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 #1
Received and published: 3 August 2016
I thought this was a very well written article, summarising a study which used the eddy covariance method to monitor variation in NO_2 + NO (NO_x) and O_3 in a field of oilseed rape. As the authors point out, there have been few papers which have measured NO_x and O_3 in the field using this technique and none which have measured them in an agricultural setting. One initial thought it that the article is fairly long, and the editor may feel that some information, particularly in the methods section, may be trimmed.
We thank referee #1 for this supporting comment. Regarding the methods section, we are open to editor's proposal to move part of it in a section of the supplementary material. We propose to suppress title in line 182 and merge with title in Line 174 as *"Spectral corrections and flux uncertainties"*. We further propose to move sections 2.6 and 2.7 in supplementary material sections S1 and S2 and write a condensed description of these sections below line 189:

"2.5 Chemical reactions, time scales and flux divergence

Chemical reactions between NO, NO_2 and O_3 are important to consider when interpreting the measured fluxes as they can affect the fluxes above the ground. A common way to determine whether these reactions may indeed affect the flux is through comparison of chemical and transport time scales. Details of the reactions rates, times scales and flux divergence calculations are given in supplementary material sections S1-S3."

The results and discussion sections are comprehensive and insightful. I have a limited number of comments/questions listed below.

Line 30 – NO_x are toxic to humans above a certain critical limit (http://ec.europa.eu/environment/air/quality/standards.htm) and are also potentially damaging to ecological systems above a critical load (http://www.apis.ac.uk/indicative-critical-load-values). There are similar, but lower, values relevant to ozone. This is worth mentioning in the introduction. I think these discussions would help to put your findings in the context of air quality issues. These could be referred to again in the discussion. What do your findings mean in relation to pushing concentrations towards critical limits?
We thank referee #1 for this comment. We already mentioned toxicity of NOx and O3 at lines 3O and 35. Indeed, NO_x and O_3 are toxic to humans and animals. Similarly nitrogen deposition leads to serious adverse effects on vegetation (eutrophication, biodiversity erosion and acidification being the most serious ones), while O_3 has a direct adverse effect on plant health through oxidation of photosynthesis pathways and direct tissue destruction above large thresholds. We propose to remove the following text lines 20-31 "NO_x, and especially NO_2, are toxic gases for humans (WHO, 2013) and national and international authorities regulate their levels", and line 35 *"is a major tropospheric pollutant, harmful for humans and ecosystems, and"*, and add the following text after line 36:
"NO_x, and especially NO_2, are toxic gases for humans, increasing risks for various respiratory diseases. World Health Organization gives guidelines for NO_2 exposure limits, both annual means (40 µg m^{-3}) and 1-hour mean (200ug/m3) (WHO, 2005: Air quality guidelines for particulate matter, ozone, nitrogen dioxide and sulfur dioxide). For ozone, only a short-term threshold is given (100ug/m3 for 8-hour mean) because there are fewer studies on long-term exposure. These thresholds are established both on epidemiological and toxicological studies on humans and animals. Similarly nitrogen deposition leads to serious adverse effects on vegetation (eutrophication, biodiversity erosion and acidification being the most serious ones), while O_3 has a direct adverse effect on plant health through oxidation of photosynthesis pathways and direct tissue destruction above large thresholds. For nitrogen, the concept of critical load has been developed which gives the amount of nitrogen deposition above which an ecosystem is impacted. These critical loads range from 5 kg N ha^{-1} yr^{-1} for sensitive habitats to 20 kg N ha^{-1} yr^{-1} for less sensitive ones (APIS, 2016). For these reasons, national and international authorities regulate atmospheric levels of these pollutants."

We propose to also refer to it in the conclusion section as follows (added after line 500):

"Our findings show that NO emissions from agricultural soils are limited (0.27% of the N-NO applied over the 8 month period, which with a conservative estimation we can extend to a yearly amount). When extended to France with an average nitrogen fertiliser use of 80 kg N ha^{-1} over a fertilised area of around 26 Mha, this

would lead to emission of NO_x of around ~5.6 t N-NO ha^{-1}, which is negligible compared to transport and industry which is several hundreds of thousand larger (CITEPA, 2015). The seasonality of these emissions may however lead to air quality issues during spring and late summer-autumn which are the main fertiliser application periods. Indeed, most of the emission we measured occurred with a few weeks following fertilisation. In terms of ozone, our findings, and previous ones, show that ozone is efficiently deposited throughout the year. This means that crops are participating through this process in the reduction of the atmospheric oxidising capacity"

Answers to referee #2 provide more details on O_3 deposition analysis.

Mention is made of 'significant difference' in the results section but I am unsure of the precise statistical methods used to derive these conclusions. Please add more detail.

We propose to explain what was meant by 'significant' each time the term is used in the text. The term was misused in line 336 where we propose to replace it by *"The NO_2 flux daily pattern was different"*. Otherwise, we used Student t-tests to check a difference in mean.

This field is surrounded by heavy trafficked roads. To what extent do these roads fall within the flux footprints? Vehicles are prolific producers of NO_x and O_3. The authors have referred to this in part in the ms, but is it possible to use statistics to unpick the contribution of the field and traffic to the different levels? Perhaps by correlation with traffic densities.

This is a good question indeed. The field is surrounded by heavy traffic roads. Unfortunately we do not have traffic statistics at that location for the given period. To answer this question, we propose to evaluate the footprint of the roads using the FIDES flux and concentration footprint model (Loubet et al., 2010), which is essentially similar to the Korman & Meixner model (Kormann and Meixner, 2001) but with a different treatment of the lateral dispersion. Overall the flux footprint from the nearby roads is smaller than 1% (which means that only 1% of the roads emission contributes to the flux at the mast) most of the time, but the concentration footprint reaches up to 10% during some episodes, with different roads contributing differently during different periods.

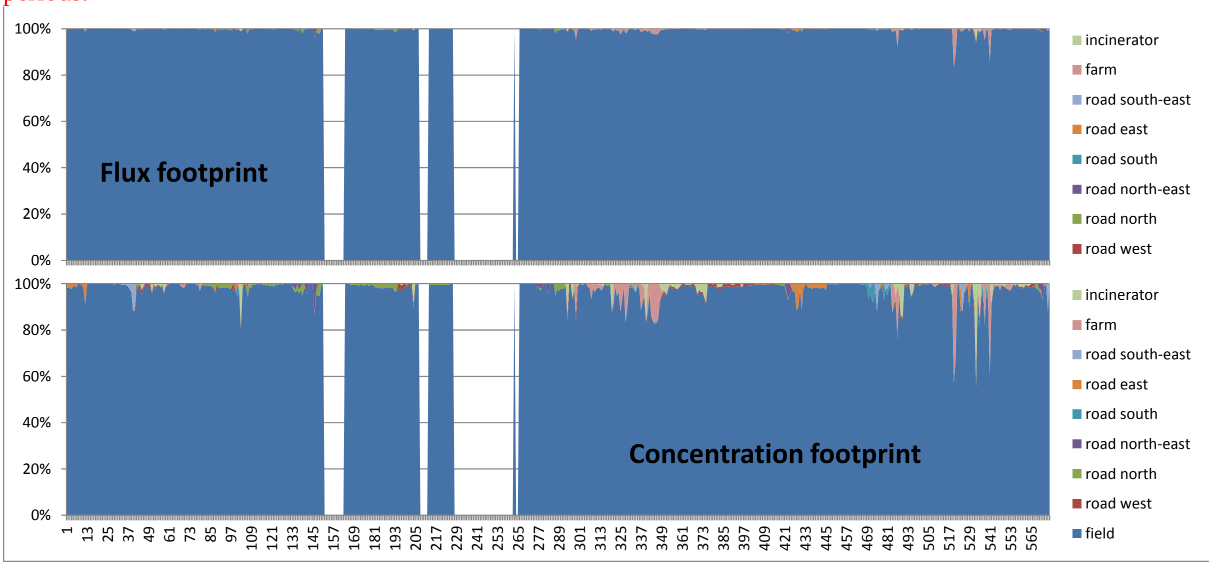

Figure R1. Flux and concentration footprints of the field and surrounding roads calculated with the FIDES model.

Using the flux and concentration footprint allows evaluating the contribution of traffic to the NO_x concentration and fluxes. For that, a conservative emission of 250 mg km^{-1} $vehicle^{-1}$ was considered. The average vehicle count per day ranges from 5000 to 13000 on the surrounding roads (2010 counts, "Statistiques du département des Yvelines pour 2010"). Using an average of 10000 vehicles per day, we can calculate that the flux due to the surrounding roads may be of magnitude 4% to 40% of the measured flux. However, the NO_x vehicles emissions have a sporadic nature: indeed, 10000 vehicles per day means a maximum of 1 vehicle every ~2 second if we consider, conservatively, that most of the traffic is condensed during 9 hours only. This vehicle is moving at say 90 km h^{-1} (25 m s-1) hence leading to a moving point source of NO_x. We therefore expect that the signal of this moving and sporadic source is not captured by the eddy-covariance method, and would be filtered out by despiking and flux calculations (Foken, 2008). From another perspective, we cannot exclude that we have not biased the flux by filtering out the flux coming from the roads as discussed by Mahrt (2010)

We propose to add the following discussion section after line 316:

Using the FIDES flux and concentration footprint model (Loubet et al., 2010) we evaluated the footprint of nearby roads. Overall the flux footprint from the nearby roads was smaller than 1% (which means that only 1% of the roads emission contributes to the flux at the mast) most of the time, but the concentration footprint reaches up to 10% during some episodes, with different roads contributing differently during different periods (Figure S1). Assuming a conservative emission of 250 mg km^{-1} vehicle^{-1} and an average vehicle count 10000 vehicles per day (2010 counts, "Statistiques du département des Yvelines pour 2010" shows range between 5000 and 15000), we evaluate a contribution from 4% to 40% of the road on the measured flux. However, since vehicles emissions of NO_x have a sporadic nature. Indeed 10000 vehicles per day means a maximum of 1 vehicle every ~2 second (if we consider, conservatively, that most of the traffic is condensed during 9 hours only). These vehicles are also moving at say 90 km h^{-1} (25 m s^{-1}) hence leading to a moving point source of NO_x. We therefore expect that the signal of this moving and sporadic source is not captured by the eddy-covariance method, and would be filtered out by despiking and flux calculations (Foken, 2008). From another perspective, we cannot exclude that we have not biased the flux by filtering out the flux coming from the roads as discussed by Mahrt (2010)."

We further propose to include Figure R1 in Supplementary section S4 and add following text to introduce the figure:

"S4 Flux and concentration footprint

The flux and concentration footprint was roughly estimated for each of the major roads around the site. Each road was geo-localised and assumed 10 m width. The FIDES model was computed with field roughness (z_0), friction velocity (u_*) and Obukhov length (L)."

Line 460 - Vehicles also emit VOC which also may affect your interpretation here.
This is true indeed, but the amount of VOC to NO_x emitted is small (below 1% for non methanic VOC, according to French national emissions inventory, CITEPA (2015), not considering CO) and hence the effect on O_3 concentrations and flux is expected to be of second order. Moreover, we see increased O_3 deposition on a period (August) which has the lowest traffic density throughout the year in this area, and we do not see increased deposition during high traffic load days throughout the year, which points towards a small effect of VOC emitted by vehicles on the O3 flux in August.
However, we have tempered our interpretation on the potential effect of VOC emitted by slurry on ozone flux since, as pointed out by the reviewer #2, the increase of ozone following fertilisation may have other physical and chemical explanations.

Technical/minor corrections
Line 10 – '7-months' should be '7 month' or 'over a period of 7 months'
Thanks for this suggestion. We propose to correct for it.

L104 – 'sheep' not 'sheeps'
Thanks for this suggestion. We propose to correct for it.

References

Foken, T.: The energy balance closure problem: An overview, Ecological Applications, 18, 1351-1367, 2008.

Kormann, R. and Meixner, F. X.: An analytical footprint model for non-neutral stratification, Boundary Layer Meteorol., 99, 207-224, 2001.

Loubet, B., Genermont, S., Ferrara, R., Bedos, G., Decuq, G., Personne, E., Fanucci, O., Durand, B., Rana, G., and Cellier, P.: An inverse model to estimate ammonia emissions from fields, European Journal of Soil Science, 61, 793-805, 2010.

Mahrt, L.: Computing turbulent fluxes near the surface: Needed improvements, Agric. For. Meteorol., 150, 501-509, 2010.