

**acp-2018-603: Surface–atmosphere exchange of water-soluble gases and aerosols above agricultural grassland pre- and post-fertilisation
by Ramsay, R. et al.**

Response to Anonymous Referee #1

We thank the reviewer for their time in reviewing our paper and providing comments. Before addressing the numbered points made by this reviewer individually, we would like to respond to the reviewer's overall question "does this manuscript offer a real advancement of the current state of knowledge?" We believe our paper provides novelty and advancement for the following reasons:

Firstly, there is currently a lack of data for simultaneous time-resolved fluxes of trace inorganic gases and associated aerosol counterparts, particularly for the reactive nitrogen species $\text{NH}_3/\text{NH}_4^+$ and $\text{HNO}_3/\text{NO}_3^-$. Our paper presents flux data for these species over agricultural grassland at hourly resolution for one month at high precision and with appropriate consideration of the uncertainties in the flux values. This dataset also includes fluxes for trace gas and aerosol species during a period of flux divergence post-application of urea fertiliser. By careful consideration of the issues present in analysing fluxes during periods of flux divergence, we present a robust dataset which considers total nitrate and total ammonium fluxes during this period and discusses the changes in flux behaviour post-fertiliser application. Furthermore, it provides strong field evidence of a ground source of both HONO and HNO_3 after fertilisation.

Secondly, this paper presents bulk deposition velocities for particulate Cl^- , NO_3^- and SO_4^{2-} , which are themselves important values for deposition modelling. From observation of these deposition velocities, it was hypothesized there was a link between deposition velocity and the proportion of fine to coarse aerosol. Using the ratio of $\text{PM}_{2.5}/\text{PM}_{10}$, as measured by a nearby instrument, we were able to demonstrate this association. While this proportion acts as a proxy measurement for particle size measurements, we believe this is novel evidence for demonstrating a link between enhancement of aerosol deposition velocity and proportion of particles contained in the coarse fraction.

Thirdly, we believe we present the first intercomparison data for nitrous acid measurements made by the Gradient of Aerosols and Gases Online Registration (GRAEGOR) and by the Long Path Absorption Photometer (LOPAP), which not only compares concentrations, but also gradients. We also present an intercomparison of ammonia measurements made by the GRAEGOR and by a Quantum Cascade Laser (QCL).

We now respond to the individual points raised in the review, with the reviewer's comments presented in blue, italicized font.

1) "As illustrated by many of the figures using gradients to determine fluxes is extremely difficult (see the concentration plots in Fig 3 & 4). Indeed direct flux measurements are also very difficult! Thus although the fluxes shown in Figure 7 and Figure 9 are presented without error bars I suspect the error bars are in fact VERY large. This is not a new problem and is certainly not unique to these authors or this study. BUT Figure 10 actually tells an important part of the story as does in Figure 14...that the concentrations are themselves rather uncertain."

We agree that it would be helpful to include error bars on the time series for fluxes and will add these to Figures 7, 9 and 13 in the revised manuscript. We have included in this response a revised version of Figure 7 – the time series of trace gas fluxes - which includes error bars as an example. We will also add a summary of median flux error values to Tables 4 and 5.

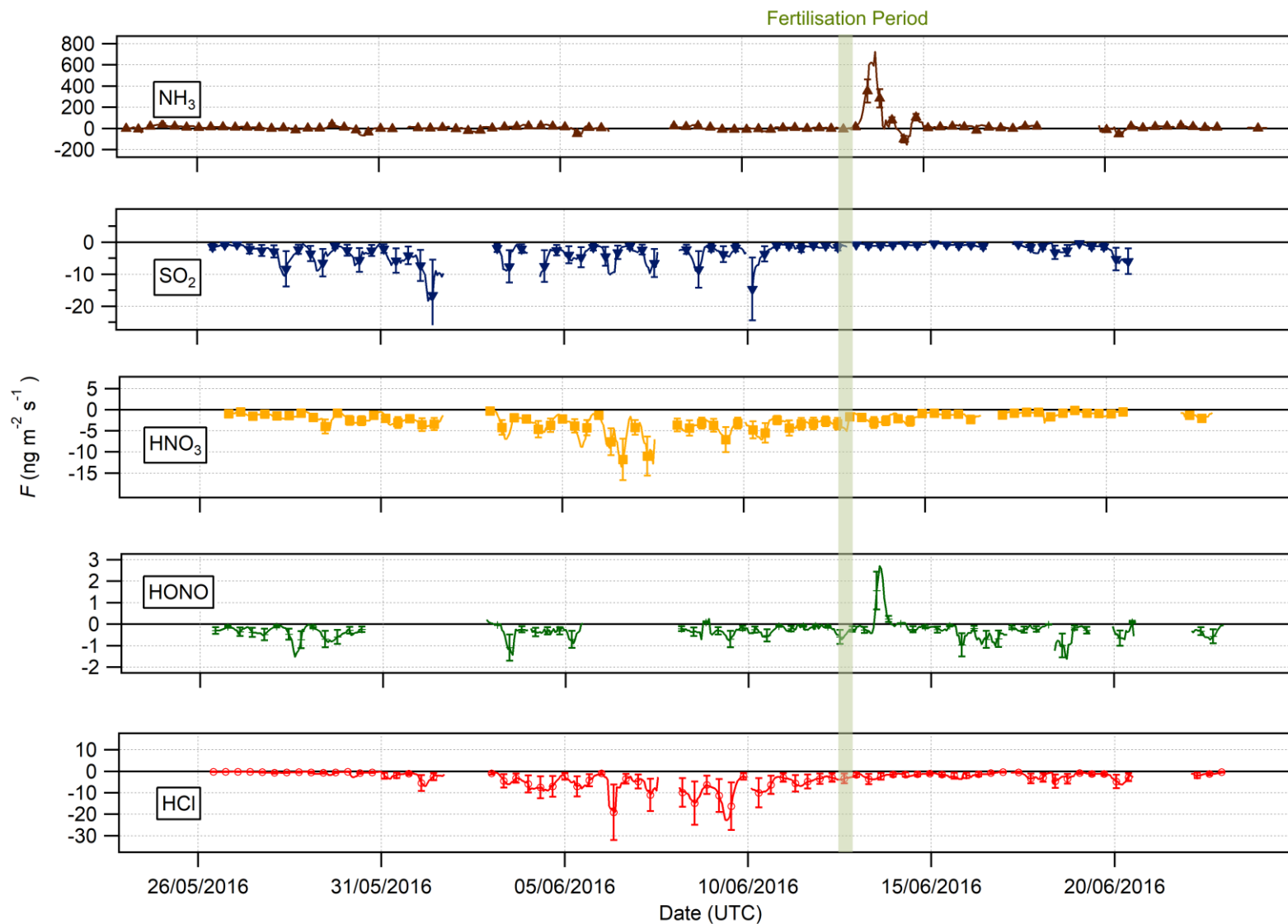


Figure 7: Time series of hourly trace gas fluxes measured during the Easter Bush campaign. Results smoothed using a 5-point moving point average. The fertilisation period was 08:00 – 09:00 on 13th June, and is highlighted in green. Flux uncertainties for each trace gas are included as error bars.

Figure 10 (which compares measurements of NH_3 taken by the GRAEGOR to that by a QCL system) and Figure 14 (similarly comparing measurements of HONO taken by the GRAEGOR to that by a LOPAP) are intercomparison studies between instruments. These comparisons do not reflect the uncertainty of GRAEGOR concentration measurements, only that there exists a difference between measurement techniques that should be accounted for when considering measurements of concentration. Crucially, the difference in measurements between two different systems does not directly impact on the error in the concentration gradient of the GRAEGOR, which is the critical part in calculating flux values. The two GRAEGOR detector boxes share the same analytical system and therefore uncertainties in the concentrations at the two heights are not independent, and the error on the gradient is significantly smaller than the combined error between the two concentrations.

It is our view that the flux uncertainties in this study are not “very large” in respect to previously published studies using the GRAEGOR. The median flux error for NH_3 , for example, was 32%, which is similar to values obtained for measurements made over grassland using the GRAEGOR by Wolff et al. (2010) and Thomas et al. (2009). By inclusion of median flux error values in Tables 4 and 5, we anticipate we can satisfy readers that our flux errors are in the range expected for use of this instrument.

2) “Fundamentally is GRAEGOR ‘fit for purpose’? Some basic statistics could be brought into play to consider what fraction of flux periods (of each of the considered species) exceeded the uncertainty bounds FOR each individual measurement.”

The reviewer raises an important point that was considered during flux calculations, but which was not included in the manuscript. As outlined by Thomas et al. (2009), it is possible to calculate the minimum flux that the GRAEGOR can measure for each species, effectively providing a limit of detection for flux measurements. Fluxes presented have been filtered using these values, but discussion of their development, beyond mentioning that fluxes were filtered according to these values was not included, nor were they included in Tables 4 and 5. We will include a brief discussion of calculating this value in the Methods section of the revised manuscript, which, together with inclusion of minimum detectable flux values for each species in Tables 4 and 5, should resolve this issue.

It is important to emphasize that the capability of the GRAEGOR to measure fluxes is dependent upon its ability to measure concentration differences with sufficient precision. As documented in the manuscript, a side-by-side comparison of the GRAEGOR sample boxes was used to develop a linear regression profile, from which – after correction – the residuals were used to determine the precision of the concentration measurements. As we state in our manuscript: “From the results obtained, it was found that for the gases NH_3 , HCl, HONO, HNO_3 and SO_2 that deviation from the 1:1 fit resulted in a precision of measurements $<4\%$ (3σ). For the aerosol species Cl^- , NO_3^- and SO_4^{2-} , precision was calculated as $<8\%$ (3σ), while for NH_4^+ was calculated as $<9\%$ (3σ).” These precision values are in line with those previously calculated by those using the GRAEGOR to measure fluxes (Thomas et al., 2009; Wolff et al., 2010; Twigg et al., 2011), and we maintain that these are sufficient precision values to resolve the vertical concentration gradients necessary for flux calculations.

The GRAEGOR shares its principle of operation and many components with other instrumentation that has routinely been used for gradient flux measurements, such as the AMANDA/GRAHAM for NH_3 (same denuder but based on selective membrane / conductivity; Erisman and Wyers, 1993; Flechard and Fowler, 1998; Milford et al., 2001, 2009; Wichink Kruit et al., 2007; Neiryneck et al., 2008) and the MARGA-based gradient system of Rumsey et al. (2016). Considering the similar architecture of the GRAEGOR to these instruments which have been successfully used to measure gradient fluxes, the statement that the GRAEGOR would not be fit for purpose is therefore surprising.

Finally, the good agreement between expected and measured deposition velocities for HNO_3 and HCl may be taken as independent evidence (though not proof) of the high quality of the measured fluxes.

“The authors describe some efforts at determining uncertainty in concentrations and fluxes but they do not appear to be applied”

As described in responses above, we will resolve issues of clarity surrounding the uncertainty measurements by revising quoted figures in the text so that they include their error values. We will also include error bars in figures where appropriate, and revise Tables 4 and 5 to include further details on error measurements.

“...the description is quiet[sic] vague and associated with statements I find it hard to comprehend; ‘Uncertainties for the trace gases and water-soluble aerosols measured calculated by error propagation ranged from 8% - 18% (3σ) throughout the campaign, varying primarily due to fluctuations in the measured flow rate and analysed concentration of the internal Br standard.’ Does this really mean ALL species for ALL hours had an uncertainty of 8-18% of the measured concentration?”

We agree with the reviewer that the wording of this section lacks clarity. The inclusion of the determination of instrument error was part of a development to determine flux error. However, as detailed in Section 2.3.4 “Alternatively, the full random error can be characterised experimentally...”, the full random error was found through side by side measurements of the GRAEGOR sample boxes. This vagueness is compounded by an error in stating that concentration errors were developed from the calculation of instrument error, rather than from the side-by-side measurements. We will clarify this issue in the revised manuscript.

‘ σ_u^ was estimated at 12% median, which, in combination with $\sigma_{\Delta c}$, was used to calculate σ_F ’ – I can’t see uncertainties are presented... ‘While most exceedances fall within the uncertainty range of the measurement’ How many do not? And why?*

3) Addressing point 2) and doing so in a manner that actually uses uncertainties for EACH measurement not for the sample as a whole would be useful in contextualizing the flux estimates and allowing the authors to determine if the ‘good enough’ threshold is achieved.”

As discussed above, we shall resolve this issue through the inclusion of the necessary values in the text.

4) “I think Figure 12 is partly a response to particle size but since no data on particle size were provided is it also a story of large measurement uncertainty?”

In our discussion of the investigation into the dependence of measured deposition velocity (V_d) on particle size, we repeatedly emphasize that our value for particle size is a proxy (the ratio $\text{PM}_{2.5}/\text{PM}_{10}$ as measured by an instrument nearby). As stated in the text – “Although measurements of particle size were not made during this campaign, measurements of aerosol species (including Cl^- and SO_4^{2-}) in the $\text{PM}_{2.5}$ and PM_{10} size fractions were taken by a two-channel Monitor for Aerosols and Gases in Ambient Air (MARGA, Applikon B.V, The Netherlands) instrument located at Auchencorth Moss, 12 km south west of Easter Bush...As a proxy for a particle size measurement, the proportion of $\text{PM}_{2.5}$ to PM_{10} was used, with a lower proportion of $\text{PM}_{2.5}$ indicating a greater proportion of coarse aerosol, and a corresponding larger deposition velocity based on process-orientated modelling”. Particle size measurements were not available. As summarised at the start of this response document, the proxy measurement was used to investigate a hypothesis that was developed from observations of aerosol V_d values. Our use of such a proxy measurement is not related to measurement uncertainty. Figure 12 shows strong and statistically significant relationships.

The scatter indicated may reflect measurement uncertainty, but could equally reflect limitations in a concentration ratio from a nearby site to describe the full size-distribution at our measurement site, the additional effect of atmospheric stability on V_d/u^* (e.g. Wesely et al., 1985) or a number of additional processes (e.g. surface wetness). We anticipate that the reviewer's concern will be resolved by further clarifying the proxy nature of the aerosol size measurement in our manuscript.

5) "The manuscript title implies a focus on fluxes ("Surface-atmosphere exchange of water-soluble gases and aerosols above agricultural grassland pre- and post-fertilisation") why are so many of the figures and so much of the text about concentrations and/or the ion balance in the aerosols?"

We believe it is necessary to include figures and text discussing concentrations as a precursor to discussion of fluxes. It is also important to present these findings for the discussions relating to (i) the deposition velocities (which makes references to elevated periods of Cl⁻ concentrations that are visually apparent in Figure 3), (ii) the HONO fluxes (the presence of HONO concentrations above the detection limit suggests a day time source for HONO; this is then linked to discussion of HONO fluxes), and (iii) the instrument intercomparison studies (which compare concentrations).

The inclusion of a brief discussion of ionic balance, with an accompanying figure, was necessary to discuss the development of the hypothesis of aerosol bulk deposition velocities being enhanced by particles in the coarse fraction. As mentioned in the text – "[the ionic balance study]...suggests a deficit of NH₄⁺, suggesting that some of the NO₃⁻ and/or SO₄²⁻ was balanced by ions other than NH₄⁺. A likely candidate is Na⁺: some of the SO₄²⁻ is likely to have represented sea-salt SO₄²⁻ and some NaNO₃ is formed by reaction of NaCl with HNO₃." This is then followed by discussion of atmospheric chemical processes that would give rise to the formation of these coarse particles, providing the framework for the eventual discussion of aerosol V_d and particle size proxy. Without the inclusion of this section, we believe that it would harm the coherence of a novel discussion point in the paper.

In conclusion, we believe that the discussion of concentration data is a necessary part of further discussion surrounding surface-atmosphere exchange. We could alternatively have called the manuscript "Concentrations and surface/atmosphere exchange fluxes of water-soluble ...", but we feel that beyond making the title even more cumbersome than it is already, this would not add any more information.

6) "With only a single fertilization event I wonder how generalizable this is? If a data set could be developed that comprises many fertilization events it may be possible to extract a signal, but at the moment the S2N ratio is very low."

Our paper provides rare field evidence of a ground source of both HONO and HNO₃ following fertilisation, corroborating previous evidence of Sutton et al. (1998) and Twigg et al. (2011). These results are quite remarkable because it is certainly not clear why the application of fertiliser, characterised by a high pH, should result in HNO₃ release. We do not suggest in the paper that our results should be generalized to fit all grassland fertilization events. However, the observations may well trigger follow-on laboratory process studies of these fertiliser emissions of HONO and HNO₃.

Here, we aimed only to observe the fluxes of trace gases and aerosols, particularly reactive nitrogen species, pre- and post- fertilisation of a grassland site with urea fertiliser, and to discuss any observed changes. We believe that through our use of the chemical conservative tracers total-nitrate and total-ammonium, we have accounted for the period of flux divergence while drawing relevant conclusions about the behaviour of reactive nitrogen species post-

fertilisation. These results add to the literature on fluxes of reactive nitrogen above fertilised grassland, much of which has also described study of only one fertilisation event.

7) "I think IF a numerical model (that accounts for flux divergence) could be brought into the research it would be very useful in trying to extract more information and provide greater insights. As it stands I did not find it compelling and thus the conclusions seem to really overstate what is shown in the manuscript."

The senior author of this publication is indeed a global leader in the 1D modelling of the NH_3 - HNO_3 - NH_4NO_3 interaction (e.g. Nemitz et al., 1998; Nemitz et al., 2000; Nemitz et al., 2009; Ryder et al., 2016). A general thread running through these model studies has been that the models are able to explore the observations qualitatively, but that it is difficult to constrain the model sufficiently to provide fully quantitative results. For example, a fully quantitative model run would require treatment and measurement information of the aerosol composition as a function of size, including any potential external mixing. Such model application is, however, well beyond the scope of this paper or the comprehensiveness of the dataset.

We do not believe that we have overstated our conclusions, as all conclusions cited in the abstract and conclusion sections are argued through the results and discussion section appropriately. We maintain that the data is robust, but we shall emphasize in the revised manuscript why we believe that to be the case, providing more information on flux errors and minimum detectable fluxes, as well as clarifying the issue of concentration measurement errors. We will also reword one conclusion in the abstract, which currently reads "providing direct evidence of a size-dependence of aerosol deposition velocity for aerosol chemical compounds" to remove the phrase "direct evidence", which we hope in combination with emphasizing the proxy nature of aerosol size measurements should clarify our hypothesis regarding aerosol V_d and aerosol size. In conclusion, we believe that the work presented in the paper remains suitable for publication by ACP, with the above-discussed amendments to highlight the robustness of our dataset.

"It's a minor point given the above but although the manuscript is quite lengthy, I did not find all the details of the measurements."

We think the reviewer may be referring here to some lack of information on the source of the NO_2 concentrations and on the MARGA instrument measurements, to which Reviewer #2 also referred. The NO_2 concentrations were determined by chemiluminescence analyser operated to standard UK national network protocols. Details will be added to the revised paper. A full description of the MARGA set-up and operation at the Auchincorth site is available in Twigg et al. (2015). The processed and ratified MARGA data are publicly available online at https://uk-air.defra.gov.uk/data/data_selector from which concentrations of any of the species measured by the MARGA can be selected. We will add the references and online resources to the paper.

References

- Erismann, J. W. and Wyers, G. P.: Continuous measurements of surface exchange of SO_2 and NH_3 ; Implications for their possible interaction in the deposition process, *Atmos. Environ. Part A. Gen. Top.*, 27(13), 1937–1949, doi:10.1016/0960-1686(93)90266-2, 1993.
- Flechard, C. R. and Fowler, D.: Atmospheric ammonia at a moorland site. II: Long-term surface-atmosphere micrometeorological flux measurements, *Q. J. R. Meteorol. Soc.*, 124(547), 759–791, doi:10.1002/qj.49712454706, 1998.

Milford, C., Theobald, M. R., Nemitz, E. and Sutton, M. A: Dynamics of ammonia exchange in response to cutting and fertilising in an intensively-managed grassland, *Water, Air Soil Pollut.*, 1, 167–176 [online] Available from: <http://link.springer.com/article/10.1023/A:1013142802662>, 2001.

Milford, C., Theobald, M. R., Nemitz, E., Hargreaves, K. J., Horvath, L., Raso, J., Dämmgen, U., Neftel, A., Jones, S. K., Hensen, A., Loubet, B., Cellier, P. and Sutton, M. A.: Ammonia fluxes in relation to cutting and fertilization of an intensively managed grassland derived from an inter-comparison of gradient measurements, *Biogeosciences*, 6(5), 819–834, doi:10.5194/bg-6-819-2009, 2009.

Neiryck, J., Janssens, I. A., Roskams, P., Quataert, P., Verschelde, P. and Ceulemans, R.: Nitrogen biogeochemistry of a mature Scots pine forest subjected to high nitrogen loads, *Biogeochemistry*, 91(2–3), 201–222, doi:10.1007/s10533-008-9280-x, 2008.

Nemitz, E., Sutton, M. A., Choularton, T. W., Wyers, P. G. and Otjes, R. P.: Investigations into vertical gradients of the gas-aerosol phase equilibrium $\text{NH}_3(\text{g}) - \text{NH}_4(\text{s, aq})$ 4 above vegetative surfaces, *J. Aerosol Sci.*, 29(SUPPL.2), S885–S886, doi:10.1016/S0021-8502(98)90625-5, 1998.

Nemitz, E., Sutton, M. A., Schjoerring, J. K., Husted, S. and Paul Wyers, G.: Resistance modelling of ammonia exchange over oilseed rape, *Agric. For. Meteorol.*, 105(4), 405–425, doi:10.1016/S0168-1923(00)00206-9, 2000.

Nemitz, E., Loubet, B., Lehmann, B. E., Cellier, P., Neftel, A., Jones, S. K., Hensen, A., Ihly, B., Tarakanov, S. V and Sutton, M. A.: Turbulence characteristics in grassland canopies and implications for tracer transport, *Biogeosciences*, 6(8), 1519–1537, doi:10.5194/bg-6-1519-2009, 2009.

Ryder, J., Polcher, J., Peylin, P., Ottlé, C., Chen, Y., Van Gorsel, E., Haverd, V., McGrath, M. J., Naudts, K., Otto, J., Valade, A. and Luysaert, S.: A multi-layer land surface energy budget model for implicit coupling with global atmospheric simulations, *Geosci. Model Dev.*, 9(1), 223–245, doi:10.5194/gmd-9-223-2016, 2016.

Sutton, M. A., Milford, C., Dragosits, U., Place, C. J., Singles, R. J., Smith, R. I., Pitcairn, C. E. R., Fowler, D., Hill, J., ApSimon, H. M., Ross, C., Hill, R., Jarvis, S. C., Pain, B. F., Phillips, V. C., Harrison, R., Moss, D., Webb, J., Espenhahn, S. E., Lee, D. S., Hornung, M., Ulyett, J., Bull, K. R., Emmett, B. A., Lowe, J. and Wyers, G. P.: Dispersion, deposition and impacts of atmospheric ammonia: Quantifying local budgets and spatial variability, *Environ. Pollut.*, 102(SUPPL. 1), 349–361, doi:10.1016/S0269-7491(98)80054-7, 1998.

Thomas, R. M., Trebs, I., Otjes, R., Jongejan, P. A. C. C., Ten Brink, H., Phillips, G., Kortner, M., Meixner, F. X. and Nemitz, E.: An automated analyzer to measure surface-atmosphere exchange fluxes of water soluble inorganic aerosol compounds and reactive trace gases, *Environ. Sci. Technol.*, 43(5), 1412–1418, doi:10.1021/es8019403, 2009.

Twigg, M. M., House, E., Thomas, R., Whitehead, J., Phillips, G. J., Famulari, D., Fowler, D., Gallagher, M. W., Cape, J. N., Sutton, M. A. and Nemitz, E.: Surface/atmosphere exchange and chemical interactions of reactive nitrogen compounds above a manured grassland, *Agric. For. Meteorol.*, 151(12), 1488–1503, doi:10.1016/j.agrformet.2011.06.005, 2011.

Twigg, M. M., Di Marco, C. F., Leeson, S., Van Dijk, N., Jones, M. R., Leith, I. D., Morrison, E., Coyle, M., Proost, R., Peeters, A. N. M., Lemon, E., Frelink, T., Braban, C. F., Nemitz, E. and Cape, J. N.: Water soluble aerosols and gases at a UK background site – Part 1:

Controls of PM_{2.5} and PM₁₀ aerosol composition, *Atmos. Chem. Phys.*, 15(14), 8131–8145, doi:10.5194/acp-15-8131-2015, 2015.

Wesely, M. L., Cook, D. R., Hart, R. L. and Speer, R. E.: Measurements and parameterization of particulate sulfur dry deposition over grass, *J. Geophys. Res. Atmos.*, 90(D1), 2131–2143, doi:10.1029/JD090iD01p02131, 1985.

Wichink Kruit, R. J., van Pul, W. A. J., Otjes, R. P., Hofschreuder, P., Jacobs, A. F. G. and Holtslag, A. A. M.: Ammonia fluxes and derived canopy compensation points over non-fertilized agricultural grassland in The Netherlands using the new gradient ammonia-high accuracy-monitor (GRAHAM), *Atmos. Environ.*, 41(6), 1275–1287, doi:10.1016/j.atmosenv.2006.09.039, 2007.

Wolff, V., Trebs, I., Foken, T. and Meixner, F. X.: Exchange of reactive nitrogen compounds: Concentrations and fluxes of total ammonium and total nitrate above a spruce canopy, *Biogeosciences*, 7(5), 1729–1744, doi:10.5194/bg-7-1729-2010, 2010.