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

Answer to Anonymous Referee #2
Received and published: 16 August 2016
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 NONO2-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-month time series 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.

We thank Referee #2 for this comment. We have put more emphasis on NO and NO_2 than O_3 in this manuscript because, as spotted by referee # 2, we have already published a lot of results on O_3 on this site while NO and NO_2 flux measurements are newer. We nevertheless propose to include a result and discussion section specifically on ozone fluxes and deposition velocity. We agree that we might have put too much emphasis on the potential reaction between VOC compounds and O_3 in the current manuscript and therefore propose to compare our O_3 deposition velocity with existing literature and especially with the parameterisation we had on bare soil in Stella et al. (2011).

MAJOR COMMENTS

1) A comparison of the observed O_3 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.
This is indeed a good comment. We have included in the Figure R2 below the ozone deposition velocity during the period as averaged daily patterns. We propose to include Figure R2 and the following short paragraph in a supplementary material S6 section on ozone seasonal pattern:

S6. Seasonal pattern of O_3 deposition velocity and NO fluxes

We found similar magnitude of ozone fluxes in August and September as those reported by Stella et al. (2013) over a meadow during the summer. We also found similar nocturnal O_3 deposition velocity as found by Stella et al. (2011) over bare soil during summer, but higher daily maximum (0.8 cm s-1 instead of 0.5-0.6 cm s-1). We further find a similar midday magnitude as Stella et al. (2011) found in April with wetter soils. Night-time ozone deposition velocity does not go lower than around 0.2 cm s^{-1} in our study, as also found by Zhu et al. (2015) over a growing wheat in China, Stella et al. (2011) over bare soil in summer, and Lamaud et al. (2009) over maize. These authors as well as Huang et al. (2016) clearly show that this is due to non-stomatal deposition being primarily driven by u_* which does not reach zero at night during these periods. We can hence conclude that we found consistent ozone deposition in August and September compared to other studies at that site or in other geographical areas. When compared to previous years on the same site the deposition velocity measured during the winter in this study was clearly smaller. We interpret this as being primarily due to u_* being smaller that winter compared to other winters as well as due to a slow growth of the winter crop due to soil drought in September (SWC =20% in the 15 cm horizon).

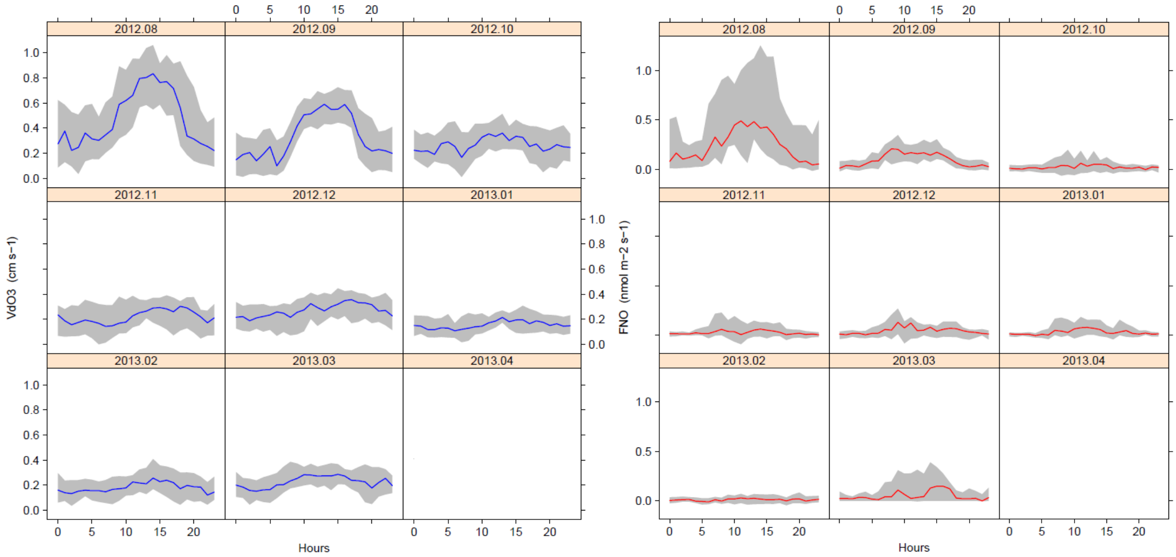


Figure R2. Seasonal changes of ozone deposition velocity VdO3 and NO fluxes. Lines show median and grey area inter-quantiles.

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 is 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.).

As just exposed in the answer to question 1) of Referee #2, we found similar night time deposition velocities as in Stella et al. (2011) but larger daytime values during the summer and similar as in April 2007, which showed also wetter soils. Regarding the other periods, the fact that we report smaller ozone deposition velocity than in Potier et al. (2015) is due to the periods which are spanned in this study: from August to March, which correspond to the period with the lowest stomatal component and also the smallest non-stomatal component because of the small leaf area index of the rapeseed. This winter also showed an especially low u_*.

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 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.

This is a very good suggestion which we followed. We propose to add Figure R3 and R4 together with the following paragraph in the supplementary material S7 section on ozone seasonal pattern:

S7. Comparison of ozone fluxes to Stella et al. (2011)

In order to compare to previous studies of ozone deposition to bare soil on the same site, we have calculated the soil surface resistance as in Stella et al. (2011) and deduced the ozone deposition velocity as $V_{dO3} = (R_{soilO3} + R_{bO3} + R_a(z_{ref}))^{-1}$*. In this way, we can compare the two studies while excluding any confounding factors (roughness and turbulent exchange intensity). We can see in Figure (R3) that the measured ozone deposition velocity during August follows most of the time the parameterisation of Stella et al. (2011) except for some days including 18 and 19 August which corresponds to slurry application and 24, 25, 26 August, which follows a small rainfall. We also see an overestimation of the Stella parameterisation before the18 August, which we interpret as being due to the straw and wheat residues laying on the ground before slurry incorporation. This comparison hence demonstrates that the ozone deposition was indeed increased slightly following slurry application and subsequently following rainfall. This may be either due to a physical reason (increased surface exchange on the soil due to tillage or humidity change due to slurry) or a chemical reason (surface reactivity* *changes due to added organic matter or VOC emissions from slurry). Figure R4 further shows that the main differences are observed for wet soils and relatively low temperatures (this is after rainfall) and to a lesser extent for dryer and hotter situation (following slurry spreading).*

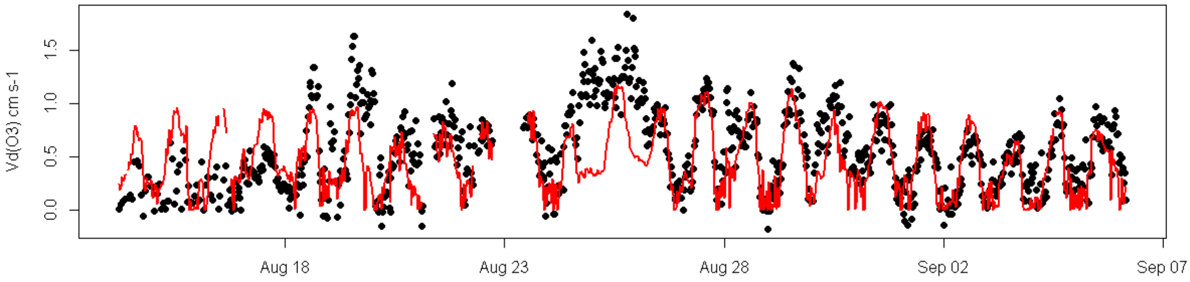


Figure R3. Comparison of ozone deposition velocity from this study (black dots), and from the parameterisation of Stella et al. (2011) (red line) based on surface temperature.

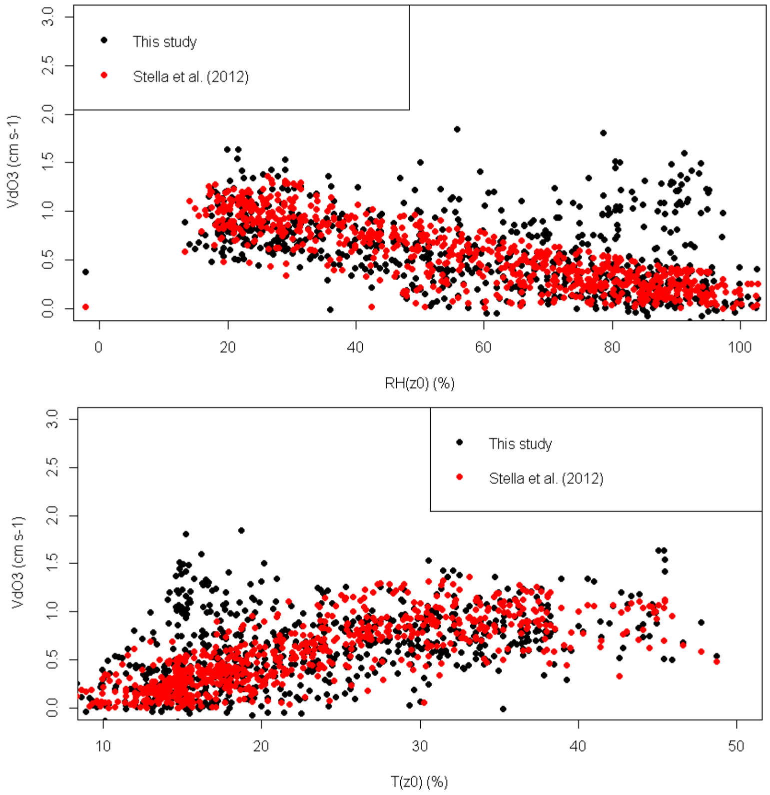


Figure R4. Response of ozone deposition velocity to surface humidity RH(z_0) and surface temperature T(z_0). Shown are data from this study and from the parameterisation of Stella et al. (2011). Period from 14 August to 6 September which is before and after slurry spreading and corresponds to Figure R3

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).
That sounds like a fair suggestion. However we feel that these are still important and therefore propose to put these two figures in a supplementary material section S5, and refer to in the text. *"S5 Wind roses and histograms of NO, NO2 and O3 concentration at the site."*

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.
This is a sound suggestion. We propose to change the title to: *“Nitrogen oxides and ozone fluxes above oilseed-rape with emphasis on organic fertilisation”*

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?
Points away from median lag ± standard deviation were considered as outliers for the lag.

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)?
Thank you for this comment. Indeed, the ratio method as described in Muller et al. (2010) and as applied here, considers that the signal has no offset. The alternative methods, computation of the flux by use of sensitivity and offset values, fixes this problem but, on the other hand, present shortcoming in terms of offset and sensitivity determination. Indeed, this kind of fast-sensor make use of cumarine disks whose sensitivity decrease on a weekly timescale, but this is not taken into account in the sensitivity estimation by signal regression or by disk calibration, that assumes sensitivity to be constant for each disk. We chose the ratio method that neglects offset but takes into account the sensitivity variation along the lifetime of the cumarine disks. An example of regression between fast- and slow- sensors signals for a three-day period is given in fig. R5. With a negative offset of 0.04V, the relative error on the flux, that can be estimated as the ratio between the offset and the raw signal, would range between about 4% to 20% (for ambient concentration of 80 and 20ppb respectively).

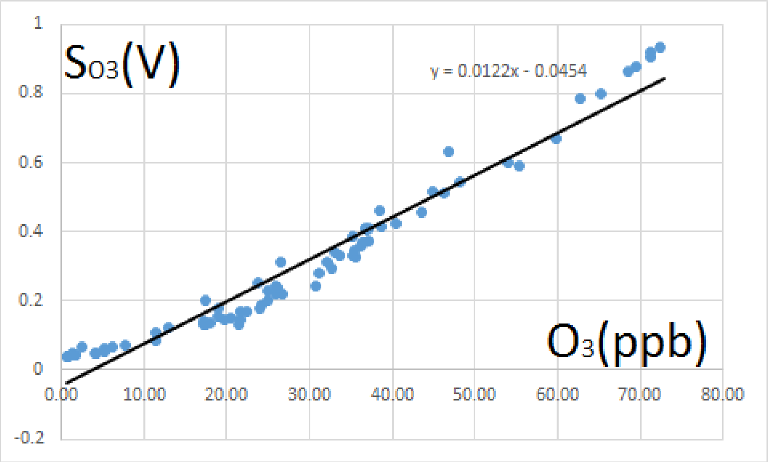


Figure R5. O3 fast sensor signal versus slow-response analyser signal. Half-hour means for a period of 3 days.

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.
We propose to use now the name of the compound instead of *s* for signals.

9) In Eq. 3 the left side should read "F_NO2" (the subscript 2 is missing in my copy)
Thanks for spotting this. We propose to change for F_{NO2}.

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 "BLCsignal", from which the NO2 flux was derived as a difference to NO (acc. to Eq. 3).
Thanks for this suggestion. We propose to use BLC signal.

11) Line 171: It is quite confusing to use the same (or a very similar) symbol for the 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".
Thanks for this suggestion. We propose to use v_{dry} instead. Overall we propose to change text and equations frm lines 165 to 173 as:.

$$F_{O3} = \frac{\overline{\chi_{O3}}}{V_{dry}} \frac{\overline{w'O_3'}}{\overline{O_3}} \qquad (1)$$

$$F_{NO} = \frac{\overline{w'NO'}}{S_{NO} V_{dry}} \qquad (2)$$

$$F_{NO} = \frac{1}{\alpha V_{dry}} \left(\frac{\overline{w'NO_x'}}{S_{NO2}} - \frac{\overline{w'NO'}}{S_{NO}} \right) \qquad (3)$$

where O_3(in mV), NO and NO_x (in counts s^{-1}) are the uncalibrated fast signals, χ_{O3} is the 30 min average of the slow-sensor reference O_3 mixing ratio (in ppb), while S_{NO} and S_{NO2} are the sensitivity of the analysers (in counts s^{-1} ppb^{-1}). α is the blue light converter conversion efficiency, and $V_{dry}$is the molar volume of dry air (in m^3 mol^{-1}). All fluxes (momentum, heat, CO_2, H_2O, NO, NO_2, O_3) were computed by the Eddypro software and final flux data were averaged for 30 min intervals. Evaluation methodologies from the CarboEurope project were applied - see (Aubinet et al., 2000 ; Loubet et al., 2011).

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 : : :"

Indeed this formulation was misleading. We propose to rephrase with *"The largest uncertainty …"*. We then rephrase Line 220 as *"The second largest uncertainty …"*

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

Actually, we have mistaken here NO_2 for NO_x. As the uncertainty analysis was performed on the NO_x channel. Hence we have changed the text accordingly: *"A higher random uncertainty was found for NOx fluxes which were smaller than NO fluxes and with a relatively low conversion ratio from NO2 to NO (30%)"*

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".

We propose to change for: *". Stella et al. (2012) measured larger peak of NO emissions following slurry spreading, but only lasting two to three days, which was probably due to a dryer soil in our study compared to Stella et al. (2012). "*

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

This is a sound suggestion we propose to move and cut this paragraph to include section 3.7.2 as follows: *"Reactive VOCs such as sesquiterpenes and monoterpenes were previously found to be emitted from soils (Horvath et al., 2012; Penuelas et al., 2014), and some of these sesquiterpenes species react with O_3 in the order of a few seconds. The reactions of O_3 with larger terpenes are important sources of OH, as well as the ozonolysis of simpler unsaturated compounds. (Donahue et al., 2005). "*

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).

This is indeed a good suggestion. We propose to move lines 402-417 to a supplementary section after the chemical time scales (actual sections 2.7):

S3 Evaluating the flux difference between ground and the reference height

When chemical timescale is shorter than transport timescale, chemical reactions affect concentrations and fluxes, resulting in flux divergence. This causes the flux at the measurement point to be different from the surface flux. The flux difference can be evaluated with a method developed by Duyzer et al. (1995) based on the early developments of Lenschow (1982) and Lenschow and Delany (1987). This method assumes a logarithmic profile of the flux divergence and depends on measured mixing ratios, stability function and friction velocity:

$$(\partial F/\partial z)_z = a \ln z + b \qquad (10)$$

$$a_{NO_2} = -a_{NO} = -a_{O_3} = -\Phi_H/ku_* \left[k_r \left(\overline{[NO]} F_{O_3,z_{ref}} + \overline{[O_3]} F_{NO,z_{ref}} \right) - j_{NO_2} F_{NO_2,z_{ref}} \right] \qquad (11)$$

Here $\overline{[NO]}$ and $\overline{[O_3]}$ are mixing ratios which should ideally refer to the geometric mean height of the profile measurements but was taken from the measurement height in our study, z_{ref} is the measurement height and Φ_H is the stability correction function for heat estimated at z_{ref} (Dyer and Hicks, 1970). Coefficient b of Eq. 10 can be computed as $b = -a \ln(z_2)$ where z_2 is the height above which the flux divergence is zero. Duyzer et al. (1995) showed with numerical simulations that the NO_x flux divergence could be approximated by Eq. 10 below a height of 4m, while it was negligible above. We refer to 4 m as the reference height z_2 at which we assume the *flux divergence to be zero. Equation 10 can be integrated from measurement height to any height, for each compound giving:*

$$F(z_{z0}) = F(z_{ref}) + a(1 + ln(z_2))(z_{ref} - z_0) - a[z_{ref} ln(z_{ref}) - z_0 ln(z_0)] \quad (12)$$

We propose to replace *"Mainly due"* at start of Line 420 by *We quantified this variation by numerically solving Eq. 12, based on the model of Duyzer et al. (1995). Due*

17) Line 420: "Mainly" can be omitted here.
We propose to delete.

18) Line 448: "is constant" should be omitted here.
We propose to delete.

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.
This is a sound remark indeed. VOCs are known to form intermediates $R\dot{O}_2$ and HO_2 radicals which react with NO, converting NO to NO_2 (Atkinson, 2000). Once VOCs are emitted, they are broken down chemically into free radicals. The degradation reactions of VOCs lead to the formation of intermediate RO_2 and HO_2 radicals that can further react with NO, converting NO to NO_2 which, after photolysis, form O_3.

$HO_2 + NO \rightarrow OH + NO_2$

$RO\cdot_2 + NO \rightarrow RO\cdot + NO_2$

The ozone formation chain is then determined by the competition between the peroxy radicals (HO_2) reactions and NO and the peroxy radical termination reactions. The factors that affect the number of NO molecules converted to NO_2 will also affect the rate of O_3 formation. These factors include radical sources and sinks, NO_x sinks and reaction pathways of NO molecules converted to NO_2 in the VOC's degradation mechanism. The photochemical formation of O_3 vs. photochemical loss of O_3 in the troposphere depends therefore on the NO concentration and is determined by the rate of the reaction of the HO_2 radicals with NO. (Atkinson, 2007; Monks, 2005).

20) Line 770: The unit "N L min-1" is very uncommon. Better use standard liter "sL min-1".
We have several example of NL min-1. However if editor suggest better using sL we propose to change for sL.

21) Figs. 4, 7, 8, 9: It would be very useful for the reader to use consistent color coding for NO, NO_2 and O_3 throughout the figures.
We propose to set all colors as blue for O_3, green for NO_2, and red for NO. We have hence changed figure 7b to the following:

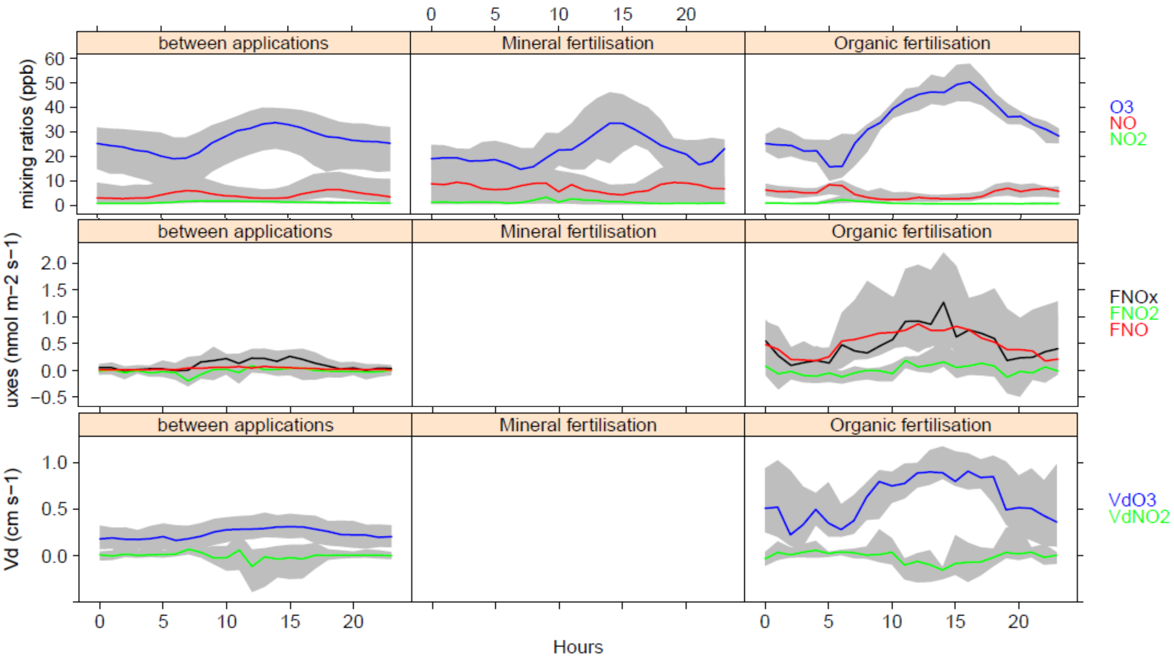
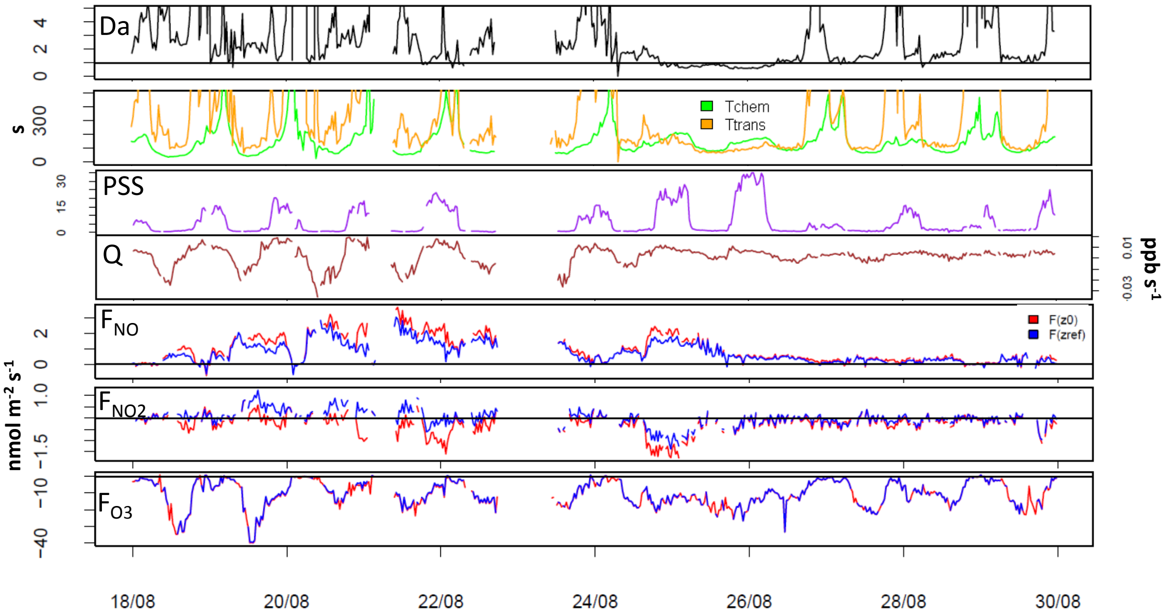


Figure 7b. Diurnal cycles of NO, NO_2 and O_3 mixing ratios and fluxes as well as the deposition velocities of NO_2 and O_3, averaged over the three periods of interest at the Grignon field site. The shaded areas represent the interquartile range.

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

Indeed, although Da and PSS has no units, Q units are missing. We propose to add labels (ppb s^{-1}). The new figure 10 looks like this:



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