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Referee's comments on bg-2022-133

Chris Flechard (Referee)

Referee comment on "Atmospheric deposition of reactive nitrogen to a deciduous forest in the southern Appalachian Mountains" by John T. Walker et al., Biogeosciences Discuss., https://doi.org/10.5194/bg-2022-133-RC2, 2022

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 NO_x 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.

Specific Comments

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?

line 265 and lines 564-569: the Gamma_s parameter in the bi-directional NH_3 exchange model should represent the emission potential (NH_4^+/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 NH_4^+/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 NH_4^+/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 NH_3 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.

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?

line 758-9: "more temporally extensive measurements of the litter NH3 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.

Technical corrections

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

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

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?

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) ?

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 ?

line 631, similar to above, suggest change to "NH_4^+ contributed more to the atmospheric NH_x load than NH_3..."

line 556: "The contributions of NO_3^- and NO_2^- were negligible." This refers to Fig. 8, but in the top part (a) of Fig. 8, I don't see that NO_3^- was negligible (here, WSON is negligible, as is NO_2^-). 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 NO_3^- ? Amend text if neccessary.

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