

Interactive comment on “

Comparison of methods for the determination of NO-O₃-NO₂ fluxes and chemical interactions over a bare soil” by P. Stella et al.

Anonymous Referee #1

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This paper presents a comparison of flux measurement methods for the NO-O₃-NO₂ triad including the influence of chemical flux divergences. The authors conclude that the eddy covariance (EC) method and the aerodynamic gradient method (AGM) agree well for O₃ fluxes, except during nighttime. However, the dynamic chamber method resulted in significantly lower NO emission fluxes than determined with the AGM. All fluxes were corrected for chemical divergence before the comparison. In general, the

C1720

paper could be a very valuable contribution to our current knowledge in the determination of surface-atmosphere exchange fluxes. However, the discussion of the results and the conclusion must be improved considerably before the paper can be published in AMT. The following comments and corrections should be taken into account by the authors.

1 General comments:

a.

The calculation of the gradient signal to noise ratio should be clarified. What is meant by “the averaged concentration standard deviation”? Ideally, the standard deviation of the averaged concentration difference should be used to calculate the ratio. It can be assumed that both heights are affected by instationarity in the same way. Please correct if required! It should also be noted that due to the inclusion of instationarity the estimate of the gradient noise presents an upper bound.

b.

Additionally, the fluxes calculated for signal to noise ratios below unity should be treated with caution. For example, these fluxes could be marked by a special symbol or color and the cases when NO and NO₂ fluxes are calculated from insignificant mixing ratio differences should be discussed in detail within the context of the method comparison (the same applies to cases when NO and NO₂ fluxes fall below the limit of detection).

c.

The authors mention several times that polluted air from Paris and nearby traffic roads is advected to the site but no discussion of the influence of advection on the NO fluxes determined by the AGM (and the differences to the dynamic chamber method) is performed. For example, on page 5498 it is mentioned that local advection of NO influences the AGM fluxes, but later in the discussion this fact is completely ignored. The

C1721

authors must assess the influence of advection on estimated fluxes based on traffic times and/or abrupt mixing ratio increases/decreases due to change in wind direction etc. at least qualitatively in the manuscript.

d.

The overall discussion and interpretation of the results must be improved. For the discussion of the discrepancy between the NO chamber fluxes and the AGM fluxes the following issues should be included in the discussion: i.) How large was the chemical correction term for the chamber flux compared to the AGM flux?, ii.) Discuss the potential influence of the reaction $\text{RO}_2 + \text{NO}$ on the underestimation of chamber fluxes (the reaction proceeds with the same rate as that of $\text{NO} + \text{O}_3$, particularly in the chamber where the residence time is longer), iii.) Potential instationarity of mixing ratios measured at the chamber inlet during the 3 min sampling interval iv.) Influence of advection (see above), v.) Influence of fluxes determined from insignificant gradients (see above).

e.

The whole conclusion section must be revised considering the missing issues from the discussion section. At the moment, only very few new scientific findings are listed in the conclusion. The fact that the application of a specific gas analyzer (i.e. the right sensor to measure a certain quantity) is needed in order to get reliable results is not a new result and should not be the last sentence of the paper (it is well known that analyzers with a molybdenum converter overestimate the NO_2 mixing ratio). For instance, one major progress of the paper is that flux uncertainties were quantified - to my knowledge for the first time in this manner for NO and NO_2 .

2 Detailed comments:

- Abstract: The fact the O_3 fluxes were also measured by EC should be mentioned in the beginning of the abstract, not at the end.

C1722

- Line 12: "unit" for year is not "yr" but "a" and should be used throughout the manuscript.
- Page 5484, Line 1: The AGM is also a micrometeorological method. Maybe, the differentiation should be made between direct (EC and derived) and indirect (AGM, profile methods) micrometeorological methods, in contrast to chamber methods.
- Page 5486: How was the lag time of 1.6 seconds determined? Besides an estimation, a lag time can be measured (practical approach) or computed (theoretical approach).
- Page 5487, Line 1: Was the effect of the ozone scrubber on the NO_2 tested?
- Page 5487, Line 3: TPG = GPT: Gas Phase Titration unit
- Page 5487, Line 13: Why a von Kármán constant of 0.41? 0.40 is more common. Please write Mr. von Kármán's name correctly.
- Line 18: LMO is the Obukhov-length. Monin and Obukhov invented the so called MO similarity theory.
- Please always use 273.15 to convert degrees celsius to Kelvin (e.g., eq. 5).
- Page 5488, eq. 5: kg (kilograms) should be set in italics and be visibly divided to be identifies as acceleration due to gravity and the von Kármán constant.
- Page 5490, Line 7: What is the Edire software? Please give details in the text.
- Page 5491, Line 18: How would the results be affected if the height of zero divergence was 3m or even 5m? Is this assumption based on more than just the low upper measuring level?

C1723

- How does the estimated turbulent timescale (eq. 13) compare to the formulation by Mayer et al. (2011)? Is a stability correction included? Please comment this in the text.
- What does eq.(14) mean exactly? What is the chemical reaction time scale for the NO-O₃-NO₂ triad? Is it the time required to achieve the photo-stationary state? Please comment in the text.
- Page 5493: The ratio between ... and ... is defined as the Damköhler Number (DA) (Damköhler, 1940): ...
- Page 5494, Line 11: "in the 0 – 10 top soil": units are missing.
- Page 5494, Line 21: Don't mix abbreviation and full name, e.g. O₃ and ozone. Use always the abbreviation after being introduced, except at the beginning of a new sentence.
- Page 5496, Line 5: a comma appears more appropriate instead of ;
- Page 5496, Line 20: better give the heights in m above ground than in words (the two highest levels, etc.)
- Page 5496: Figure 3 shows a good correlation for NO analyzers but still the scatter is quite large at higher mixing ratios. Please comment on that.
- Page 5497, Line 14: "not affected in the same extend in terms of percentages": What do the authors want to say here? The fact that the same absolute divergence affects fluxes of different magnitudes in relative units differently is trivial. It is not surprising that O₃ fluxes are always less affected by chemical divergence than fluxes of NO and NO₂. Please reformulate.
- Page 5498, Line 20ff: Here, the authors miss to discuss the potential interference of PAN in the fast analyzer and how this was treated in the evaluation. How

C1724

was the large interference in the slow NO₂ analyzer accounted for in the data evaluation?

- Page 5499, Line 2: The lifetime of NO_x is not the same as lifetime of NO and NO₂. NO_x can be regarded as a quasi-conservative species (as was stated elsewhere in the manuscript).
- Page 5500: What is the reason for the decrease of the flux error with increasing measurement frequency? Is the value of σ_{c*} decreasing?
- Page 5501: Line 18 (Fig. 5a to c) must be replaced with (Fig. 6a to c)
- Page 5501: Line 24-26: It is well established that only for cases when DA < 0.1 the reactive species can be considered as inert tracers. As long as DA > 0.1 chemical reactions are expected to influence measured fluxes. Consequently, it is expected that the corrected surface flux was still different than the AGM flux. Please correct that in the text.
- Page 5502, Line 22: How much of the discrepancy could be explained by chemical reactions?
- Page 5503: Mention here that vd was determined from the AGM method. The reference height should be that geometric mean of the two heights used for the AGM. Was it 0.2 and 1.6m or 0.7 and 1.6m? Please state this in the method section.
- Page 5504: Please also provide R_c for ozone here.
- Page 5506: Please state here how large the difference between the NO fluxes from the AGM and the chamber fluxes was.
- Please always use mixing ratio and not concentration when referring to ppb. This was not corrected yet for some cases.

C1725

- Please increase the text size in Figure 2.
- The last sentence in the caption of Figure 8 is a repetition and can be deleted.
- The deposition velocity in Figure 11 should be presented a median diurnal cycle with interquartile ranges (0.25, 0.75).

3 Language corrections:

- Page 5482, Line 4-5: The determination of surface-atmosphere exchange fluxes of these trace gases are a prerequisite to establish their atmospheric budget. . .
- Line 14: The application of the aerodynamic gradient and the eddy covariance methods resulted in comparable O₃ fluxes. . . The NO chamber fluxes. . .
- Page 5483, Line 16-17: . . .and depends on several factors, such as the amount of nitrogen. . .
- Page 5483, Line 29: . . .What does “and those derived such as. . .” mean? Please correct! Page 5484:
- Page 5483, Line 16-17: . . .would require several fast analyzers. . .
- Page 5483, Line 21: . . .reported similar results using these two. . .
- Page 5486, Line 25-26: The flow inside the subsample lines was . . .
- Page 5487, Line 6-7: . . .was calculated with the AGM. . .
- Page 5488, Line 1: Eddy covariance is a direct measurement method to determined fluxes without application of. . .

C1726

- Page 5488, Line 11: . . .correction for the latent heat flux. . .
- Page 5492, Line 2: . . .may occur during the transport. . .
- Page 5495, Line 14-15: The friction velocity featured a marked diurnal variation.
- Line 17: Delete “Globally”. The end of the. . .
- Line 18: . . .was characterized by higher friction velocities. . .
- Page 5496, Line 15: . . . with a very small difference. . .
- Page 5496, Line 28: . . .the increase in turbulent mixing. For ozone, this ratio was systematically. . .
- Page 5497:
- Line 6: . . .whereas the C_{*} relative. . .
- Line 22: . . .were always much larger than . . .
- Page 5500, Line 8: . . .the use of the fast response sensor was. . .when the friction velocity. . .
- Page 5500, Line 25-26: delete “Indeed”. The ozone flux (. . .
- Page 5501, Line 3: The overall chemical reaction time. . .
- Page 5502, Line 5: . . .measured using the aerodynamic. . .
- Page 5505, Line 13: . . .were mainly due to uncertainties of the friction velocity.
- Page 5505, Line 23-24: . . .ozone fluxes are significantly higher than . . .
- Page 5505, Line 27: . . .methods resulted in comparable O₃ fluxes. . .

Please decide if you use night-time or nighttime. The referee prefers that latter case.

C1727

4 Literature:

- Damköhler, G.: Der Einfluss der Turbulenz auf die Flammengeschwindigkeit in Gasgemischen, Zeitschrift für Elektrochemie und Angewandte Physikalische Chemie, 46 (11), 601-652, 1940.
- Mayer, J. C., Bargsten, A., Rummel, U., Meixner, F. X., and Foken, T.: Distributed Modified Bowen Ratio method for surface layer fluxes of reactive and non-reactive trace gases, Agricultural and Forest Meteorology, 151, 655-668, 10.1016/j.agrformet.2010.10.001, 2011.

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