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Atmospheric Chemistry and Physics Discussions

Interactive comment on "Biogenic emissions of NO_x from recently wetted soils over West Africa observed during the AMMA 2006 campaign" *by* D. J. Stewart et al.

D. J. Stewart et al.

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Referee #1

1. Flux calculation: time dependent vs. steady-state

Comment The authors do not justify the way they have set up their flux calculation (section 3.4). They assume that at sunrise NOx concentrations are the background concentrations measured over dry soil. Then between sunrise and the time of observation (˜8-10 hours later), constant soil NOx emissions are applied. Are there no biogenic emissions at night? The observations were typically 18 hours-3 days after a rain event, so why assume that the soil NOx production only occurred since sunrise?

Response Yes there are biogenic emissions at night and on previous days but as explained in the paper (p16264 lines 7-9) emissions are only considered from sunrise on the day of the flight as the night time monsoon flow would tend to disperse NOx accumulated before dawn. The dispersal of this NOx overnight may also explain the significant concentrations of NOx over the dry soils although the reviewers comment that NOx is emitted from dry soils could also explain this.

Comment Why assume that the initial NOx concentrations at sunrise are at the values observed over the dry soil? The dry soil measurements are also taken in the afternoon and that NOx is also subject to the same NOx processes as the NOx over wet soils.

Response The NOx over the dry soils are taken as the background as it is assumed in the absence of NOx emitted due to recent rainfall over the wet patch on the day of the flight the concentrations over the two regions would be the same, i.e. we have calculated the flux required to produce the extra NOx observed following recent rainfall.

Comment Why not, more simply, assume that the NOx concentrations are at steady-state, such that H = H L Cwet. This eliminates the need to assume a time over which soil NOx emissions occur and also does not require any assumptions about the background NOx concentrations. In practice this gives results that are very similar to the ones obtained with equation (3), especially for short lifetimes (for OH = 5e6 and 1e7 molec/cm3, the NOx lifetime is 4 and 2 hours, respectively using the values given by the authors). For OH = 0 and 1e6 molec/cm3 the NOx lifetimes are much longer: 9 days and 21 days. Actually a 9 day lifetime for NOx is unrealistically long and there is no reason to believe that OH concentrations would be zero and there would be no chemical loss. I suggest removing the case where OH = 0 from the paper.

Response We thank the reviewer for the suggestion of using the steady-state approach to calculate the NOx fluxes. The paper has now been revised to include calculations of this kind. We also agree that the case for OH = 0 is not realistic, it was originally included to the paper to give an extreme limit of the possible fluxes but we concur with

ACPD

7, S9470–S9481, 2008

the referee that it should be removed.

Comment Also, a more detailed discussion of the OH observations on board the aircraft would be useful. What range of values were observed under what conditions?

Response The OH data requires further work before a definitive discussion of OH measurements can be made. This work is currently being carried out by the FAGE group at the University of Leeds and will be the subject of their own paper in due course. The authors feel that at the present time a range of observed values throughout the West African boundary layer is the best we can do at this stage of the analysis.

2 Flux calculation: Dry vs. wet

Comment It appears that the authors assume that soils that have not been wetted recently do not emit NOx. Field measurements (for example summarized by Davidson et al., 1997) show that semi-aid soils emit little NOx during the dry season, but then after an initial pulsing following the first rains of the season, soil NOx emissions are lower but still significant during the remaining of the wet season. Indeed Stewart et al. measure significant background NOx concentrations over dry regions (outside the wet regions), with values ranging from 210-400 ppt. If there are no other significant sources in this region (biomass burning or fossil fuel combustion) as suggested by low VOC and CO correlations, then significant soil NOx emissions would be needed to maintain these high NOx concentrations, especially given the deeper boundary layer height. In fact assuming steady-state and the same OH levels as the authors, I find that the soil NOx emissions needed to maintain these observed NOx levels are about 25-60% lower than over wet soils. The factor of 3 difference in NOx concentrations is counterbalanced by the factor of 2 difference in boundary layer height. These fluxes cannot be neglected.

Response We agree with the referee that we should have considered emission of NOx from the “dry” soils. In light of the referees comments we have included calculations of the steady-state flux from dry soil required to maintain the NOx concen-

ACPD

7, S9470–S9481, 2008

trations over the dry soil. These are discussed along with the other flux calculations in the revised manuscript.

3 Significance of calculated flux (section 3) Comment The authors scale up their flux over a wet patch to a 2.3 million km2 over the Sahel. They assume that at any given time 11% of that region has seen recent rainfall and apply the following formula:

Total N = F x A x 0.11 x t

For a 2-month period between July and August they find these regions account for 0.01-0.05 TgN. They assume that the regions outside these recently wetted areas do not emit biogenic NOx. Again, this is not realistic (see section 2 above). Using flux values inferred from NOx observations over dryer areas, I calculate that these dryer regions emit significant levels of NOx. Applying the following formula (assumeing that these fluxes occur over the remaining 89% of the region):

TotalN (dry) = Fdry x A x 0.89 x t The resulting NOx emissions range from 0.001 (OH=0) to 0.3 Tg! Adding the two together, NOx emission over the Sahel range of 0.01 to 0.36 Tg. Combined to the top-down satellite estimates in Jaegle et al. (1994) of 0.19 Tg, these values are not too different, and even exceed them by a factor of 2 at the high end of the OH concentrations assumed.

Response The authors acknowledge this point and the upscaling calculation has been reconsidered to include the contribution from the dry soils over the Sahel region.

4 Comparison to Delon et al paper in ACPD

Comment The authors briefly mention the Delon et al paper which applies a mesoscale model and a neural network approach to modeling the soil NOx emissions. Given that there is significant overlap between the two papers, it would be useful to see more of a discussion comparing the results of the Stewart et al. paper. For example how do the model calculated soil NOx emissions in Delon et al compare to the simpler upscaling approach presented in the present paper?

ACPD

7, S9470–S9481, 2008

Response In the revised paper the fluxes calculated for B227 are compared to those derived from the model of Delon et al. Also the results of upscaling the fluxes to the Sahel region are also compared.

5 Other comments + page 16257, line 2. What is the detection limit and accuracy of the TECO instrument? The values are given for the UEA NOxy instrument but not for the TECO.

Response This information has been added to the relevant part of the paper.

Comment Given the main argument against an anthropogenic origin for the NOx is the lack of correlation with CO, I suggest that the authors show the CO measurements on Figure 3.

Response The authors thank the referee for his suggestion but feel that the addition of another trace to these figures would be detrimental to the clarity reducing the effectiveness of the figures. We believe that stating that there is poor correlation and providing the correlation coefficient should be sufficient.

Referee #2

Comment Page 16255, line 22-24 It is strongly recommended, that in a revised version of the paper, a certain piece of text should be found, where the issue of the atmospheric transformation of NO to NO2, the (fulfilled/not fulfilled) assumption of photostationary equilibrium between NO-NO2_O3, etc. is elucidated to potential (non-specialised) readers of ACP.

Response Text has been added so the relevant sentence now reads: “Although emissions from soils are in the form of NO (Conrad 1996), once in the atmosphere NO is rapidly converted to NO2 by reaction with ozone, some of this NO2 can subsequently be photolysed back to NO, through this cycle of reactions a photostationary state between NO-NO2 and ozone can be established.” Whether the system is in photostationary state or not does not matter for the calculations presented here as

ACPD

7, S9470–S9481, 2008

the concentration of NOx (NO + NO2) is considered.

Comment Page 16257, lines 3-6 (and elsewhere) The problem of non-specific conversion of the molybdenum converter (TECO) is addressed; however, discussion and conclusions from the data $<$1ppb certainly still need more quantitative elaboration (particularly some enhanced statistical uncertainties).

Response More statistical analysis has been done on the data, the uncertainties in the gradient of the comparison plot have been calculated based on the standard deviation and 95% confidence interval, these values have been added to the paper.

Comment The results of Steinbacher et al (2007) would expect 27-50% systematic overestimation by the TECO instrument (rather that only 16% as found by the authors). The findings of Dunlea et al (ACP, 7, 2691-2704, 2007) would rather support 50% systematic overestimation. In this respect the authors’ own findings on page 16265, line 16-19, namely “in the latter case the PAN levels were of the order of 60 ppt whilst the TECO instrument was overestimating NOx by around 200 ppt” will certainly grab the attention of any (experienced) reader.

Response The results of Steinbacher et al. and Dunlea et al. are representative of environments very different from those experienced in West Africa during AMMA. The magnitude of the overestimation of NO2 by TECO type instruments is of course dependent on the concentrations of oxidised nitrogen species such as PAN, nitric acid and organic nitrates. Nitric acid would be expected to be low in the region discussed in this paper as in the boundary layer nitric acid is rapidly deposited to the surface. PAN concentrations were also generally low (up to 60 ppt in regions with active photochemistry) due to the rapid thermolysis of PAN in the tropical boundary layer. Also the organic nitrate concentrations observed during AMMA are also low with an estimated upper limit of 20 ppt for the sum of organic nitrates for flight B227 (G. Mills pers. Comm.). In view of these low concentrations it is not surprising that the observed overestimation of the TECO is lower than that reported in the literature as the measurements of Dunlea

ACPD

7, S9470–S9481, 2008

et al were conducted in a polluted urban atmosphere (Mexico City) and those of Steinbacher et al. although conducted in rural Switzerland are not far from the industrialised areas of Northern Europe and so PAN and organic nitrate concentrations would be expected to be much higher. In summary the atmosphere of West Africa is generally much cleaner that that of Mexico City and Switzerland – this means that the potential to form high concentrations of compounds that would cause an overestimation of the TECO type method of NOx measurement is low.

Comment Page 16264; eq. (1) The validity of eq. (1) presumes a variety of (justified?) assumptions (as stated by the authors), e.g. negligible horizontal and vertical advection of NOx, as well as negligible vertical divergence of NO-, NO2- and O3-fluxes in the entire atmospheric boundary layer. The serious problem of (NO-, NO2-, O3-, etc.) advection has been already addressed by referee #2 (Delon et al.), as well (to some extent) by referee #1 of this paper. However, the neglecting vertical divergence entirely (just on the assumption of complete vertical mixing) seems a bit risky (without any further proof). Is there no support (for “complete” mixing) from vertical profiles of (virtual) potential temperature, or any other scalar quantity? How, Delon et al (2207) have handled this problem?

Response As we state in the paper, page 16264 lines 14-17 “These assumptions are simplifications, not least the neglect of horizontal and vertical mixing of NOX, which will be significant at the length scales analysed here. A more realistic mixing assumption would increase the flux required to maintain the observed concentrations” We unfortunately have no chemical data in profiles over the wet regions but the paper of Taylor et al. 2007 (fig. 3) shows dropsonde data from B224 of potential temperature and humidity mixing ratio. These are very uniform in the boundary layer. A sentence stating this is included in the revised paper.

Comment Page 16246, eq. (2) This equation contains definitely the wrong sign in the exponent of the (most right hand side) exponential function.

ACPD

7, S9470–S9481, 2008

Response We thank the reviewer for pointing out this typographical error, the equation has been corrected.

Comment The dry deposition of NO2 to west African soils (vegetation?) may be low, but vd(NOx) = 9 x 10-2 cm/s could be considered dramatically low. Giving the rich treasure of related literature, the authors are kindly asked to consider more than one reference for it (a few examples are given below; “references(1)”).

Response The referee is correct in his statement on the wealth of literature available on NO2 deposition velocities, however, the importance of the deposition velocity on the flux calculation is a small factor due to the much faster loss by reaction with OH (increasing the deposition velocity from 0.09 to 1 cm/s changes the calculated fluxes by less than 0.25% for OH greater than 1e6 cm-3. The value used in the paper may be on the low end of the available literature values but even if the higher ones were chosen the effect on the calculated fluxes would be small.

Comment Page 16255, line 18-21, page 16260, first para, page 16266, line 17-18, page 16267, first para, and page 16267, line 16-18 The authors obviously do not belong to the biogeochemistry/soil flux community. For a revised version of their paper, the authors may consider the fact that, that the biogenic NO emission (F(NO)) from soils is a strongly non-linear function of soil moisture (water filled pore space, WFPS), i.e. the emission follows an optimum curve (the reviewer suggests for semi-arid, sandy soils: a narrow maximum of F(NO) around WFPS <=0.2). This fact may help in particularly interpreting the results in sub-chapters 3.2 and 3.3. It will particularly address the question of biogenic NO emission vs. wetting and/or (fast?) drying of soils. By the way, on page 16267, line 5, the authors claim to have used data of satellite measurements of soil moisture. So, if the data on soil moisture are available, why not to make explicitly use of the known dependence of F(NO) vs. WFPS? The authors will find a lot of information and helpful support in this direction in the papers cited at the end of referee#2’s comments (“references (2)”).

ACPD

7, S9470–S9481, 2008

Response The spatial resolution of the AMSR-E soil moisture data is of the order of 50 km, though the data are gridded at 25-30 km. Due to this resolution the data do not resolve the fine scale surface features which we identified from boundary layer concentrations as producing large NO fluxes. Also the satellite data used in the estimation of the area of the Sahel that had been recently wetted detects soil moisture only in the top ˜1cm of the soil and soil moisture in this layer decays rapidly after rainfall (within hours), soil moisture at greater depths will persist for longer. Satellite overpasses occur typically once per day, so the sensor cannot accurately quantify surface soil moisture away from the overpass times. Also in order to obtain WFPS from this data a map of soil porosity would be needed, this could be obtained from the FAO map but in W. Africa this data is not terribly accurate and the information used to produce it is not of high spatial resolution. Therefore we feel that calculation of WFPS from the satellite data would not add value to the paper. What the AMSR-E data can provide, however, is a qualitative indication at the larger scale of whether the soil has been wetted. This is how the data is used on page 16267.

Comment Page 16265, ff Like referee#1 of this paper, referee#2 also wonders that “the authors assume that soils that have not been wetted recently do not emit NOx”. The authors are kindly referred to corresponding literature which will provide them with some helpful data and material (given at the end of referee#2’s comments, (“references (3)”). Particularly, the authors may find Otter et al. (1999) interesting on the effects of “pulsing” and re-wetting on the biogenic emission from semi-arid African soils.

Response In light of the comments of both reviewers a section will be added to the paper in which the steady state fluxes required to maintain the NOx concentration over the wet and dry soils are calculated and text has been added to the paper to clarify the effect of rainfall and drying on NO fluxes.

Comment Page 16266, line 12 There is a more recent review on “NO from soils…for a variety of land surface types in Africa and other tropical re-

ACPD

7, S9470–S9481, 2008

Interactive Comment

gions” than the 1977 review of Davidson and Kingerlee (namely Meixner and Yang, 2006, see “references (3)”).

Response We thank the reviewer for bringing to our attention this review, we have taken some of the data presented in this review and added it to Fig 6. We have also added this review to the reference list.

Comment Page 16267 and 16268, section 3.6 Referee#2 agrees 100% with the referee#1 of this paper, as far as criticism on the authors’ flux estimate is concerned.

Response The calculation has been redone in light of the comments of referee#1

Comment Page 16269, line 6-8 To judge whether or not “Figure 7 shows a good correlation” some more information, e.g. statistical quantities (n=?, P(0.05, P(0.01), etc.) might be helpful

Response The uncertainties in the gradient of this plot have been calculated using the 95% confidence interval. This results in a 95% probability that the gradient lies between 6.99 and 7.91. The authors believe this shows that the correlation is good. This (as well as the number of points in the graph) has been added to the figure caption. An “F-test” on the data shows that the correlation is significant at the 99.9% level.

Comment The referee of this manuscript (Stewart et al.) is also the referee of another paper (Delon et al., Nitrogen oxide biogenic emissions from soils: Impact on NOx and ozone formation in West Africa during AMMA ACPD 7, 15155-15188, 200&), which has been also submitted to the ACP Special Issue on the AMMA 2006 campaign. The authors of the present paper have mentioned that in their manuscript once, page 16256, line 10-18. There are only two more citations of the paper by Delon et al., namely page 16262, line 2-5 and page 16269 line 10-21. In turn, Delon et al. made only two (minor level) references to Stewart et al. namely on page

ACPD

7, S9470–S9481, 2008

15167, line 19-22 and page 15168 line 15-16. Both papers make some mutual use of data and/or results. It is undoubtful that both papers share an identical aspect of one of the major present time scientific endeavours (the AMMA project). On the other hand, the reader of both papers (in their present form) is hardly able to deny a substantial lack of coordination between both papers. However, that would not only be desirable from a scientific point of view, it is being supposed to have occurred with respect to the well-known and high level of (scientific) coordination within the AMMA project. In their present form, both papers received substantial criticism (see: http://www.cosis.net/members/journals/df/article.php?paper=acpd-7-15155, particularly with respect to “not very thorough comparison between the different soil NOx emission methods/simulation results with the measurements” and to considerable “flaws in the interpretation of the flux measurements and their extrapolation”. The referee feels, that more and also more comprehensive coordination of both papers would easily overcome these criticisms. Moreover, with respect to the high importance of the common scientific issue, it is strongly recommended to join both papers; any (anticipated) arguments about an (oversize) length of such a joined paper should not discourage the authors: two (companion) papers sharing the same title, but separated into “Part I” and “Part II” should even increase the attractiveness and importance of both papers.

Response The titles of both manuscripts (Stewart et al. and Delon et al.) have been changed to Biogenic nitrogen oxide emissions from soils: Impact on NOx and ozone over West Africa During AMMA (African Monsoon Multidisciplinary Analysis with the current paper adding “Observational Study” and that of Delon et al. adding “Modelling Study” to emphasise the connectivity of the two papers. To further emphasize this connectivity the following text has been added to the manuscript: “Delon et al (2008) is a companion paper to this one which models the impact of soil NOx emissions on the NOX and ozone concentrations over West Africa during AMMA. It employs an artificial neural network to define the emissions of NOX from soils, integrated into a coupled chemistry-dynamics model. The results are

ACPD

7, S9470–S9481, 2008

Interactive Comment

compared to the observed data presented in this paper. Here we compare fluxes deduced from the observed data with the model-derived values from Delon et al.” at the end of the abstract. Also parts of the manuscript have been reworded to bring more attention to the study of Delon et al. and how the two manuscripts are related.

Minor corrections

Page 16255, line 3 “Prather and Enhalt” rather than “Prater and Enhalt”

The authors thank the referee for pointing out this typographic error. The error has been corrected.

Interactive comment on Atmos. Chem. Phys. Discuss., 7, 16253, 2007.