Atmos. Chem. Phys. Discuss.,
https://doi.org/10.5194/acp-2018-603-AC1, 2018

Atmospheric Chemistry and Physics
Discussions

Interactive comment on "Surface–atmosphere exchange of water-soluble gases and aerosols above agricultural grassland pre- and post-fertilisation" *by* Robbie Ramsay et al.

Robbie Ramsay et al.

robams56@ceh.ac.uk

Received and published: 15 August 2018

We thank the reviewer for their time spent reading our paper and providing comments.

Clearly we have failed to convince this reviewer of the merits of our dataset and of our interpretations of this dataset. Below we provide responses to the reviewer's criticisms on a point-by-point basis (the reviewer's comments are provided in quotation marks, and are numbered), but first we wish to reiterate the aims of our study and the relevancy of its conclusions.

The aim of this work was to determine, at hourly resolution for a month, the concentrations and fluxes of water-soluble trace gases and their associated particle-phase ionic counterparts as measured by the Gradient of Aerosols and Gases Online Registration (GRAEGOR) at two heights over agricultural grassland. The vertical fluxes of these species were calculated using the modified aerodynamic gradient method and co-located micrometeorological measurements. Simultaneous time-resolved fluxes of these atmospheric components have not been widely determined because of the sophistication of the instrumentation required to do so. We carefully considered issues of limits of detection and flux divergence.

A further aim of this study was to discuss any change in flux of reactive nitrogen species after an inorganic fertilizer application to the grassland part way through the measurement period. Such a change was observed.

It was not an aim of this study to measure fluxes of particles, total or size-resolved. The use of the word 'aerosol' without qualification in the title of this paper may have unintentionally raised expectation that full particle flux characterisation is included – we expand on this remark, and suggest a refinement to the title, further below.

Our paper presents bulk deposition velocities of the water-soluble aerosol-phase ions Cl-, NO3- and SO42- which is important knowledge for deposition models. In examining the deposition velocities we derived we hypothesised a relationship with the proportion of fine and coarse particulate matter. We were able to demonstrate this association by plotting hourly deposition velocity as a function of the temporal PM2.5/PM10 ratio measured nearby. We emphasise throughout our paper that use of this ratio is a proxy only for particle size. This reviewer might have liked to see additional measurements that would have allowed a more quantitative analysis. However, to our knowledge, this is the first study that through composition-resolved bulk flux measurements confirms the enhancement in the bulk deposition velocity of aerosol constituents partly contained in the coarse fraction. Direct particle number flux measurements in the coarse fraction are notoriously difficult due to the limited counting statistics. The only ambient measurements available are from fog droplet deposition (see reviews, e.g. by Pryor et al., 2008), based on the (non-validated) assumption that aerosols and fog droplets interact with vegetation in similar manner.

A final aim of our work was to present a novel intercomparison between measurements of nitrous acid as gathered by two wet-chemistry instruments.

We maintain that fundamentally the depth of our dataset, its presentation and the conclusions it supports are appropriate for publication in ACP.

1. "After thorough reading the manuscript I come to the conclusion that it does not meet the standards of atmospheric chemistry and physics and has to be rejected. My rating is based on several points: Title and abstract promise measurements, findings, and discussions which are not given. Title and abstract are very broadly formulated, while the paper itself lacks of focus."

We do not agree that the abstract is broadly formulated or promises measurements and discussions that are not subsequently presented. The method by which the trace gases and associated aerosol counterparts were measured is specifically mentioned in the abstract, as is the method by which flux was calculated. All findings referred to in the abstract are directly referred to in the results section, and the discussion points in the abstract are likewise presented in the discussion sections of the paper. We acknowledge, however, that the following wording in the abstract “direct evidence of a size-dependence of aerosol deposition velocity” is overstated, since aerosol size distributions were not directly measured at the site; but the conclusion itself is supported by use of a proxy measurement of aerosol size, which we stress is a proxy measurement throughout the text, including later in this same sentence in the abstract. We will reword this sentence in the revised paper to remove the phrasing “direct evidence.” We will also add to the abstract the location of the study. Other than that we do not see anything in the abstract which is not supported by data discussed in the paper.

We do acknowledge that the title of the paper is potentially too broad in that it does not specifically qualify that the aspect of aerosol fluxes measured are the water-soluble

ionic counterparts of the measured trace gases not full particle distribution fluxes. However, we believe that the exact scope of the aerosol-phase measurements made in our work is readily clear from the abstract and the main text. To avoid ambiguity we will extend the title of our paper to “Surface-atmosphere exchange of inorganic water-soluble gases and associated ions in bulk aerosol above agricultural grassland pre- and post-fertilisation.”

2. "Substantial supportive measurements are lacking (e.g. aerosol size distribution or even size resolved chemical analysis of the aerosol)."

We believe that the origin of this comment may relate to the issue raised above concerning the abstract, which mentions aerosol size, but which is clarified within the abstract and throughout the text as being a proxy measurement of fine to coarse particle ratio. As indicated above, we will amend the phrasing on this in the abstract and in the title. Measurement of aerosol size distributions and full size-dependent chemical composition was not a component of our study, and we only base our conclusions on data that were available to us. We state in Section 4.2.2 that we did not make size-resolved aerosol measurements: “Although measurements of particle size were not made during this campaign, measurements of aerosol species (including Cl- and SO42-) in the PM2.5 and PM10 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 proxy for a particle size measurement, the proportion of PM2.5 to PM10 was used, with a lower proportion of PM2.5 indicating a greater proportion of coarse aerosol, and a corresponding larger deposition velocity based on process-orientated modelling”.

We also state in our Conclusions section that “Future measurements of aerosol deposition velocities should aim to investigate the effect of particle size upon deposition velocity, using a more robust measurement of particle size than used here”.

We believe that re-emphasis of the proxy nature of aerosol measurements in the abstract will clarify this matter.

3. "The text is not structured clearly and way too long."

The reviewer has not amplified on aspects of the paper that they feel are not structured clearly. We have followed the standard structure of presenting primary results and discussions in separate sections. The Discussion includes secondary analysis of the results data, and/or other data brought in, where this supports the points we wish to draw out at a particular place in the Discussion.

4. "Some sections contradict each other."

We cannot provide a response to this since the reviewer has not specified where they believe there is contradiction. We do not see a contradiction in what we present.

5. "When studying reactive trace gas exchange fluxes, possible flux divergence needs to be addressed. The typical sources for flux divergences are introduced in the introduction but not analyzed and discussed in the paper. There are several indications for flux divergence in the results. Nonetheless the authors calculate a 'flux' from the measured gradients and even derive a canopy resistance."

We agree that the period of measurement includes periods of flux divergence due to changes in the gas-aerosol partitioning. However, this has been explicitly addressed throughout the manuscript. At the end of Section 2.3.3 we state that we initially process the data ignoring chemistry and discuss the validity of this assumption later. Divergence of Vd(HNO3) (as calculated neglecting chemistry) from Vmax has often been taken as an indicator of the importance of flux divergence as have very large deposition velocities of NH4+. Thus, in Section 4.2.3 it is shown that the influence of chemistry is within the measurement uncertainty, except for the period after fertilisation. To overcome this problem, this period is treated separately by calculating the conservative tracers of total-ammonium and total-nitrate, as per our text: "It should be noted that during this period the aerodynamic gradient method does not derive accurate fluxes

because the condition of flux conservation is not met… By contrast, fluxes of total ammonium and total nitrate would be conserved, as the effect of gas-particle interactions are not considered, and their assessment provides additional information on the processes occurring during periods when fluxes are not conserved with height." Our conclusions based on the behaviour of ammonia, ammonium nitrate and nitric acid fluxes are grounded in this analysis.

We have also taken care to exclude the period of flux divergence from the statistical analysis of canopy resistance and deposition velocity for the entirety of the campaign. This latter point was perhaps not clear in the paper and we will add text to stress this exclusion.

It is also worth noting in this context, that previous analyses indicate that size-segregated particle number fluxes (e.g. Nemitz and Sutton, 2004) and even total particle number fluxes (Nemitz et al., 2009) can be highly perturbed by gas-aerosol partitioning, an artefact that is usually completely ignored. This implies that eddy-covariance particle number fluxes do not have a methodological advantage over the bulk composition gradient flux measurements presented here.

6. "Flux limits of detection are explained in the material and method section, but no results are given. Small and bidirectional fluxes most probably were within the detection limit."

The flux limits of detection for all trace gas and aerosol species measured will be added to Tables 4 and 5, respectively, of the manuscript. The bidirectional fluxes of HONO and NH3 that were observed throughout the campaign – including the period before fertilisation – remained above the flux detection limit calculated. This point will also be added to the text.

7. "At a well-studied site like Easter Bush there should be more information on aerosol chemistry than just the GRAEGOR measurements. The comparison with MARGA results (measured at a distance of 12 km) itself plus the very rough aerosol size analysis

is not sufficient."

As outlined in Section 2.1., Easter Bush periodically hosts campaigns but it is not a site which hosts a suite of long-term measurements of aerosol chemistry. Aerosol size measurements, if they had been available, would have been used. Standard continuous measurements of size distribution would not have greatly aided this campaign: scanning mobility particle sizers (SMPS) and Aerosol Mass Spectrometers (AMS) measure in the sub-micron fraction and the AMS only non-refractory aerosol, whilst analysis focuses on the influence of the coarse fraction and refractory material on deposition velocity. Whilst impactor measurements of aerosol size segregated ion composition would have been helpful, they were not available and indeed are not a routine measurement even at Supersites.

8. "Furthermore the supportive measurements of the MARGA are not described in the corresponding section. Nor are the NO2 measurements."

We thank the reviewer for pointing out these omissions. A full description of the MARGA set-up and operation at the Auchencorth 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.

We also acknowledge that whilst measurements of NO2 are mentioned in Section 4.4.1 the details of this measurement are not included. The NO2 concentrations were determined by chemiluminescence analyser operated to standard UK national network protocols. Details will be added to the revised paper.

9. "In the comparison of GRAEGOR measurements with LOPAP and QCL measurements discussion is mixed with contents that should better be placed in the material and method and/or the results section. Data for both comparison lack in number, range and supportive measurements, which would help to understand agreement and disagree-

ment."

During the preparation of this paper the authors discussed the best placements within the paper of the material on the LOPAP and QCL comparisons. We consider that the comparison between GRAEGOR and LOPAP, and GRAEGOR and QCL, is best placed in the Discussion Section as this was not the motivation of the study and we felt that it would become disjointed if material was split between several sections. If reviewers collectively feel strongly on this point we are happy to rearrange the sections.

With respect to the comment on amount of intercomparison data, for the comparison between the QCL and the GRAEGOR there is a limited (n = 72) number of measurements. This is considered in the discussion of the comparison (Section 4.4.2), where we mention that lack of measurements restricted comparison to only concentrations of ammonia. On the other hand, the comparison between the LOPAP and the GRAEGOR spans 6 days (n = 148). We are mindful of the ovelty of the comparisons – the first that we are aware of to be presented for publication – and we believe the data and our observations on it are worth inclusion in the paper.

10. "The presented measurements and results do not lead to the presented conclusions... Conclusions remain speculative, unfounded and airy... The discussion paper does not keep up to the promising title and abstract. The data basis does not appear to bring sufficient material to a paper on its own. Maybe the data can be presented as supportive data in another paper, such as the cited Di Marco et al. one on HONO fluxes."

These final comments from the reviewer essentially re-iterate the same concerns the reviewer has expressed in their earlier comments, and to which we have responded. In summary, we present one full month of hourly-resolved multi-species flux measurements, and throughout the results and discussion section, present carefully considered findings and conclusions which we have made based on our understanding of atmosphere science, the scientific literature, and analysis of the data gathered. We will make modifications to the title and the abstract to avoid any interpretation that this study included size-resolved aerosol flux measurements, plus the other modifications indicated above.

References - Pryor, S. C.; Gallagher, M. W.; Sievering, H.; Larsen, S. E.; Barthelmie, R. J.; Birsan, F.; Nemitz, E.; Rinne, J.; Kulmala, M.; Groenholm, T.; Taipale, R.; Vesala, T., A review of measurement and modelling results of paricle atmosphere-surface exchange. Tellus B 2008, 60, 42-75.

Nemitz, E.; Sutton, M. A., Gas-particle interactions above a Dutch heathland: III. Modelling the influence of the NH3-HNO3-NH4NO3 equilibrium on size-segregated particle fluxes. Atmospheric Chemistry and Physics 2004, 4, 1025-1045.

Nemitz, E.; Dorsey, J. R.; Flynn, M.; Gallagher, M. W.; Hensen, A.; Erisman, J. W.; Owen, S.; Daemmgen, U.; Sutton, M. A., Aerosol fluxes and particle growth above grassland following the application of NH4NO3 fertilizers. Biogeosciences 2009, 6, 1627-1645.

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.; Cape; J. N., Water soluble aerosols and gases at a UK background site – Part 1: Controls of PM2.5 and PM10 aerosol composition, Atmospheric Chemistry and Physics 2015, 15; 8131–8145; doi:10.5194/acp-15-8131-2015; 2015.

Interactive comment on Atmos. Chem. Phys. Discuss., https://doi.org/10.5194/acp-2018-603, 2018.