

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

Anonymous Referee #1

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Review of Surface–atmosphere exchange of water-soluble gases and aerosols above agricultural grassland pre- and post-fertilisation by Robbie Ramsay et al. I find this manuscript somewhat difficult to evaluate, because while on the one hand there is a need for improved understanding of (and model tools for estimating) volatilization of reactive species after fertilization, on the other-hand does this manuscript offer a real advancement of the current state of knowledge? I think not in its current state and FEAR that the measurements are not actually to a standard necessary to address the key points that authors wish to resolve. My key concerns are; 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

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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. 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 authors describe some efforts at determining uncertainty in concentrations and fluxes but they do not appear to be applied and the description is quiet 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? ‘ 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. 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? 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? Perhaps this reflects the author’s own assessment that GRAEGOR is not adequate to derive robust fluxes. If it is not then the manuscript really does not meet the bar for ACP but parts of the research could be published in another forum. 6) With only a single fertilization event I wonder

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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. 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 over-state what is shown in the manuscript. 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.

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