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

I think this is an excellent study, with the MS including particularly detailed discussion of the underlying processes which have driven the fluxes measured. I think this adds to our knowledge of NO, NO_2 and O_3 fluxes and would be of interest to the readership of Biogeosciences. Whilst I find the scientific updates to have been well implemented in general, for example I am impressed by the detail given for the response to the influence of the surrounding roads (3.7) I think that some minor changes will still be required before publication. There is still no mention of the statistics in the methods section. I think that this is essential if the reader is to make an informed decision about the drivers of flux increases. What has been tested against what? What was the magnitude of change and what is the statistical output?

The different measurements and their relationship are analysed in sections 3.3 to 3.8. In particular, we focus on the relationship between NO_x and O_3 fluxes and meteorological and soil parameters (sections 3.3.2 and 3.3.4), nitrogen input (section 3.4), surrounding traffic (section 3.5), chemical interactions (sections 3.6 and 3.7), and VOC emitted from slurry (section 3.8). Statistical outputs are given in some cases as level of significance according to the Student-t test, histograms and correlation coefficients, but in several cases we can only argue that a correlation exists because available data only covered one event of interest (for example, one slurry application).
We have also added in the text the statistical following outputs in all Students t-test: the p-values (the probability of the null hypothesis) and the means (lines 256, 399 and in the conclusions section).

Also, whilst I understand that it is not always easy to generate perfect scientific prose, I think that the scientific English should be improved. I have listed a few items which need to be corrected below, but I suggest that the paper be re-read with spelling and grammar in mind.
Specific comments below, though this list is not exhaustive:

21: at all time(s)
Thank you for the suggestion, this was corrected for.

70 and others: nowadays – is not a very scientific term
Thank you for the suggestion, we replaced by "a well-established method" and "currently"

73: is this a quote – ""?
Yes it is indeed. It is actually from Corrsin (1975). We have added some quotes as well as the reference to Corrsin (1975).

83-98: The section reads very much like a list
The idea was to make reference to the studies reporting (to our knowledge) simultaneous NO, NO_2 and O_3 fluxes and to report their main findings. We have slightly rearranged this section with a section on forests then grasslands and other surface types

128: on the oilseed rape field
Thank you for the suggestion, this was corrected for.

131: French for December is included
Thank you for the suggestion, this was corrected for.

136: ~monthly -> approximately monthly
Thank you for the suggestion; this was corrected for (approximately once a month).

169: equation has been included in the main text
Thank you for the comment. We put the expression in a new line.

232: (Paris) – items in brackets must be elaborated upon, or not put in brackets.

Thank you for the suggestion, this was corrected for.

243: NO fluxes were slightly negative part of the time - reword
We replaced “part of the time” by “for some events”

248: and were mostly negative (deposition) – again brackets
We replaced “deposition” by “indicating deposition”

257: during bare soil periods – reword
This text was replaced by the one of the Supplementary Material (see comments of Anonymous Referee #3)

350: stats in brackets in discussion, not enough detail and no statistical output
The t-test statistical outputs are now added here and also each time it was mentioned: the p-value and the means of each sample were added.

421: numbered bullets very long – bullet points are unusual and if included, very brief
Thanks for this suggestion. We have suppressed the bullet points and add some short sentences to follow which hypothesis is addressed in each chapter.

Answer to Anonymous Referee #2

With the revised version, the authors have considerably improved the manuscript. However, there are still some issues that need further revision before the manuscript can be published (see detailed comments below).

MAJOR COMMENTS
It needs to be considered, that the Supplementary material is not an integral and equally valid part of the peer-reviewed manuscript. Therefore, information that is necessary for understanding the discussion and conclusions must not be placed in the Supplementary material but has to be included in the main manuscript. This concerns the following comments 1 and 2.

1) Supplementary section 6 should be integrated in Section 3.3.2 of the main manuscript. The latter is named 'Seasonal dynamics ...' but presently contains only one sentence (Line 260) about seasonal variations, although this is one major aspect of the presented dataset. In contrast, the overall flux statistics presented in Lines 240-250 could be shortened.
We thank anonymous Referee #2 for this remark, and we integrated the ozone deposition velocity subject in section 3.3.2.

2) Fig. S5 and the corresponding text in supplementary section 7 need to be integrated into the main manuscript, in order to make the discussion in Section 3.8.2 understandable.
We thank anonymous Referee #2 for this remark, and we integrated the ozone deposition velocity comparison subject in the main manuscript as subsection 3.3.3.

3) In Section 3.8.2 the authors should probably differentiate more between (a) empirical explanations of the observed ozone deposition velocity by measurable driving parameters like e.g. the parameterisation of Stella et al. and (b) identification of real physical/chemical adsorption and destruction processes like e.g. gas-phase chemical reactions with NO and various VOCs (above soil or within soil pore-space) or heterogeneous chemical and physico-chemical reactions at dry and wet soil surfaces.
This is an interesting comment. Actually in the three hypothesis discussed, the first one corresponds indeed to the empirical explanations based on existing knowledge of the ozone fluxes (specific to that site), while the other two hypotheses belongs to the identification of destruction processes in the gas-phase or at the surface. We however feel difficult to organise the discussion as proposed by anonymous Referee #2 since empirical models by nature include the destruction processes at the surface. We have therefore left this section as such.

4) Line 505ff.: Instead of assessing the significance of agriculture for total NOx emissions from this single site and crop, it would be much more useful to compare the observed NO emission factor to comparable emission factors used in national or international inventories (e.g. EMEP, IPCC, etc.).
Thank you for the comment. We have added the value of emission factor that is cited in the last EMEP/EEA air pollutant emission inventory guidebook, which refers to the 2006 IPCC report. Nevertheless, this is an average

value that does not take into account site-specific parameters as soil pH and fertilizer type. We have added the following sentences in the text:

"… emission factor of 0.27%, which is similar to values reported earlier for the same site (Laville et al., 2011) but one order of magnitude larger than the EMEP/IPCC default value of 0.04 (EEA, 2016). Nevertheless, this is an average value calculated with the Tier 1 approach, which does not take into account correction factors depending on soil pH or fertilizer type. This more detailed approach, the Tier 2, has not been developed for NO."

5) Line 508: The value ~5.6 t N-NO ha-1 is clearly erroneous (concerning value and/or units ha-1). 0.27% of 80 kg N ha-1 yr-1 multiplied by 26 Mha results in an annual total of 5600 t N-NO for the entire country.
Thank you for the remark, indeed the units were wrong (kt instead of t ha-1), this was corrected for. As a consequence, this means also that our estimation would be a factor 40 smaller than the emission from transports, industry and heating.

6) Line 508-512: The argumentation is contradicting here. First it is said that the annual total of agricultural NO emissions is "several hundreds of thousand" times smaller than the other emissions; and then it is argued that if concentrated within a few weeks in spring and autumn, they can nevertheless be important. A concentration of the annual emission to a few weeks (say 2-3 weeks) increases the relative magnitude (compared to other emissions during these weeks) only by a factor of 20, which is still much smaller than a factor of "several hundreds of thousand"
Thank you for this comment. We agree that during most of the year the weight of agricultural emissions probably remains small compared with other sources. Nevertheless, as pointed out in the previous comment we made a mistake in the units used in our national estimation. It turns out that considering few weeks only, would increase the relative magnitude by a factor of 20 leading to a contribution from crops only half of that from transport. This means indeed that agricultural emissions, concentrated in a short period of the year and under certain meteorological conditions, can potentially make atmospheric NO_x concentrations increase above the thresholds that are critical for human health and ecosystems.

7) Figure 5b: It would be most interesting to see the effect of the chemical correction on the NO2 deposition velocity.
This is an interesting suggestion. Indeed we see that the NO_2 deposition velocity switches from slightly negative to slightly positive. The Figure 7b was modified and some text was added in section 3.3.4: ". In terms of deposition velocity, the ozone deposition velocity followed a clear diurnal cycle with a maximum during the day and a minimum at night. The measured NO_2 deposition velocity showed slightly negative values, but slightly positive ones when corrected for reactions with NO and O_3."

MINOR COMMENTS AND LANGUAGE CORRECTIONS

- Line 15 (abstract): Replace "Mean NO emissions" by "Cumulated NO emissions"
Thank you for the suggestion, this was corrected for.

- Line 19/20: This statement about the ozone deposition velocity is incomplete. It 'was significantly larger' than ...?
It was meant "than before fertilization". The expression was replaced by "deposition velocity increased significantly after organic fertilisation"

- Line 84: write more precisely "...none over an arable crop."
Thank you for the suggestion, this was corrected for.

- Line 85: This sentence needs rephrasing. It is not the question whether the gases are interacting (they do so according to general chemical and physical laws). Better write "...whether the reactions between NO, NO2 and O3 significantly influence their fluxes above crops and ..."
Thank you for the suggestion, we rephrased as you suggested.

- Line 99: It is not clear what 'adapted' means here. Better use e.g. 'suitable' or 'adaptable'.
Thank you for the suggestion, this was corrected for.

- The numbering of the (Sub-) Sections in Chapter 3 is obviously not correct. E.g. there is no Section 3.4 or 3.5
Thank you for the suggestion, we re-numbered and ordered the sub-sections titles.

- Line 276-278: This argument should be related to the chemical correction and derivation of the surface fluxes in Section 3.8.1 and Fig. 8 later in the manuscript. Does the chemical correction of the NO fluxes lead to diurnal cycle that is more in phase with temperature?
Thank you for the interesting comment. Indeed, the derivation of surface flux lead to a diurnal cycle that is peaked later in the day, more in phase with temperature. We added comments and figure 9 to show this finding.

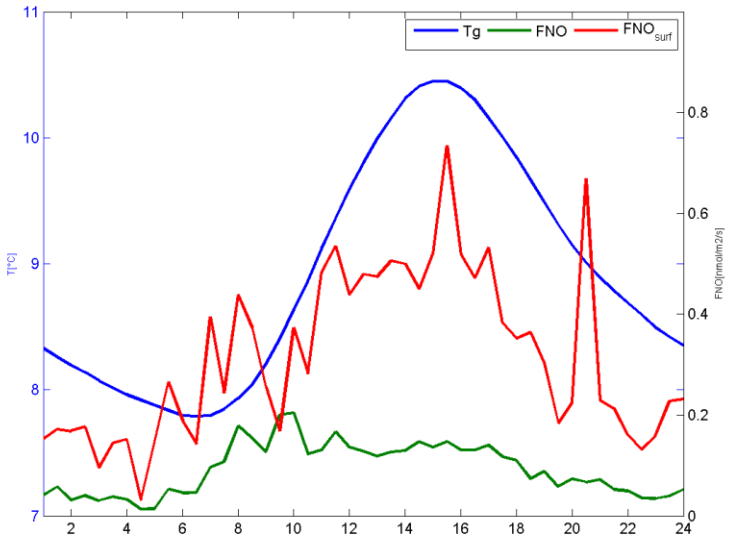

Figure 9. Diurnal cycles of ground temperature, NO flux at measurement height and at surface by the logarithmic profile.

- Line 282-284: These statements are contradicting: 0.09 nmol m-2 s-1 is not smaller than the previous result of 0.07 nmol m-2 s-1!
Thank you for the comment, we replaced “smaller” by “in the range of”

- Line 287: Correct to "...flux distributions ..."
Thank you for the comment, but we keep here the singular as we refer to one singular distribution (the NO one)

- Line 288: Change to "...the ones for the whole period"
Thank you for the comment, we add “the one for…” but we keep the singular as we refer to one singular distribution (see previous comment)

- Line 295: "Following the slurry application" is quite unspecific. Please specify the length of the time period attributed to this event.
We added here the period (two weeks)

- Line 297: What is the difference of this emission factor (0.27%) to the one in Line 295 (0.25%)? Maybe Lines 295-296 are obsolete?
Thank you for the comment. The first factor (0.27%) is referred to the whole period, while the smaller one (0.24% indeed) is referred to the nitrogen losses during two weeks after fertilization. We have synthetized the information.

- Line 309: " the soil was only humidified ... and occurred ..." This formulation is syntactically incorrect and needs rephrasing.
Thank you for the comment. We rephrased as follows:
“… while in August no significant rain event occurred after the first week. In this period indeed, the soil was only humidified by the organic manure supply (on a layer 4.8 mm thick) that was applied on a dry soil.”

- Line 359-360: It is quite unusual to present correlation coefficients in %. In addition it is not fully clear whether the normal correlation coefficient or the squared correlation is meant here. here the normal correlation coefficient (that assumes the value of 100% or 1, when the variables are linearly correlated). We added “normal” in the text. - Line 387f.: This statement needs rephrasing. The gaseous transfer in the soil is always driven by molecular diffusion. Here, the important assumption is that the soil surface deposition is quantitatively limited by molecular diffusion in the soil pores. I thus suggest to modify to: "...if molecular diffusion in the soil pores is the main limitation factor"
Thank you for the comment, we rephrased as suggested.

- Line 394: Replace "to the mast" by "to the EC measurement height"
Thank you for the comment, this was corrected for.

- LIne 408-410: This sentence can be omitted because it is a repetition of statements that have been introduced before.
Thank you for the comment, but we think that it is important here to synthetize the connection between Damköhler number and NO fluxes, also to introduce fig. 8.

- Line 418: "O3" is misplaced here.
Thanks for that comment. Yes indeed, “O3” was on the wrong side of the brackets. We corrected that typo.

- Line 427: Correct to "using the Stella et al..."
Thank you for the comment, this was corrected for.

Answer to Anonymous Referee #3

The manuscript titled ‘Nitrogen oxides and ozone fluxes for an oilseed-rape management: influence of organic fertilisation’ by Vuolo et al. discusses fluxes of NO, NO2 and O3 measured using the eddy covariance method. The paper is well written and structured and describes an interesting dataset which I believe the flux community will like to see. I recommend that the paper should be published subject to some small edits which I leave to the editors and author’s discretion. I hope that my comments aid the authors and look forward to seeing the paper published.

Comments:

It may be prudent to change the title to ‘Nitrogen oxides and ozone fluxes from an oilseed-rape management cycle: the influence of cattle slurry application’. The term organic fertilisation covers a wide variety of possibilities and as the authors point out, much of the chemistry occurring can be dominated by VOC emissions which will vary widely depending on fertiliser type and consistency.
We have followed the referee suggestion and changed the title to: “Nitrogen oxides and ozone fluxes from an oilseed-rape management cycle: the influence of cattle slurry application”

As mentioned in the previous review of the paper, it is a fairly long submission. The author’s attempts to shorten the paper by converting some of the methodology section to supplementary material do help with this. I don’t believe that shortening the paper further would improve its readability and would only serve to damage its scientific value.
We agree with the referee comments.

The soil pH is relatively high (7.6). Is this normal for the field or due to recent liming? There is little mention of this on nitrification rates.
The site is naturally characterized by alkaline pH that revealed to be of the same order of magnitude or larger in previous studies: 8.3 in Laville et al., 2009 and 2013 and 7.6 in Loubet et al., 2011. The following text has been added in the manuscript:
“The soil organic carbon content was ~20 g C kg^{-1}, pH (in water) = 7.6, and bulk soil density was 1.3 g m^{-3}, in agreement with previous measurements on the same site (Laville et al., 2009 and 2011, Loubet et al., 2011). High pH are common in soils over calcareous layers and with high fine fraction content (clay and silt) as is the one of the Grignon site. It is known that alkalinity fosters the nitrification process and this range of pH is optimum for it to occur (e.g. Nieder and Benbi, 2008).”

There is mention of the FIDES footprint analysis which shows that the effect of pollution from the cars would be minimal, but no graphical representation of this. Would it be possible to include a rough sketch of the field site and location of the roads with a representation of the footprint contribution during the measurement period?
This is a good suggestion. We have added a small map of the field with the surrounding roads.

What percentage of eddy covariance measurements passed QC steps for each compound? What is the total time coverage for each? Which version of eddy pro was used? Were any other settings changed in eddypro outside of the carboEurope settings to accommodate NO, NO2, O3. (i.e. spike removal, outliers etc…) If so please include a brief summary.
NO_x and O_3 half-hourly fluxes were filtered by the quality check test included in EddyPro (version 5), according to the 0-1-2 labelling proposed by Mauder and Foken (2006). As recommended in the framework of the CarboEurope project, we discard fluxes with quality check index value of 2. This lead to keep the 74%, 84% and 76% of the records, for NO, O3 and NO2 respectively. The total records of NO and O3 half-hourly fluxes were 11329 (from 07/08/2012 to 13/03/2013), while for NO2 they were 2257 (during the period 14/08/2012 to 30/09/2012). This information has been added in Section 3.1, whose title has been changed into "Quality check and uncertainty in NO, NO_2 and O_3 flux measurements".

L190: It would be useful to give the reader a range of Reynolds number that would be in the turbulent range for the site in brackets. i.e (xxxx to xxxx)
We added (Re>4000) to specify the turbulent range.

I would like to see a bit more detail in how the fluxes were quality controlled. What were the cut-off values for outliers and why? Was u_* limited used as a cut-off? If so, what limit was chosen and why? If not, why not?
To compute yearly averages, we used as cut-off values to exclude outliers the 99.9 percentiles separately for the positive and negative parts of the fluxes distributions, as we observed that the values outside this range were isolated and do not have physical meaning. These values resulted to be ±5nmol/m^2/s for NO and NO_2, and -60 and +10nmol/m^2/s for O_3.
As regards u_* we did not use a threshold for it but observed that very low values of u_* were already discarded with the quality check classification, that included the test for well-developed turbulence (Mauder and Foken, 2006).

L213: At what point would the authors deem the eddy covariance method unusable?
Section 3.3.1: These observations seem worrying when applying eddy covariance to such reactive compounds which are constantly changing as they disperse from sources. Later in Section 3.7 an estimate of 4 to 40% of contribution to fluxes is described based solely on estimated stats. Horizontal transfer of the species being measured in and out of the storage area of the fetch and the resultant advection effect seems to be a very significant source of uncertainty and one which cannot be fully accounted for in this study even with de-spiking etc... It is understandable that no field site is perfect, but as one of the aims of this study is to asses if eddy covariance is suitable for the measurements it seems odd to accept such a large source of error as a given. Perhaps some of the more negative aspects of the methodology should be embraced as a discussion point for future studies?
Thank you for that very sound comment indeed. This is true that the site is particularly challenging for studying NO_x fluxes, and we agree that some of the most challenging aspects should be retained for future studies. We added some considerations in the conclusions, and made suggestions for additional measurements:
"Nevertheless, random uncertainty were particularly important (>20%) during morning traffic peaks due to non-stationarity of NO_x and O_3 mixing ratios. As concerns NO_2, uncertainty was even higher (up to 40%) due to the indirect measurement method. We thus recommend caution in the use of the method in non-stationary conditions, and combined measurements of horizontal gradients of mixing ratios to quantify the effect of advection. Also, additional measurements of surface mixing ratios would be useful to check the reconstruction of surface fluxes that we performed by using the logarithmic-profile model of Duyzer. Finally, high NO_2 to NO conversion efficiency should be assured to reduce uncertainty on NO_2 fluxes."

Is it possible to report a detection limit for each of the measured fluxes?
This would be possible but makes the figures less readable. For that purpose, we prefer to stick with the hourly averages

Perhaps this comment is beyond the scope of the paper and I do not expect the authors to amend the manuscript. Was short term changes in PAR (i.e. the effect of clouds) compared to the random error of Ozone fluxes? Is this not an issue when looking at fluxes over a 30 min period when UV exposure can change so dramatically over very short time periods? If fluxes were calculated over a 60 min period instead of 30 minutes are the same fluxes

and correlations observed? Would it reduce cumulative flux uncertainty at the cost of data points and the observation of diurnal patterns?
As indeed mentioned by the reviewer this is a bit beyond the scope of this manuscript. We do have the data to look at 5 minutes PAR and O3 fluxes correlations but this would require to re-process all eddy-covariance data. We prefer to leave that question out of the way for the moment but we agree that it would be interesting to look at short-term correlations between ozone fluxes and UV radiations.

Section 3.6: How were cumulative totals estimated? Linear regression between points or using the diurnal cycles to gap fill? With such consistent patterns and correlations it seems like gap filling could be modelled relatively well?
We did not perform gapfilling but averaged fluxes that passed the quality check (74%, 84% and 76% of the records for NO, O_3 and NO_2 respectively). We preferred to avoid any reconstruction of the lacking records with models (for example the one of Henault et al., 2015) because of the high variability of emissions and dependency on many factors on which measurements were not available at the required frequency (nitrate and water soil content, soil temperature). We however acknowledge that our cumulative totals may hence be biased.

Axis Text on Fig 7 has overlapped in places

Optional:
I don't like the phrase 'changed sign' referring to fluxes switching between emission and uptake at different levels. L23 & L 526**.** If possible please re-word.
Thank you for the suggestion, we adopted the expression "switched from deposition to uptake".

L21: replace 'at all times during' with 'constantly throughout'
Thank you for the suggestion, this was corrected for.

L 37: replace 'increasing risks for' with 'exposure to which increases risk to'
Thank you for the suggestion, this was corrected for.

L48: replace 'mostly due to' with 'primarily the by-products of'
Thank you for the suggestion, this was corrected for.

L136: replace ~monthly with 'approximately once a month'
Thank you for the suggestion, this was corrected for.

L193*This is assumed to be "white noise" and……
Thank you for the suggestion, this was corrected for.

L241: replace 'on' with 'over'
Thank you for the suggestion, this was corrected for.

L246: replace 'strongest' with 'highest'
Thank you for the suggestion, this was corrected for.

L258: …it can be deduced that deposition velocities were around…
Thank you for the suggestion, this was corrected for.

L337: probably similar to those measured in September
Thank you for the suggestion, this was corrected for.

Technical:
Indents throughout the manuscript are inconsistent. Editorial team will correct?
Thank you for the remark, we added indents at each paragraph.

Dates are presented inconsistently throughout. Choose either (18th of February) or (18/02/16) format and stick with it.
Thank you for the suggestion, we adopt the notation dd/mm/yyyyy.

L131: *December
Thank you for the suggestion, this was corrected for.

L124 * performed on
Thank you for the suggestion, this was corrected for.

L223: *7 month period
Thank you for the suggestion, this was corrected for.

L250: replace ‘than’ with ‘of’
Thanks for the suggestion. Changed.

L297: 0.27 or 0.25? See line295
The correct value is 0.24, we replaced it.

L330*24th
We replaced by 24/08 to keep the notation dd/mm/yyyy

L397: delete ‘of’
Thank you for the suggestion, this was corrected for.