

## ***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 #2**

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The paper presents a 2.5-year long dataset of dry deposition of total reactive nitrogen (Nr) to a forest site, interpretation of the results in the light of measurements of Nr speciation, and a comparison of the results with alternative approaches: the prediction of a chemistry and transport model, a site-specific inferential model and a canopy budget technique. Direct measurements of Nr dry deposition is rare and such a long dataset of Nr dry deposition measurements to forest is unique and important, and thus generally publishable in Biogeosciences. I had high hopes for this paper, especially because the Nr flux measurements were accompanied by NH3 flux measurements (by QCL), which I hoped would have been used to elucidate the non-NH3 component of the Nr flux. However, I was let down in various aspects: the NH3 fluxes are not used in this

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paper (only concentrations). It is not stated whether they just did not work or whether they are left for another paper. However, this paper speculates a lot about the nature of the NH3 exchange and its impact on the total Nr flux and with NH3 flux data presumably available to explore this explicitly, this seems rather odd. In addition, the Discussion section is quite long and lacks structure and aim. The advantage of the TRANC is that it captures most of the Nr flux with one instrument. The disadvantage is that it does not shed light on the behaviour of the individual Nr components. Yet, much of the discussion is dedicated to relating the measured flux to the behaviour of individual compounds reported in the literature. I do not think this adds to the manuscript and should be shortened. Instead the paper should be more focussed on describing the flux in its totality. For example, the Nr dry deposition budget is not discussed in the context of the additional wet deposition which could be taken either from nearby measurements (if available) or the LOTOS-EUROS prediction. A number of serious concerns need to be addressed as raised below before the manuscript can be accepted for publication. This will require significant reworking and refocussing of the manuscript.

Main scientific comments:

1. As mentioned above, if the NH3 fluxes could be worked into the manuscript this would strengthen the analysis a lot.
2. The paper confuses the rate of deposition (deposition velocity) and the actual deposition. Ignoring the effects of compensation points on NH3 exchange and the contribution of soil NO emissions to the net flux of NO and NO<sub>2</sub>, and also changes in the relative contribution of different compounds to Nr, the deposition of Nr is expected to scale approximately with its concentration. This is trivial and fundamentally also the way the deposition is calculated in LOTOS-EUROS and DEPAC-1D. Changes in concentration therefore mask the mechanisms that regulate the deposition rate. Thus, the analysis would be much more meaningful if the authors examined the controls of the deposition velocity rather than of the flux. This is what is done in the literature for the different compounds and, currently, comparisons are not correct. For example, it is

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stated that NH<sub>3</sub> fluxes are largest under wet conditions. In fact most studies report that Vd is larger for wet conditions, but at the same time the concentration may be reduced. For this reason statements like “dry conditions seem to favour nitrogen dry deposition (line 13, also line 793f)” are maybe not incorrect, but certainly misleading. Throughout the analysis it is rarely clear whether an association between the flux and drivers is due to their effect on concentration or Vd. For example, Fig. 4 would be more meaningful if presented for Vd. In fact, an analysis in terms of Rc would be even more meaningful as it would normalise for the effect of turbulence on Ra and Rb both of which contribute to Vd. Because particles are not really subject to a boundary-layer resistance in the way it is applied to gases, Rc is not really meaningful. However, the analysis could be done in terms of Vds = Vd(z0), i.e. after normalising at least for Ra.

3. The interpretation of the measurements is not helped by the lack of showing absolute concentrations. The relative composition of total Nr (Figs. B1 and E1) is useful, but also the absolute concentrations are needed to interpret the results. Again, because fluxes are discussed in terms of their magnitude and not their Vd the reader is left wondering whether it is really the change in relative composition that changes the flux or whether it is just the overall Nr concentration. By the way, it is unclear what time periods are shown by each pie chart and what frequency this maximum refers to (Caption and text Line 305ff). Presumably, these are monthly results given that the lowest data resolution (from the DELTA) is monthly? Indeed, I would find a figure showing monthly stacked bar graphs of the individual Nr components very useful. This would convey how the total and their contribution to total Nr changed seasonally. Also, an assessment of how well the sum of the individual N compounds compares with the total Nr concentration needs to be added as quality control.

4. The measurements are compared to those made over other ecosystems and differences are explained by differences in ecosystems. Again, this is only part of the story, mainly the part that affects Vd. The pollution climate the ecosystem is in is equally important and does not necessarily correlate with the ecosystem type (think of an urban

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woodland or a heavily grazed pasture in otherwise pristine environment). The comparison needs to be reworded. Generalisation that Nr fluxes always behave above natural vegetation as they do at this particular site is not tenable (e.g. line 13 and throughout).

5. The analysis of the effect of precipitation on the flux (Fig. F1a and associated text) is particularly problematic. During rain the eddy-covariance flux measurement of water soluble compounds (and many Nr compounds are) is highly uncertain because fluxes cannot be assumed to be constant with height due to the washout process. An increased Vd during rain may just reflect the presence of an additional sink (the washout process) below the measurement height. Rain episodes should potentially be filtered out, but certainly no process understanding should be derived from data taken during rain. How do the measurements demonstrate that wet deposition is important (Line 595)?

6. The paper does not distinguish different types of error (e.g. lines 617f and 652f). The flux error according to Finkelstein and Sims describes a random error, whereas the uncertainty in the DEPAC-1D estimate is more likely to be systematic and thus provide a bias. The input parameters are considered the largest uncertainty in DEPAC-1D (lines 619f), but actually different inferential models give very different results which highlights their uncertainty (e.g. Flechard et al., 2011).

7. This then also relates to an apparent contradiction between the discussion of the importance of stomatal exchange (Line 575) which is temperature dependent but mainly regulated by PAR and the statement that the canopy resistance is mainly driven by water solubility (Line 702).

8. Still on the topic of drivers of the exchange, a similarity in the diurnal cycle between global radiation and flux is no proof of causality (line 549ff). A lot of parameters are driven by the radiation: turbulence, photochemistry etc.. Neural networks also do not derive causalities or ‘drivers’, only associations and determinants.

9. The filtering criteria will have removed preferentially the smaller fluxes during low

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turbulence conditions and the remaining dataset will therefore be biased. Whilst this is not an issue if a model is used for gap filling that accounts for changes in turbulence, it does impact the straight averages of the fluxes (Figure 2) the value of which then becomes questionable and also the MDV gap filling method. These issues and implications need to be discussed.

10. The use of monthly mean concentrations for some of the compounds (DELTA measurements) adds significant uncertainty to DEPAC-1D model results. The first mention that the DELTA measurements are monthly seems to come in line 303 and the uncertainties are not mentioned until Line 622 (and there without references to, e.g., Schrader et al. 2018). The limitations of this approach should be more visible earlier on. Was the gap-filling of NH3 (Line 257) done in a mass-conserved way, i.e. was the available data removed from the long-term NH3 average to work out what the average concentration during the gaps might have been? I suppose this would lower the uncertainty somewhat? Was a diurnal cycle superimposed on the long-temporal resolution measurements?

11. I do not follow the introduction of the DEPAC algorithm (Section 2.4.1). Erisman et al. (1994) does not describe a bidirectional resistance model (Line 224). Similarly, the references in lines 230-231 all describe deposition parameterisations, but most are almost certainly not the ones used in this version of DEPAC and contradict each other. The most correct description probably comes in Lines 243-247. Much of the description of the DEPAC-1D (Section 2.4.3), including the resistance parameterisations, probably also apply to the DEPAC version implemented in LOTOS-EUROS? It is all a little confusing. I did not realise until the Discussion section that DEPAC-1D does not treat the aerosol. This is a major and seemingly unnecessary shortcoming. My understanding was that DEPAC-1D is a stand-alone version of the deposition scheme implemented in LOTOS-EUROS and surely the latter treats the aerosol components. This seems hardly justifiable.

12. I am confused throughout about the use of a compensation point for NH3 in the  
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versions of LOTOS-EUROS and DEPAC-1D used. What is its magnitude for the forest types under consideration and where does it come from? Line 264 says that the DELTA concentrations were used for determining compensation points and additional deposition corrections? How was this done? Does this mean the models were not run with the standard scheme for these ecosystem types? Monthly concentrations do not lend themselves to deriving compensation points. Lines 671ff discuss uncertainties around cuticular compensation points. This would suggest that this was somehow adjusted based on the measurements?

13. Given all this discussion about compensation points it is then highly surprising that Vd for HNO3 and NH3 are virtually identical (Line 374). How can this be? Apart from potential of evaporating NH4NO3 on leaf surfaces, HNO3 exchange is well understood and follows a near-zero Rc. NH3 does not.

14. I am similarly unclear about the discussion of the landcover (Lines 236-242). Given the resolution of LOTOS-EUROS of 7 x 7 km<sup>2</sup> it is not surprising that the landcover of the grid cell containing the measurement site does not match that of the flux footprint which is much smaller. But I also do not see a big problem: is LOTOS-EUROS not based on a mosaic / tiling approach and predict fluxes to each landcover type separately? The associated description of the LAI values (Lines 273-279) is also unclear. Surely DEPAC-1D and LOTUS-EUROS simulate the deposition to all landuse types in a gridcell and from those a landcover-weighted average can then be calculated? In general, it should be made clearer what is identical and what is different between the LOTOS-EUROS and the DEPAC-1D simulation. What measurements were used for DEPAC-1D? Concentrations, meteorological parameters, canopy characteristics?

15. The December emission fluxes are insufficiently explained. Were temperatures really sufficiently high to drive NH3 emissions from decomposition (Line 489)? Is there any evidence of freeze-thaw cycles affecting NH3 fluxes (Line 496)? Possibly, freeze-thaw cycle effects on soil NO are a more likely explanation? However, does the flux direction actually correlate with freeze-thaw events? Could it be caused by a problem

with the measurement setup for a period of time given that December measurements differed between the two years?

Minor scientific comments

The abstract seems overly long and should be shortened. This can be done linguistically (e.g. remove phrases such as "We further showed that") and in terms of content. For example, it is sufficient to list the results in terms of annual deposition inputs and remove the numbers for the 2.5-year timeframe (line 19ff).

In Section 2.2 I am missing a fuller statement on the response of the TRANC to Nr compounds in the aerosol phase. What is the size-cut? What is the response to nitrate other than ammonium nitrate (e.g. sodium nitrate, calcium nitrate, ...)? Presumably they are not volatilised?

Line 33ff. I am not aware that deposition of Nr components threatens human health. They do so by acting as precursors to PM2.5 and O<sub>3</sub>.

Line 80f. The critique of the MDS method is difficult to understand because it is not explained what it is. The introduction of CTM approaches is a little messy. Line 90 explains their workings by needing meteorological data and land-use information. Emissions and chemistry are only mentioned much further down.

The introduction of the principle of operation of the TRANC is also not very logical. First reduced N is oxidised and then NH<sub>3</sub> is formed from NH<sub>4</sub>NO<sub>3</sub>? Surely this happens before the oxidation (or in the same step).

The description of turning the leaf wetness value into a boolean value needs to be improved (line 158ff). At present, a value of 10 in arbitrary units is meaningless.

Line 166ff. Please state the temporal resolution of the DELTA measurements. Also, later the text refers to ammonia diffusion samplers and NO<sub>x</sub> measurements, which do not appear to be mentioned in Section 2.2.

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Line 199. Does the flux loss depend on the chemical composition of Nr?

Line 207. Please state the relative magnitude of the water correction. What is its uncertainty?

Line 211. Removal of fluxes outside a certain range appears to be arbitrary and subjective. Are these extreme fluxes not caught by the other tests, e.g. Foken's stationarity test or testing for stochastic significance via the random flux error? I presume the latter is what the "threshold of two times 1.96sigma" (Line 213) refers to? Currently, sigma is not defined and its calculation remains unexplained.

Line 264f. How were compensation points derived from long-term measurements of SO<sub>2</sub> and NH<sub>3</sub>? This would seem problematic.

Line 266. Why was the LAI modelled for a site-based application? Why was this not based on a measured value?

Line 390. How do the diurnal cycles compare between measurements and model results? Does this shed add additional light on model deficiencies?

Line 434. No, concentration is not proportional flux. The flux is proportional to the concentration. The concentration is the driver.

Line 468. What do the concentration ranges refer to?

Line 501. Both NO and NO<sub>2</sub> contribute to Nr. So even if soil NO is converted to NO<sub>2</sub> it will still contribute to the Nr flux except for the fraction that is removed by the canopy.

Line 507. The DELTA samplers does not measure NO<sub>x</sub>.

Line 514. There is a range of coatings available for the DELTA denuders. Clarify here and possibly also in the Methods section that carbonate coating was indeed used.

Line 551. Presumably in addition to total Nr concentration, its speciation also affects the net deposition rate and thus the flux.

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Line 721. Is it worth adding DELTA, QCL and passive sampler data all to the graph to have an intercomparison between measurements? How do HNO<sub>3</sub> compare between model and measurement? The modelled values of NH<sub>3</sub> could also be too high because HNO<sub>3</sub> in the model is too low (thus forming less NH<sub>4</sub>NO<sub>3</sub>).

Line 739. The model presumably calculates u\* from the ascribed canopy height and does not know about the complexity of the terrain. Are you saying that the measured u\* is elevated because of topography? Would this not imply that the conditions for eddy-covariance are not met?

Line 754. "input NH<sub>3</sub> concentrations" Do you refer to emissions or long-range transport?

Line 763. If the deposition event wasn't measured it maybe did not exist. I suggest to rephrase: "All models predicted at 2nd emission event which was not confirmed by the measurements."

Line 793f. But you say the Vd of NH<sub>3</sub> is very high almost as high as HNO<sub>3</sub>. Thus, a large relative contribution of NH<sub>3</sub> should give you large deposition fluxes.

Line 795f. The wash-out could have occurred upwind and not contributed to the local wet deposition.

Line 798f. The good agreement seems entirely fortuitous given aerosol was not included in DEPAC-1D ...

Line 803f. Maybe the gap filling methods are designed for compounds whose fluxes are actively regulated by production and consumption processes rather than the consequence of turbulence and concentrations such as deposition.

Technical corrections / suggestions:

The English needs to be improved throughout the manuscript, especially the use of articles. The list of corrections suggested here is not complete and since major changes

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to the text will follow when addressing the points above it should be checked again anyway.

General: avoid starting sentences with numbers. E.g. line 23 could better read "Deposition of 16.8 kg N ha<sup>-1</sup> was calculated"

General: there are numerous places where an article is missing. E.g.

- line 86: "due to the low number"
- Line 146: "as a reducing agent"
- Line 179: "on an annual basis"

General: there are several instances where the word "after" seems to be a mistranslation from German and needs to be replaced.

- Line 105: "were taken following the approaches of the International ..."
- Line 108: "nitrogen deposition using the canopy budget technique"
- Line 179: "bases following the CBT approach"

General: in many cases units are incorrectly combined. For example ms-1 should read m s<sup>-1</sup> and  $\mu$ gm<sup>-3</sup> should read  $\mu$ g m<sup>-3</sup>.

Line 7. I was surprised to see Nr concentration given in ppb rather than  $\mu$ g N m<sup>-3</sup>, especially since Nr contains aerosol compounds for which the use of ppb is rather unusual.

Line 62. Better "EC studies of ..."

Line 69 refers to "that site", but it is not clear which site is meant at this point.

Line 96. "validation with flux measurements" (or "against").

Line 116. "Measurements were carried out in". Actually, the authors should consider the alternative "Measurements were made" here and elsewhere.

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Line 117. Remove “and”.

Line 130. Remove “which is remote from significant sources of emissions.” This is repeating what was said before.

Line 139. “which was housed in an”

Line 142. “oxidation”

Line 145. “during which remaining oxidised Nr species”

Line 219. “was caused by”

Line 249. “filling the gaps in the flux data.”

Line 274. “weighted using the actual land-use fractions” ?

Line 275. “when considering only deciduous”

Section 3.1. Much of the section here and elsewhere should be put into past tense.

Line 303 and elsewhere. Please add charges to NO<sub>3</sub><sup>-</sup> and NH<sub>4</sub><sup>+</sup> (NO<sub>3</sub> is a radical).

Line 305. Redundant “with”

Line 308. “the relative contribution of NH<sub>3</sub> is significantly higher”

Line 310 and elsewhere. A colon is followed by lower case in English.

Line 311 “done following the criteria mentioned”

Line 380 & 447. Should be “consequently” instead of “consequentially”

Line 384. Should the units here be “kg N ha<sup>-1</sup> a<sup>-1</sup>”?

Line 391. “Clearly, …”

Figure 6. The colours between upper and lower CBT estimate seem to be reversed.

Line 417 and also line 816. “the range of …”

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Line 450. “LOTOS-EUROS states out NH<sub>3</sub> …” – meaning unclear.

Line 479. “Apart from management events, fluxes above the arable …”

Line 528. “Munger et al. (1995) also made NO<sub>y</sub> flux measurements …”

Line 607. “sometimes lead to non-stationarities”

Line 612 “under certain circumstances”

Conclusions. Re-introduce all acronyms, including Nr.

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