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Atmospheric Measurement Techniques Discussions



# *Interactive comment on* "The dynamic chamber method: trace gas exchange fluxes (NO, $NO_2$, $O_3$) 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 p. 5201, l. 20: Why is the efficiency of the BLC so low, and how does that effect the LOD? Please state why the efficiency is higher under field conditions. Is it due to higher concentrations?

Reply The conversion efficiency of the BLC depends on the residence time of the air

sample in the cell of the BLC after the laboratory measurements and before. Field measurements we performed considerable improvements of the NO/NO2 analyzer. To get a higher efficiency during field measurements we increased the residence time inside the cell of the BLC. The actually measured quantity of the NO/NO2 analyzer is NO (therefore NO2 is converted into NO by BLC), thus the LOD of NO2 is dependent on the LOD of NO. The higher the conversion efficiency of the BLC, the lower are the detectable NO2 concentrations. For example if LOD(mNO) = 0.5 ppb a NO2 concentration of 1 ppb can only be measured if the efficiency is 50 % or higher.

Comment 2 p. 5204, l. 10: This is a rather low flow rate (and much lower than under field conditions) resulting in a rather long exchange time of the air volume in the chamber. How does this affect the results? And does it affect the comparison to field data?

Reply The exchange rate of the air volume in the chamber under laboratory conditions was indeed smaller (14 L min-1) than under field conditions (60 L min-1). But under laboratory conditions a lower exchange rate will not cause a problem because we excluded any photo-chemical reactions inside the chamber by suitable set-up. Therefore, to our knowledge no effects on chemical reactions inside the chamber were related to a longer exchange rate. Consequently it does not affect the comparison to field data.

Comment 3 p. 5206, Sect. 3.3.4: I wonder for how long time the branches were enclosed. It seems that the lid is not opened during the whole experiment?

Reply Our chamber system is a dynamic chamber system, which means there is a constant flow of air through the chamber. The chamber itself is not featured with a lid and the branches were enclosed continuously for the whole experiment. We checked that the enclosure had no effects on the physiological performance of the branch (see Sect. 5.1).

Comment 4 p.5208, l. 13. I would suppose that a temperature increase might occur in the chambers. Was this measured?



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Reply Indeed, the temperature inside the chamber was a bit higher than outside. We measured these temperatures as well. The difference was 1.53 ±0.98 K for the entire experiment. For a more general approach see Pape et al.: An automated dynamic chamber system for surface exchange measurement of non-reactive and reactive trace gases of grassland ecosystems, Biogeosciences 6, 405-429, 2009.

Comment 5 p. 5214, l. 20. I suppose the improvement was due to higher concentrations under field conditions. Please add this information.

Reply As mentioned above (reply to comment 1) the improvement was due to modification of the NO/NO2 analyzer. The residence time of the air sample in the cell of the BLC was increased. This will be mentioned in the revised manuscript, page 5214, line20: "After considerable improvement of the NO/NO2 analyzer, by what the residence time of the air sample in the cell of the BLC has been increased, precision at 1 ppb improved to nearly 10 % in the field (however, precision was still 35 % at LOD(mNO2) = 0.31 ppb (13.8 nmol m-3))."

Comment 6 p. 5526, Sect. 5.3.2: I understand the "statistical" reason to select for higher delta m,NO2, but I also think that this will bias the resulting average v_dep,NO2. Could you comment on this?

Reply The referee is 100 % correct: selecting "higher" $\Delta$m,NO2 will "bias" the resulting v_dep,NO2. However, the selection is by for not only "statistical". The selection bases on measured (!) uncertainties (errors) of the two concentration measurements (m_a,NO2 and m_s,NO2). In other words only those $\Delta$m,NO2 are accepted which are significantly different from zero considering observed errors of concentration measurements (see Sect. 3.4.5). Keeping "smaller and smaller" $\Delta$m,NO2 data would consequently result in v_dep,NO2 values which reflect more and more the noise of the concentration measurements rather than a real (significant!) small difference of m_a,NO2 and m_s,NO2. In other words, keeping those $\Delta$m,NO2 values will consequently lead to v_dep,NO2 of lower significance; i.e. "likely" to "unlikely". Therefore, we decided to use



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only those ∆m,NO2 data which are "justified" by a statistical evaluation of observed quantities including measured errors.

Comment 7 p. 5230, l. 14 to p. 5231, l. 1: I find this too speculative and not fair to the original authors because you actually assume some errors in their experiments that are not documented. Therefore, I highly suggest that you delete these lines and leave in the discussion the other parts which are justifiable.

Reply We revised the paragraph page 5230, line 14 to page 5231, line 5: "Nevertheless, we tried to estimate the potential impact of NO2 photolysis on these, previously reported v_dep,NO2. For that, the quantities Aleaf, V, j(NO2), v_dep,NO2, and transmissivity of used chamber material have to be a priori known or they must be derived from other (accompanying) data. We made an educated guess of Aleaf an available accompany date. The transmissivity for the wavelength range of j(NO2) was estimated on basis of available 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(NO2) ranged between 6.02x10-3 and 3.48x10-3. In summary: if actual NO2 photolysis would not have been considered at all, v_dep,NO2 values would have potentially been overestimated by 20 up to more than 100 % (according to Eq. (15.1)). However, applying an empty ("reference") chamber (see Sect. 5.2), the impact on NO2 photolysis on the reported vdep,NO2 values might be smaller if the underlying assumption would be correct, that the effect of NO2 photolysis is identical in the plant and in the empty chamber."

Comment 8 p. 5233, l. 19-25. This is not documented in the present paper. It might be a conclusion of the companion paper mentioned somewhere else in the text.

Reply We modified Conclusion 1, in order that it corresponds to our remarks mentioned in Sect. 5.1: Conclusion 1: "One of the most important characteristics of our dynamic chamber system is the minimal disturbance of plant physiology and growth. The check of the plant status after long-term field experiment resulted in no detectable differences



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of photosynthetic capacity between enclosed and not enclosed plant material."

Comment 9 Figure 12: It is clear that the concentration of NO and NO2 in the measurement interval is not always very stable: in the presented data-set e.g. intervals 16-20 min. and 28-32. What would be the fate of such data after your data quality check procedure?

Reply In Figure 12 the individual measurements of concentrations during a measurement cycle are presented. For our calculations we used the average of 4 minutes. However, before averaging we excluded the first nine measurement points (first 90 s), the remaining data were tested for outliers. In the mentioned intervals the significance of the difference between the two averages of m_s,i and m_a,i resulted in a significant difference for NO between sample chamber 1 and ambient air, but in a not significant difference for NO2. Between sample chamber 2 and ambient air (data for this ambient air not shown, interval 32 - 36 min) are significant for NO2 difference but not significant for NO difference.

Comment 10 Technical corrections: p. 5184, l. 9. I suggest: "detection of the photolysis product". p. 5193, l. 5. I suggest to delete "which"

Reply Text will be corrected in the revised manuscript.

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