

## ***Interactive comment on “Field investigations of nitrogen dioxide (NO<sub>2</sub>) exchange between plants and the atmosphere” by C. Breuninger et al.***

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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 #1

### GENERAL COMMENTS

This manuscript reports results of chamber measurements of NO<sub>2</sub> fluxes of Norway spruce branches, compares them with earlier observations, and seeks for reasons for

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discrepancies. Contrasting some previous studies, the authors did not find a significant compensation point of the NO<sub>2</sub> flux and their deposition rates were lower than in most earlier published data. When discussing the reasons for this, the authors emphasize the accuracy of their measurements compared with some earlier studies, because they used a highly specific NO<sub>2</sub> detection system, unlike many of the earlier ones. Overall, this study seems careful and measurements and data analysis reliable. There are no novel revolutionary findings about the NO<sub>2</sub> fluxes between vegetation and the atmosphere, but it is good to get more data on this phenomenon, and the authors seem to have done their best to avoid known sources of error within this kind of chamber measurements. There are, however, some points that need to be clarified and I think the analysis requires more discussion on the implications of the findings, to give the paper more value. About the language: the paper is mainly clear and the message easily understandable but there are some errors with grammar and phrasing. I recommend a native proofreader.

Reply: We will involve a native proofreader.

### SPECIFIC COMMENTS

- I would like to see you explicitly stated what it means, in practice, if there is no compensation point. Does the NO<sub>2</sub> concentration inside the plant leaves equal zero? Is there an infinite NO<sub>2</sub> sink in the plants? You conclude that, based on your statistical tests, it is unlikely that there is a compensation point for the NO<sub>2</sub> flux. However, you also report “significant” emission of NO<sub>2</sub> (page 18179). How is that possible if there is no compensation point? Please clarify this.

Reply: The NO<sub>2</sub> concentration inside the plant leaves does not equal zero, but production and uptake are at a very low steady state. NO<sub>2</sub> concentrations inside leaves can be regarded as very low. Due to the cytotoxicity of nitrite, it can be assumed that this compound is underlying a fast turnover to be reduced to ammonia and incorporated into amino acids (Morot-Gaudry-Talarmin et al. 2002).

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We further agree with the referee, that our reported emissions contradict the phrasing that there is no compensation point concentration. We apologize for this diction. However, the emissions were very low comparing to the NO<sub>2</sub> exchange flux densities. Furthermore, the released NO<sub>2</sub> may represent a release from the leaf surface instead being an emission from inside the leaves. An evidence for that circumstance is given by the separation and classification of the NO<sub>2</sub> exchange flux densities for leaf conductance (see Fig. 4 and 5). It became apparent that at higher classes (i.e. higher leaf conductance) the NO<sub>2</sub> emission decreased and the compensation point concentration declined.

To avoid misunderstandings and to keep our estimation comprehensible we will reshape the paragraph dealing with the emissions. Basically, we will replace “no compensation point” by “negligible compensation point”. Based on our previous publication in AMT (Breuninger et al. 2012) we can define the accuracy of our measurements. We propose to add: “In Breuninger et al. (2012), we have simulated (random number application) the effect of different NO<sub>2</sub> detection limits (1.0, 0.1, and 0.01 ppb) on the minimum possible, but still highly significant NO<sub>2</sub> compensation point concentration considering several ambient and quality parameters (s. Fig. 2 there). For the given performance parameters of the NO/NO<sub>2</sub> analyzer used for this study, but otherwise optimal conditions, the minimum possible, but still highly significant NO<sub>2</sub> compensation point concentration would be < 0.1 ppb. Henceforth, when the term “negligible NO<sub>2</sub> compensation point concentration” is used, it should be understood as  $m_{comp,NO_2} < 0.1$  ppb.”

- Photolytic conversion of NO<sub>2</sub>. You very much stress the others have had insufficient measurement techniques and that is why their results differ from your highly specific ones. It would be nice if you discussed what this means. Did the others detect a real flux, of biological origin, of some other NO<sub>y</sub> compound (HONO, PAN, ?) visible to their analyzer but not yours? Or do you think their extra fluxes were purely an artifact?

Reply: It is not possible for us to distinguish if the others measured artifacts like other

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NO<sub>y</sub> compounds. As we described in Sect. 2.2.2 it is well known that molybdenum converters are non-specific for NO<sub>2</sub> because other oxidized nitrogen compounds and other organic nitrates were found to be also converted to NO, which leads to systematic and considerable overestimation of the measured NO<sub>2</sub> values. Ferrous sulfate (FeSO<sub>4</sub>) converter also overestimates the mixing ratio of NO and NO<sub>2</sub> and are not recommended for measuring NO<sub>2</sub>. Also the luminol technique is noted for interferences by ambient O<sub>3</sub> and PAN, and exhibits non-linear response at low NO<sub>2</sub> concentrations. The interferences due to O<sub>3</sub> and PAN are significant especially at low NO<sub>2</sub> concentrations. Consequently, we used the highly NO<sub>2</sub> specific photolytic blue light converter from which no interferences or any artifacts were reported. Regardless if the others measured artifacts or other compounds, we believe that there exists a substantial potential to overestimate the NO<sub>2</sub> fluxes by using unspecific measurement techniques.

We propose to add some text in the MS, approx. at page 18179, line 20 ff. (Last line of chap. 4.2. sounds as follows: Thus, discrepancies reported in the literature may be understood to be caused by the use of insufficiently specific NO<sub>2</sub>-detection techniques. “However, it might be discussed, whether or not those measurements which have used either non-photolytic converters (molybdenum or ferrous sulphate) or the luminol technique are just measurement artefacts or reflect additional (extra?) fluxes of PAN, HONO, HNO<sub>3</sub>, ethyl nitrate, and ethyl-, methyl-, n-propyl-, and n-butyl nitrate. All of these compounds generate positive interferences of the NO<sub>2</sub> detection, partially up to 100% (s. Table 2 in Breuninger et al, 2012). Therefore, if those compounds may be actually emitted from vegetation elements, either biologically or by surface (catalytic) reactions, then those measurements would be (a) an indication of additional N-fluxes (hardly to quantify), but (b) would fake enhanced NO<sub>2</sub> compensation point concentrations.” - What are the implications of your findings: do the lower deposition velocities and the non-existing compensation point affect something, for instance, in air chemistry models? Do you have an idea of how much?

Reply: Questioning a NO<sub>2</sub> compensation point concentration results in a sink which

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is much stronger than discussed so far. A high NO<sub>2</sub> compensation point would mean that remote re-gions like large rainforest would be strong sources of NO<sub>2</sub>, which is not true (see Rummel et al. 2001). But to calculate the consequence for air chemistry is something for another paper dealing with air chemistry models.

- Page 18167: Aim of the paper is: "to investigate the stomatal NO<sub>2</sub> uptake comparing field and laboratory measurements of spruce..". This sounds like you had done both field and lab measurements, which you haven't. I suggest rephrasing the aim so that it will be clear you only have field data, but you compare it with existing published data from field and lab.

Reply: We will rephrase this sentence to make clear that in this paper we present the field measurements only and that the also realized laboratory measurements were presented in a recently published paper.

- In the Methods chapter, you do not explain how the nutrient concentrations of needles were analyzed. Please add it.

Reply: We will add this information in the MS, at page 18173, line 24 ff:

"Therefore at first all the samples were grounded by a ball mill. Carbon and nitrogen were measured by an C/H/N elemental analyzer by combust the sample in an oxygen stream at temperatures of 900 °C and subsequently measured by a thermal conductivity detector. The other elements were measured by using inductively coupled plasma optical emission spec-trometry (ICP-OES).

- Page 18168: It seems your chamber walls were not rigid. How accurate is the volume of the Teflon bag chamber?

Reply: The accuracy of the chamber volume should be around 10 %. However, the volume of the chamber is not the determining issue. The essential factor is flow through the chamber (for emission calculation) and a small residence time of the air inside the chamber to follow fast reactions and to limit chemical reactions. During our study our

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residence time was short, just 75 seconds.

- The reference chamber: a) Page 18169: Please explain more clearly how the measurements were done. So you had an empty reference chamber, but it in fact was not used in the NO<sub>2</sub> measurements, only for the CO<sub>2</sub> and H<sub>2</sub>O measurement? Did you monitor the inlet and outlet NO<sub>2</sub> concentrations of the reference chamber simultaneously with the branch measurements, or did you just trust the previous empty-chamber tests reported in your earlier paper (Breuninger et al. 2012)?

Reply: The reference chamber was used for the CO<sub>2</sub> and H<sub>2</sub>O measurements which were per-formed with a two channel analyzer. So we could measure the difference between the cham-bers directly. For the other trace gases we used analyzers with only one channel, so we had to measure the inlets successively. Simultaneously measurements were not possible. The refer-ence chamber was used to detect basic contamination in the system, adsorption/desorption, as well as to investigate gas-phase chemical reactions within the chamber volume and at the wall surface.

b) If you used the earlier results: You say deposition of NO<sub>2</sub> onto the walls of the chamber was not significant. Have you tested the chamber blank in near-zero concentration, or only within the range reported in Breuninger et al 2012 (6 ppb and higher)? If not in near-zero, is it possible the chamber acted as an NO<sub>2</sub> source when the ambient concentrations decreased close to zero?

Reply: The chamber wall effects in near zero concentrations were tested during previous studies by Chaparro-Suarez et al. (2011) and were found to be negligible. For the present study we used the same materials, therefore we trust these results.

- It would be helpful especially for a first-time reader if you had the definition of symbols (m<sub>s</sub>,NO, b<sub>NO2</sub>, F<sub>ex</sub>,NO<sub>2</sub> etc) in a separate table, to make it easier to check what was what. Although some of the symbols are quite self explanatory, all are not.

Reply: We add a list of symbols and abbreviations in Appendix B

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- Page 18176: Why did you filter away the NO<sub>x</sub> concentration peaks coming from the traffic? It would have been interesting to see the flux data.

Reply: We filtered the peaks because we have no simultaneous measurements and the peaks coming from the traffic were faster than our measurement cycle. This means the peak could reach the chamber and we measured it but when measuring the ambient air the peak was gone, so we have no reference measurements for the chamber measurement.

- Chapter 3.2: This is a Results chapter. Please move to the Discussion the general background information (about how plant physiological processes and nutrient concentrations may vary) and speculation about whether the differences in potassium concentration were significant, and include only your results.

Reply: We will check the paragraphs and where required we will rearrange some paragraphs with regard to the comments of Referee #2.

- Significance of the compensation point a) Page 18177: It is a bit confusing (although apparently correct) to call the same percentages first "significance probability for  $m_{comp,NO_2} = 0$ ", then "unlikely probability for  $m_{comp,NO_2} = 0$ ". I suggest you write it for dummies, e.g. 'with a probability of 19.98% to 91.22%, the compensation point was zero' or something like that.

Reply: We respect your difficulties with the term "unlikely". Thus we will revise the text and remove the brackets.

b) Discussion: You say 'Moreover, the significance probability of the compensation point concentrations in our study was always "unlikely".' What is the limit for an "unlikely" percentage? Greater than zero? Greater than 50%? If the latter, you cannot say it was always unlikely.

Reply: For the decision whether or not a compensation point concentration exists we tested the hypothesis whether or not the average of the compensation point concentra-

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tion is different from zero. The limits are highly significantly ( $\bar{t}A_{\alpha} = 0.999$ ), significantly ( $\bar{t}A_{\alpha} = 0.99$ ), and likely ( $\bar{t}A_{\alpha} = 0.95$ ). Therefore the limit for significance was greater than 95 %.

- In the abstract and conclusions you say the compensation point was 7.4+-6.4 to 29.0+-16.3 nmol m<sup>-3</sup>, but on page 18177 you write the range started from 2.4+-9.63.

Reply: We checked it and corrected the values. The right values are 2.4+-9.63 to 29.0+-16.3.

- Page 18178: do you have any idea of why the potassium concentration was higher for the young enclosed needles?

Reply: No, we have no idea why the potassium concentration was higher for the enclosed young needles.

- Page 18179: Mention the tree species used in Chaparro-Suarez et al. (2011)

Reply: We will add this information in the revised manuscript. - Page 18181: You could refer e.g. to the study by Rondón & Granat 1994. They conclude that "the relationship between NO<sub>2</sub> needle conductance and stomatal conductance was close to 1:1." And they had a photolytic converter.

Reply: We agree and add this reference.

- Page 18183: You suggest one source of discrepancies between your results and others could be that the others did not use the bi-variate regression analysis. It is difficult for a reader to know how much this affects the results, since you do not show it. Would your deposition velocities and compensation points move closer to those observed by others, if you used the simple linear regression?

Reply: We analyzed the effect of applying simple linear regression or bi-variate weighted linear regression for our laboratory results. However, applying simple linear regression analysis the existence of a NO<sub>2</sub> compensation point becomes mostly

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not significantly different from zero. The impact of different statistical treatments on the evaluation of NO<sub>2</sub> deposition velocities is small. Using simple regression influences mainly the probability for the existence of a compensation point concentration.

We propose to add in the MS, approx. at page 18183, line 21 ff.:

Lines 17-21 on page 18183 sound as follows: In most of the previous studies simple linear regression between exchange flux density  $F_{ex,NO_2}$  and the trace gas concentration at the outlet of the sample chamber  $c_{ms,NO_2}$  were applied (Rondon et al., 1993; Rondon and Granat, 1994; Thoene et al., 1996; Sparks et al., 2001; Hereid and Monson, 2001), only Geßler et al. (2000, 2002) applied a bi-variate algorithm.

“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 different values (numbers?), neither of NO<sub>2</sub> compensation point concentrations nor NO<sub>2</sub> deposition velocities. However, the statistical significance of  $m_{comp,NO_2} \neq 0$  changes from “highly significant ( $P=0.999$ )”, if simple linear regression is applied, to “unlikely ( $P<0.95$ )”, if we used bi-variate weighted linear regression analysis.”

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