

Interactive comment on “Dry and wet deposition of inorganic nitrogen compounds to a tropical pasture site (Rondônia, Brazil)” by I. Trebs et al.

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1. Overall Comment

The manuscript makes a very valuable contribution to the sparse literature on N deposition in the tropics and is generally well written and presented. The authors use state-of-the-art measurement technology for continuous measurement of gas and aerosol concentration, which under tropical conditions is certainly no small feat. In applying inferential techniques to estimate dry deposition of compounds such as HNO_3 and NH_3 , the work relies on the applicability of, in many cases sparse, data from European sites,

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which may not be representative for conditions found at Rodonia. This necessarily induces uncertainties, which can only be reduced through direct flux measurements over such surfaces, which clearly goes beyond the scope of the current study. The following scientific and technical errors, especially in the application, terminology and interpretation of the inferential modeling approach need to be addressed before the manuscript can be published in ACP.

2. Specific Comments

1. Page 3134, line 6. For compounds whose exchange is controlled by compensation points, the direction and magnitude of the flux also depends on the concentration in air, not just the production / consumption processes. This needs to be mentioned.
2. The dependence of particle deposition velocity on particle density (Page 3134, Line 16) needs to be supported with a literature reference.
3. Page 3134, line 21. It is not necessarily the 'urban receptor sites' that are most affected by N deposition. By contrast, the deposition of agricultural ammonia dominates N deposition in major parts of Europe.
4. Page 3134, line 26. Co-author Luciene Lara has been involved in measurements of N wet deposition at several sites in Brazil. I am surprised there is not more work that can be quoted here.
5. Section 2.1. Please add information on management of the pasture (grazing, stocking density, fertilisation, cutting) which will be useful for the interpretation, in particular of the ammonia exchange. Please note here also that *B. brizantha* is a C4

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grass which may have consequences for the modeling of NH_3) exchange (see below).

6. Eq. (1), Eq. (2) and throughout the document: V_d and R_a) are height dependent and the reference height should always be stated, i.e. " $V_d(1\text{ m})$ " to enable intercomparison between studies.

7. Page 3137, line 2. Just out of curiosity: why were the IC sampling times different during the different measurement periods?

8. Page 3137, line 17. I am not fully convinced that a contribution of PAN to NO_x can be ruled out. PAN concentrations of 0.5 ppb or above have been reported for temperatures similar to those encountered at FNS. In addition, high emissions of isoprene in the area may result in elevated concentrations of PAN like compounds?

9. Page 3140, line 23 and also Section 4.4.3. The authors apply the term 'compensation point' very loosely. The existence of a 'compensation point' requires the presence of competing (typically biological) consumption and production mechanisms. The concentration point is then the air concentration at which these processes balance to give a zero net flux (cf. discussion following the paper by Sutton et al. 'Plant-Atmosphere Exchange of Ammonia' Phil. Trans. Roy. Soc. 351, 261-278, 1995). If a single chemical equilibrium determines the flux, the term 'compensation point' is inappropriate. The terminology should be revised here.

10. Related to this, the authors need to bear in mind that the canopy compensation point is a notional concentration, with the main aim to solve the flux equation mathematically. They need to be careful not to give the impression that this entity describes the canopy, as it is also affected by the air concentration (e.g. page 3142, line 6; Section 4.5.3). For example, it is not surprising that χ_c lies in the range of former studies (Page 3153, line 13), as the values for the underlying pa-

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rameters (Γ and the resistances) are taken from these other studies and χ_c follows. Although it should be noted that the authors are comparing χ_c for an extensive agricultural surface with values of χ_c that have been derived for intensive agricultural surfaces.

11. I am surprised that the authors opted for the more complicated dynamic capacitor model rather than the simpler static canopy compensation point model, given that the additional modeling parameters required by the dynamic model (i.e. R_d , C_d) are highly uncertain and depend on factors such as the absorption capacity of the plant species and pH of the leaf water layer. What is the benefit of this more complicated model over the simpler one? What is the difference in the net flux? A diagram of the resistance model would help to define the different component fluxes, emission potentials and resistances. Interestingly, the increased NH_3 concentration around 9 am (Fig. 2a) could be indicative of a desorption peak.

12. Page 3143, line 3. There are several models and semi-empirical approaches to estimate V_p for particles $> 1 \mu\text{m}$ and nitrate. I agree that the Wesley et al. (1985) approach, which was derived from SO_4^{2-} , should be applicable to ammonium sulphate and ammonium nitrate. Here the main uncertainty would be the difference in the morphology of different grasses pointed out in theoretical studies. However, these values of V_p are most likely an underestimate for NO_3^- concentration contained in particles $> 1 \mu\text{m}$. From the balance of NH_4^+ and the sum of SO_4^{2-} and NO_3^- the authors could attempt to estimate the importance of NO_3^- not associated with NH_4^+ . Is there any indication for the presence of organic NO_3^- in the coarse mode, e.g. associated with humic-like substances, in the tropics?

13. Section 3.4. The way wet deposition was measured (estimated?) is unclear, especially the use of 'historical time series'. Are the authors saying that wet deposition was not measured continuously, but on a campaign basis, and that long-term estimates of wet deposition were estimates by combining precipitation weighted

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mean concentrations from these campaigns with long-term data on rainfall amounts?

14. There is an apparent contradiction between page 3148, line 3, where the authors suggest NO emission with O₃ reaction is responsible for the build-up of NO₂ in the nocturnal boundary layer and page 3147, line 23, where the authors claim that O₃ concentrations in the morning were too low to oxidize NO.

15. The lower estimate of the chemical time-scale (Case 2) is calculated on the assumption of a unity accommodation coefficient and that inorganic and organic water soluble aerosol is available for the reaction. However, especially in the remote environment, the aerosol will be internally mixed. Hence, either all aerosol will be available or, in the presence of organic surface coatings, the reaction with all aerosol may be impeded (although this effect may be subsumed in the value of α). For the lower estimate all aerosol should be taken into account.

16. The authors need to distinguish more clearly between the R_c modeling approach and the canopy compensation point modeling approach for NH₃, which are mutually exclusive. The term R_c is defined as the bulk canopy resistance for a zero surface emission potential. As soon as there is a non-zero surface concentration (e.g. as represented by χ_s and χ_d), the term R_c should not be used. This implies in particular that R_c cannot be calculated as the reciprocal sum of R_s and R_d (page 3151, line 5; Section 4.5.2). Rather than depicting ' R_c ', Figure 5 should present the component resistances R_s and R_d .

17. Section 4.4.2. I do not understand the authors' approach to estimating R_s . R_s is a plant-physiological parameter and differs between chemical compounds only because of differences in their molecular diffusivity. Any further constraints on the stomatal pathway should be expressed as a further resistance in series or through a stomatal compensation point. Hence, R_s derived from LE should (after correction

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for differences in diffusivity) be appropriate as long other sources do not contribute to the evaporation. The uptake limitation for NH_3 , compared with H_2O , is then taken into account through the non-zero stomatal compensation point. I am not certain how the authors justify the use of $R_c(\text{O}_3)$ in the calculation of $R_s(\text{NH}_3)$. The interaction of O_3 with vegetation surfaces is very different to that of NH_3 and hence the non-stomatal resistance for O_3 cannot be approximated by $R_d(\text{NH}_3)$. The authors should compare the values of R_s derived from LE with literature values on *B. brizantha*. Was there any effect of stomatal drought closure on R_s ?

18. Section 4.4.4. The authors should spell out more clearly whether the pasture received any fertilizer, in addition to the cattle excreta. Since they apply stomatal compensation points that are representative for semi-natural vegetation, I assume that this is not the case. However, the cattle excreta affect NH_3 exchange in two ways: (a) direct emission from the manure and urine patches, (b) raising the N status of soils and plants, leading to higher NH_3 compensation points. Here, double-counting is a potential problem, as the 8% volatilization may include this second effect.

19. Page 3153, line 21. In addition, to the increase in temperature, epicuticular water films evaporate, further increasing the cuticular emission potential (χ_d), which increases χ_c .

20. Page 3155, line 6. For a compound that is exchanged with a very small R_c (as is the case for HNO_3), V_d is mainly dependent on $R_a + R_b$. Hence, in comparing $V_d(\text{HNO}_3)$ between studies one is mainly comparing the turbulence and surface roughness.

21. Section 4.6.1. The model by Sutton et al. (1998) does not 'use' non-zero values of R_c , it calculates them. It needs to be emphasised again that R_c is a theoretical, calculated entity and not a descriptor of the canopy. The calculation

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of the 'net deposition scenario' is unclear and appears to be inconsistent. Firstly, Page 3156, line 11 refers to Eq. (1), which does not contain χ_c . Secondly, χ_c is 0 only if $R_s = R_d = 0$ and $\chi_d = \chi_{is} = 0$. Therefore, this scenario does not make sense scientifically. Instead, the deposition-only scenario could be calculated by setting $\Gamma = 0$.

22. The upper estimate of NH_3 deposition is derived by combining the χ_c , modeled with the canopy compensation point model, with R_c values. Here, χ_c is the result of competing pathways and its magnitude is somewhere between the values of $\chi(z_{ref})$, χ_d and χ_s . In particular, χ_c will exceed $\chi(z_{ref})$ in situations where the canopy compensation point model predicts net emission. By combining these values of χ_c with R_c the authors are in danger of grossly overestimating deposition. Instead, the authors should use $\chi(z_{ref})$ combined with estimates of $R_a(z_{ref})$, R_b and R_c to predict the upper estimate for the deposition.

23. Page 3156, line 24ff. "... suggests that surface-atmosphere exchange of NH_3 may be significantly smaller ...". The authors should clarify if they are talking in terms of emission, deposition or modulus flux. In addition, the factors listed here don't all have the same effect. Deposition increases with lower epicuticular pH, lower Γ , and lower R_c .

24. Page 3157, line 11. Where would the night-time emission come from? Surely the stomates are closed and increase in RH (and thus leaf water layer thickness) would lead to an increased epicuticular reservoir?

25. Page 3157, line 13. Most former measurements were made at lower temperatures. It is not impossible that the high temperatures at the measurement site result in large emissions, even at moderate Γ . The Γ values applied in this study have been taken from C3 grasses in cooler climates. An interesting question would be if C4 plants have developed mechanisms to minimize gaseous N losses in warm

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climates, e.g. by minimizing the time of stomatal opening or by reducing apoplastic NH_4^+ concentrations. While NH_3 exchange has been measured over fertilized maize, I am not aware of NH_3 flux measurements over semi-natural C_4 canopies with low N status. Some research appears to be needed here ...

26. Do the authors know what neutralizes the excess aerosol NH_4^+ . I assume it is SO_4^{2-} ? (Page 3158, line 21).

27. Section 4.7. What exactly do the authors mean by 'only cases of net deposition were considered'? Surely, what matters is the net N input. It may be worth splitting the net flux into an upward and a downward component, i.e. sum up hourly upward fluxes and downward fluxes separately. Also, in Section 4.8 the authors state that $2.7\text{--}6.8 \text{ kg N ha}^{-1} \text{ yr}^{-1}$ are net re-emitted from the pasture site. Why is this re-emission not included in the estimate of the bi-directional exchange? Some clarification is needed what the deposition estimates actually represent.

28. The authors state that N deposition at FNS was always dominated by NO_2 and NH_3 (Page 3159, line 24). However, this surely depends on the scenario, given the 'high' scenario predicts net NH_3 emission during the dry season (e.g. Fig. 9).

3. Technical Comments

29. Abstract, line 3: "... data sets exist of wet N deposition ..."

30. Page 3134, line 9: "... Earth's surface."

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31. Section 2.2. Please add model numbers, manufacturers and/or references to the instrumentation used (e.g. DMPS, APS).
32. Eq. (2). Denominator should read " $(z_{ref} - d)$ " (two occurrences). Same again three lines below Eq. (2).
33. d (zero-plane displacement height) is used in the text but does not appear to be defined.
34. Throughout the text u^* should read u_* (i.e. subscript rather than superscript).
35. Section Heading 3.3. Suggestion: "Determination of Chemical Time Scales for Turbulent Transport and Chemistry"
36. Eq. (4): R_c should not appear in this equation (cf. 2nd RHS of Eq. 5, which is correct).
37. Eq. (9): Why write " $(\sigma_w^2/u_*)^{-1}$ " rather than " u_*/σ_w^2 "?
38. Page 3144, line 5. 're-formed' instead of 'formed back'.
39. First sentence after Eq. (10). This seems to be back-to-front. Better: "... whereby the mass size distribution ($m(R_p)dR_p$) is related to the measured aerosol number size distribution."
40. Page 3145, line 12: Better English: "provides a test" rather than "allows to test". Alternatively: "allows ... to be tested ..."

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41. Section 4.1. Please state measurement heights for the meteorological parameters. For example, RH was measured at several heights and is probably higher close to the canopy.
42. Section 4.1, last sentence. Suggestion: '... conditions was presented by Trebs et al. (2005)."
43. Section 4.2, first sentence. Better: 'Median diel variations in concentrations of NO, ...'
44. Section 4.3. Write "NH₃-HNO₃-NH₄NO₃" instead of "NH₃-NO₃-NH₄NO₃" (at least 4 occurrences).
45. How was WOSC measured? Did I miss this in the methods section?
46. Without looking up the references of Kramm and Dlugi (1994) and Meng and Seinfeld (1996) it is currently unclear how the laboratory time-scales were derived. Are these really more experimental than the time-scales calculated for the Brazilian field site? Some more detail is required to evaluate this part of the manuscript.
47. At various locations throughout the text parentheses are used incorrectly in literature references, e.g. "... in the recent study by (Stutz et al., 2002)." should read "... in the recent study by Stutz et al. (2002)."
48. Suggestion: Change heading of Section 4.4 to "The inferential approach: selection of input parameters"
49. Page 3157, line 10. "If the epicuticular water film were >4.5 and Γ constant

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..."

50. Page 3159, line 14. "As may be expected, estimated wet N deposition (Fig. 11b) is ..."

51. Section 4.8 and elsewhere. "PM10" should read "PM₁₀" (several occurrences)

52. Page 3162, line 11. "... were considered to be bi-directional. All ..."

53. Acknowledgements: "... the authors are grateful to L. Ganzeveld ..."

54. Literature list: Please correct missing superscripts and subscripts.

55. Eq. (8b): As it stands the equation is dimensionally incorrect. I suggest using a symbol (e.g. a) for the -300 and introduce it as $a = 300$ m

56. Table 2 and Fig. 2. Mixing ratios (ppb) are not suitable units for aerosol concentration. I suggest the use of either $\mu\text{eq m}^{-3}$ or $\mu\text{g N m}^{-3}$ throughout, possibly with the exception of O₃. This will maintain inter-comparability between compounds.

57. Fonts of symbols (i.e. italics vs. non-italics) and sub/superscripts need to be unified throughout the manuscript.

58. Figures 7 and 9 are quite small. Maybe a matrix of 2 x 2 panels would lead to an increased size in print? Also the word 'median' does not need be repeated in the legend of Fig. 9.

Eiko Nemitz.

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