

## ***Interactive comment on “Forest-atmosphere exchange of reactive nitrogen in a low polluted area – temporal dynamics and annual budgets” by Pascal Wintjen et al.***

### **Anonymous Referee #1**

Received and published: 9 December 2020

This manuscript presents 2.5 years of measurements of total reactive nitrogen (Nr) fluxes above a mixed forest in Germany. The measurements are used to assess annual dry deposition budgets and are then compared to deposition estimates derived from a field scale model and a gridded chemical transport model. This study directly addresses the need for new Nr flux measurements to improve Nr deposition budgets, assess exceedances of critical loads of Nr, and improve models of reactive N deposition. The dataset developed is novel and should prove useful to the ecological and atmospheric chemistry communities interested in N deposition. Furthermore, the interpretation of the measurements in relation to micrometeorology and atmospheric chemistry sheds new light on the processes influencing air-surface exchange of Nr and the

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relative importance of Nr species to the dry Nr deposition budget. However, there are a number of technical details of the analysis and discussion, along with some organizational issues, that should be addressed before the paper is suitable for publication.

In general, the paper would benefit from a more thorough quantitative analysis of the flux patterns and their relation to micrometeorology and atmospheric chemistry. Section 4.2 touches on these relationships but could be extended along the lines of several suggestions outlined below. As also suggested below, the current content of Section 4.2 could be reorganized and shortened by eliminating some redundancies, making it possible to expand the analysis without significantly lengthening the Section overall. Sections 4.3.2 and 4.3.3, which describe uncertainties in the modeling approaches, as well as the Conclusions section, could be significantly reduced in length. More specific comments are detailed below.

Specific comments: Line 83: Change “pattern” to “patterns”.

Line 90: Should the first word be “methods”?

Line 94: CTM should be plural

Line 117: “site located” should be “site is located”

Line 145: For clarity, consider rewording this sentence to something like: “In a 2nd step, a gold tube passively heated to 300C catalytically converts the remaining oxidized Nr species to NO.”

Line 148: Is 2.1 L/min the flow rate through the converters (atmospheric pressure) or through the reduced pressure portion of the tubing downstream of the orifice? If the latter, please indicate the flow rate through the converters.

Line 164: What type of passive sampler was used? What was the sampling duration?

Line 166: Is there a reference specific to the QCL NH<sub>3</sub> measurements performed at this site?

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Line 207: What was the typical magnitude of this correction to the total Nr flux?

Line 216: What caused the reduced sensitivity of the CLD and how was it identified?

Line 266: How was the quality of the DELTA measurements assessed?

Line 275: Has LAI been measured at this site? How variable is the LAI throughout the seasons, given the relative fractions of spruce and beech.

Line 285: Should be "gaps in micrometeorological".

Figure 1: The blue bar in the lower plot is incorrectly labeled NH<sub>3</sub>.

Line 296: The findings here relative to concentrations of NO<sub>x</sub> > 20ppb make me question the description of this site as being situated in a "low pollution" area. Some additional justification of this site characterization is needed.

Line 302: The figure numbering configuration for the Appendices (e.g., Figure B1) was not immediately clear to me. I believe the format for Biogeosciences is for such material to be included as "Supplemental Material".

Line 303: How does the sum of the concentrations measured by the DELTA compare to the TRANC Nr measurement?

Line 317: What fraction of the non gap-filled half-hourly fluxes exceeded the flux detection limit?

Line 350: Should "based on" be "are based on"?

Line 352: I might expect the sensor nearest the ground to remain "wet" later into the morning than the sensor closest to the top of the canopy.

Line 398: "It seems that. ...most likely driven by particulate Nr compounds." Is this supported by the particulate measurements? Do the DELTA measurements show relatively higher concentrations of particulate NH<sub>4</sub>NO<sub>3</sub> during this period? Given the lower V<sub>d</sub> of particles relative to gases, the concentrations would need to be much higher to

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drive the high total N deposition during this period, correct?

Lines 404 and 405: So a linear interpolation is used? Please clarify.

Line 411: "...significantly higher lower and upper." I understand what you mean here but it is a little confusing. Consider rewording for clarity.

Line 425: "4.6 kg N/ha/a are determined as a lower estimate." Please clarify how this estimate was determined.

Line 426: Should this section heading read "Sensitivity of deposition estimates to measured vs. modeled input parameters"?

Line 428: Remove comma after "class" and add "the" after "considering".

Line 432: Specify that you are referring to the apoplastic ratio of NH<sub>4</sub><sup>+</sup> to H<sup>+</sup>. I would also suggest you clarify that you are referring to the stomatal compensation point in the latter part of this sentence. Have any measurements of the soil and vegetation chemistry been conducted at this site such that compensation points could be estimated?

Line 435: "...global radiation enhances the opening of the width of the stomata" It may be more straightforward to say that the stomatal resistance is influenced by global radiation.

Line 439: I would suggest that reporting the bias (absolute percent) in the modeled values relative to the measured values is more informative than the correlation in this context.

Lines 450 - 455: A table comparing the measured Nr species concentrations (Delta compounds, NO<sub>x</sub>, QCL NH<sub>3</sub>, passive NH<sub>3</sub>) to LOTOS\_EUROS would help clarify this section.

Line 458: "... are very low compared to other studies" This statement is true relative to the three references cited but perhaps not so for Nr flux studies in a global sense. Some additional context is required for this statement, e.g., low relative to sites influenced by

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agricultural activities, previous studies in European ecosystems, etc.

Line 464: Consider modifying sentence to “. . .higher ground-level concentrations. . .”.

Line 470: “Values. . .” This sentence seems incomplete.

Line 472: “. . .confirm the seasonal pattern of Nr”. Do you mean that those studies show patterns consistent with the current study?

Line 473: “Obviously, measured concentration levels were significantly higher since the observed ecosystems were subject of agricultural management or in close proximity to industrial or agricultural emissions.” Are the authors referring here to the studies listed in Line 471? At least for the Geddes study, NO<sub>x</sub> was lower than in the present study. Please clarify and correct this statement as needed.

Line 477: This sentence should include references for the “few studies focusing on Nr”.

Line 483: Please consider changing “their flux pattern” to “the flux pattern observed by Ammann et al. (2012). . .”

Line 486: Please reference the “few studies” that measured fluxes Nr compounds mixed forests.

Lines 488 – 497: The discussion of the high emission fluxes observed in December requires some additional detail and clarification. The authors refer to decomposition of fallen leaves beneath a snow layer. Are the authors suggesting that the decomposition is enhancing emissions of NH<sub>3</sub> or NO or both? Decomposition rates typically decrease at low temperatures. The authors mention that they “discovered an increase in nitrogen concentration in the investigated samples”. Samples of what? Soil? How were these samples taken and analyzed and for which compounds? How frequently were they collected and at what depths? How much did the N concentrations increase and over what time period? The statement regarding the influence of the freeze-thaw cycle on the emission fluxes is interesting but very speculative. Can a soluble gas like NH<sub>3</sub> diffuse through a partially wet snow layer to the atmosphere? Do the fluxes correlate

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with air temperature in a pattern that would support this statement? Looking more closely at the December diurnal profiles in Figure 3 it appears the emission fluxes were mostly observed in 2017, which also had much higher variability in general than 2016. Were there more periods of snow cover in 2017? Did the two years differ in other ways in terms of meteorology or air concentrations that might help explain the emissions observed in 2017?

Line 508: Change “proposed” to “reported”.

Line 511: Change “by DELTA” to “by the DELTA”.

Line 528: Change “high” to “large”.

Line 529: Change “at less” to “at a less”.

Line 530: Change “It shows” to “These studies indicate”

Line 539: Please consider splitting up this long sentence for clarity.

Lines 544 – 547: The last two sentences of this paragraph seem more appropriate for the conclusions section.

Section 4.2: In general this discussion would benefit from some reorganization and a more thorough quantitative evaluation of relationships between flux, micrometeorology, and air concentrations. The authors discuss radiation/photosynthesis, air concentration, dryness/RH/temperature, and precipitation as important variables. Perhaps these can be discussed in sequence, rather than jumping back and forth among them throughout the section, to make the discussion read more smoothly and to eliminate redundancies. For example, the role of air concentration is mentioned in numerous places, as are relative humidity and temperature. Some care should be given to revising this section as it will be of particular interest to readers seeking a better understanding of the processes driving Nr fluxes above forests.

Line 548: Section heading 4.2 only mentions micrometeorology but much of the follow-

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ing discussion involves the relationship between flux and air concentrations. Consider rewording.

Line 549: What is the proposed mechanistic relationship between Nr flux and global radiation? What about the diurnal pattern of turbulent mixing and its role in air-surface exchange?

Line 551: The authors discuss the relationship between air concentration and flux in several places in Section 4.2. Can the authors be a bit more quantitative in this analysis? What is the relationship (scatterplot) between concentration and flux if, for example, the dataset is filtered to include only mid-day fluxes (i.e., periods of high global radiation and friction velocity)? Is a clear relationship observed? What are the observed diurnal patterns in concentration? Do these patterns confound the relationship with global radiation mentioned in line 549? The authors should consider adding figures similar to figures 2 and 3 but for TRANC Nr concentration in supplemental material.

Line 553: What do the authors mean by “favor” in this sentence?

Line 556: How is the last sentence in this paragraph justified by the preceding sentence? I must be missing something here.

Line 558: The authors compare March and April of 2017 and 2018 as an example of the potential role of photosynthesis in the interannual variability of fluxes. The explanation cites the role of temperature in stomatal function (and therefore the stomatal resistance) but what about the role of radiation? Are there differences in radiation between the two years that would also support this explanation?

Line 562: “. . . confirmed by the similar daily cycle for May 2017 and 2018.” Similar daily cycle of what? Please specify.

Line 567: “Almost the same average. . .”. This sentence is out of place relative to the rest of the paragraph. Please consider removing or consolidating with analysis of relative humidity and temperature in next paragraph.

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Line 571: The first sentence of this paragraph should either be removed or reworded. The use of “Therefore” implies a missing introductory sentence.

Line 572: What is the proposed mechanism by which dry conditions enhance Nr deposition? Are the authors proposing that the stomatal processes are a larger overall source of variability in the net canopy-scale flux than the cuticular processes? It is unclear from this paragraph, which seems to include multiple lines of analysis the connections or which are unclear as currently written. Please see my previous comment regarding the organization and clarity of section 4.2

Line 573: The sentence “Higher concentrations values lead to higher deposition values through the entire daily cycle.” seems out of place. How does this statement relate to the preceding sentence?

Line 576: “Higher temperatures increase the opening size of the stomata leading to increased photosynthetic activity.” What do the authors mean by “photosynthetic activity” in the context of the Nr fluxes?

Line 580: The role of wetness and RH with respect to cuticular deposition of NH<sub>3</sub> are reviewed by Massad et al. 2010 <https://acp.copernicus.org/articles/10/10359/2010/> and Flechard et al. 2013. <https://bg.copernicus.org/articles/10/5183/2013/>.

Line 584: “Thus we examined the influence of precipitation on fluxes.” Would it not be more straightforward to compare fluxes during wet versus dry conditions as indicated by the leaf wetness sensors, perhaps binning by day versus night or air concentration to examine the relationship while controlling for other sources of variability? I’m not sure what precipitation rate in figure F1 is telling us about the relationship between flux and canopy wetness. Is the canopy any less wet (or leaf water layers thinner) after a prolonged 0.5 mm/h rainfall compared to short duration 5 mm/h rainfall? To clarify, are these flux measurements conducted during active precipitation? What is the quality of the EC fluxes during such periods? Please add another figure to F1 similar to plot b) but for the fluxes and include in discussion.

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Figure F1: Please begin the caption by describing plot a) rather than plot b).

Line 587: "It has to be considered that the catchment, in which the flux tower is located, has a size of approximately 0.69 km<sup>2</sup> (Beudert and Breit, 2010) and is larger than the catchment of Wyers and Erisman (1998). Also, the surrounding forested area is much larger and the entire area is mountainous. The forest stand is relatively young since it is recovering from a bark beetle outbreak in the 1990s and 2000s (Beudert and Breit, 2014)." Please clarify how these statements are relevant to discussion of the relationship between surface wetness and flux.

Line 592: "Presumably, if NH<sub>3</sub> concentrations are low, Nr dry deposition seems to be favored by dry conditions." Please clarify how this conclusion follows from the analysis of the Wyers and Erisman (1998) and Woff et al (2010) studies. What would be the underlying leaf-level mechanism?

Lines 595-598: It is unclear how the sentences on wet deposition relate to the rest of the paragraph. Please consider removing.

Line 609: "the implementation of Nr species like HNO<sub>3</sub> is relatively straightforward compared to NH<sub>3</sub>" is out of place in this sentence. Consider removing.

Line 618: Change "uncertainties sources" to "sources of uncertainty".

Line 633: Change "much needed approach" to "much improved approach"

Line 663: "most of the studies. . ." Please indicate which studies the authors are referring to.

Line 667: "and the inclusion of exchange mechanisms for NO<sub>3</sub> and NH<sub>4</sub> should be considered in-situ modeling approaches." Please clarify what is meant here.

Line 671: As a general question, how well does the DEPAC total Nr flux reflect the relationships between measured TRANC Nr flux and radiation, temperature/RH/dryness described in section 4.2?

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Line 682: And at sites with sparse vegetation.

Line 685: Change "almost similar" to "similar".

Line 688: Has VDI been explained/defined?

Line 689-690: The two sentences here related to NH<sub>3</sub> should be move to the preceding paragraph.

Line 696: The use of "positive" to describe the deposition velocity is not necessary.

Line 712: Why is CBT mentioned here in the discussion of LOTOS-EUROS?

Line 720: As previously mentioned, a summary and comparison of the various measurement techniques would be helpful to this discussion. Could the authors add a table summarizing the statistics of QCL, DELTA, and passive measurements, along with the LOTOS\_EUROS predictions, as supplemental material? How well did the measurement techniques agree?

Line 722: "The difference to LOTOS-EUROS NH<sub>3</sub> concentrations was highest during periods with significant amount of NH<sub>3</sub> in the atmosphere like in spring and autumn, which is caused by emissions from fertilizer leading to a high load of modeled concentrations." Please reword this sentence, avoiding the use of "like" and "load".

Line 726: I encourage the authors to revisit the point and usefulness of this paragraph. As written I can't see that it adds anything to the discussion.

Line 760: "The deposition event in February 2018 seen by the TRANC seems to be driven by particulate Nr." Do the DELTA measurements reflect higher NH<sub>4</sub><sup>+</sup> and NO<sub>3</sub><sup>-</sup> concentrations during this period compared to other months? These data should be presented.

Line 775: The details here (i.e., "were selected from a matured tree stand") highlight that more information is needed in the method section regarding CBT as it was specifically applied at this site.

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Line 783: And to CBT.

Line 779: Conclusions section. Much of the information contained in this section is a direct recap of the preceding results and discussions. The length of this section could be significantly reduced.

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