

Interactive comment on “Nitrogen oxides and ozone fluxes following organic and mineral fertilisation of a growing oilseed-rape” by Raffaella M. Vuolo et al.

Anonymous Referee #2

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The manuscript presents eddy covariance flux measurements for O₃, NO and NO₂ over an arable field during 8 months between August and the following April. The flux data processing and quality assessment appears sound. The discussion of the NO fluxes (with influence of fertiliser application) and the chemical reactions of the NO-NO₂-O₃ triad show that the related gas phase chemistry below the flux measurement height can have a considerable effect on the NO and NO₂ fluxes but only a very small relative effect on the O₃ flux. This finding is in agreement with previous similar studies (e.g. Stella et al., 2012).

However the discussion of the O₃ deposition (velocity) and its temporal variation is quite disappointing in its present state. In the discussion of the 8-months time series

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of ozone fluxes, the authors mainly concentrate on 2 weeks in August pointing out that the deposition velocity after slurry spreading (average midday values around 0.6 cm/s) was much larger than for the rest of the observation period (average midday values around 0.2 cm/s). They then search for processes that can explain the higher deposition velocity and identify reactive VOC compounds as the most likely cause. I see major shortcomings in this evaluation and interpretation that are detailed in the following comments.

MAJOR COMMENTS

- 1) A comparison of the observed O₃ deposition velocities with previously published data is largely lacking, although it would be very important to compare the magnitude of the values observed in this study with literature results.
- 2) It is particularly astonishing that the authors do not compare their observations with results for the O₃ deposition velocity by Stella et al. (2011) observed over bare soil at the same site. This comparison would reveal that the deposition velocities after slurry application presented here are very similar to previous results over bare soil up to 1 cm/s (also without slurry application). Thus the deposition velocity after slurry spreading are obviously not exceptionally high, but quite normal for bare soil. The need for a special additional chemical sink is therefore not so clear. It rather needs to be discussed why the deposition velocities in the other periods were exceptionally low in the present study, i.e. lower than in other studies over arable/wheat fields (see e.g. Potier et al., 2015, Agric. For. Meteorol.).
- 3) As shown by Stella et al. (2011) the O₃ soil resistance, and thus the deposition velocity, for bare soil strongly depends on the soil surface temperature and/or on the relative surface humidity (for an overview of related processes, see Fowler et al., 2009, Atmospheric Environment).

In Figure 8 (and 7a/b) it can be seen that the strong increase of the dep. velocity at slurry application coincides with a strong increase of the daytime surface temperature

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by about 15°C (from <25°C to >40°C). I suggest that the authors apply the relationship for R_soil derived by Stella et al. (2011) to their own dataset, and discuss the deviation of the measurements from that relationship.

4) Figures 5 and 6 are mentioned only shortly in the text and do not provide much additional insight. They could either be omitted or at least reduced (Fig. 5 to one season/whole experiment; Fig. 6 to flux histograms).

5) Title: I am not sure if the title is really appropriate. It makes not much sense to focus on the comparison of "fluxes following an organic and a mineral fertilization" if the first was in high summer and the second in deep winter. It would be more appropriate to mention the observed seasonal/management cycle for the winter crop in the title, and also to discuss it more profoundly.

MINOR COMMENTS

6) Line 160: Please explain what "filtered for outliers" means here. I guess it was a kind of smoothing and gap filling procedure?

7) Line 165: This equation is only valid, if the raw ozone signal has no offset. Why did you not use an analyser sensitivity here (like in the following equations)?

8) Line 166/167: It is unnecessarily confusing to use "s" in these equations twice for two different quantities (in size scaled equations the uppercase and lowercase "s" are often difficult to distinguish). I would recommend to use two different symbols instead for the raw signal and the analyser sensitivity.

9) In Eq. 3 the left side should read "F_NO2" (the subscript 2 is missing in my copy)

10) Line 169: It is not fully appropriate to talk of a "NO2 sensor signal" because there was no NO2 sensor. It would be more correct to name it "NOx sensor signal" or "BLC signal", from which the NO2 flux was derived as a difference to NO (acc. to Eq. 3).

11) Line 171: It is quite confusing to use the same (or a very similar) symbol for the

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molar volume and for the deposition velocity in this manuscript. Volumes are generally represented by an uppercase "V". I would suggest to use here the symbol "V_dry".

12) Line 226: This formulation is confusing. Were there two high frequency losses? I think this should be rephrased to "The first main uncertainty was ..."

13) Line 235f.: How was this high uncertainty effect for NO2 quantified in the uncertainty calculation?

14) Line 298: "which was probably due to a dryer soil in this study." It is not clear which study is meant here. Please make a clearer distinction between "this/these" and "that/those".

15) Lines 346-356: this paragraph is oddly placed here. It should be combined with the text in chapter 3.7.2.

16) Line 401-417: This paragraph with Eq. 10 to 12 should be moved from the discussion to the method section, since this calculation already has been applied previously for the same site (e.g. Stella et al., 2012).

17) Line 420: "Mainly" can be omitted here.

18) Line 448: "is constant" should be omitted here.

19) Line 481f.: If it is assumed that very reactive VOCs significantly contribute to the gas phase destruction of O3 it should also be discussed what the effect of these VOCs on NO could be.

20) Line 770: The unit "N L min-1" is very uncommon. Better use standard liter "sL min-1".

21) Figs. 4, 7, 8, 9: It would be very useful for the reader to use consistent color coding for NO, NO2 and O3 throughout the figures.

22) Fig. 10: The axis labelling is not complete.

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