Response to reviewer 2

Reviewer's comments on Biogeosciences manuscript "Atmospheric Deposition of Reactive Nitrogen to a Deciduous Forest in the Southern Appalachian Mountains" by J.T. Walker

General Comments

This manuscript describes the atmospheric reactive nitrogen (Nr) deposition budget over a deciduous forest in the Southern Appalachian Mountains. Extensive measurements of the wet and dry deposition components of total deposition of inorganic and organic, reduced and oxidized, gas- and aerosol-phase Nr, are reported for the years 2015-2016, when intensive measurement campaigns were conducted at a forest site in Coweeta Basin as part of the SANDS programme.

Wet deposition was measured in straightforward manner by precipitation collectors, while dry deposition was mostly modelled from measured air concentrations and surface-atmosphere exchange (inferential) modelling. Some aerodynamic gradient-flux measurements were made for gases and aerosols over a limited period of time, providing measured reference points to assess the performance of the surface-atmosphere exchange model.

The detailed, speciated, multi-season, multi-site measurements of most of the dominant and also less documented (e.g. organic) forms of Nr concentrations in air and water offer a rare, measurement-based glimpse into the diversity of all Nr forms contributing to total Nr deposition over a US forest, and into the technical challenges and solutions implemented to close the deposition budget.

The data from the 2015-2016 SANDS intensive campaigns are examined in the light of multi-year or multi-decadal observation datasets from CASTNET, AMoN, NADP and EPA measurement networks, showing the decreases observed in total Nr deposition to the site over the last 3-4 decades (mostly from a long-term reduction in NOx emissions), but highlighting the increasing importance of reduced nitrogen in total deposition and the continued exceedance of critical loads for this ecosystem. The paper is therefore very well suited for the readership and scope of Biogeosciences.

The manuscript presents a very detailed and clear description of the measurement methods used in the extensive data collection, and assimilation by inferential modelling, which I find very useful for this type of paper, where the objective and scope include a thorough methodological component to document the manifold aspects required to compute a comprehensive Nr deposition budget. Such methodological aspects deserve not to be trivialized and glossed over, and will be useful to other researchers in this field, confronted by the complexities of total Nr deposition budgetting.

The paper is very well written, and I have only very few and minor comments before recommending eventual publication in Biogeosciences.

Response: We sincerely thank the reviewer for their comments and questions. We have addressed each in detail below.

Specific Comments

Comment: line 153: some gas and aerosol components of total Nr were measured at 1-10m above ground , while the canopy height is 30m. I presume this means the samplers were located in a clearing of the forest. How was this accounted for in inferential modelling of dry deposition, knowing that the model supposes that concentrations are measured above the canopy, and that concentrations measured in a (small) clearing are likely to represent sub-canopy levels rather than above-canopy concentrations? Was there a correction scheme to account for this effect?

Response: This is a good point. As the reviewer points out, some measurements were taken above the canopy on the eddy flux tower while another set of measurements was collected in an open area nearby the tower. We did not make any attempt to correct for potential differences in concentration due to measurement height but will clarify this point in the text, noting potential dilution effects of sub-canopy drainage into the open area, particularly at night.

Comment: line 265 and lines 564-569: the Gamma_s parameter in the bi-directional NH3 exchange model should represent the emission potential (NH4+/H+) of the apoplast, i.e. the inter-cellular fluid that is exposed to the air within sub-stomatal cavities. Here the assumption is made (implicitly) that the NH4+/H+ ratio of bulk tissue extracts (whole leaf, i.e. whole cells inc. vacuole, symplast and apoplast all mixed) is equal to the apoplastic emission potential. Many publications have previously reported vastly different NH4+/H+ ratios for bulk tissue and apoplast (e.g. Sutton et al, Biogeosciences, 6, 2907–2934, 2009, fig.7 over grassland, 1-2 orders of magnitude difference; Wang et al., Plant Soil (2011) 343:51–66, conclude p64: "...bulk leaf tissue Ð“ can not be used as a tool to predict the potential NH3 exchange of beech leaves"). Some publications do assert that there is a positive relationship between bulk and apoplastic Gamma ratios, and bulk ratios are of course much more easily measured than apoplastic extraction methods, so it is tempting to use the bulk tissue ratio as a proxy, for simplicity. Do the authors have evidence that it is justified in the case of this particular forest ecosystem? They do present a sensitivity analysis later on, using upper and lower percentiles, but I didn't see any explicit discussion of why or how the bulk tissue ratio could be used as a proxy for the apoplastic ratio. Please comment.

Response: The reviewer raises an important point here. We are indeed using the NH_4^+/H^+ ratio (stomatal emission potential, Γ_s) from measurements on leaf bulk tissue as a proxy for that of the apoplast. As rightly pointed out by the reviewer, while a number of studies have shown positive correlations between bulk tissue chemistry, apoplastic chemistry, and independently quantified compensation points (David et al., 2009; Hill et al. 2002; Massad et al. 2010; Mattsson and Schjoerring 2002; Mattsson et al. 2009), absolute differences between ratios derived from bulk tissue versus apoplast measurements can be large. For example, Sutton et al. (2009) and Personne et al. (2015) both show that ratios derived from bulk tissue chemistry exceed those derived from apoplast chemistry. As will be clarified in the text, we did not perform experiments to validate the use of bulk tissue as a proxy for apoplast chemistry.

To put our bulk tissue derived Γ_s into broader context, our results fall within the range, but on the lower end, of Γ_s reported for forests in the meta-analysis of Massad et al., 2010. Using data from studies in which Γ_s was reported along with the concentration of NH_4^+ in bulk tissue, Massad et al. (2010) derived a general relationship:

$$\Gamma_s = 19.3 \times \exp\,(0.0506 \times [NH_4^+]_{bulk} \qquad (1)$$

where $[NH_4^+]_{bulk}$ is the concentration of NH_4^+ in leaf tissue (µg g^{-1} tissue). Using our measured median value of $[NH_4^+]_{bulk}$ in equation (1) gives Γ_s = 210, which is larger than our tissue derived median value of Γ_s = 36 but on the same order as the 75th percentile (Γ_s = 171) used as the upper value in our model sensitivity analysis. In general, our estimates of Γ_s are reasonable in the context of existing observations and the general relationship between $[NH_4^+]_{bulk}$ and Γ_s put forth by Massad et al. (2010). That being said, we certainly acknowledge the reviewer's point regarding uncertainty in the validity of our use of bulk tissue chemistry as a proxy for apoplastic chemistry and will expand on this point in the text. As the reviewer points out, measurements on bulk tissue are easier and therefore more tempting to use compared to apoplastic extractions. More studies comparing apoplast and bulk tissue derived Γ_s are needed to extend the meta-analysis of Massad et al. (2010) to a wider range of natural ecosystems, particularly deciduous forests. This point will also be emphasized in the revised text.

Comment: line 647: "This pattern largely reflects the seasonal cycle in leaf area index". Could seasonal patterns in wind speed, turbulence, surface wetness (rainfall), also contribute to seasonal Vd patterns, aside from LAI?

Response: Yes, we agree that seasonal patterns in other drivers could also contribute to seasonality in V_d and will clarify this point in the text.

line 758-9: "more temporally extensive measurements of the litter NH_3 emission potential are also needed". I would add that a better understanding (and modelling) of the leaf litter decay dynamics, constrained by weather (temperature, moisture) are needed if one aims to reproduce litter N emissions in surface exchange models.

Response: Thank you for the comment. We agree and will add this point to the text.

Technical corrections

Comment: line 290: add "by eddy covariance" after "heat flux measured..."

Response: OK

Comment: lines 427-428: the sentence " To estimate the concentration of NO2 from the measured "other" NOy, we examined the ratio of NO2 to the quantity NOy – HNO3 – PANS – NTR (e.g., "other" NOy) simulated by CMAQ (V5.2.1) for the Coweeta site over the year 2015418-419..." feels a little like a repeat of lines 418-419

Response: Thank you for point this out. We will shorten the sentence at line 418 to eliminate redundancy.

Comment: line 442, figure 2 and figure S9: the decrease of SOx emissions and concentrations over 30 years had a large impact on NHx chemistry, and is useful to explain the NHx trends. It would be good to show the SO2/SO4= data of Fig S9 in Fig.2 of the main text, alongside long-term trends of Nr?

Response: Good suggestion. We will add the sulfur time series to Figure 2 of the main text.

Comment: line 505, fig. 5: NOy concentrations are expressed in ppb, it might be good to harmonize with the rest of the figures as µg m-3 (easier to compare NOy with TNO3- and NHx of figs 6-7, for example) ?

Response: Agreed. Concentrations will be harmonized to µg m^{-3} in the revised text.

Comment: line 517: suggest change "the same proportions of the NOy budget..." to "the same proportions of the atmospheric NOy load ..." ? The word budget may suggest deposition ?

Response: Agreed. Wording will be changed to “atmospheric NOy load”

Comment: line 631, similar to above, suggest change to "NH4+ contributed more to the atmospheric NHx load than NH3..."

Response: Agreed. Wording will be changed to “atmospheric NHx load”

Comment: line 556: "The contributions of NO3 - and NO2- were negligible." This refers to Fig. 8, but in the top part (a) of Fig. 8, I don't see that NO3- was negligible (here, WSON is negligible, as is NO2-). And subsequently, "Organic compounds (WSON) contributed 11.6% of WSTN...", again that is not what the top figure shows, but it is what the lower part (b) of Fig. 8 apparently shows. There is a contradiction between the two parts (a) and (b): which is WSON, and which is NO3- ? Amend text if neccessary.

Response: This was a mistake in the color coding of the top chart and will be corrected.

Comment: Fig. 8 caption: suggest change to "Contributions of N aerosol species to WSTN..."

Response: Thank you. Wording will be changed as suggested.

References

David M, Loubet B, Cellier P, Mattsson M, Schjoerring JK, Nemitz E, Roche R, Riedo M, Sutton MA (2009) Ammonia sources and sinks in an intensively managed grassland canopy. Biogeosciences 6: 1903–1915. doi:10.5194/bg-6-1903-2009

Hill PW, Raven JA, Sutton MA (2002) Leaf age-related differences in apoplastic NH4+ concentration, pH and the NH3compensation point for a wild perennial. J Exp Bot 53: 277–286. doi:10.1093/jexbot/53.367.277

Massad RS, Nemitz E, Sutton MA (2010) Review and parameterization of bi-directional ammonia exchange between vegetation and the atmosphere. Atmos Chem Phys 10:10359–10386. doi:10.5194/ acp-10-10359-2010

Mattsson M, Schjoerring JK (2002) Dynamic and steady-state responsesof inorganic nitrogen pools and NH3 exchange in leaves of Lolium perenne and Bromus erectus to changes in root nitrogen supply. Plant Physiol 128:742–750. doi:10.1104/pp.010602

Mattsson M, Herrmann B, Jones S, Neftel A, Sutton MA, Schjoerring JK (2009) Contribution of different grass species to plant-atmosphere ammonia exchange in intensively managed grassland. Biogeosciences 6:59–66. doi:10.5194/bg-6-59-2009

Personne, E., Tardy, F., Genermont, S., et al. (2015) Investigating sources and sinks for ammonia exchanges between the atmosphere and a wheat canopy following slurry application with trailing hose. Agricultural and Forest Meteorology 207:11-23.

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. (2009) Dynamics of ammonia exchange with cut grassland: synthesis of results and conclusions of the GRAMINAE Integrated Experiment, Biogeosciences6: 2907–2934. https://doi.org/10.5194/bg-6-2907-2009.