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Atmospheric Chemistry and Physics Discussions

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

I. Trebs et al.

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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, which may not be representative for conditions found at Rondônia. 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.

The authors are grateful to Eiko Nemitz for the time-consuming work of carefully reviewing the manuscript. The very detailed and useful comments are greatly appreciated.

Due to the length of the review, the specific comments of Eiko Nemitz will not be added here. The numbered items refer directly to the each specific comment of Eiko Nemitz (see: Atmos. Chem. Phys. Discuss., 5, S1273-S1284, 2005 www.atmos-chem-phys.org/acpd/5/S1273/)

1. Response: This will be changed.

2. Response: A reference will be added.

3. Response: This will be changed.

4. Response: Some more references about the work of Luciene Lara will be added.

5. Response: The information will be added.

6. Response: Since throughout the manuscript, the deposition velocity for each compound is written as e.g., $V_d(HNO_3)$, the authors found it more appropriate and also sufficient to add the height in the caption of Figure 7a-d. The turbulent resistance will be changed to R_a(5.3 m) throughout the document.

7. Response: This was done because the software of the instrument was running more stable when fewer injections were done. During the cleaner periods, diel variations decreased such that a higher time resolution was not strictly needed.

8. Response: Increased concentrations of PAN due to high isoprene emissions are indeed very likely. The argumentation regarding PAN will be revised.

9. Response: The meaning of the term canopy compensation point is quite clear to the authors. However, it is true that the manuscript contains some misleading statements,

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which will be changed. The term “chemical equilibrium” is never used to describe the compensation point. Regarding HONO the knowledge about a canopy compensation point is very limited and therefore the discussion was focused on the influence of NO_2. However, to avoid misunderstandings, we will add a definition to introduce the canopy compensation point concentration.

10. Response: see previous responses; The fact that χ_c lies in the range of former studies (from Europe or North America) is just stating that we have modeled fluxes in such a way that the overall results found in temperate regions can be reproduced. Surely, this is accompanied by a large uncertainty, but given the lack of surface-atmosphere exchange measurements in tropical regions, this was the only choice we had. In this context we would like to note that although most parameters (e.g., pH) were the same as in temperate regions, the temperature was much higher in our study, an effect that was compensated by implying a low N status of the ecosystem (low Γ). $R_c(NH_3)$ was not directly compared to other studies, we just explained how it was approximated (see below).

11. Response: The ammonia desorption peak after sunrise (and also the high ammonia concentration after sunrise, Fig. 2a) was explained in section 4.5.3 and is also described in:

Trebs, I., F.X. Meixner, J. Slanina, R.P. Oties, P. Jongejan, and M.O. Andreae (2004), Real-time measurements of ammonia, acidic trace gases and water-soluble inorganic aerosol species at a rural site in the Amazon Basin, Atmospheric Chemistry and Physics (4), 967-987.

And

Trebs, I., S. Metzger, F.X. Meixner, G. Helas, A. Hoffer, Y. Rudich, A. Falkovich, M.A.L. Moura, R.J. Da Silva, P. Artaxo, J. Slanina, and M.O. Andreae (2005), The NH_4^+-NO_3^--Cl^--SO_4^{2-}-H_2O system and its gas phase precursors at a pasture site in the Amazon Basin: How relevant are mineral cations and soluble organic acids?, Journal of Geo-

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physical Research-Atmospheres, 110 (D07303), doi:10.1029/2004JD005478.

Exactly this peak was the reason for applying the dynamic resistance model. When using the static canopy compensation point model the overall net deposition flux is higher (about a factor of two). The apparent ammonia emission from drying surfaces after sunrise cannot be modeled using the static approach. When the static model is applied, the net emission peak after sunrise is modeled as a large net deposition and the overall daytime net emission is correspondingly smaller. The authors do not consider this to be representative for the ecosystem under study, since the ammonia flux was certainly determined by absorption/desorption processes by/from epicuticular water films at this tropical site (characterized by high RH and wet surfaces at night and high temperatures during the day). A diagram of the resistance model used was not considered to be necessary since this has been presented in detail by Sutton, M. A., Burkhardt, J. K., Guerin, D., Nemitz, E., and Fowler, D.: Development of resistance models to describe measurements of bi-directional ammonia surface-atmosphere exchange, Atmospheric Environment, 32, 473-480, 1998. A statement regarding the emission peak will be added.

12. Response: The attempt to estimate the importance of coarse aerosol NO_3^- for the dry deposition would clearly go beyond the scope of this study. Aerosol NO_3^- concentrations were low compared to other N compounds and the contribution of the aerosol phase to the total N deposition was found to be marginal. Impactor measurements during SMOCC indicate that there was NO_3^- present in the coarse aerosol fraction. However, it is well known that these types of measurements are not very reliable for semi-volatile aerosol species. Association of NO_3^- with HULIS might be possible, but to our knowledge this was not investigated in detail yet.

13. Response: It is true that wet deposition (NO_3^-, NO_2^- and NH_4^+) was measured on a campaign basis, covering September, October and November 2002. At the same site, but for another period (wet and dry season) wet deposition of NO_3^- was measured (not NH_4^+). see Lara, L.L.; Holland, E.A.; Artaxo, P.; Camargo, P.B.; Martinelli, L.A.

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(2005) Linking biomass burning and nitrogen pattern deposition in tropical regions. Biogeochemistry (in press). Pauliquevis, T; Lara, L.L. (2005) Precipitation chemistry in Amazonia in two different land use sites. Atmospheric Environment (Submitted)

The annual result obtained in this paper for wet deposition of NO_3^- is consistent with the results of Lara et al., 2005 and Pauliquevis Lara, 2005. The rain water concentration values measured during SMOCC (dry, transition and wet seasons) were extrapolated for the whole year. In order to ensure the accuracy of the data long-term data on rainfall amounts (historical time series) were used to estimate the annual wet deposition. See Lara, L., Artaxo, P., Martinelli, L. A., Victoria, R. L., Camargo, P. B., Krusche, A., Ayers, G. P., Ferraz, E. S. B., and Ballester, M. V.: Chemical composition of rainwater and anthropogenic influences in the Piracicaba River Basin, Southeast Brazil, Atmospheric Environment, 35, 4937-4945, 2001.

Some more explanations about this will be added to the manuscript.

14. Response: The accumulation of NO_2 in the nocturnal boundary layer took indeed place during the night due to reaction of NO with O_3. Hence, O_3 is consumed during nighttime in the absence of photochemistry. The minimum of the O_3 mixing ratios was around 7 am (two times lower than during the night), exactly the time when NO was peaking. The sun rises just after 6 am and the convective boundary layer started to develop. This means that the two statements are totally independent from each other since one process takes place during nighttime and the other one during sunrise. Additionally, rapid HONO photolysis during sunrise may be partially responsible for the large NO peak. This comment will be added to the paragraph.

15. Response: This calculation will be changed and the entire aerosol mass will be taken into account.

16. Response: This is correct and the authors are very grateful for this comment. The use of the term R_c within the framework of the bi-directional surface-atmosphere exchange model needs to be revised (particularly the corresponding equations). The

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differences between the R_c modeling approach and the canopy compensation point modeling approach for NH_3 will be elaborated. Figure 5 will be changed to Figure 5a and 5b presenting the component resistances R_s and R_d. Moreover, R_c(HONO) will be eliminated from the calculation and from Table 3, which implies that no scenario will be calculated for the HONO flux (Figures 7b and 9b will be adapted).

17.Response: That comment is related to the previous one and the same answer is valid. Clearly, the approach for the calculation of $R_s(NH_3)$ needs to be corrected. R_s will be derived from LE during daytime for the high and low flux scenario. The authors are not aware that literature data of R_s derived from LE for B. brizantha grass species exist. Stomata might have partially closed due to high vapor pressure deficit in the afternoon. (cf. Kirkman, G.A., A. Gut, C. Ammann, L.V. Gatti, A.M. Cordova, M.A.L. Moura, M.O. Andreae, and F.X. Meixner (2002), Surface exchange of nitric oxide, nitrogen dioxide, and ozone at a cattle pasture in Rondonia, Brazil, Journal of Geophysical Research-Atmospheres, 107 (D20), 8083, doi:10.1029/2001JD000523.

18. Response: The pasture does not receive any fertilizer. A statement will be added in section 2.1. The value of 8 % refers only to direct NH_3 emissions from excreta, but not the second effect. The low soil N status was mentioned in section 4.4.4.

19. Response: The sentence will be changed to: “After sunrise when the increase in surface temperature causes the NH_3 partial pressure above the epicuticular solution to increase in accordance to Henry’s law, χ_d increases, which increases χ_c.”

20. Response: A comment on this will be added.

21. Response: This comment is related to comments 16 and 17. The first sentence of section 4.6.1 (... ’use’ non-zero values of R_c ...) will be changed accordingly. However, the deposition only scenario was calculated using equation 1. For this approach, R_c can be calculated from R_s and R_d , which should be valid. The statement that χ_c was set to zero will be deleted because is it misleading in that context. Setting $\Gamma = 0$ will not lead to a deposition only scenario since only χ_s will be zero, but χ_d will not.

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22. Response: There seems to be some misunderstanding here. The upper estimate for NH_3 deposition was calculated exactly by using $\chi_{(zref)}$ combined with estimates of $R_c(z_{ref})$, R_b and R_c according to equation 1. This means that the existence of a canopy compensation point was totally neglected (see last comment).

23. Response: This will be clarified.

24. Response: As stated in the paper, the nighttime emission would be due to higher epicuticular pH values, which are attributed to surface water chemistry. A high concentration of alkaline compounds or a lower acid concentration in surface water films may be responsible.

25. Response: This is true.

26. Response: Excess NH_4^+ is only partially neutralized by sulfate, but a large fraction is neutralized by organic acids. See: Trebs, I., S. Metzger, F.X. Meixner, G. Helas, A. Hoffer, Y. Rudich, A. Falkovich, M.A.L. Moura, R.J. Da Silva, P. Artaxo, J. Slanina, and M.O. Andreae (2005), The The NH_4^+-NO_3^--Cl^--SO_4^{2-}-H_2O system and its gas phase precursors at a pasture site in the Amazon Basin: How relevant are mineral cations and soluble organic acids?, Journal of Geophysical Research-Atmospheres, 110 (D07303), doi:10.1029/2004JD005478.

27. Response: “Only cases of net deposition were considered” means exactly that hourly upward fluxes and downward fluxes were separately summed up for each season. The statement is simply that 7.3 - 9.8 kgN ha^{-1} yr^{-1} are deposited and 2.7 - 6.8 kgN ha^{-1} yr^{-1} are emitted. The formulation will be revised. Some of the discussion and Figure 13 will be changed.

28. Response: This will be clarified.

Reply to technical corrections:

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

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Response: This will be changed.

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

Response: This will be changed.

31. Section 2.2. Please add model numbers, manufacturers and/or references to the instrumentation used (e.g. DMPS, APS).

Response: The DMPS was home-built at the division Div. of Nuclear Physics, Lund University (Sweden) and a reference was used for this in the paper. Rissler, J., Swietlicki, E., Zhou, J., Roberts, G., Andreae, M. O., Gatti, L. V., and Artaxo, P.: Physical properties of the sub-micrometer aerosol over the Amazon rain forest during the wet-to-dry season transition - comparison of modeled and measured CCN concentrations, Atmospheric Chemistry and Physics, 4, 2119-2143, 2004.

The APS was the type TSI APS 3310, this information will be added.

32. Eq. (2). Denominator should read "(z_{ref}-d)" (two occurrences). Same again three lines below Eq. (2).

Response: For z_{ref} = 5.3 m and a zero-plane displacement of about 10 cm the difference between z_{ref} - d and z_{ref} is about 2 %, such that zero-plane displacement was neglected in our study.

33. d (zero-plane displacement height) is used in the text but does not appear to be defined.

Response: "d" appeared accidentally in the text, this was removed.

34. Throughout the text u^* should read u_* (i.e. subscript rather than superscript).

Response: This will be changed.

35. Section Heading 3.3. Suggestion: "Determination of Chemical Time Scales for Turbulent Transport and Chemistry"

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Response: The authors don't agree on this change.

36. Eq. (4): R_c should not appear in this equation (cf. 2nd RHS of Eq. 5, which is correct).

Response: This will be corrected.

37. Eq. (9): Why write "$(\sigma_w{}^2/u_*)^{-1}$" rather than "$u_*/\sigma_w{}^2$"?

Response: This will be changed.

38. Page 3144, line 5. 're-formed' instead of 'formed back'.

Response: This will be changed.

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."

Response: This will be changed.

40. Page 3145, line 12: Better English: "provides a test" rather than "allows to test". Alternatively: "allows ... to be tested ..."

Response: This will be changed.

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.

Response: This will be changed.

42. Section 4.1, last sentence. Suggestion: '... conditions was presented by Trebs et al. (2005)."

Response: This will be changed.

43. Section 4.2, first sentence. Better: 'Median diel variations in concentrations of NO,

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...'

Response: This will be changed.

44. Section 4.3. Write "NH_3-HNO_3-NH_4NO_3" instead of "NH_3-NO_3-NH_4NO_3" (at least 4 occurrences).

Response: This will be changed.

45. How was WSOC measured? Did I miss this in the methods section?

Response: WSOC was measured using filter samplers. This information was not included in the methods part because, as mentioned in the paper, these results are presented in detail by: Response: WSOC was measured using filter samplers. This information was not included in the methods part because, as mentioned in the paper, these results are presented in detail by: Fuzzi, S., Decesari, S., Facchini, M.C., Cavalli, F., Emblico, L., Mircea, M., Andreae, M.O. Trebs, I., Hoffer, A., Guyon, P., Artaxo, P., Rizzo, L.V., Lara, L.L., Pauliquevis, T., Maenhaut, W., Raes, N., Chi, X., Mayol-Bracero, O.L., Soto, L., Claeys, M., Kourtchev, I., Rissler, J., Swietlicki, E., Tagliavini, E., Schkolnik, G., Falkovich, A.H., Rudich, Y., Fisch, G., Gatti, L.V. : Overview of the inorganic and organic composition of size-segregated aerosol in Rondônia, Brazil, from the biomass burning period to the onset of the wet season, to be submitted to Journal of Geophysical Research, 2005. That reference will be added.

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.

Response: Yes, these time scales were derived experimentally. Some more explanations will be added to that paragraph.

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

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the recent study by Stutz et al. (2002)."

Response: This will be changed.

48. Suggestion: Change heading of Section 4.4 to "The inferential approach: selection of input parameters"

Response: This will be changed.

49. Page 3157, line 10. "If the epicuticular water film were >4.5 and Γ constant

Response: This will be changed.

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

Response: This will be changed.

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

Response: PM 2.5 and PM 10 is generally not written in subscript throughout the manuscript.

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

Response: This will be changed.

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

Response: This will be changed.

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

Response: This will be done.

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

Response: This will be changed.

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56. Table 2 and Fig. 2. Mixing ratios (ppb) are not suitable units for aerosol concentration. I suggest the use of either μeq m^{-3} or μg N m^{-3} throughout, possibly with the exception of O_3. This will maintain inter-comparability between compounds.

Response: Mixing ratios were used to make the paper and corresponding measurement values compatible to papers by Trebs et al. published before. Conversion factors from ppb to μg m^{-3} will be added to the figure caption for each species.

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

Response: This will be done.

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.

Response: This will be changed.

Interactive comment on Atmos. Chem. Phys. Discuss., 5, 3131, 2005.