

***Interactive comment on* “The dynamic chamber method: trace gas exchange fluxes (NO, NO₂, O₃) between plants and the atmosphere in the laboratory and in the field” by C. Breuninger et al.**

C. Breuninger et al.

c.breuninger@mpic.de

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We appreciate the positive evaluation of our manuscript. We thank the referee for his comments. Our replies and indications of changes to be made to a revised manuscript are listed below.

Comment 1 The manuscript is not easy understandable because of some unnecessary lacks. In several cases I cannot understand equations as the abbreviations used therein are not explained directly. Examples therefore are the equations 1.1 to 1.3. Reading the text near to these equations I cannot find a remark wherefore ma, ms k or

j(NO₂) stand. Other examples are equations 4.1 to 4.3. Here crossbars emerge without any explanation. Not until two pages later averaging is mentioned giving a reader an advice regarding the meaning of the crossbars. Nevertheless, the meaning of the crossbars is still not mentioned. The reader of this manuscript is forced to first read the appendix before understanding several equations written short after the introduction. This should be avoided and I therefore ask the authors to check their text for such unnecessary flaws. These make it hard to read the manuscript and redirect from the basic message.

Reply We respect your difficulties with the equations. Thus we have revised the text and inserted the missing explanations for the abbreviations and crossbars.

Comment 2 The authors should give some comments on their quality criterion of significant concentration differences (ma, ms). The authors' requirement of significant concentration differences (ma, ms) is certainly justified if concentrations in the chamber are well above a hypothetical compensation point. It allows obtaining reliable flux densities because artificially low concentration differences are not taken into consideration. But, if ms would be near to a hypothetical compensation point, this criterion is not clear to me: At concentrations near to the compensation point these concentration differences should be low. The authors should state how they distinguished between concentration differences being insignificant due to an artifact or insignificant due to trace gas concentrations near to the compensation point. There are two questions connected to this item. These also should be commented. Does a strict requirement of significant concentration differences introduce a bias to the results because it may rule out data points obtained near to a hypothetical compensation point where small differences are correct? If the requirement is strict, compensation points will only be obtainable by extrapolations. Is that true or can compensation points also be measured if concentration differences are zero?

Reply We like to thank referee#3 (as well as referee#1 Comment 6) for this comment. It allows us to clarify again why we used the Δm_{NO_2} (Δm_{NO} ; Δm_{O_3}) criterion as

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described in section 3.4.5. As far as the “bias” to the results (i.e., compensation point concentration, deposition velocity) is concerned we refer to our answer to comment 6 if referee#1. As far as our procedure for Δm_{NO_2} (Δm_{NO} ; Δm_{O_3}) near to the (hypothetical) compensation point is concerned: At the compensation point itself, the corresponding Δm are definitely equal to zero. Since even the best available analyzers do have (small) errors of (any) measured concentration, a $\Delta m = 0$ can not be determined on a statistically significant level (by definition). It also holds for $\Delta m \approx 0$, since only a certain $\Delta m > 0$ can be determined significantly when considering observed errors of concentration measurements. Otherwise (i.e. without considering the observed errors of m) Δm 's may be small or even zero, but resulting deposition velocities and/or compensation points will reflect the analyzer's errors only and will turn out to be “likely” to “unlikely” only.

Comment 3 The data from the laboratory experiments do not give any important information and the whole section can be deleted without abating the quality of the manuscript. The only justification for a detailed description of the laboratory results would be some important information on top of those from field experiments. But due to the sub-optimal performance of the analytic device the results from the laboratory experiments do not give such information. It is therefore unnecessary to describe the laboratory experiments. Focus of the manuscript is a description of analytical and mathematical procedures. These procedures are described in detail at hand of the field experiments. The authors should therefore consider deleting the whole section dealing with the laboratory experiments.

Reply After due consideration we disagree about deleting the laboratory experiment and results from manuscript. During laboratory experiments the conditions are different from field measurements, at least due to avoiding gas phase chemistry effects. Moreover, one of our intentions for this paper was to introduce a dynamic chamber method which can be used under field and laboratory conditions. Furthermore, the agreement of conclusion based on laboratory data with those from field with gas phase

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chemistry, demonstrates the general applicability of the methods.

Some minor points

Comment Chapter 2.1 refers to basic equations explained in the appendix (A7.1 – A7.3). Please give these equations directly at the beginning of this chapter (justification can be left in the appendix A). This will also help for easier understanding of the equations 1.1 to 1.3. as also the abbreviations can directly be explained.

Reply see answer to your comment 1.

Comment P. 5193 lines 4 ff.: it is written: “purging rate Q and leaf area A_{leaf} are unchanged”. Equations 8.1.1 to 8.2.3 on the same page contain averaged quantities. If both quantities are unchanged why are averaged values used? Please explain.

Reply For plausibility and for the sake of clarity we do not removed the overbars. The Eqs. (8.1.1) - (8.2.3) were derived from Eqs. (5.1) - (6.3) where Q and A_{leaf} changed. If Q und A_{leaf} are constant σ_Q and $\sigma_{A_{leaf}}$ are zero, for corresponding error propagations we need σ_Q and $\sigma_{A_{leaf}}$ anyway.

Comments P. 5196 line 11: typo: “99u4” P. 5210 line 7: check grammar “depends from” P. 5215 line 8: sample flow (1.42 – 1.67 m³ s⁻¹ or 8.5 – 10 L/min). These data do not fit together. Check for the typo.

Reply We checked the typo and corrected them.

Comment P. 5232 lines 1 to 3: The m_{comp,NO_2} values reported in previous studies .. would be overestimated between 3 and 17% if the photolysis of NO_2 was not considered. “ Give more information on the $j(NO_2)$ values that are the base for this estimation.

Reply We added the $j(NO_2)$ range for the estimation into the revised paragraph page 5230, line 14 to page 5231, line 5 (see also answer to referee#1 comment 7): “The transmissivity for the wavelength range of $j(NO_2)$ was estimated on basis of available

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material information, borosilicate glass (Schott Glaswerke, Mainz, Germany) and FEP Teflon film (Thoene et al., 1991, 1996; Rondón et al., 1993, Geßler et al., 2002), $j(\text{NO}_2)$ ranged between 6.02×10^{-3} and 3.48×10^{-3} ”.

Comment P. 5235 Conclusion No. 6 can be drawn without any experimental results. Conclusion no. 6 is therefore trivial and should be deleted.

Reply We agreed and deleted conclusion no. 6 and added part of the statement into Sect. 4.2.: After page 5216, line 18: “Consequently application of future NO/NO₂ analyzers (lower detection limit (3σ) $< 2.2 \text{ nmol m}^{-3}$ ($< 0.05 \text{ ppb}$) will be useless, unless the uncertainty of the NO₂ blending for fumigation experiments is improved significantly.”

Comment P. 5235 Conclusion no. 8 is not clear to me. I can read it as request to adjust a reference cell properly (which is trivial) or as a hint that reference cells are anyhow useless. What is the conclusion no. 8? Please clarify.

Reply We modified this conclusion, which became no. 7 after deleting conclusion no. 6. Conclusion 7: “The use of an empty (“reference”) chamber for measuring non-reactive trace gases is trivial. Using it for measuring reactive trace gases it becomes more difficult because for considering (compensating) photo-chemical reactions implies that NO₂ photolysis, and the concentrations of NO₂, NO, and O₃ in the empty and in the plant chambers are identical; however, this is generally not the case, neither under laboratory or under field conditions.”

Comment Page 5237, lines 13 ff: Here seems to be a misunderstanding regarding the conception of a steady state condition. Steady state condition just means that the respective quantity does not change with time. Equilibrium is another matter. Please correct.

Reply We agreed and corrected it.

Comments Page 5238 line 19 typo “Atkinson” Page 5242 standard error listed twice, delete once

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Reply We checked the typo and corrected them.

Interactive comment on Atmos. Meas. Tech. Discuss., 4, 5183, 2011.

AMTD

4, C2504–C2509, 2011

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