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## ***Interactive comment on “Processes of ammonia air-surface exchange in a fertilized *Zea mays* canopy” by J. T. Walker et al.***

**J. T. Walker et al.**

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Author response: “Processes of ammonia air-surface exchange in a fertilized *Zea mays* canopy” by J. T. Walker et al.”

We appreciate the comments and suggestions of the two reviewers of this manuscript. The reviews are included below along with responses to each comment.

Interactive comment on “Processes of ammonia air-surface exchange in a fertilized *Zea mays* canopy” by J. T. Walker et al.

Anonymous Referee #1 Received and published: 27 July 2012 This paper deals with the description and the quantification of the ammonia (NH<sub>3</sub>) exchange between the soil-crop system and the atmosphere in a corn crop, grown in an agricultural site in

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North Carolina, USA. The crop was fertilized with urea ammonium nitrate solution (UAN) containing a urease inhibitor and the dynamic of  $\text{NH}_3$  exchange has been followed for 10 weeks. The work is excellent, both from the experimental and the results presentation points of view. All the sections are well written and clearly presented, with the right dose of details and synthesis when the ammonia exchange processes are described and illustrated for the different compartments: soil, soil-crop interface, foliage, canopy-atmosphere interface, atmosphere. The measurements of all the variables were carried out by well established methods and equipment, in order to minimize all the possible uncertainty linked to the values determination. The interesting results, relative to the chance of improving nitrogen efficiency considering crop managements to optimize the re-adsorption of soil  $\text{NH}_3$  by overlying vegetation, should be investigated also for other important agricultural crops, which need to be highly fertilized for assuring stable yields, also under different climates. Particularly important seems to be the outcome of the research concerning the  $\text{NH}_3$  emitted from the soil and its recapture by leaves in function of their moisture status. The study suggests that further research is needed for understanding the ammonia dynamics during the whole crop growth cycle, from plantation to harvest, by following the different sources/sinks by suitable measurement at different LAI values. New experimental approaches are requested by the authors in order to improve the parametrization in the models of the  $\text{NH}_3$  bi-directional exchange. Further, specific experiments should be performed for better understanding the role and the behaviour of a urease inhibitor, for different types of soils and under different climates. Considering the large number of reported results, the only improvement for helping the reader is to add letter label “a, b, c. . .” in Figures with more than one graph and to cite them in the text with the right number and letter label (e.g Figure 4 has to be cited as 4a, 4b and 4c).

Response: We have labeled figure 4 and referenced the figure in the text as suggested.

Moreover, maybe a few details about the cited source/sink model (Bash et al., 2010) could be added in an appendix.

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Response: We have added a short description of the source/sink model as supplemental material.

Therefore, this article is surely acceptable under the present form for the discussion on Biosciences.

Minor points 1. Page (P) 5 Line (L) 10: delete one comma.

Response: Corrected

2. P6 L21: a dot is missed after “. . .experiment”.

Response: Corrected

3. P6 L23: delete comma before “and 500 ppb” and be coherent with unit for concentration (ppb or microg/m3).

Response: Comma has been deleted. Liquid standards, as opposed to gas phase standards, are often reported in ppb. We have left the liquid standard concentration units unchanged.

4. P7 L2: delete comma before “and 2-D”.

Response: Corrected

5.P10 L7: delete comma before”and moisture”.

Response: Corrected

6. P11 L11: delete sentence “AMANDA. . . 214”, it is a repetition.

Response: Sentence has been removed as suggested.

7. P12 L18 and L24: it is Wolff et al., (2010).

Response: Corrected

8. P18 L11:add “u\*,” after “Friction velocity,” to introduce the symbol.

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Response: The symbol for friction velocity is now defined at first occurrence.

9. P19 L22: it is “emission”.

Response: Corrected

10. P20 L24-25: in the section Material and method add how these analysis (K+, Mg<sup>2+</sup>, Ca<sup>2+</sup>) are performed.

Response: Information has been added as suggested.

11. P21 L24: add the range of night time temperature.

Response: Range of hourly median night time temperatures has been added.

12. P22 L2: define RH.

Response: Relative humidity (RH) is now defined at first occurrence.

13. P28 L18, L19 and L23: be consistent with the form of time (hh:mm or hhmm).

Response: Corrected

14. P23 L25-27 and P24 L1-6: it is a repetition: you have already discussed it at P17 L3-13.

Response: This section has been removed and a reference to section 3.4 has been added.

15. P25 L8: delete comma before “and the resistance to turbulent. . .”.

Response: Corrected

16. P25 L16-19: define the average time of data plotted in Fig 10.

Response: The averaging times for soil volumetric water and air concentrations have been added to the figure caption.

17. P26 L22: delete comma before “and Fw”.

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Response: Corrected.

18. P33 L12: it is “Mecklenburg”

Response: Corrected

19. P37: add meaning of S.D and N.

Response: S.D. and N have been defined as standard deviation and number of observations, respectively.

20. P38: could you add pH in order to better follow the description in the text?

Response: We were unsure of the meaning of the reviewer’s question.

21. P43: there are not references to trend in RH in the text.

Response: The trend in RH is mentioned in reference to the morning period in which the canopy dries on page 18, line 25.

22. P44: indicate the period of senescence on Fig. 6. 2

Response: The approximate onset of senescence (DOY 200) is now indicated in the text (Page 19, line 13).

3. P45: delete comma before “and leaf”.

Response: Corrected.

24. P46: could you plot also standard deviation?

Response: The data points represent individual measurements.

25. P47: add meaning of N.

Response: N has been defined as number of observations.

Interactive comment on “Processes of ammonia air-surface exchange in a fertilized Zea mays canopy” by J. T. Walker et al. C. Flechard (Referee) [chris.flechard@rennes.inra.fr](mailto:chris.flechard@rennes.inra.fr)

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Received and published: 16 August 2012

Referee's comments on bg-2012-225 discussion paper : "Processes of ammonia air-surface exchange in a fertilised *Zea mays* canopy" by J.T. Walker et al.

General comments This excellent paper reports measurements of the net surface/atmosphere NH<sub>3</sub> exchange above a fertilised maize field over a 2.5-month period up to peak LAI, and identifies the main internal ecosystem cycling processes and gross fluxes within the plant/soil system that control the overall net exchange. By using a combination of micrometeorological techniques, plant bioassays, soil and leaf surface chemistry, incanopy measurements of turbulence and vertical NH<sub>3</sub> profiles, and an analytical in-canopy first-order closure source/sink model, the authors hardly left a stone unturned, and were able to quantify the individual source-sink contributions of soil/fertiliser, plant stomata and other (non-stomatal) foliar surfaces. The authors also present a very useful error analysis for measured NH<sub>3</sub> fluxes. Key findings are the large fraction (73%) of fertiliser-emitted NH<sub>3</sub> that was re-captured by the overlying foliage, and the counterintuitive notion that wet foliage was a less efficient sink for NH<sub>3</sub> than a dry canopy at this site, due to a large leaf surface pH. The paper is very well written, logically constructed, and certainly a welcome addition to the NH<sub>3</sub> flux literature and to the Nitrogen and Global Change Special Issue of Biogeosciences, and may be published in its present form (subject to very minor technical corrections, see below), although the authors might wish to address/comment on the few discussion points I raise hereafter.

Specific comments Abstract, p7894, l28 to p7895, l1: "Inverse source/sink and resistance modeling indicated that the canopy recaptured \_73% of soil emissions near peak LAI". The last 3 words are important, but they are missing from Fig. 11, which may suggest to the unobservant reader that the canopy recaptured 73% of soil emissions averaged over the whole season.

Response: This point has been clarified in the legend of Fig. 11.

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As the in-canopy profile experiments were carried out near peak LAI (DOY 187-213, i.e. last 3 weeks of July), the recapture rates are representative of a fully closed canopy, but not of a developing canopy with lower LAI and higher wind penetration. During the in-canopy experiment, the canopy recaptured a large fraction of what may have been a much reduced flux (compared with early season). The soil emission potential ( $\gamma$ ) was around 100,000 on DOY 190 and declined to around 5,000 on DOY 207 (versus 250,000 on DOY 150) (Fig. 6), and Fig.10 may indicate that the decline from DOY 192 to DOY 214 was exponential and continuous. On the other hand, from DOY 150 to DOY 180, LAI was lower (range 0.5-2.5) and the emission potential much higher. In short, it might be interesting to speculate what the overall recapture rate was for the whole growing season, rather than just at peak LAI, since the soil/fertiliser emission and capture efficiency are (temporally) inversely correlated. Fig.4 (top panel) may suggest that  $\text{NH}_3$  is lost to the atmosphere as long as the canopy is not closed, and then there is a large recapture rate, but another interpretation is that by the time the canopy is closed, there is not much emitted  $\text{NH}_3$  to recapture anyway. In many agricultural situations fertiliser can only be applied onto a short, young, open canopy, and thus the potential for recapture by the canopy should not be over-rated.

Response: We agree with the reviewer. While we have not speculated on the potential for total recapture of soil emissions by the canopy over the entire growing season, we do add this point of clarification in the conclusions section.

p7899, l15-17, "Glass impactors with cutpoints of  $2.5 \mu\text{m}$  aerodynamic diameter were used to remove particles from the air sample stream". Should there not be an  $\text{NH}_3$ -specific capture by denuders, without interference by  $\text{NH}_4^+$  aerosols which should pass unaffected through the tubes due to much lower lateral diffusion to the inner tube surface? Why use impactors?

Response: Yes, that is true. We used impactors to avoid sampling of large soil particles, particularly at heights very close to the ground, which would have a greater tendency to deposit on the denuder walls.

p7906, I2-3: "Uncertainty is greatest in the early morning when the heat flux and temperature gradient are small (Fig. 2)". Actually Figure 2 shows highest flux uncertainty during the night and before sunrise (00 - 05 am), not really in the early morning. The highest uncertainty occurs at night during temperature inversion, when there is a negative heat flux and an inversed T gradient.

Response: We have modified our interpretation of the uncertainty profile base on the reviewer's comments. We have also added some additional detail to the uncertainty analysis.

p7910, I19-22: "...concentrations increase rapidly in the morning with the post sunrise increase in the momentum flux. This spike in concentration, which is accompanied by an emission pulse, likely represents the upward mixing of NH<sub>3</sub> that accumulates near the ground..." Could such rapid changes in concentration and storage in the air column have induced a significant error in flux measurements during the morning NH<sub>3</sub> peak? Were any tests for instationarity, and/or corrections, applied?

Response: It is possible that instationarity may have induced some error in the flux measurements during the post sunrise period. However, this was not quantitatively addressed in our uncertainty analysis. We have added a point of clarification in the text.

p7910, I22: "... below the lowest NH<sub>3</sub> measurement height...": was there any evidence of this from the in-canopy denuder NH<sub>3</sub> measurements ?

Response: As discussed on page 7910, the early morning peak in emissions was coincident with decreasing concentrations within the canopy.

p7914, I8: "As shown in Table 3, net canopy-scale emissions at night were larger when the canopy was wet, indicating that the wetting of the canopy, and the accompanying high pH of the surface water, increased the cuticular resistance to NH<sub>3</sub> uptake and reduced the capacity of the canopy to recapture soil emissions". An alternative expla-

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nation may be that wet canopy conditions may correlate with rainfall (unless only dew conditions were selected?), and thus with wet soil, which triggers urease hydrolysis (Fig. 10). The increased cuticular resistance hypothesis for wet conditions (versus dry conditions) only holds if the soil emission potentials are similar for both sets (wet vs dry) of data. If the soil emission potential was generally higher in wet conditions, then the analysis may be biased. A first indication could be given in Table 3 with the average SWC values, and if possible  $\gamma_{\text{soil}}$  or near-surface  $\text{NH}_3$  concentrations, for the 4 categories. Another option is to analyse dew-only conditions (exclude nights with a rain-wetted canopy).

Response: The reviewer raises an important point, which is that nights with dew may also correspond to nights in which soil emissions are larger. In an attempt to remove the possible bias in soil emissions between wetness categories we removed days on which rain was measured. For period 1 the results were similar and soil volumetric water was very similar between dry nights and dew wetted nights. We therefore assume that the differences in night time fluxes between wetness categories are not the result of differences in soil emissions. The results for period 2 are not as easily interpreted. After removing days on which rain was measured, there persists a difference in soil volumetric water between night wetness categories of about 0.05, the higher content corresponding to wet canopy conditions and higher net canopy fluxes. It is therefore possible that the higher soil volumetric water associated with nights on which dew occurred also resulted in higher soil emissions and net canopy scale emissions. Therefore, larger emissions for dew wetted canopy conditions may not have been entirely due to high pH of the leaf surface water. We have included this additional analysis in the text.

p7917, I21-23: "The correlation between the concentration of  $\text{NH}_3$  just above the soil surface and soil moisture likely reflects the linkage between soil moisture and the resistance to  $\text{NH}_3$  diffusion through the soil profile, which decreases non-linearly with increasing soil moisture". This may be true, but over the same time period,  $\gamma$

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values in soil decreased by a factor 20 from 100,000 (DOY 190) to around 5,000 (DOY 207) (Fig. 10). Unfortunately there were no intervening measurements of gamma to tell if this decrease was continuous and exponential. It could be that the decrease in gamma alone can explain the decrease (by a factor of 3) in near-soil-surface NH<sub>3</sub> concentration over the same interval.

Response: This is a very good point. We have added this possible explanation to the text and modified the discussion on page 7917 accordingly.

#### Technical corrections

Table 3: It seems there is an error in the calculated  $V_e$  for Period B/wet, with  $V_e = 8.1/2.2 = 4 \text{ mm/s} = 0.4 \text{ cm/s}$ , not  $0.22 \text{ cm/s}$  ?

Response: In this analysis the mean  $V_e$  was calculated from individual 30 minute observations of F/C. This yielded a mean value of  $V_e = 0.22$ , which was driven by a small population of very high concentrations. We now include median values in the summary table to account for the effects of skewed F and C distributions.

Reference to Flechard et al 1999: the actual title is "A dynamic chemical model of bidirectional ammonia exchange between semi-natural vegetation and the atmosphere." (not "Modelling of ammonia and sulfur dioxide exchange over moorland vegetation").

Response: This embarrassing oversight has been corrected.

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Interactive comment on Biogeosciences Discuss., 9, 7893, 2012.

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