

Atmos. Meas. Tech. Discuss., 4, C2510–C2516, 2011

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AMTD

4, C2510–C2516, 2011

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Comment

## ***Interactive comment on* “The dynamic chamber method: trace gas exchange fluxes (NO, NO<sub>2</sub>, O<sub>3</sub>) between plants and the atmosphere in the laboratory and in the field” by C. Breuninger et al.**

**C. Breuninger et al.**

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Received and published: 30 December 2011

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 Overall it is a bit disappointing that the authors do not discuss more the physiological reason for NO<sub>2</sub> compensation point. They should also discuss the reason for the negative NO<sub>2</sub> compensation point found in the field experiment.

Reply We discussed the physiological reasons for NO<sub>2</sub> compensation point concen-  
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trations not in detail because this manuscript concerns more with the method of the dynamic chamber, as well as the analytic and mathematical techniques. But we added a reference to the present state of knowledge in the introduction. after page 5188, line 6: “While the internal plant physiological processes of atmospheric NO<sub>2</sub> consumption are known (NO is oxidized to NO<sub>2</sub> in aqueous solutions to deliver NO<sub>2</sub> (Ghaffani et al., 2005)), NO<sub>2</sub> is converted to HNO<sub>3</sub> and HNO<sub>2</sub> in water (Takahashi et al., 2007) and NO<sub>3</sub><sup>-</sup> / NO<sub>2</sub><sup>-</sup> are metabolized by corresponding reductases to NH<sub>4</sub><sup>+</sup> which is incorporated into amino acids (Lea and Mifflin, 1974; Yoneyama et al., 2003), possible NO<sub>2</sub> production processes inside plants and are to our knowledge entirely unknown.” In Table 8 (page 5221, line 3) are negative compensation point concentrations listed. Negative NO<sub>2</sub> compensation point concentrations could be generated, according to Eq. (7.1), if additional chemical processes in the chamber air volume would exist, which finally leads to NO<sub>2</sub> production. In such a case the numerator on the left side of Eq. (7.1) becomes negative, consequently the NO<sub>2</sub> compensation point will also be negative.

Comment 2 The introduction very nicely details the potential drawbacks of chamber flux measurements of O<sub>3</sub>-NO-NO<sub>2</sub>. However they do not consider at all other compounds like VOCs. Does it mean that the only significant interaction in such chambers is between O<sub>3</sub> and NO<sub>x</sub>?

Reply In the chamber VOC's are only relevant if they will generate radicals. However, we believe that the necessary OH radicals can not enter the chamber

Comment 3 There is a great number of equations which may be given as one equation for all the three gases using index notations (e.g. 1, 3, 8, . . .). This may get the paper smaller and may be easier to read. The reference to the large number of equations makes also the paper hard to read. Please consider whether this may be useful.

Reply We are thankful for this suggestion. However, after closer inspection, we are sure that the equations may eventually become easier to read, but more difficult to

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follow if we would use index notations.

Comment 4 Regarding the argument that highly sensitive instruments are needed to determine the NO<sub>2</sub> compensation point: Could one not argue that the compensation point may be determined by extrapolation of the “ms” versus “ma” line (Fig 1b) down to low concentration?

Reply Agreed! But than the error (determined by extrapolation) will become larger and larger as more the extrapolated compensation point concentration is different from the lowest measured data point(s).

Comment 5 Please consider simplifying the results presented in section 2.2 “constraints of precision”, by synthesising the results in tables. The text is very hard to read at the moment with many symbols and numbers.

Reply We agreed and added a table after page 5197, line 23 (see supplement).

Comment 6 In the constraints of design, I would suggest to consider the need to have the smallest possible aerodynamic resistance in order to be able to retrieve stomatal exchange parameters. The leaf temperature should also be characterised in order to estimate water concentrations in the stomatal cavity. I would like to know the authors opinion about these points.

Reply To establish the smallest aerodynamic resistance possible, we used mixing fans inside the chamber for continuous and complete turbulent mixing of the chamber air (see Sect. 3.3.1). As mentioned in Sect. 3.3.2 we measured the leaf temperature with thermocouples and used it for calculations of leaf conductance.

Comment 7 The authors have used a Model 49C (Thermo Electron Corporation, USA) for O<sub>3</sub> concentration measurements. They also have used electro-valves to switch between chambers and between inlet and outlet. However these analysers have been shown to have large negative readings if switching between different humidity regime, which is expected between inlets and outlets. Did the authors had to face such an issue

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and if so, how did they get round this problem? (see ref: Wilson and Birks, Environ. Sci. Technol. 2006, 40, 6361-6367).

Reply Here only a fast change between different humidity regimes may effect the analyzers readings. To avoid that influence, we skipped the first 90 s after each switching (to be sure that the signal is stable). Moreover, independent profile measurements (during EGER field measurements) of in- and above canopy concentrations of NO NO<sub>2</sub> O<sub>3</sub> performed simultaneously to our dynamic chamber measurements have shown very similar values for the ambient concentrations. Therefore we consider the effect of switching between different humidity regimes as negligible.

Comment 8 The authors speak of deposition velocity measured from the chamber. Since the mixing is very efficient, should they not rather talk of leaf conductance?

Reply We believe that one can only talk of leaf conductance, if within the series of turbulent, boundary and stomatal resistances the first two can be definitely neglected. Agreed, mixing in our chamber is complete, therefore the turbulent resistance is very low. But even if mixing is complete, the boundary layer resistance has still a finite value. So since the deposition velocity considers all resistances inside the chamber, we would still prefer to use “deposition velocity”.

Detailed comments

Comment P5185L25: Should it not be “leaf area indexes” rather than “leaf are indices”?

Reply Both notations may be used for the plural of index.

Comment P5188L24: Please specify if Aleaf is a one or a two-sided leaf area index?

Reply Which Aleaf will be used depends on the plant species and their stoma distribution at the leaf. In the case of spruce we used a two-sided leaf area index. We mention this in Sect. 3.3.5 where we described the plant material. To prevent misunderstandings (see Sect. 3.3.5) we changed in the revised manuscript one-sided Aleaf values for the field studies into the two-sided Aleaf values, so that the reader does not have to

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calculate the used two-sided values.

Comment P5189L5-L7: This statement is only true if NO/NO<sub>2</sub> is not emitted from the leaves.

Reply If we understand this comment right, it seems not to be correct. The Equation (1.4) is also true for trace gas emission, in that case the sign of the fluxes will change because concentration inside will be greater than outside the chamber.

Comment P5189L12-13: There may be a flux without “consumption” and “destruction”, as for instance in the case of a compensation point which is a concentration in equilibrium with a liquid phase. Please consider rephrasing.

Reply We do not agree with this definition of compensation point because in our opinion a equilibrium with a liquid phase is something else than the definition of the compensation point what we have considered (according to Conrad (1994)).

Comment P5190L1-L2: Wouldn't “inward” and “outward” fluxes be more appropriated here?

Reply We added the two definitions.

Comment P5190L4 & L16: Consider using italics for Latin “sensu stricto” and “a priori”.

Reply According to manuscript preparation instructions of AMT words, phrases and abbreviations referenced in the Webster's are not italicized.

Comment P5190,eq4.1 and onwards: Overbars notations have been introduced without definitions.

Reply We agree and we will integrate the definitions of the overbars in the revised manuscript.

Comment P5198L7: “stomatal” instead of “stomata”.

Reply That is right. We changed it.

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Comment P5201L6: “Air liquide”

Reply The company’s name is written as “Air Liquide” (see [www.airliquide.com](http://www.airliquide.com)).

Comment P5201L20-21: How do the authors explain this increase in conversion efficiency of the BLC?

Reply As we answered to comments of referee#1 the improvement was due to modification of the NO/NO<sub>2</sub> 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/NO<sub>2</sub> 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(mNO<sub>2</sub>) = 0.31 ppb (13.8 nmol m<sup>-3</sup>)).”

Comment Fig. 3: The color line are difficult to see: I could not identify the “dark purple line” . . . Try to use other colors.

Reply We corrected the figure captions. We labeled the lines with the wrong colors, instead of “dark purple, purple, and pink lines” it should say “black, gray and dashed line”.

Comment Fig. 7: How do you explain the negative values observed just after the step change?

Reply The negative values after the step change resulted from the internal compensation process for temperature and pressure of the analyzer after switching being too slow. Therefore we rejected the first 90 seconds after switching. We included a note into the figure caption.

Comment Appendix A: To me “molar mass” is the “mass per unit of moles”. I think there is a confusion here with “number of moles”: The “molar mass flux” is rather a “molar flux” i.e. the total number of moles leaving or entering the chamber. I suggest the authors to clarify the nomenclature.

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Reply We agreed and we changed it in the manuscript.

Please also note the supplement to this comment:

<http://www.atmos-meas-tech-discuss.net/4/C2510/2011/amtd-4-C2510-2011-supplement.pdf>

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

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