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.
Atmos. Chem. Phys. Discuss., https://doi.org/10.5194/acp-2020-275-RC1, 2020

RESPONSE TO REVIEWER 2

(Referee)

The authors thank reviewer 2 for their 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.

“This manuscript describes measurements collected within the EU NitroEurope (NEU) network during the period 2006 – 2010. While some of this data has been previously published, as noted by the authors, the current manuscript provides a comprehensive description of the data quality as well as temporal and spatial patterns of atmospheric chemistry over the lifetime of the network. The data will make a valuable contribution to the field of atmospheric chemistry, in particular with respect to better understanding the role of reduced forms of reactive nitrogen in aerosol processes and for model evaluations. The manuscript is generally well written and the analyses are appropriate, though the manuscript is somewhat lengthy. I recommend publication subject to treatment of the relatively minor comments outlined below, some of which are technical in nature and others seek to reduce the length of the paper.”

Individual remarks:

1. *“Page 5 – Replicate measurements. It would be useful to see a bit more detail on the replicated measurements to get a better sense of overall precision. For example, scatterplots and summary statistics could be added to the Supplemental Material.”*

Author Response 1:

- ➢ Regression analyses and statistics, including t-tests are added in Supp. Figures S2 to S5 for the 4 parallel sites:
  - UK Auchencorth Moss: UK-AMoP vs UK-AMo
  - UK Easter Bush: UK-EBuP vs UK-EBu
  - French Fougéres: FR-FgsP vs FR-Fgs
  - Slovakian EMEP site: SK04P vs SK04
- ➢ Comparisons of annual and overall means for the above 4 sites added in Supp. Tables S2 to S5 (attached at the end of this document)
- ➢ Subsequent Supp. Figures and Supp. tables renumbered accordingly after insertion of above.

<u>Page 14:</u> references to Supp. Figures and Tables are inserted in text (see highlighted text in the text copied below). Months where paired data are not available have been excluded in the updated regression analyses, t-tests and in the comparisons of mean concentrations, whereas previous analyses included all data points. Numbers are therefore also updated to reflect the updated analyses (see highlighted text).

3.3.1 Comparisons according to ecosystem types, paragraph 3

“Sites with parallel (P) DELTA® measurements were Auchencorth Moss (UK-AMoP), Easter Bush (UK-EBuP), Fougéres (FR-FgsP) and SK04P (EMEP site in Slovakia) (Figure 7). Overall, good reproducibility in DELTA® measurements was demonstrated by the parallel measurements (Supp.

Figures S3 - S6). At the Auchencorth Moss parallel site (UK-AMoP), NH_3 and NH_4^+ only were measured, and agreement for these 2 components were on average within ~~5~~4 % at the low concentrations measured at this site (annual mean: 0.5 – 0.9 µg NH_3 m^{-3} and 0.3 – 0.5 µg NH_4^+ m^{-3}) (Supp. Table S5). Parallel measurements at Easter Bush (UK-EBuP) stopped in March 2010. With the exception of Ca^{2+} and Mg^{2+}, the comparison of annual mean data from the replicated measurements for 200~~7~~6 to 2009 provided excellent agreement of ~~2~~4 % (NO_3^-) to ~~13~~12 % (~~SO_4^{2-}~~NH_3) at Easter Bush (Supp. Table S6). At Fougéres (Supp. Table S7), HNO_3 concentration measured on K_2CO_3/Glycerol coated denuders (FR-Fgs) was about 2-fold higher than on NaCl coated denuders in the parallel DELTA® system (FR-FgsP), consistent with over-estimation of HNO_3 (on average 45 %) on carbonate coated denuders (see Sect. 2.2.3). The disadvantage of a NaCl coating, however, is that it can only collect HNO_3 and not the other acid gases. A third carbonate denuder is necessary in the sample train to collect and measure SO_2, since SO_2 is only partially captured and HCl cannot be measured on NaCl denuders (Tang et al., 2015, 2018b). This explains the smaller SO_2 concentrations reported by the FR-FgsP site, with break-through of SO_2 (inefficiently captured by NaCl denuders) onto the aerosol filters resulting in larger particulate SO_4^{2-} concentrations than the Fr-Fgs site. For the SK04 site, measurement reproducibility for the 4 years of parallel data for N and S component was good, with agreement ranging from ~~0.4~~1.2 % (NH_4^+) to ~~5~~9 % (SO_4^2) (Supp. Table S8). HCl and Na^+ and determinations were however more uncertain with differences of ~~21~~67 and ~~28~~43 %, respectively (Supp. Table S8). It has to be noted, however, that the concentrations of the two components were very low, at < 0.2 µg HCl m^{-3} and < 0.4 µg Na^+ m^{-3}. The differences in concentrations are therefore actually within ± 0.1 µg m^{-3} for HCl and within ± 0.2 µg m^{-3} for Na^+. ”

2. *Page 6 – Coordinating laboratories. Some brief discussion of the analytical methods employed by the laboratories (ion chromatography or colorimetry) should be included, along with some discussion or reference to method detection limits (MDL). This information could also be included in the Supplemental.*

Author Response:
Supp. Table S3 added:
“Supp. Table S3. Details on analytical methods used in the analysis of anions (NO_3^-, SO_4^{2-}, Cl^-) and cations (NH_4^+, Na^+, Ca^{2+}, Mg^{2+}) in aqueous denuder and filter extracts in the NEU DELTA® network (all labs) and in precipitation samples from the NEU wet deposition network (INRA and SHMU).”
In manuscript:
Text added (see highlighted text below)

Page 6, Section 2.1.1 Coordinating laboratories, paragraph 1, line 3:

“A team of seven European laboratories shared responsibility for running the network. Measurement was on a monthly timescale, with each laboratory preparing and analysing the monthly samples with documented analytical methods (see Supp. Table S3 for information on analytical methods and limit of detection (LOD)) for between 5 and 16 DELTA sites (Figure 2).

3. *Page 8 – Bulk precipitation measurements. These measurements will no doubt be useful for deposition assessments. However, as currently written the data do not add much to the current manuscript and could be removed to reduce overall length.*

Author Response:
Cutting out the Bulk precipitation measurement sections would reduce the overall length by about a page only and it would be a shame to cut out this valuable dataset which might otherwise not be so readily available to the community. We feel it is important to retain the wet deposition measurements in the paper, as it highlights where DELTA® and bulk wet deposition data are co-located and provides parallel information on gas and aerosol concentrations (for dry deposition modelling) and wet deposition at those sites. The co-located data is important for deriving N budgets and linking to ecosystem response (e.g. recent paper by Flechard et al. 2020) and invaluable for modellers.

Section 3.6 Bulk wet deposition measurements
Page 29, lines 27 - 30

"The intention of the bulk network at the outset was to provide wet deposition data at DELTA® sites that do not already have such measurements on site. The wet deposition data on NH_4^+ *and* NO_3^-*, combined with a wider precipitation chemistry dataset (e.g. from EMEP and other national precipitation networks) was used to estimate total* N_r *deposition to a site (Flechard et al., 2011; 2020)."*

This has been reworded to set out the intentions of the bulk wet deposition measurements and moved to Introduction (last paragraph).

"In this paper, we present and discuss four years of monthly reactive gas (NH_3, HNO_3, HCl) and aerosol (NH_4^+, NO_3^-, SO_4^{2-}, Cl^-, Na^+, Ca^{2+}, Mg^{2+}) measurements from the Level 1 network set up under the NEU integrated project (Figure 2). A harmonised measurement approach with a simple, cost-efficient time-integrated method, applied with high spatial coverage allowed a comprehensive assessment across Europe. The gas and aerosol network was complemented by two years of bulk wet deposition data made at a subset of the sites (Figure 3). The intention of the smaller wet deposition network was two-fold, i) to provide wet deposition estimates at DELTA® sites that do not already have such measurements on site, and ii) to compare the relative importances of reduced and oxidized N versus sulfur in the atmospheric pollution load. Measurements across the network were coordinated between multiple European laboratories. The measurement approach and the operations of the networks, including the implementation of annual inter-comparisons to assess comparability between the laboratories, are described. The data are discussed in terms of spatial and temporal variation in concentrations, relative contribution of the inorganic nitrogen and sulfur components to the inorganic pollution load, and changes in atmospheric concentrations of acid gases and their interactions with NH_3 gas and NH_4^+ aerosol.

Additional text is also added at the end of Section 3.6. Bulk wet deposition measurements on the relevance of the wet deposition data:

"The wet deposition measurements in this paper highlights where DELTA® and bulk wet deposition data are co-located and provides parallel information on gas and aerosol concentrations (for dry deposition modelling) and wet deposition at those sites. The co-located data is important for deriving N budgets and linking to ecosystem response (e.g. Flechard et al. 2020) and invaluable for modellers."

And in Section 3.4. (page 23, lines 40 - 43) (highlighted text)

This demonstrates that sea salt SO_4^{2-} (ss-SO_4^{2-}) aerosol makes up a large and variable fraction of the total SO_4^{2-} measured, consistent with observations of the contribution by ss-SO_4^{2-} to the total SO_4^{2-} in precipitation observed in the wet deposition measurements in this study (Figure 11) and across Europe (ROTAP, 2012).

4. *Page 11 – Line 20. The comparison is referred to here as "field inter-comparison" but as "laboratory inter-comparison" in the 3.2 section heading. I understand the distinction, but it is a little confusing at first glance.*

Author Response:
Thank you. On re-reading, we agree with the reviewer that the section heading is misleading.

"Section 3.2. Laboratory inter-comparison results: DELTA® measurements"
Changed to
"Section 3.2. Field inter-comparison results: DELTA® measurements"

Section 2.5. Laboratory inter-comparisons: DELTA® measurements"
Also changed to:
Section 2.5. Field inter-comparisons: DELTA® measurements"

5. *Page 12 – Line 14. Knowledge of the laboratory blanks would be very helpful. Is there no way to recover the results from original chromatograms? Granted it might be time consuming but interlaboratory comparison of blanks, particularly for NH_3 which is notoriously difficult, could be enlightening as to some of the laboratory comparisons.*

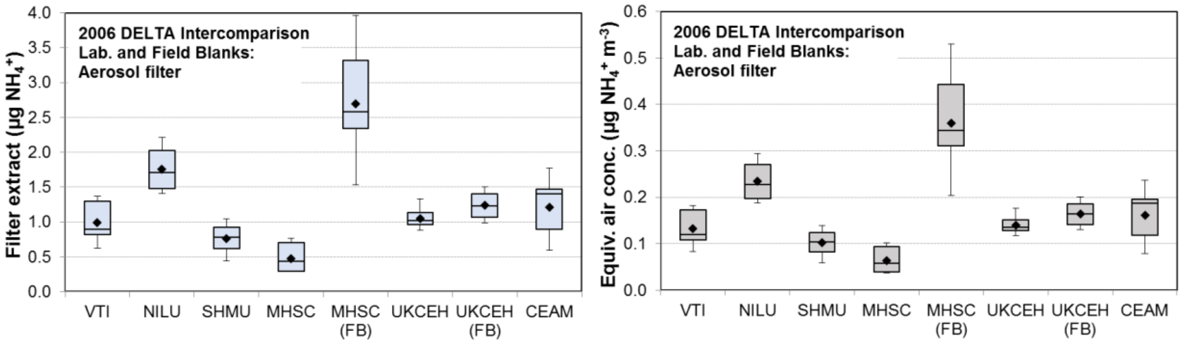
Page 12, Lines 12 - 14
"A possible cause may be the quality and/or variability in the aerosol filter blank values for NH_4^+, as laboratory blanks are subtracted from exposed samples to estimate aerosol NH_4^+ concentrations. Laboratory blank results were however not reported to allow this assessment."

Author Response:
We have managed to extract laboratory and field blank data from the original submitted laboratory files (covering the DELTA intercomparison periods).
Supplementary Figure S2 with boxplots comparing lab and field blanks added (see below):

Text has been amended to:

"A possible cause may be the quality and/or variability in the aerosol filter blank values for NH_4^+, as laboratory blanks are subtracted from exposed samples to estimate aerosol NH_4^+ concentrations. While the laboratory blanks reported by MHSC for aerosol NH_4^+ were low (mean = 0.48 µg NH_4^+) and smaller than other laboratories (mean = 0.64 – 1.20 µg NH_4^+) (Supp. Fig. S2), their field blanks in the 2006 DELTA intercomparison exercise were on average 5.5 times larger than the laboratory blanks. This is likely due to extensive delays in getting samples released from customs in Slovakia at the start of the network."

The comparison shows similar range in blank values in the acid coated aerosol filters and denuders between laboratories. The mean amount of ammonium (NH_4^+) in the acid coated aerosol filters ranged between 0.48 to 1.76 µg across all laboratories. This is equivalent to an atmospheric concentration of 0.06 to 0.23 µg NH_4^+ m^{-3}, based on air volume of 7.5 m^3 sampled by DELTA® system over a 2-week exposure period in the 2006 DELTA intercomparison at the clean site (Auchencorth).



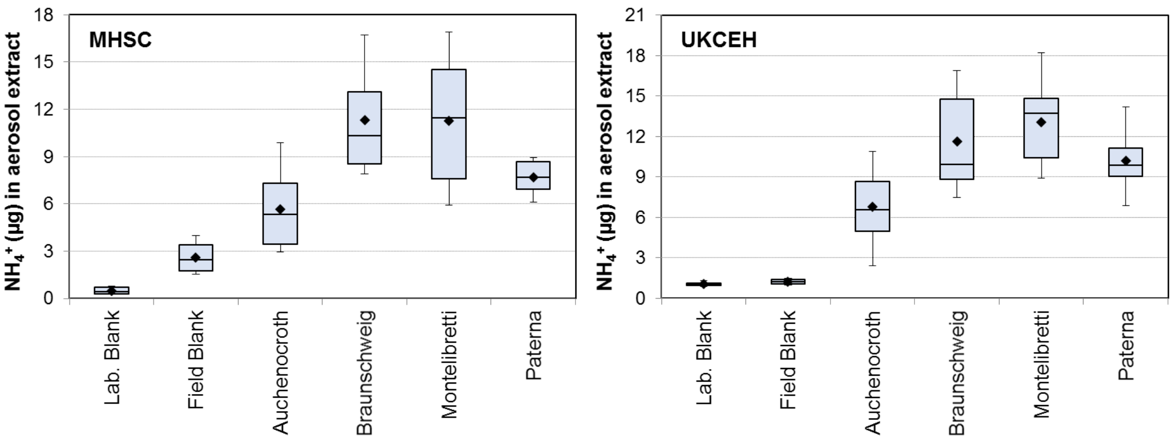
	Aerosol filter: Lab Blank		Aerosol filter: Field Blank (FB)	
	µg NH_4^+ in extract	Equivalent aerosol concentration for 2 week exposure (µg NH_4^+ m^{-3}) [1]	µg NH_4^+ in extract	Equivalent aerosol concentration for 2 week exposure (µg NH_4^+ m^{-3}) [1]
VTI	mean = 0.99 (*n* = 8) range = 0.62 – 1.37	mean = 0.13 (*n* = 8) range = 0.08 – 0.18		
NILU	mean = 0.99 (*n* = 8) range = 0.62 – 1.37	mean = 0.23 (*n* = 8) range = 0.19 – 0.29		
SHMU	mean = 0.64 (*n* = 4) range = 0.44 – 1.05	mean = 0.10 (*n* = 4) range = 0.06 – 0.14		
MHSC	mean = 0.48 (*n* = 9) range = 0.28 – 0.76	mean = 0.06 (*n* = 9) range = 0.04 – 0.10	mean = 2.70 (*n* = 9) range = 1.53 – 3.97	mean = 0.36 (*n* = 9) range = 0.20 – 0.53
UKCEH	mean = 1.05 (*n* = 10) range = 0.88 – 1.33	mean = 0.14 (*n* = 10) range = 0.12 – 0.18	mean = 1.24 (*n* = 6) range = 0.98 – 1.50	mean = 0.16 (*n* = 6) range = 0.13 – 0.20
CEAM	mean = 1.21 (*n* = 7) range = 0.59 – 1.78	mean = 0.16 (*n* = 8) range = 0.08 – 0.24		

Equivalent aerosol concentrations, based on air volume of 7.5 m^3 sampled by DELTA® system over a 2-week exposure period in the 2006 DELTA intercomparison.

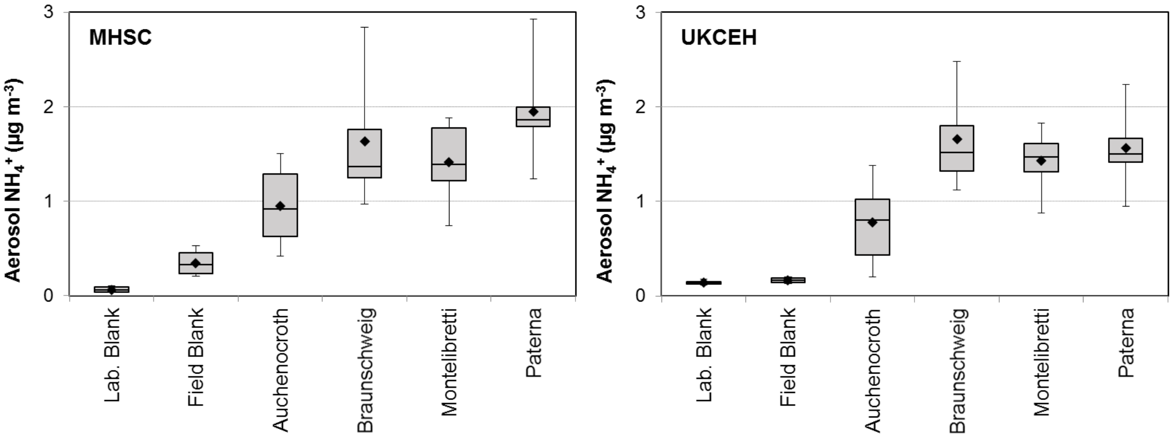
Figure S2: Comparison of laboratory and field blanks (where reported) for ammonium aerosol filters from the 2006 DELTA intercomparison exercise between six participating laboratories.

To put the blank values into context, the amount of NH_4^+ in the lab. and field blanks are compared with amount of NH_4^+ collected in exposed DELTA aerosol samples in the 2006 DELTA intercomparison. At the four intercomparison sites (Auchencorth, Braunschweig, Montelibretti and Paterna), the amount of ammonium (µg NH_4^+) ranged between 2.9 to 16.9. The lab. blank values were therefore acceptably low, being ~1/10th of the smallest concentrations at the cleanest site, Auchencorth.

Field blanks were reported by two laboratories only (MHSC and UKCEH), and compared in the box plots below. While the reported lab and field blanks were not dissimilar from the UKCEH lab, the field blanks for MHSC were on average 5.5 times larger than their lab. blanks. In the DELTA protocol, lab. blanks are subtracted from exposed samples, whereas field blanks serves as a quality check on potential contamination during storage and transport. The larger MHSC field blank values may be due to returned samples being held for extended periods of time in customs in Slovakia and may account for the larger aerosol NH_4^+ concentrations reported by MHSC.

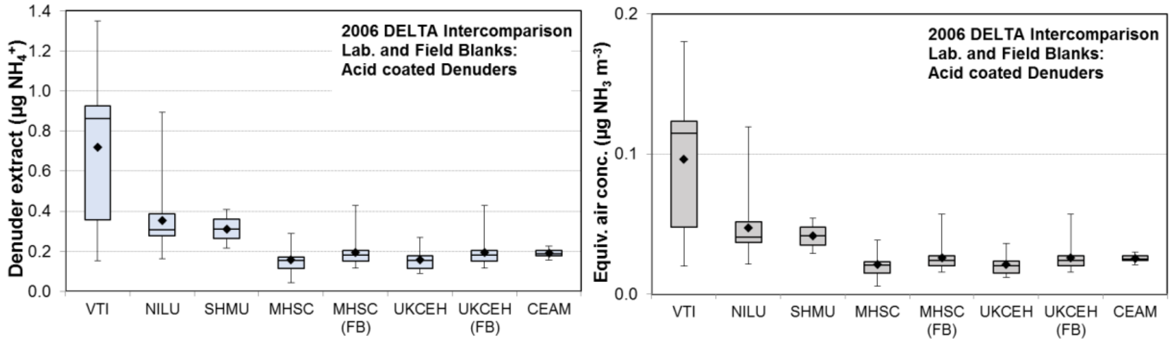


Comparison of the amount of NH_4^+ in the lab. and field blanks (where available) with amount of NH_4^+ collected in exposed DELTA® aerosol samples in the 2006 DELTA intercomparison.



Equivalent gas concentrations estimated for lab and field blanks, based on air volume of 7.5 m^3 sampled by DELTA® system over a 2-week exposure period in the 2006 DELTA intercomparison.

A comparison of denuder lab and field blanks (where reported) are also shown below, to demonstrate the good quality of denuder blanks achieved in ammonia measurements by the DELTA® method.



6. *Page 12 – Line 23. Was CEAM the only laboratory that used colorimetric analysis for NH4+? See previous comment on summarizing analytical techniques used by the various laboratories.*

Author Response:
No, see author response to Comment 2
Other labs that used colorimetric analysis for determination of aqueous NH_4^+ are:

- INRA (Salicylic acid)
- NILU (Indophenol)

7. *Page 15 – Line 4. The overestimation of HNO3, or at least that the HNO3 measurement includes other oxidized N compounds, could be noted again here.*

Author Response:
Text added – see below (highlighted)
"Most of the N_r concentrations at each site in turn are dominated by reduced N (NH_3-N, NH_4^+-N), rather than by oxidised N species (HNO_3-N (includes other oxidized N compounds, see Sect. 2.2.3) and NO_3^--N)."

8. ***Page 15 – Line 30. See previous comment regarding LOD/MDL for different laboratories/chemical species.***

Author Response:
Supp. Table S3 with details of analytical methods and LODs is now added.
Reference to Supp. Table S3 added in text
"The concentrations of Ca^{2+} and Mg^{2+} were very low across the network, with values (mean of all sites < 0.1 µg m^{-3}) that were at or below method limit of detection (LOD = ~ 0.1 µg m^{-3}) (Supp. Table S3)."

9. *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.*

Author Response:

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 analyses 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."

10. *Page 17 – Line 25. Were the high concentrations at IT-BCi indicative of highly local emissions, i.e., adjacent to the field site, or is this concentration more indicative of a broader area? It would be impractical to include a description of every site but where such details are relevant, they should be included. In the same regard, it would be good to know if all of the grassland sites are grazed (Page 17 – Line 41). It appears so.*

Author Response:

IT-BCi is an ecosystem station located in a 15 ha field (arable crops) on the Sele Plain, an agricultural area with intensive buffalo farming in Southern Italy. The site is not affected by close proximity to sources (e.g. animal housing or manure stores), so the annual mean concentrations of 8 ug NH_3 m^{-3} is indicative of the broader area. Close to sources (e.g. within 300 m), annual mean concentrations can be expected to be even higher.

"Borgo Cioffi (IT-BCi) in an intensive buffalo farming region of Southern Italy provided the highest 4-year average of 8.1 µg NH_3-N m^{-3} (cf. group mean = 3.8 µg NH_3-N m^{-3} , n = 10) (Table 4, Supp. Table S4)."

Further details of the site has been added in text:
"Borgo Cioffi (IT-BCi) is an ecosystem station located in a 15 ha field (arable crops) on the Sele Plain, an agricultural area with intensive buffalo farming in Southern Italy and this provided the highest 4-year average of 8.1 µg NH_3-N m^{-3} (cf. group mean = 3.8 µg NH_3-N m^{-3} , n = 10) (Table 4, Supp. Table S4)."

11. *Page 18 – Line 38/39. I believe "will dominate dry NH3-N dry deposition" should be changed to "will dominate dry N deposition", correct?*

Author Response:

Thank you.
"…then NH_3 will dominate dry NH_3- N dry deposition and exert the larger ecological impact."

Corrected (highlighted):

"…then NH_3 will dominate dry N deposition and exert the larger ecological impact."

12. *Page 19 – Line 11. Remove "that are".*
13. *Page 19 – Line 12. Change "emission" to "emissions"*

Author Response:
"….ranging from 0.05 to 6.7 µg NH_3-N m^{-3} that are consistent with smaller NH_3 emission from the UK (Figure 9A).

Amended (highlighted):

"….ranging from 0.05 to 6.7 µg NH_3-N m^{-3}, consistent with smaller NH_3 emissions from the UK (Figure 9A).

14. *Page 21 – Line 7. The sentence beginning "This corroborates. . . ." is quite lengthy.*

Author Response:
"Annual averaged SO_2 concentrations measured across the network were between 0.9 and 2.3 µg SO_2-S m^{-3} (Figure 9C, Supp. Table S9). This corroborates observations from monitoring made in the EMEP networks of large reductions in ambient concentrations and deposition of sulfur species during the last decades (EMEP, 2016), reflecting successes of air quality policies across Europe in achieving substantial reductions in SO_2 emissions, which decreased by 74 % between 1990 and 2010. Annual mean SO2 concentrations of 0.03 to 5.5 µg SO_2-S m^{-3} were reported from the EMEP network from 58 rural background sites across Europe over the period of 2007 – 2010, with largest SO_2 concentrations from North Macedonia and Serbia (EMEP, 2016). Since the highest emitting countries in European countries were not included in the DELTA® network, the SO_2 concentrations provided by the DELTA® network are smaller, but are within the range reported by EMEP (EMEP, 2016)."

Paragraph rephrased – see below:
(Supp. Table numbering also updated)

"Annual averaged SO_2 concentrations measured across the network were between 0.9 and 2.3 µg SO_2-S m^{-3} (Figure 9C, Supp. Table S14). By comparison, the EMEP network of 58 urban background sites reported annual mean concentrations of 0.03 and 5.5 µg SO_2-S m^{-3} over the same period, with largest SO_2 concentrations from North Macedonia and Serbia. Since these high emitting countries were not included in the DELTA® network, the range of SO_2 concentrations are smaller. Together, the small SO_2 concentrations reflect the substantial reductions in SO_2 emissions across Europe (-74 % between 1990 and 2010) and large reductions in ambient concentrations and deposition of sulfur species across Europe during the last decades (EMEP, 2016).

15. *Page 23 – Section 3.4. It appears that Figure 13 is incorrectly referred to as Figure 12 throughout this section.*

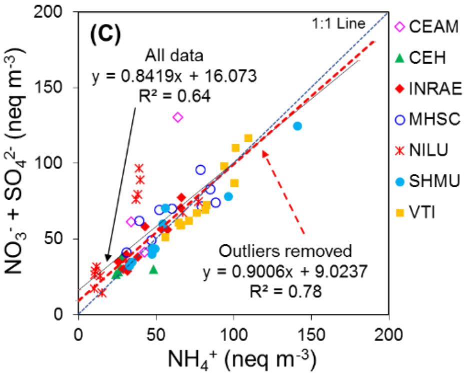
Author Response:

Thank you for spotting the mistake.
Page 23 – Section 3.4
Throughout this section:
1st paragraph: Figure 11 corrected to Figure 12 (two times)
Rest of section: Figure 12 corrected to Figure 13 (eleven times)

16. Page 24 – Line 16. Are there other potential reasons for the higher sulfate measurements at these sites? Seems worthy of additional investigation/discussion.

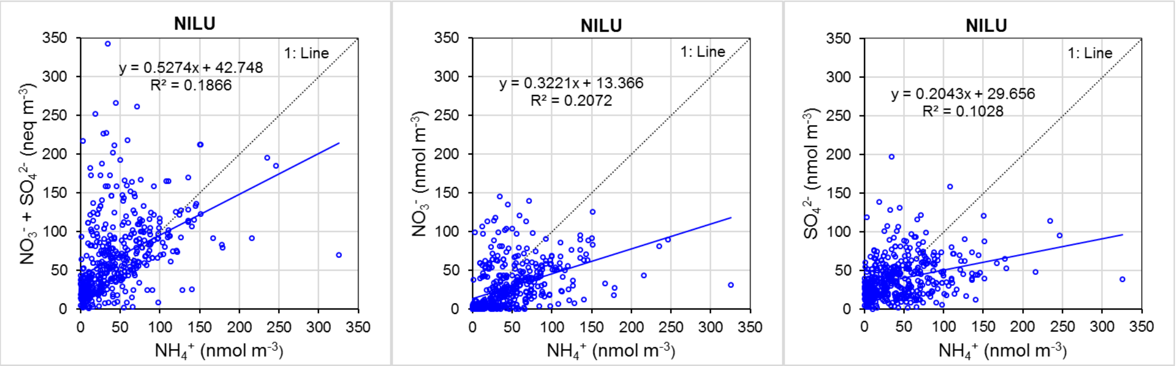
Author Response:

Figure 13C from paper is copied below, showing outliers in the regression plot.



Regression plots of individual monthly measurements at all sites managed by NILU are shown below. Ratio [neq NH_4^+: sum (neq NO_3^- + neq $SO_4^{=}$)]

- Ratio = 0.9 – 1.1: 10.4% of data
- Ratio < 0.5: 42.7 % of data
- Ratio > 1.5: 7.9 % of data



This indicates either an over-read of the anions (NO_3^-, SO_4^{2-}), or under-read of NH_4^+ concentrations. On closer examination of individual monthly site data:

- 14.6 % of aerosol $NH_4^+ \leq 0.1$ µg m^{-3}.
- 17.1 % of NO_3^- (µg m^{-3}) ≤ 0.1 µg m^{-3}
- Only 0.7 % of all SO_4^{2-} (µg m^{-3}) data were ≤ 0.1 µg m^{-3}.

This then points to a potential under-read of NH_4^+ and NO_3^-. Possible reasons:

i) loss of NH_4^+, NO_3^- from filters (e.g. microbial degradation),
ii) non-capture on the aerosol filters (e.g. aerosol filters installed wrong way round),
iii) filters mixed up and wrong analysis performed on the respective acid and base-coated filters,
iv) high NH_4^+, NO_3^- blanks subtracted from already low concentrations at clean sites.

Possibilities also still remain of an over-read in SO_4^{2-}.

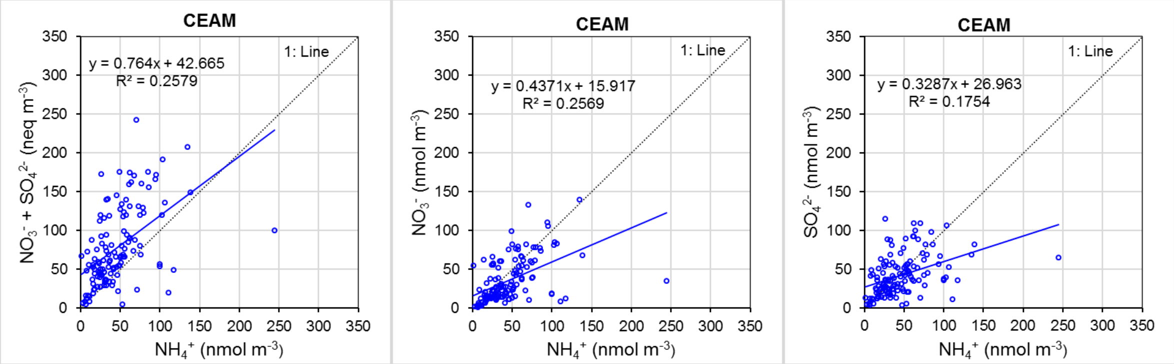
Regression plots of individual monthly measurements at all sites managed by CEAM are shown below. Ratio [neq NH_4^+: sum (neq NO_3^- + neq $SO_4^=$)]

- Ratio = 0.9 – 1.1: 5.4 % of data
- Ratio < 0.5: 36.2 % of data
- Ratio > 1.5: 6.2 % of data

This indicates either an over-read of the anions (NO_3^-, SO_4^{2-}) or under-read of NH_4^+ concentrations. On closer examination of individual monthly site data:

- 1.5 % of aerosol NH_4^+ < 0.1 μg m^{-3}.
- 0.8 % of NO_3^- (μg m^{-3}) < 0.1 μg m^{-3}
- All SO_4^{2-} (μg m^{-3}) > 0.1 μg m^{-3}

This does not show any apparent low outliers in the data. The regression plots also show points distributed on either side of 1:1 line.



In manuscript

"Removal of the outlier NILU (7 out of 16) and CEAM (1 out of 3) data points with ion balance ratio < 0.5 improved both the slope (new slope = 0.90) and correlation (new R^2 = 0.78) (Figure 13C). This indicates either an over-read of the anions (NO_3^-, SO_4^{2-}) or under-read of NH_4^+ concentrations by the two laboratories at some sites. Results reported by NILU in the DELTA® field inter-comparisons (Sect. 3.2) showed that, with the exception of a few high NH_4^+ and NO_3^- readings, there was on average no overall bias in the NH_4^+, NO_3^- or SO_4^{2-} measurements by the NILU laboratory that could account for the high SO_4^{2-} outliers in the regression (Figure 13). The ion balance checks suggest possible over-read and increased uncertainty in the SO_4^{2-} measurements for 7 sites: Hyytiälä (FI-Hyy), Sodankylä (FI-Sod), Rimi (DK-Rim), Risbyholm (DK-Ris), Soroe (DK-Sor), Skyttorp (SE-Sk2) and Vielsalm (BE-Vie). For the CEAM lab, the uncertainty in SO_4^{2-} measurements affected 2 sites, El Saler (ES-Els) and Las Majadas (ES-Lam) (see also Sect. 3.3.4)."

Text revised to:

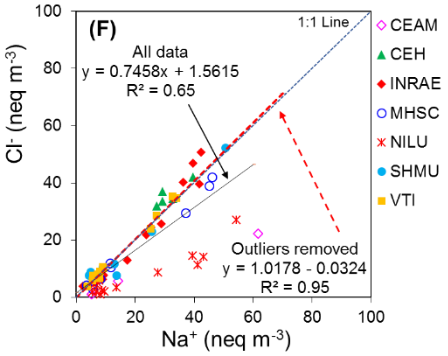
"Removal of the outlier NILU (7 out of 16) and CEAM (1 out of 3) data points with ion balance ratio < 0.5 improved both the slope (new slope = 0.90) and correlation (new R^2 = 0.78) (Figure 13C). An inspection of individual monthly site data reported by NILU showed that 15 % of aerosol NH_4^+ and 17 % of NO_3^- concentrations were below 0.1 μg m^{-3}, compared with only 0.7 % of all SO_4^{2-} data. This then points to a potential under-read in NH_4^+ and NO_3^-. Possible reasons include:

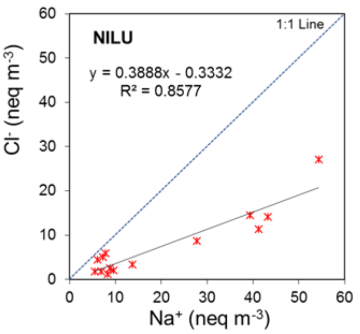
i) loss of NH_4^+, NO_3^- from filters (e.g. microbial degradation),
ii) non-capture on the aerosol filters (e.g. aerosol filters installed wrong way round),
iii) filters mixed up and wrong analysis performed on the acid and base-coated filters,
iv) high blanks subtracted from already low concentrations at clean sites.

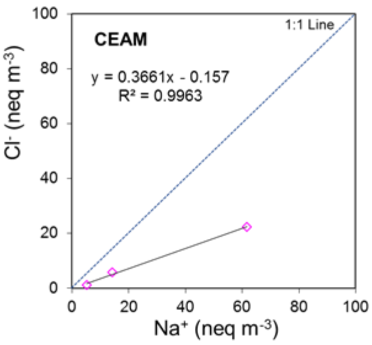
Possibilities still remain, however, of a potential over-read in SO_4^{2-}. The ion balance checks suggest increased uncertainty in the NH_4^+, NO_3^- and SO_4^{2-} measurements for 7 sites: Hyytiälä (FI-Hyy), Sodankylä (FI-Sod), Rimi (DK-Rim), Risbyholm (DK-Ris), Soroe (DK-Sor), Skyttorp (SE-Sk2) and Vielsalm (BE-Vie). Examination of monthly site data from CEAM showed only 1.5 % of aerosol NH_4^+ and 0.8 % of NO_3^- concentrations below 0.1 µg m^{-3}, whereas all SO_4^{2-} data were above 0.1 µg m^{-3}. For the CEAM lab, the uncertainty in NH_4^+, NO_3^- and SO_4^{2-} measurements affected 2 sites, El Saler (ES-Els) and Las Majadas (ES-Lam) (see also Sect. 3.3.4)."

17. *Page 24 – Line 16. Regarding the discussion of the CEAM and NILU Na+/Cl- regressions and the data below the 1:1 line, there does seem to be correlation among these outliers. Could this be an issue in the way filter blanks were applied? Perhaps an average Cl- blank biased high by an outlier was subtracted from all of the field measurements?*

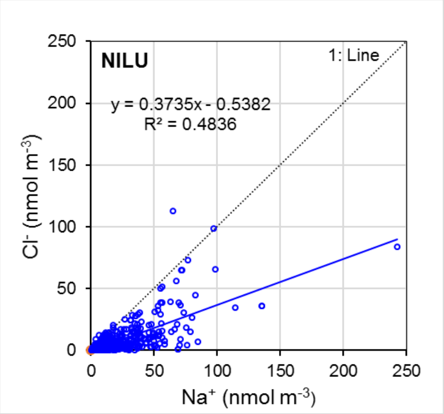
Author Response:
Na and Cl data for NILU and CEAM are plotted separately below, which shows good correlation, but with a slope of 0.37 and 0.28, respectively.

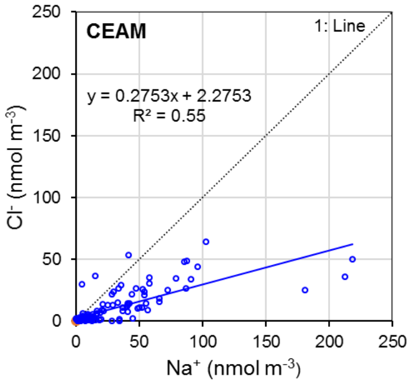






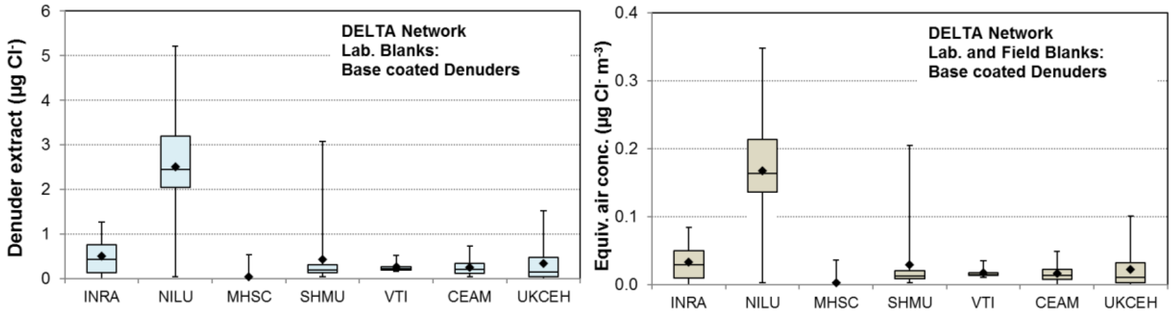
All data points





As the reviewer suggests, the under-estimate in Cl^- concentrations could be caused by high aerosol Cl^- blank values. Aerosol blank values were unfortunately not reported by the labs, but denuder blanks were. Box-plots of blank Cl^- data from base-coated denuders (K_2CO_3-Glycerol, same coating as that used to coat the aerosol filters to collect Cl^-) from the network measurements are shown below. An average blank value was submitted by the laboratories for each month between 2006 to 2010. The plots show a larger range of blank Cl^- values reported by the NILU lab (mean = 2.51 µg Cl^- (0.05 – 5.22)), equivalent to an average air concentration of 0.17 µg Cl^- m^{-3} (range = 0.0 – 0.35 µg Cl^- m^{-3}), based on

15 m^3 of air sampled over a month. So if the blank Cl$^-$ values in aerosol filters were similarly variable, then uncertainty in blank Cl$^-$ values could contribute to the error. However, blank denuder Cl$^-$ values reported by CEAM (mean = 0.26 ug Cl$^-$) were less variable (range = 0.05 to 0.73 µg Cl$^-$, equivalent to 0.0 – 0.05 µg Cl$^-$ m^{-3}, based on 15 m^3 of air sampled over a month) and comparable with other labs.



18. Page 26 – Line 19. Should "Figure 13A" be "Figure 14A"?

Author Response:

Yes, thank you. Corrected to Figure 14A in paper.

19. Page 26 – Line 23. ". . .with possible uptake and removal of NH3 from the atmosphere". Could results from the GRAMINAE project be cited here?

Author Response:

Yes, thank you. Graminae reference added:

Sutton, M. A., Nemitz, E., Milford, C., Campbell, C., Erisman, J. W., Hensen, A., Cellier, P., David, M., Loubet, B., Personne, E., Schjoerring, J. K., Mattsson, M., Dorsey, J. R., Gallagher, M. W., Horvath, L., Weidinger, T., Meszaros, R., Dämmgen, U., Neftel, A., Herrmann, B., Lehman, B. E., Flechard, C., and Burkhardt, J.: Dynamics of ammonia exchange with cut grassland: synthesis of results and conclusions of the GRAMINAE Integrated Experiment, Biogeosciences, 6, 2907–2934, https://doi.org/10.5194/bg-6-2907-2009, 2009.

20. Page 26 – Line 24. Please change "thermodynamic shift to" to "thermodynamic shift of NH4NO3 to".

Author Response:

Yes, thank you. Changed to "thermodynamic shift of NH_4NO_3 to"

21. *Page 26 – Section 3.5.2. To what extent could the temporal patterns in HNO3 be confounded by the collection of other oxidized N species on the denuder?*

Author Response:

Oxidized N species that are potentially also collected on the denuders include HONO, NO_2, N_2O_5 and PAN, as well as other inorganic and organic nitrogen species.

NO_x emissions are dominated by vehicular sources which are not expected to show large seasonal variations. Co-collection of NO_2 (estimated to be between 3 – 5% on carbonate coated denuders) should therefore exert negligible effect on the temporal patterns in HNO_3.

Of these, HONO is most likely to contribute the largest interference, since it is collected effectively on a carbonate coating.

Tropospheric HONO sources include chemical formation and direct emissions.

$NO + OH (+ M) \rightarrow HONO (+ M)$

$H_2O + 2 NO_2 \rightarrow HNO_3 + HONO$

Emission sources include fossil fuel combustion, microbial activities in soil, and biomass burning.

The diurnal cycle in HONO is well established, but there remains limited information on its seasonal behaviour.

Li et al. (2018) reported maximum HONO concentrations in winter and elevated HONO/NO_2 ratio in summer at an urban site in China.

Wang et al. (2017) reported highest HONO concentration in autumn, and lowest in winter at an urban site in Beijing.

The temporal patterns in HNO_3 derived from the DELTA network is therefore likely to be HONO seasonal cycle superimposed onto the HNO_3 seasonal cycle.

Dandan Li, Likun Xue, Liang Wen, Xinfeng Wang, Tianshu Chen, Abdelwahid Mellouki, Jianmin Chen, Wenxing Wang, Characteristics and sources of nitrous acid in an urban atmosphere of northern China: Results from 1-yr continuous observations, Atmospheric Environment, 182,
2018, 296-306, https://doi.org/10.1016/j.atmosenv.2018.03.033

Jiaqi Wang, Xiaoshan Zhang, Jia Guo, Zhangwei Wang, Meigen Zhang, Observation of nitrous acid (HONO) in Beijing, China: Seasonal variation, nocturnal formation and daytime budget, Science of The Total Environment, 587–588, 2017, 350-359, https://doi.org/10.1016/j.scitotenv.2017.02.159.

Additional text added:

"Since the HNO_3 data is actually the sum of HNO_3 and HONO, with a small contribution from NO_2 (see Sect 2.2.3), the temporal patterns seen are likely to be the superimposed profiles of both HNO_3 and HONO. NO_2 are predominantly from vehicular sources which are not expected to show large seasonal variations and should therefore exert negligible effect on the temporal patterns in HNO_3. "

22. *Page 28 – Line 12. Consider changing "were provided by" to "were observed at".*

Author Response:

Yes, thank you. Changed to "were observed at"

23. *Page 29 – Section 3.6. See previous comment regarding inclusion of precipitation measurements*

Author Response:
Please see our response above regarding inclusion of precipitation measurements.

24. *Page 29 – Section 4.0. It seems like the material in this section could be greatly condensed and integrated into the Conclusions.*

Author Response:
Section 4.0 has been removed and integrated into the Conclusions – see author response to final reviewer comment.

25. *Page 30 – Line 10. The sentence beginning "However, SO2 (by mass). . .. . ." is quite lengthy.*

Author Response:
"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)."

Has been reworded to:

"However, 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), SO_2 will remain important in contributing to exceedance of critical loads for acidification in European ecosystems (EEA, 2019). "

This paragraph has also been moved to conclusions, in response to the previous reviewer comment.

26. *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 the reviewer comments (as also provided in response to reviewer 1):
(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 µg 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.

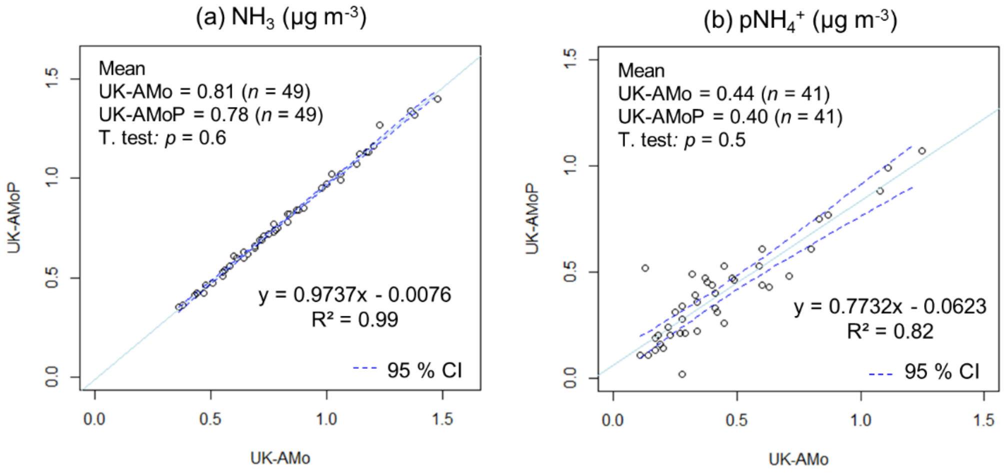


Figure S3: Comparison of replicated DELTA monthly measurement of (a) NH_3 and (b) particulate NH_4^+ concentrations at the UK Auchencorth (UK-AMo) and its' parallel site (UK-AMoP). Months where paired data are not available were excluded from analysis. Independent samples t test was carried out using R. $p < 0.05$ = statistically significant difference in mean concentration between replicated measurements. $p > 0.05$ = not a statistically significant difference.

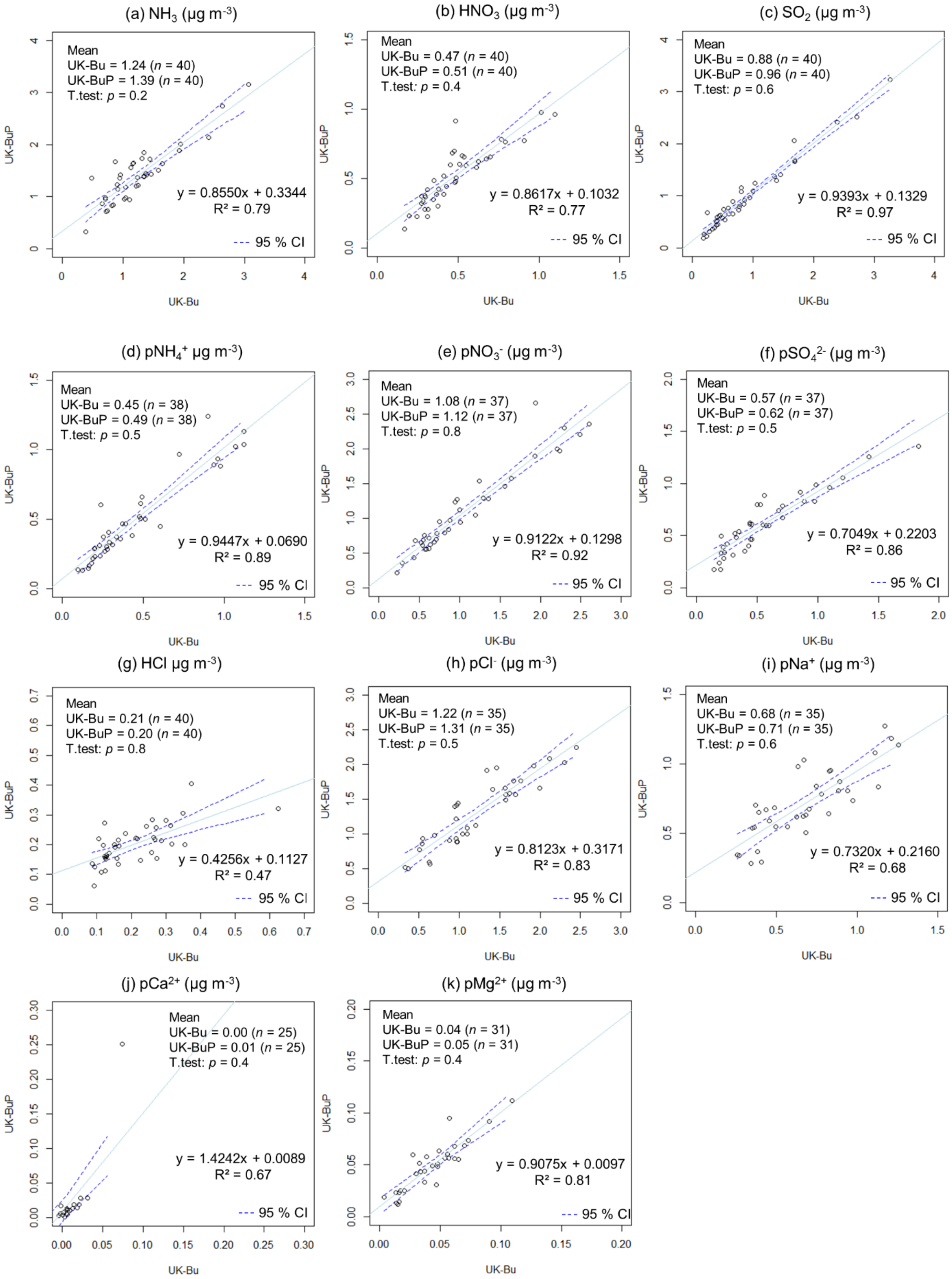


Figure S4: Comparison of replicated DELTA monthly measurement of gases (a: NH_3, b: HNO_3, c: SO_2, g: HCl) and particulates (d: NH_4^+, e: NO_3^-, f: SO_4^{2-}, h: Cl^-, i: Na^+, j: Ca^{2+}, k: Mg^{2+}) at the UK Bush site (UK-Bu) and its' parallel site (UK-BuP). Independent samples t test was carried out on R ($p < 0.05$ = statistically significant difference in mean concentration between the replicates; $p > 0.05$ = not a statistically significant difference).

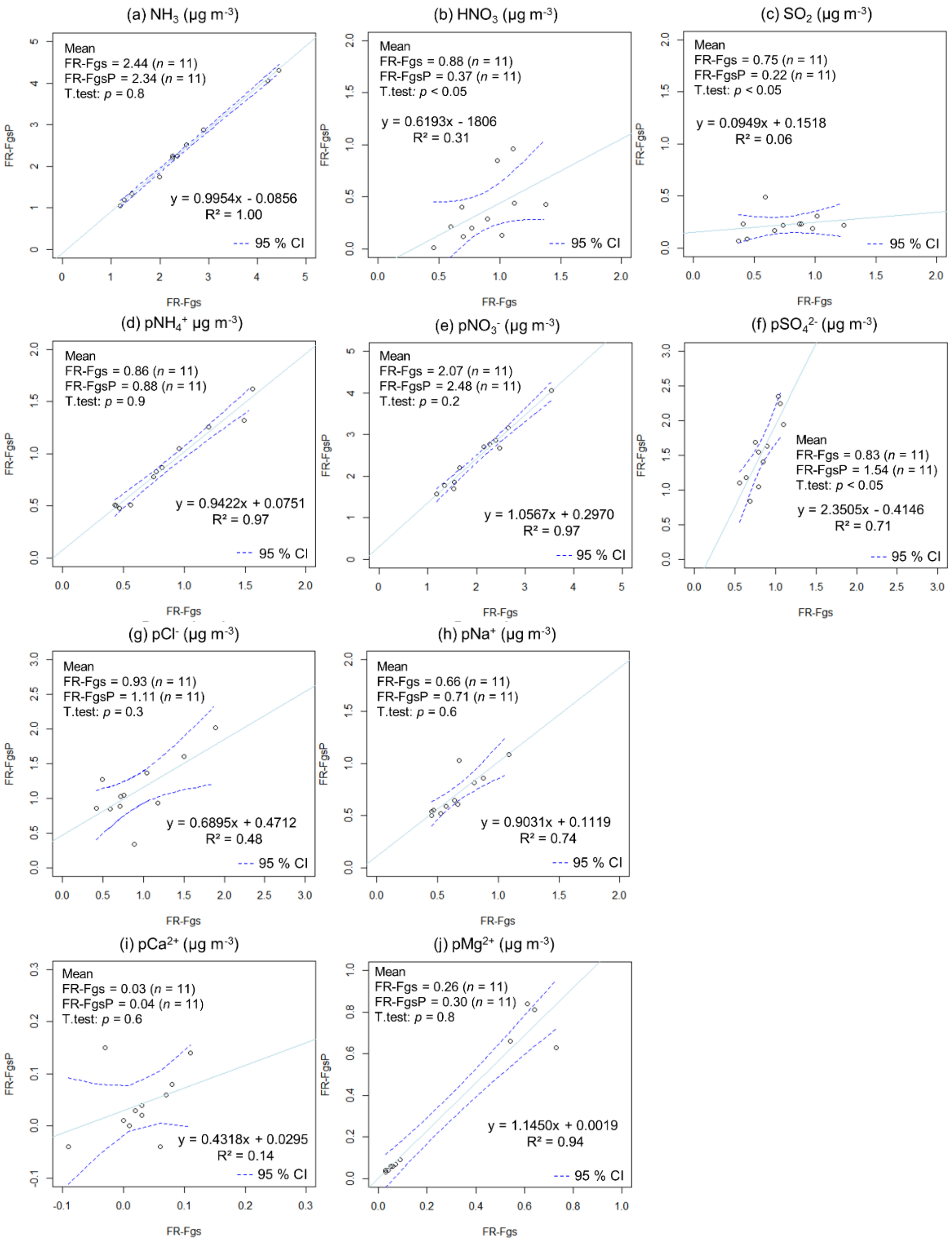


Figure S5: Comparison of replicated DELTA monthly measurement of gases (a: NH_3, *b: HNO_3, **c: SO_2) and particulates (d: NH_4^+, e: NO_3^-, **f: SO_4^{2-}, g: Cl^-, h: Na^+, i: Ca^{2+}, j: Mg^{2+}) at the French Fougéres site (FR-Fgs) and its' parallel site (FR-FgsP). Independent samples t-test was carried out on R ($p < 0.05$ = statistically significant difference in mean concentration between the replicates; $p > 0.05$ = not a statistically significant difference). *K_2CO_3/glycerol coated denuder used at FR-Fgs (HNO_3 determination includes potential inteference from co-collected oxidised N species) *vs* NaCl coated denuder at FR-FgsP.(selective for HNO_3). ** SO_2 is partially captured on NaCl coated denuders only, with break-through of SO_2 onto the aerosol filters resulting in larger particulate SO_4^{2-} concentrations than the Fr-Fgs site.

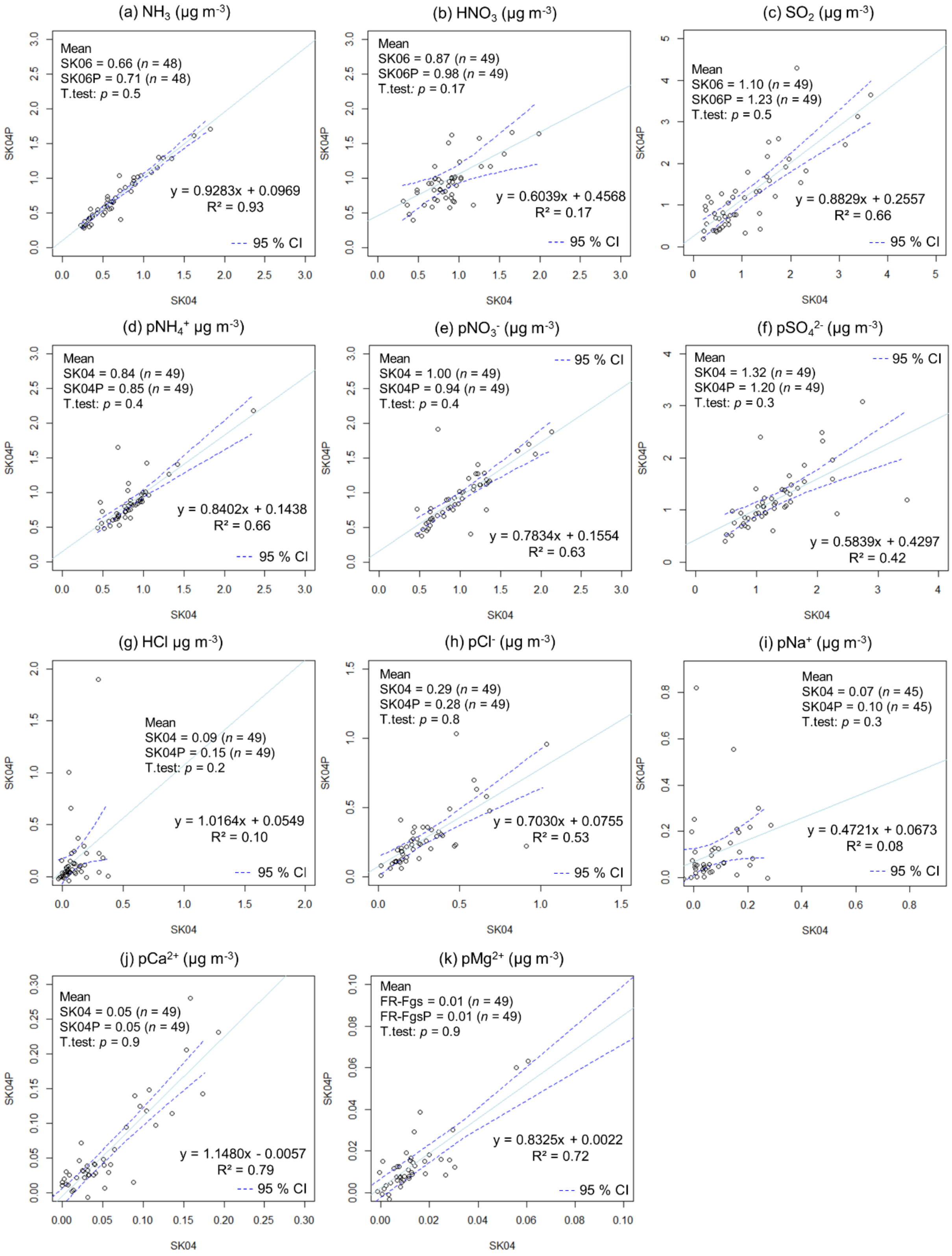


Figure S6: Comparison of replicated DELTA monthly measurement of gases (a: NH_3, b: HNO_3, c: SO_2, g: HCl) and particulates (d: NH_4^+, e: NO_3^-, f: SO_4^{2-}, h: Cl^-, i: Na^+, j: Ca^{2+}, k: Mg^{2+}) at the Slovakian site (SK06) and its' parallel site (SK06P). Independent samples t test was carried out on R ($p < 0.05$ = statistically significant difference in mean concentration between the replicates; $p > 0.05$ = not a statistically significant difference).