

Dear Referee#1,

We first would like to thank you for your comments. We modified the manuscript according to your comments and answered them in details in the following.

P. Stella et al.

1/General comments

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.

We meant, as you suggested, the standard deviation of the averaged concentration difference. In addition, we included in the revised manuscript Student's t-test in order to define if mixing ratio profiles were significant. Stationarity test on mixing ratios were also carried out and added to the revised manuscript (see also answer to Referee #2 comments).

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).

As indicated previously, we performed both stationarity test and Student's t-test. For NO₂, the stationarity test systematically failed which eventually led us to ignore this data for flux calculation. For NO and O₃, Student's t-test were also carried out on paired sample (in our case for mixing ratios measured (i) at 0.2 meters and 0.7 meters and (ii) at 0.7 meters and 1.6 meters). The procedure was as follows: if mixing ratio difference between both (i) 0.2 meters and 0.7 meters and (ii) 0.7 meters and 1.6 meters, fluxes were calculated using the three levels. If at least one or the two mixing ratio difference was not significant, Student's t-test was carried out for mixing ratios difference between 0.2 meters and 1.6 meters. If mixing ratio difference between 0.2 meters and 1.6 meters was significant, fluxes from AGM were calculated without including mixing ratios measured at 0.7 meters. Otherwise, mixing ratio gradient was considered as insignificant and fluxes were not calculated. We added in the revised manuscript one table and one figure concerning these results and modified the text in consequence. Finally, only fluxes satisfying both stationarity criteria and significance of the mixing ratio difference using T-test were kept for further analysis.

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 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.

We included in the revised manuscript a discussion concerning this issue, especially the effect of local advection on the stationarity of NO₂ mixing ratio. Unfortunately, not enough data were available during this study, i.e. only ten days, to establish robust relationship between wind direction or traffic time with fast changes in mixing ratios. Local advection may also artificially increase NO fluxes measure by micrometeorological method at a given height above the ground. This issue is also discussed qualitatively in the manuscript.

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 RO₂ + NO on the underestimation of chamber fluxes (the reaction proceeds with the same rate as that of NO+O₃, 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).

Concerning the issue i), for the chamber method the chemical correction term accounted for 0.13 nmol m⁻² s⁻¹ on average over the whole study period but could reach 0.92 nmol m⁻² s⁻¹ during the large NO emission period. These values were comparable with chemical correction term for the AGM (i.e. 0.12 nmol m⁻² s⁻¹ on average, 1.44 nmol m⁻² s⁻¹ in maximum). This was included in the revised manuscript.

ii) The potential error in the chemical correction method we used for the chamber measurements, which only included reaction with NO and O₃ was discussed in the revised manuscript. Unfortunately, since no measurements of peroxy radicals were available, the discussion concerning this issue is quite limited.

iii) This was not an issue because the flow rate of the chamber inlet was very small (1 L min⁻¹) compared to the chamber headspace volume (55 L)

For the issues iv) and v), we referred the Referee to the above comments.

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 NO₂ 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 NO₂.

Done

2/Detailed comments

Abstract: The fact the O₃ fluxes were also measured by EC should be mentioned in the beginning of the abstract, not at the end.

Done

Line 12: "unit" for year is not "yr" but "a" and should be used throughout the manuscript.

We are not sure to understand this remark. Indeed, "yr" is usually used as the unit for year (see for example Wild, 2007; Derwent et al., 2008; Butterbach-Bahl et al., 2009). Thus, we choose to keep "yr" 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.

We modified the sentence as follows: "it is possible to distinguish between the direct micrometeorological methods (such as the eddy-covariance (EC), the relaxed eddy-accumulation and the disjunct eddy-covariance), the indirect micrometeorological methods (such as the aerodynamic gradient method, AGM, and profile methods) (Foken, 2008), and the chamber methods (Meixner et al., 1997; Denmead, 2008)".

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).

The lag time of 1.6 seconds was determined theoretically. However, during an other experiment using the same profile system with additional sonic anemometers at each level, we measured the time lag by estimating the cross-correlation functions of $w'T'$, $w'O_3'$, $w'NO'$ and $w'NO_2'$ (Loubet B., Stella, P., Fanucci, O, and Mascher, N.: Evaluation of a modified disjunct eddy covariance method for estimating the fluxes divergence of nitrogen oxides and ozone, Poster presentation, NitroEurope Conference, Edinburgh, United Kingdom, April 11-15, 2011) (see figure below). The measured lag time for O_3 , NO_2 and NO were 0.5 s, 2.9 s and 1.1 s. The Figure below shows one example of cross-correlation functions for O_3 , NO_2 and NO .



We modified the text to specify that the lag time of 1.6 s is a theoretical estimate.

Page 5487, Line 1: Was the effect of the ozone scrubber on the NO_2 tested?

Unfortunately, the effect of the ozone scrubber on the NO_2 was not tested

Page 5487, Line 3: TPG = GPT: Gas Phase Titration unit.

Corrected.

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.

We used the von-Kármán constant of 0.41 because it was used by Dyer and Hicks (1970) to establish this universal function. This issue was also pointed out by the Referee#2. For more details concerning this issue, please see the response to the Referee#2.

The Mr von Kármán's name was corrected for.

Page 5787, Line 18: LMO is the Obukhov length. Monin and Obukhov invented the so called MO similarity theory.

Corrected.

Please always use 273.15 to convert degrees Celsius to Kelvin (e.g., eq.5)

Done

Page 5488, eq. 5: kg (kilograms) should be set in italic and be visibly divided to be identified as acceleration due to gravity and the von Kármán constant

Done

Page 5490, Line 7: What is the Edire software? Please give details in the text.

It is the software developed by Robert Clement from the University of Edinburgh. We used it for EC flux calculation and quality control. We included these 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?

This issue was also pointed out by the Referee #3. We estimated that the fluxes with chemical corrections differed from less than 1% for O₃, 3.8% for NO and 4.6% for NO₂ if we assumed z₂ = 1.6 m or z₂ = 4 m.

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.

Eq. 13 differs from Mayer et al. (2011) by the fact that Mayer et al. did not integrate the diffusivity K_m (or K_H or K_C) with height but they took the value of K_C at mid height of the considered layer. In eq. 13 $R_a(z)$ is the integral of $(1/K_c(z) dz)$ from z_0 to z . So virtually the two approaches should give exactly the same τ_{turb} when $\Delta z \rightarrow 0$. If the considered layer is large ($\Delta z \gg 1$), the integral approach (using R_a) should be preferred. For instance in this study, with $z_m = 1.6$ m, and under neutral stability, Mayer et al. would give a τ_{turb} 2.7 times larger as the one in Eq. 13.

The stability correction was included in the estimate of the turbulent timescale through R_a calculation. It was added in the revised manuscript.

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.

The equation (14) gives the characteristic time scale of the set of reactions $NO + O_3 \rightarrow NO_2 + O_2$ and $NO_2 + O_2 + hv \rightarrow NO + O_3$. This timescale is namely the time at which the O₃ concentration *significantly* changes from its “initial” value when reacting with NO and NO₂ (which also have an initial value and evolves). It is indeed somehow the time required to reach a new photo-stationary state each time the concentrations of NO, NO₂ or O₃ or the chemical constants k or J_{NO_2} change. It was specified in the revised manuscript.

Page 5493: The ratio between...and...is defined as the Damköhler Number (DA) (Damköhler, 1940):...

Done

Page 5494, Line 11: “in the 0 – 10 top soil”: units are missing.

Corrected

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.

It was corrected throughout the manuscript.

Page 5496, Line 5: a comma appears more appropriate instead of ;

Done

Page 5496, Line 20: better give the heights in m above ground than in words (the two highest levels, etc.)

Done

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.

This is a sound remark. We can hypothesise here that the larger concentrations of NO (and NO₂) correspond to advective situations. Under such situations, the plume exhibit large spatial and temporal variability in NO and NO₂ concentrations. Since the CLD780 was sampling at sequentially at the three levels, the concentration measured at one level would miss some periods. Similarly, the 42i has an internal cycling and samples successively NO, NO₂ and a pre-chamber and does therefore not sample NO (NO₂ as well) all the time. Finally, the two analysers masts were located at a few meters from each other and may have seen variable NO concentrations. The discrepancy is larger at larger NO (and NO₂) since the temporal and spatial variability is larger under advective episodes than under non advective ones (the atmosphere is better mixed).

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.

It is trivial indeed, but we wanted to give the order of magnitude of the divergence on each gas. We reformulate this as: "The absolute chemical correction was 0.12 nmol m⁻² s⁻¹ on average for both NO and O₃, but could reach 1.44 nmol m⁻² s⁻¹ during the large soil NO emission period. Due to the magnitude of each trace gas fluxes, the weight of chemical correction did not affect NO and O₃ fluxes to the same extent: the mean flux correction over the whole campaign was estimated to be less than 1 % for O₃, while it accounted for 10 % for NO."

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

Unfortunately, we had no indication about the interference of PAN and other compounds on both fast and slow response sensors. Thus, it was not evaluated.

Page 5499, Line 2: The lifetime of NOx is not the same as lifetime of NO and NO2. NOx can be regarded as a quasi-conservative species (as was stated elsewhere in the manuscript).

Corrected

Page 5500: What is the reason for the decrease of the flux error with increasing measurement frequency? Is the value of σ_{C^*} decreasing?

The decrease of the flux error was effectively due to the decrease of σ_{C^*} . It was precised in the revised manuscript.

Page 5501: Line 18 (Fig. 5a to c) must be replaced with (Fig. 6a to c)

Done

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.

We agreed with this statement and corrected the sentence in the revised manuscript.

Page 5502, Line 22: How much of the discrepancy could be explained by chemical reactions?

The discrepancy between AGM and chamber measurements explained by the chemical reactions was highly variable throughout the period. As indicated in the manuscript, the difference between chamber and AGM fluxes was around a factor five without taking into account chemical reactions a around a factor three taking into account chemical reactions. In the revised manuscript, we indicated the absolute chemical correction term and the difference between the NO fluxes estimated with the two methods to comment on this issue.

Page 5503: Mention here that v_d 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.

This section was removed in the revised manuscript. However, the V_d was defined in the submitted manuscript at the AGM reference height, i.e. 0.61 m (the geometric mean of the three heights 0.2, 0.7 and 1.6 m).

Page 5504: Please also provide R_c for ozone here.

This section was removed in the revised manuscript. Indeed, according to quality analysis, we could not present results for NO_2 , and in our opinion it would be the comparison between V_d (or R_c as suggested here) for O_3 and NO_2 that would be interested. In addition, the R_c for ozone on bare soil was already published in a previous study (Stella et al., 2011). So we choose to focus only on measurement method and quality, which is more in the scope of this journal.

Page 5506: Please state here how large the difference between the NO fluxes from the AGM and the chamber fluxes was.

Done

Please always use mixing ratio and not concentration when referring to ppb. This was not corrected yet for some cases.

Done

Please increase the text size in Figure 2.

Done

The last sentence in the caption of Figure 8 is a repetition and can be deleted.

Done

The deposition velocity in Figure 11 should be presented a median diurnal cycle with interquartile ranges (0.25, 0.75).

This figure was removed in the revised manuscript

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...

Done

Line 14: The application of the aerodynamic gradient and the eddy covariance methods resulted in comparable O₃ fluxes...The NO chamber fluxes...

Done

Page 5483, Line 16-17: "... and depends on several factors, such as the amount of nitrogen..."

Done

Page 5483, Line 29: What does "...and those derived such as..." mean? Please correct.

Done

Page 5484, Line 16-17: "...would require several fast analyzers..."

Done

Page 5483, Line 21: "... reported similar results using these two..."

Done

Page 5486, Line 25-26: The flow inside the subsample line was....

Done.

Page 5487, Line 6-7: ...was calculated with the AGM...

Done

Page 5488, Line 1: Eddy covariance is a direct measurement method to determine fluxes without application of...

Done

Page 5488, Line 11: ...correction for the latent heat flux...

Done

Page 5492, Line 2: ...may occur during the transport...

Done

Page 5495, Line 14-15: The friction velocity featured a marked diurnal variation.

Done

Line 17: Delete "Globally". The end of the...

Done

Line 18:...was characterized by higher friction velocities...

Done

Page 5496, Line 15: ... with a very small difference...

Done

Page 5496, Line 28:...the increase in turbulent mixing. For ozone, this ratio was systematically...

Done

Page 5497 Line 6:...whereas the C_o relative...

Done

Page 5497 Line 22:...were always much larger than ...

Done

Page 5500, Line 8:...the use of the fast response sensor was...when the friction velocity....

Done

Page 5500, Line 25-26: delete "Indeed". The ozone flux (...)

Done

Page 5501, Line 3: The overall chemical reaction time...

Done

Page 5502, Line 5:...measured using the aerodynamic...

Done

Page 5505, Line 13:...were mainly due to uncertainties of the friction velocity.

Done

Page 5505, Line 23-24:...ozone fluxes are significantly higher than...

Done

Page 5505, Line 27:...methods resulted in comparable O₃ fluxes...

Done

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

Done

References

Butterbach-Bahl, K., Kahl, M., Mykhayliv, L., Werner, C., Kiese, R., and Li, C.: A European-wide inventory of soil NO emissions using the biogeochemical models DNDC/Forest-DNDC, Atmos. Environ., 43, 1392-1402, 2009.

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Dyer, A.J., and Hicks, B.B.: Flux-profile relationship in the constant flux layer, Q. J. Roy. Meteor. Soc., 96, 715-721, 1970.

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Wild, O.: Modelling the global Tropospheric ozone budget: exploring the variability in current model, Atmos. Chem. Phys., 7, 2643-2660, 2007.