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Biogeosciences Discussions



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

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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 NH3 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, in-canopy measurements of turbulence and vertical NH3 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 NH3 fluxes. Key findings are the large fraction (73%) of fertiliser-emitted NH3 that was re-captured by the overlying foliage, and the counter-intuitive notion that wet foliage was a less efficient sink for NH3 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 NH3 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. 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 developping 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



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capture efficiency are (temporally) inversely correlated. Fig.4 (top panel) may suggest that NH3 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 NH3 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.

p7899, l15-17, "Glass impactors with cutpoints of 2.5 $\mu$m aerodynamic diameter were used to remove particles from the air sample stream". Should there not be an NH3-specific capture by denuders, without interference by NH4+ aerosols which should pass unaffected through the tubes due to much lower lateral diffusion to the inner tube surface? Why use impactors?

p7906, l2-3: "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.

p7910, l19-22: "...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 NH3 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 NH3 peak? Were any tests for instationarity, and/or corrections, applied?

p7910, l22: "... below the lowest NH3 measurement height...": was there any evidence of this from the in-canopy denuder NH3 measurements ?

p7914, l8: "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 NH3 uptake and



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reduced the capacity of the canopy to recapture soil emissions". An alternative explanation 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_soil or near-surface NH3 concentrations, for the 4 categories. Another option is to analyse dew-only conditions (exclude nights with a rain-wetted canopy).

p7917, l21-23: "The correlation between the concentration of NH3 just above the soil surface and soil moisture likely reflects the linkage between soil moisture and the resistance to NH3 diffusion through the soil profile, which decreases non-linearly with increasing soil moisture". This may be true, but over the same time period, gamma 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 NH3 concentration over the same interval.

Technical corrections

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

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

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