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Atmospheric Chemistry and Physics Discussions

Interactive comment on "Field investigations of nitrogen dioxide (NO_2) exchange between plants and the atmosphere" *by* C. Breuninger et al.

C. Breuninger et al.

c.breuninger@mpic.de

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Answers to the referee comments

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.

Referee #2

1 General comments

The paper presents results of NO2 exchange measurements between the atmosphere and branches of spruce made by dynamic chambers over a period of 1.5 months. The

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main results are rather low deposition velocities and compensation point concentrations that are not differ-ent from zero.

The applied methodology is very good and well documented. One main point of the paper is that the method for analyzing NO2 is precise in the terms of the applied photolytic converter, which has negligible interference from other nitrogen compounds.

The authors discuss their results in relation to previously published results and conclude that their deposition velocities are lower than those of many other studies and that they do not find a compensation point as claimed in some other papers. This is an important statement, but it is quite difficult to judge the possible error of previous studies, because it is not known how important interferences from other nitrogen compounds could have been. The present paper could be improved by giving information of the magnitude of the possible errors due to con-version of other nitrogen compounds by the analyzer, due to chemical reactions in the cham-ber, and due to chamber wall effects.

In general, I find that the paper is well written and structured, however, I suggest that the authors are more stringent in what material goes into “Materials and Methods” and “Results” and what goes into “Discussion”. E.g. the discussion of the advantages of photolytic convert-ers (p.18169, l.23 to p.18170, l.1) should be moved.

Reply: We will check the paragraphs and where required we will rearrange some paragraphs with regard to the comments of Referee #1.

2 Specific comments

p.18164, l.17: “unequal to zero”

Reply: Text will be corrected in the revised manuscript.

p.18164, l.21: more specific than what?

Reply: We revised the sentence: “It is essential to use a more specific NO2 analyzer

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than applied at the studies before. . . “

p.18166, l.24-27: I do not get the point here: Why is this an argument for the lack of a com-pensation point?

Reply: Compensation point concentrations of NO2 between 0.3 and 3 ppb have been reported by several authors suggesting plants act as a NO2 sink or as a source of NO2. According to Lerdau et al. (2000), these results contradict the findings of Jacob and Wofsy (1990), who demonstrated that even at ambient NO2 concentrations of 0.2 to 0.4 ppb a strong uptake by plants (primary rainforest) is required to align measured NO2 concentrations in the canopy with the measured NO soil emission rates. Lerdau et al. (2000) emphasized the importance of finding an explanation for this discrepancy.

p.18168, l.10: With respect to what was the scanner calibrated and how?

Reply: The system to determine the leaf area index was calibrated by using scale paper.

p.18174, l.8: How large was the total set of observations? And how many flux values were disregarded due to this criterion?

Reply: During the field experiment nearly 3000 pairs of ma,i and ms,i have been obtained. Ap-plying the significance criterion around 60 % of the NO2 data pairs remained. We will add this information in the revised manuscript.

p. 18170, l.4: Does the (low) conversion efficiency affect the accuracy and precision of the measurements?

Reply: The conversion efficiency of the blue light converter (BLC) depends on the residence time of the air sample in 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 limit of detection (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

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if the efficiency is 50 % or higher.

p.18175, l.11: “enclosure” p.18178, l.24: I suppose it should be: “atmospheric NO2 concentrations”

Reply: Text will be corrected in the revised manuscript.

p.18181, l.3-5: I do not understand this sentence; should it rather be “results in 11-37% lower deposition velocities”?

Reply: We agree and corrected it in the manuscript.

p. 18183, l.4: It would be useful to include the size of the corrections (eq. 1) in this study to make the reader reflect on the possible size of the error.

Reply: If we differentiate our calculated NO2 exchange flux densities into the (chamber) flux densities and the gas-phase flux densities (gas phase production and destruction of NO NO2 O3), we can identify the fraction of the gas-phase reactions. For example for a se-lected leaf conductance category (high PAR radiation) the fraction of the gas-phase flux den-sities at the exchange flux density of NO2 was just +8 %, but in particular cases it could be +22 % or 12 %, respectively. We will added this information in the manuscript.

We propose to add the following text in the revised MS, approximately at page 18183, line 21ff. “In Breuninger et al. (2012), we have analyzed the effect of applying simple linear regression or bi-variate weighted linear regression (s. Table 7 there). Applying simple linear regression instead of bi-variate weighted linear regression analysis does not lead to considerably differ-ent values (numbers?), neither of NO2 compensation point concentrations nor NO2 deposition velocities. However, the statistical significance of mcomp,NO2 ïĆź 0 changes from “highly signifi-cant (P=0.999)”, if simple linear regression is applied, to “unlikely (P<0.95)”, if we used bi-variate weighted linear regression analysis.”

p.18184, l.20: Rather than using the term “unlikely”, I prefer to say that the values were

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not “significantly different from zero”. Actually this does not necessarily mean that there is no compensation point, just that the current precision of measurements are not able to detect it. The rephrasing should also be done elsewhere in the manuscript e.g. p. 18177, l.14.

Reply: We fully agree, the referee is right, “significantly different from zero” should be used instead of “unlikely” just to avoid any confusion on the fact, that nobody might ever detect mcomp,NO2 = 0, due to the still finite detection limit even of future analyzers.

We will exchange “no compensation point” in the MS against “negligible compensation point” and we will add a short chapter for definition. (see reply to referee 1).

Interactive comment on Atmos. Chem. Phys. Discuss., 12, 18163, 2012.