

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 #3

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GENERAL COMMENTS

The authors present a 10-day time series of NO-NO₂-O₃ gradient measurements with fast-response sensors, from which fluxes are derived using a relatively simple parameterisation for the necessary chemical corrections proposed by Duyzer et al. (1995). For O₃ the chemical correction turns out to be small and generally negligible. The

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gradient-derived O₃ fluxes were compared with simultaneously measured EC fluxes and showed a good agreement on average, yet with a considerable scatter for individual fluxes (especially problematic for small fluxes). Gradient-derived NO fluxes were compared with simultaneously measured NO fluxes by static chambers. Here the agreement was not good with gradient fluxes being 2-3 times larger (if significantly different from zero). Finally resulting mean deposition velocities (diurnal cycle) for O₃ and NO₂ over the bare soil are shown.

1) Although only ten days of measurements over bare soil are presented, the deposition velocity and, more specifically, the surface resistance results for O₃ and NO₂ deposition (in parallel) under such conditions are very useful, because such results are relatively rare in the literature. Some discussion on the relative magnitude of O₃ and NO₂ deposition velocities (or surface/soil resistance) used in the literature could be added.

2) The authors argue that the use of fast response sensors is preferable over slow response sensors to reduce the uncertainty of the gradients and fluxes (although they state that u^* is the main source of uncertainty?, see detailed comments below). Although the use of fast vs. slow response sensors is a scientifically interesting topic, it is treated in a too simple way in this MS. This is not just a problem of statistical error propagation but mainly of instrument performance. Fast response sensors usually have a higher noise level, are less stable (see e.g. the fast ozone sensor used here) and suffer more from interferences than slow response sensors. In order to really demonstrate the advantage of fast response sensors for gradient measurements it would be necessary to perform and present a careful evaluation of the time dependent noise as well as drift effects of both instruments. Alternatively, AGM fluxes from both slow and fast response sensors could be presented and compared to EC. Also the optimum switching interval between measurement heights would be an interesting problem in this context. Finally there remains the question why available fast response sensors should be used for gradient measurement and not for EC directly (especially for chemically reactive

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species)?

3) The discussion of the NO fluxes by gradient and chamber methods seems to be quite biased. Only potential errors for the chamber methods are considered (spatial heterogeneity, not representative concerning rain etc.). Yet it has to be mentioned that also the gradient method may become problematic for heterogeneous conditions because the concentration measurements at different heights do not have the same footprint. In addition, the chemical correction performed relies on assumptions that could not be really proven, and it is probably incomplete because there are other chemical reactions beside the ones considered here (e.g. NO with peroxy radicals). Given the importance of the applied chemical correction in this study, its uncertainty and problems with the assumptions should be assessed and discussed in more detail.

4) The applicability of the presented calculation of the AGM flux uncertainty and detection limit should be discussed critically. A detection limit of $0.08 \text{ nmol m}^{-2} \text{ s}^{-1}$ is reported for the O₃ flux. However, when looking at Fig. 9a, the detection limit (= individual fluxes clearly discernable from zero) seems to be rather at about $2 \text{ nmol m}^{-2} \text{ s}^{-1}$, if the EC fluxes are taken as a reference. So either the effective detection limit for AGM fluxes is more than 10 times larger than expected or the EC flux results have a much lower quality than the AGM fluxes!

DETAILED COMMENTS

p5482 L15: "...gave similar O₃ fluxes (within 4%)" This formulation is misleading, since the 4% refer to the slope of the overall linear regression line. The agreement of half-hourly fluxes is generally much less than 4%!

p5484 L21-22: "...the few previous comparison studies..." Either give additional references here or specify (if applicable) "...the two studies mentioned above..."

p5485 L15-16 and following paragraph: Omit all method descriptions for which no results are included in the current manuscript.

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p5486 L27: Give a detailed description of the used fast ozone sensor (FOS) since it seems that it has not been described before in scientific literature. This is especially important considering the topic of the paper and the focus of this journal.

p5487 L3: How large was the variability from one 6h calibration to the next?

p5487-88: Equations 3-5 (as well as Eq. 11) could be omitted since they represent common textbook knowledge and are referenced in the text (e.g. Dyer and Hicks, 1970).

p5489 Eq.6: This method for the flux determination only works, if there is no offset in the raw fast ozone sensor signal. Was that checked regularly? Please comment on this issue in the manuscript.

p5489 L7: What does "averaged concentration standard deviation" mean here? Averaged over both levels? For the ability to resolve the gradient between two mean concentrations, wouldn't the standard error of the means be more meaningful?

p5489 Eq. 7: It should be pointed out that this uncertainty estimation is only valid for the non-reactive case.

p5491 The definition of the trace gas fluxes in Eqs. 10 and 12 (and throughout the manuscript) is not consistent and partly confusing. Define and use a clear and consistent nomenclature for fluxes (with/without chemical corrections and at different heights z) throughout the manuscript (also in Figures).

p5491 L17-18: Is this assumption reasonable? What is the uncertainty introduced with the assumptions in this relatively simple chemical correction?

p5495 L17: Replace "the end" by "the second half"

p5496 L14-15: This statement is clearly misleading. It does not apply to (individual) measured NO concentrations, but describes the systematic overall deviation determined by a linear regression. This has to be clarified.

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p5497 L14-19: Relative corrections alone are not very informative (because the respective fluxed and thus the absolute correction could be close to zero). Additionally give and discuss absolute effects of chemical corrections for the fluxes.

p5498 L3-22: In the formulation of this paragraph the issue of fast vs slow response sensors is mixed with the selectivity (specific detection of NO₂) of the analysers, which is confusing. When discussing the issue of selectivity, use the names of the sensor instead of 'slow-response' and 'fast-response'. The selectivity of an analyser has no direct relation to its time response (at least not in this study).

p5499 L6-12: There is an obvious contradiction in this paragraph! First the authors say that the flux uncertainty are mainly due to u^* -uncertainty. But later it is said that the (relative) O₃ flux uncertainty was considerably lower than for NO and NO₂ because of the higher precision of the O₃ gradient measurements. (same problem on p5505 L13-16) If the precision of the gradient measurement has such a clear influence on the resulting flux uncertainty, the gradient uncertainty is the limiting factor for the flux uncertainty (and not mainly u^*)!

p5504 L18-20: It seems not very meaningful to compare deposition velocities for bare soils with literature values for vegetated surfaces like turfgrass or other vegetation. If no values for bare soil are available, the present results could be compared to nighttime values over vegetated surfaces (excluding stomatal uptake) or deposition measured at the forest floor.

p5505 L21-23: This statement is misleading. As mentioned earlier in the manuscript (p5501) high flux divergence typically occurred during nighttime when turbulence was weak. It is trivial that NO₂ photolysis does not play a role in the dark!

p5516 Tab.2: A classification of the results with u^* (or z/L) would be useful here.

p5517 Fig.1: If possible give a better illustration of the relative tube lengths (before/after the branching off of the subsample lines to the analysers).

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LANGUAGE CORRECTIONS

p5482 L9-10: "It was demonstrated that ... appeared to be negligible for O₃ fluxes ..." This formulation is awkward and has to be changed.

p5484 L1: interchange "and" and "or" in this sentence

p5484 L12-17: Rephrase this two sentences. The term "Alternatively" is not appropriate here.

p5485 L13-14: The formulation is not clear. Do the author mean "slurry application ... and incorporation by tillage ..."?

p5486 L14: "The aerodynamic gradient method was used to determine ..." (It is a very general rule in literature that titles must not be treated as integral parts of the flow text!)

p5486 L20: Replace "tension" by "voltage"

p5489 L14: "basic" instead of "basics"

p5489 L19: "deviations of w and u "

p5495 L14-15: "...had a marked daily dynamics." Rephrase this sentence.

p5495 L17: Omit or replace "Globally"

p5496 L20: Replace "daily" by "diurnal"

p5496 L7: Replace "day cycle" by "diurnal cycle"

p5499 L2: Replace "these" by "those"

p5504 L6: "variable" instead of "variables"

p5504 L14: "... of about 0.35 cm s⁻¹"

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