechard et al., 2011), a canopy compensation point and the bi-directional exchange of NH3 between vegetation-type and the atmosphere are also considered (e.g. Sutton et al., 1995; Massad et al., 2010; Flechard et al., 2011)."

10. *Page 14 line 36-43: The comparison between N and S is based on mass here. Given the scope on ecosystem deposition provided elsewhere I could imagine that a comparison based on acid equivalents makes more sense than the mass. I do not see the consistency between the currently higher N levels and emission reductions since the nineties as the emissions did not start from a ratio of 1:1.*

Author Response to the first part of the comment:
"The comparison between N and S is based on mass here. Given the scope on ecosystem deposition provided elsewhere I could imagine that a comparison based on acid equivalents makes more sense than the mass."

We have tried to avoid using too many different units, to permit comparability of concentrations, and to avoid confusion, e.g. we have used units of µg N m^{-3}, µg S m^{-3} when referring to mass of gas and aerosol concentrations, and neq. m^{-3} when doing ion balances. Readers should be able to make the conversion to acid equivalents.

A comparison of acidification potential is made in "Section 4. Implications for a chemical climate dominated by NH_3 and NH_4NO_3 in Europe"

"However, SO_2 (by mass) has a higher acidification potential (1 kg SO_2 = 1.00 kg eq. SO_2) than NO_x (1 kg NO_2 = 0.70 kg eq. SO_2) (see Hauschild and Wenzel, 1998), so SO_2 will remain important in contributing to exceedances of critical loads for acidification, estimated to be exceeded in 5 % of the European ecosystem area in 2015 (EEA, 2019). "

Please note that the sentence was reworded following reviewer 2 comment to simplify sentence (see below) and integrated into Conclusions:

"Although the concentrations of SO_2 have fallen to very low levels at all sites, SO_2 will continue to be important in contributing to the exceedance of acidification in European ecosystems (EEA, 2019), since SO_2 has a higher acidification potential than NO_x (0.70 kg SO_2 = 1 kg eq. NO_2 in acidity) (see Hauschild and Wenzel, 1998).

Please note Section 4.0 has been removed and integrated into the Conclusions.

Author Response to the second part of the comment:
I do not see the consistency between the currently higher N levels and emission reductions since the nineties as the emissions did not start from a ratio of 1:1.

The paragraph in question:
"A key feature in Figure 7 is the dominance of N over S species at most sites, when expressed as µg m-3 of the element. The mean percentage contribution of sumNr (NH_3-N, HNO_3-N, NH_4^+-N, NO_3^--N) concentrations to the total mass of gas and aerosol species measured is 52% (range = 24 – 80%), twice as much as from sumS (SO_2-S and SO_4^{2-}-S; mean = 23 %, range = 7 – 53%) (Figure 8). This is consistent with more substantial reductions in SO_2 emissions (−72%) than achieved with NO_x 40 (−43%) or NH_3 (−18%) in Europe between 1991 – 2010 (EEA, 2019). The differences in atmospheric composition of S and N species in the present assessment therefore reflected changes in emissions of the precursor gases, and are also in agreement with a recent assessment of air quality trends showing important changes in S and N composition in air and rain across the EMEP networks (EMEP, 2016)."

Perhaps the paragraph is a bit ambiguous, so we have rephrased it to:

"A key feature in Figure 7 is the dominance of N over S species at most sites, when expressed as µg m^{-3} of the element. The mean percentage contribution of sumNr (NH_3-N, HNO_3-N, NH_4^+-N, NO_3^--N) concentrations to the total mass of gas and aerosol species measured is 52% (range = 24 – 80%), twice as much as from sumS (SO_2-S and SO_4^{2-}-S; mean = 23 %, range = 7 – 53%) (Figure 8). This reflects the smaller emissions in SO_2 (4-year average = 319 kt SO_2 yr^{-1}), compared with emissions of nitrogen gases (4-year average = 614 kt NO_x yr^{-1} and 220 kt NH_3 yr^{-1}) across the 20 countries in the NEU network. The differences in atmospheric composition of S and N species in the present assessment therefore reflected changes in emissions of the precursor gases, and are also in agreement with a recent assessment of air quality trends showing important changes in S and N composition in air and rain across the EMEP networks (EMEP, 2016)."

11. *Page 15, line 16. The 10-50% contributions in Putaud et al refer to the ammonium salts, not only ammonium. Please correct. Moreover, this paragraph seems more appropriate in the discussion or implication section than in the results chapter.*

Author Response:

Thank you. We have corrected in the text – see below:

"Secondary NH_4^+ particles are mainly in the 'fine' mode with diameters of less than 2.5 µm ($PM_{2.5}$) and estimated to contribute between 10 to 50 % of ambient $PM_{2.5}$ mass concentration in some parts of Europe (Putaud et al., 2010, Schwartz et al., 2016)."

Amended to:

"Secondary NH_4^+ particles are mainly in the 'fine' mode with diameters of less than 2.5 µm ($PM_{2.5}$), with ammonium salts estimated to contribute between 10 to 50 % of ambient $PM_{2.5}$ mass concentration in some parts of Europe (Putaud et al., 2010, Schwartz et al., 2016)."

Section 3.3.1. Comparisons according to ecosystem types is under Chapter 3: Results and Discussions

12. *Page 16 line 3. Here the correlation between precursor and aerosol is discussed in the paragraph on the correlation with emission densities. Right place?*

Author Response:

"The particulate components NH_4^+ and NO_3^- were also correlated with both precursor gases NH_3 and HNO_3 (Table 3). By contrast, there was no relationship between SO_4^{2-} with any of the three gases, possibly because of contributions to SO_4^{2-} from long-range transport. All regression plots of concentrations against emission densities, including summary statistics are provided in Supp. Figure S2. "

To clarify, the comparison of particulate components NH_4^+ and NO_3^- are with emission densities of NH_3 and NO_2.

Text amended (Supp Figure no. also updated):

"The particulate components NH_4^+ and NO_3^- were also correlated with emission densities of NH_3 and HNO_3 (Table 3). By contrast, there was no relationship between SO_4^{2-} with emission densities of any of the three gases, possibly because of contributions to SO_4^{2-} from long-range transport. All regression plots of concentrations against emission densities, including summary statistics are provided in Supp. Figure S7. "

13. *Page 17 line 3. HNO3 maybe highest in eastern Europe, but NOx emissions aren't. Could it be that the lower ammonia and hotter summer climate plays a pronounced role in the explanation as indicated in the seasonal cycle with summer maxima in the region (in contrast to western Europe). Similarly, in the presentation of the oxidized nitrogen on page 20 (L 24) the limitation on ammonia availability could be mentioned. The higher correlation between nitrate and ammonia emissions is indicative for this issue as well. Ammonium nitrate formation could be checked with the ammonium salt ion balance. Often inverse relationships between nitric acid and ammonia are modelled due to the limiting impact of the equilibrium with ammonium nitrate. Do you see this feature in the data?*

Author Response to the first part of the comment:
"HNO3 maybe highest in eastern Europe, but NOx emissions aren't. Could it be that the lower ammonia and hotter summer climate plays a pronounced role in the explanation as indicated in the seasonal cycle with summer maxima in the region (in contrast to western Europe)."

The larger SO_2 concentrations in Eastern Europe (mean 1.8 µg SO_2 m^{-3}) could also mop up available NH_3 (mean = 1.4 µg NH_3 m^{-3}), limiting available NH_3 to react with HNO_3.

Additional text added:

"HNO_3 formation by photochemical processes may be enhanced in hotter, sunnier summer weather in Russia. Since SO_2 concentrations (mean = 0.49 µg SO_2-S) at the Russian site (RU-Fyo) is in molar excess over the low levels of NH_3 (mean = 0.32 µg NH_3-N m^{-3}), removal of HNO_3 by reaction with NH_3 will also be limited."

Author Response to the second part of the comment:
"Similarly, in the presentation of the oxidized nitrogen on page 20 (L 24) the limitation on ammonia availability could be mentioned."

An explanation is already offered for the higher HNO_3 at the Russian site, so we feel that mentioning the limitation on ammonia availability as a possible mechanism in controlling atmospheric concentrations of HNO_3 is unnecessary repetition.

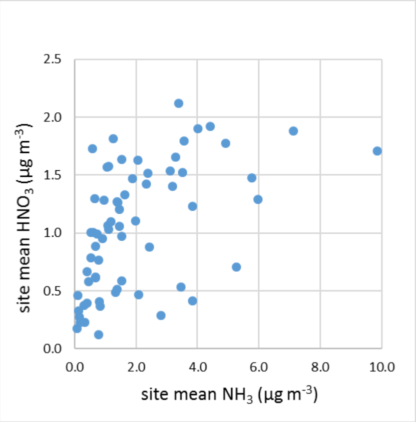
14. *" The higher correlation between nitrate and ammonia emissions is indicative for this issue as well. Ammonium nitrate formation could be checked with the ammonium salt ion balance. Often inverse relationships between nitric acid and ammonia are modelled due to the limiting impact of the equilibrium with ammonium nitrate. Do you see this feature in the data?"*

Author Response to the first part of the comment:
Ammonium nitrate formation could be checked with the ammonium salt ion balance: this is already covered in Section 3.4 Correlations between gas and aerosol components.

"In the aerosol phase, NH_4^+ correlated well with NO_3^- ($R^2 = 0.75$, $p < 0.001$, Figure 13A) and SO_4^{2-} ($R^2 = 0.75$, $p < 0.001$, Figure 13B) (Tables 5 and 7), but not with Cl^- (Table 5). Regression of the molar equivalent concentrations of the sum of NO_3^- and SO_4^{2-} against NH_4^+ show points close to the 1:1 line (slope = 0.84) and significant correlation ($R^2 = 0.64$, $p < 0.001$), which demonstrates the close coupling between the base NH_4^+ and the acid $NO_3^- + SO_4^{2-}$ aerosols (Figure 13C, Table 7)."

Author Response to the second part of the comment:
"inverse relationships between nitric acid and ammonia"

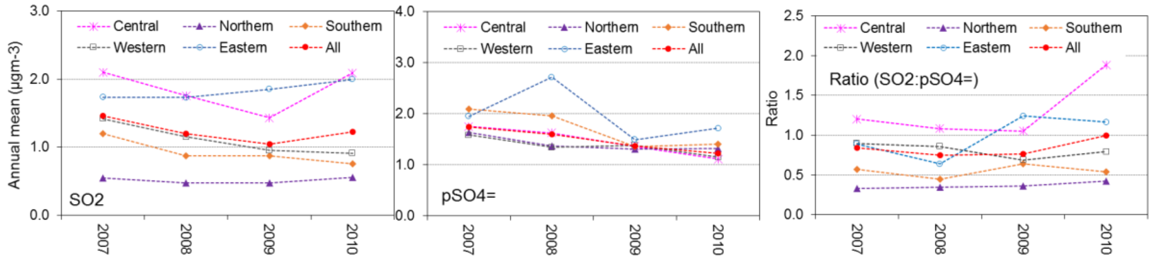
Below is a plot of mean HNO_3 versus site mean NH_3. We don't see an inverse relationship, although there appears to be a curvilinear relationship, with HNO_3 concentrations plateauing at $NH_3 > 2$ µg NH_3 m^{-3}.



The analysis is provided here to address the reviewers question only and has not been added to the paper.

15. *Page 21, the current levels are interpreted in relation to emission reductions which are not indicated from this network. The SO2 to SO4 ratio variability across the network may be the most interesting feature concerning sulfur for model developers. Did you see the anticipated systematic behavior for this ratio?*

Author Response:
Please see plots prepared below:
There appears to be different trends in SO_2 and SO_4^{2-} according to geographic regions.
The SO_2 to SO_4^{2-} ratio therefore also varies according to grouped regions.



A decrease in ratio of SO_2 to SO_4^{2-} : would suggest increased dry deposition of SO_2 ("co-deposition due to increasing ratio of NH_3 to SO_2 in the atmosphere). This results in a larger decrease in atmospheric SO_2 concentrations than would be achieved by emissions reduction alone.

A stable ratio of SO_2 to SO_4^{2}: would suggest that maximum deposition rates for SO_2 may have been reached with the smaller SO_2 concentrations since 2006.

Since there are only 4 years of data, the analysis and discussion is provided here to address the reviewers question only and have not been added to the paper.

16. *Page 21 the Bugac discussion interrupts the main information flow.*

Author Response:

We have simplifed / shortened the text. Discussions on gridded emissions was removed, since

i) section on comparison with gridded emissions has been deleted, and
ii) does not add substantively to understanding of what is happening at the site.

See amended text below:

"SO_2 concentrations were also correlated with SO_2 emission density ($R^2 = 0.65$, $p < 0.001$, $n = 20$) in each country (Figure 10A3, Table 3). The smallest and largest SO_2 annual average concentrations corresponded with the lowest emissions in Norway and highest in the Czech Republic (Figure 9C). By contrast, SO_2 concentrations from the single measurement site Bugac in Hungary (HU-Bug) are much higher than expected on the basis of SO_2 emission density estimated for the country. This suggests that Bugac is likely to be affected by proximity to sources. This contrasts with the BKFores site in the Czech Republic (CZ-BK1) which had smaller NH_3 concentrations due to its location away from sources. "

~~Gridded emissions for the single grid (0.1° x 0.1°) containing the semi-natural Bugac site are all at the low end of the range of gridded emissions across Hungary for SO_2, NO_x and NH_3:~~

- ~~SO_2-S: t yr^{-1} = 2.1 (range = < 0.1 to 5144)~~
- ~~NO_x-N: t yr^{-1} = 11 (range = < 0.1 to 3230)~~
- ~~NH_3-N: t yr^{-1} = 63 (range = < 0.1 to 589)~~

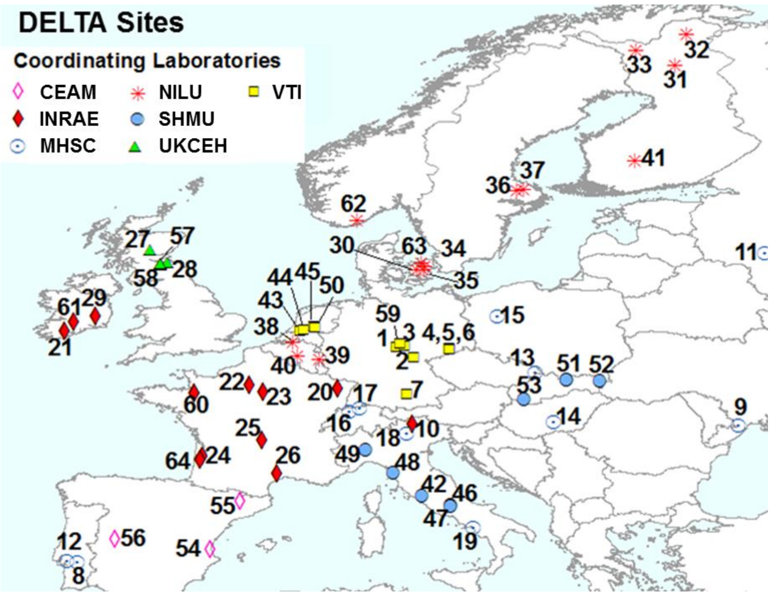
~~Although the Bugac site is located in a grid with low emissions of all the gases, the higher SO_2 (1.2 µg S m^{-3}), together with elevated NH_3 (2.6 µg N m^{-3}) and HNO_3 (0.3 µg N m^{-3}) concentrations measured at this site suggests that it is likely to be affected by proximity to sources. This contrasts with the BKFores site in the Czech Republic (CZ-BK1) which had smaller NH_3 concentrations due to its location away from sources. "~~

17. *Page 22. The ion balance for southern Scandinavia may be affected by sodium nitrate formation and not so much by an overestimation of SO4. Na:CL depletion ratio may give a hint here. Further down on the same page the remark is made but no connection is made.*
 On page 24 another check is made on ion balances with hard statements on lab quality– are these issues not connected and is one actually looking at sea salt depletion reactions?

Author Response:

Southern Scandinavian sites

		µg m^{-3}									Ratio	
id	name	NH_3	HNO_3	SO_2	HCl	pNH_4^+	pNO_3^-	pSO_4^{2-}	pCl^-	pNa^+	Na:Cl (neq)	NH_4^+: (NO_3^- + SO_4^{2-}) (neq)
63	Brandbjerg	0.77	0.76	0.85	0.25	1.16	1.74	2.01	0.21	0.63	4.6	0.93
34	Rimi	1.47	1.05	0.74	0.26	0.74	2.46	2.34	0.88	1.28	2.3	0.47
35	Risbyholm	5.26	0.70	0.61	0.20	0.71	1.82	2.00	0.33	1.02	4.8	0.56
30	Soroe	1.54	0.97	0.91	0.33	0.74	2.55	2.32	0.53	0.92	2.7	0.46
62	Birkenes	0.29	0.37	0.17	0.34	0.28	0.42	1.03	0.26	0.43	2.5	0.55
36	Norunda	0.32	0.23	0.17	0.14	0.25	0.22	1.09	0.05	0.21	6.1	0.52
37	Skyttorp	0.14	0.33	0.17	0.17	0.19	0.30	1.14	0.09	0.20	3.5	0.37



The four Danish sites Brandbjerg (63), Rimi (34), Risbyholm (35) and Soroe (30) are all very close together (see map).
The Na:Cl ratios varied between 2.3 at Rimi to 4.8 at Risbyholm.
The appearance of excess sodium at the sites may be due to uncertainty (underestimation of chloride concentrations) at these sites, as discussed in the manuscript.

The two Swedish sites Norunda (36) and Skyttorp (37) are also close together (see map).
The Na:Cl ratios varied between 3.5 at Skyttorp to 6.1 at Norunda.
The appearance of excess sodium at the sites may therefore likely be due to underestimation of chloride concentrations, which are very close to or below the detection limit of the method. The quality (e.g. variability) of the blanks (data not available) at such low concentrations will also have a proportionately large effect on the calculated Cl$^-$ concentrations.

Finland

		µg m^{-3}									Ratio	
id	name	NH_3	HNO_3	SO_2	HCl	pNH_4^+	pNO_3^-	pSO_4^{2-}	pCl^-	pNa^+	Na:Cl (neq)	NH_4^+: (NO_3^- + SO_4^{2-}) (neq)
41	Hyytiälä	0.11	0.46	0.54	0.19	0.22	0.20	1.38	0.03	0.17	9.8	0.3
31	Sodankylä	0.17	0.23	0.57	0.17	0.17	0.09	1.24	0.06	0.16	3.8	0.3
32	Kaamanen	0.79	0.12	0.93	0.17	0.32	0.05	0.64	0.15	0.14	1.4	1.3
33	Lompolojänkkä	0.09	0.17	0.25	0.22	0.19	0.06	0.79	0.06	0.12	3.0	0.6

The three sites in Finland Sodankylä (31), Kaamanen (32) and Lompolojänkkä (33) are all inland sites, in close proximity to each other in the North of Finland (see map).
The Na:Cl ratio at Kaamanen was 1.4, whereas the two nearby sites showed ratios of 3.0 and 3.8.
At Hyytiälä (41), a site that is further south in Finland, the ratio was even larger, at 9.8.

The LOD for aerosol chloride measurement on the DELTA system is around 0.1 – 0.16 µg Cl$^-$ m^{-3} for monthly exposures. The appearance of excess sodium at the sites may therefore likely be due to underestimation of chloride concentrations, which are very close to or below the detection limit of the method. The quality (e.g. variability) of the blanks (data not available) at such low concentrations will also have a proportionately large effect on the calculated Cl$^-$ concentrations.

18. *Page 22: does the HCl distribution provide a hint at the importance of the marine source for it?*

Author Response:
At coastal sites, HCl released from the reaction of sea salt with HNO_3 and H_2SO_4 can be a significant source. Part of the chloride of sea salt can be substituted by SO_4^{2-} and NO_3^- through a reaction with H_2SO_4 and HNO_3, known as the Cl^- deficit

Seasalt depletion: $NaCl (p) + H^+ (p) => Na^+ (p) + HCl (g)$
H^+ = from H_2SO_4, HNO_3
p = particle, g = gas

Looking at the spatial distribution of HCl, site mean concentrations varied between 0.06 at Renon (Italy, inland, site 10) to 0.50 at Espirra (Portugal, coastal, site 12). So it appear at first glance that HCl is elevated at the coastal Espirra site, possibly from the reaction described above.
However, site mean HCl concentrations at other coastal sites in the network were in the range of 0.14 (Solohead, Ireland) to 0.34 µg HCl m^{-3} (Birkenes, Norway), similar to the range across the entire network (0.06 = 0.50 µg HCl m^{-3} described above)
It cannot therefore be concluded that there is a potential marine source for HCl.

19. *Page 27 line 1-5: the impact of ammonia and temperature on seasonality of nitric acid is not discussed ad should be mentioned. OK, it is done in the next paragraph. Why not combine these?*

Author Response:
Paragraph 1 focuses on the influence of photochemistry on the formation of HNO_3.
Paragraph 2 goes on to look at other drivers: temperature and NH_3 on formation and partitioning between the gas and aerosol phase. We feel that the discussion can be split into two paragraphs in this way.

Other updates made to paper:
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Updated