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Interactive comment on "Nitrogen oxides emission from two beech forests subjected to different nitrogen loads" *by* B. Kitzler et al.

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The editor shares the appraisal ("general comments") of referee #2 of the present manuscript (Biogeosciences Discussions, 2, S652, 2005).

However, there are more (specific) comments:

section 2.2 & 2.3 The wealth of new data presented in the manuscript provides the scientific potential of the paper. However, there is some confusion about data coverage and frequency of measurements during year 1 and year 2, as far as the individual components of N budget in both forests are concerned (N2O and CO2 and NO/NO2 flux measurements (chambers); throughfall, stemflow and litterfall measurements; dry deposition estimates (passive samplers). May be, Table 5 could be extended correspondingly (including number of individual measurements/month); alternatively, a bar diagram (monthly time steps) of data availability would be helpful.

p 1385, line 1 The closing time of the static chambers is up to two hours, which might cause a (serious) underestimation of N2O fluxes. Since the results of N2O flux measurements are crucial for the paper, a convincing verification should be presented, that the fluxes are not underestimated (more then referring to Zechmeister-Boltenstern et al., 2002). This topic may also be considered, when the authors will explain the difference in N2O fluxes measured by the automatic system (AGPS) and the manual boxes (also addressed by referee's #2 comment to p. 1394)

p 1386, line 9-12 at least when considering the partly considerably low (and sometimes even downward directed) N2O fluxes in Fig. 4b and 5b, the detection limit of the N2O flux is of substantial importance; however, a corresponding number (and/or discussion of it) is missing in the present manuscript. A precise error analysis should be done including the uncertainty in gas analysis and other possible sources of errors.

p 1386, line 14 ff. since the N2O and CO2 flux measurements have been performed by static chambers, it should specifically be mentioned, that NO and NO2 flux measurements have been performed by dynamic chambers. In this context any information about material, volume, enclosed area, rate of through-flow, dimensions and material of soil rings is entirely missing.

p 1386, line 16 ff. whereas 1ppb is given as the detection limit for the NO concentration, a corresponding detection limit of the NO and NO2 flux is missing. Also here, a precise error analysis is necessary including the uncertainty in gas analysis and other possible sources of errors. Moreover, since NO and NO2 fluxes are derived from measurements by a dynamic chamber system (flux is inferred from corresponding concentrations at in- and outlets of each chamber), precision of the NO and NO2 concentration measurements becomes of equal importance and should be considered correspondingly.

p. 1386, line 19 ff (see also list of specific comments of referee#2) The "steady state" inside the dynamic chambers depends on flow rate and volume, but particularly on the turbulent (complete) mixing of the chamber air (see Ludwig 1994; Meixner et al., 1997). There is no statement of the authors how (complete) mixing of the chambers was guaranteed. In this context, it should be mentioned, that the fact to install a fan in a dynamic chamber is by far not a self-evident proof of (complete) turbulent mixing. Using ozone as a test agent and a saturated potassium iodide solution as a perfect ozone absorber (see Galbally and Roy 1980), complete turbulent mixing in a dynamic chamber can be experimentally demonstrated (see Ludwig 1994, Meixner et al. 1997).

p 1386, line 20-26 Considering the basically bi-directional nature of NO exchange, the operation of dynamic chambers under "zero-gas" conditions (NO free air) leads definitely to a certain overestimation of NO fluxes (due to exposing the enclosed soil to low NO concentrations), e.g. Ludwig et al. 2001. How have the authors quantified this fact in their estimation of monthly and annual NO fluxes (besides the statement on p 1401, line 16-19 : "It has to be mentioned that NOx and O3 was measured in year 2003, but not in year 2002 where we used a filter to remove air impurities. We couldn't compare the differences in NO emissions between the two years regarding the different methods") ?

p 1387, line 21 ff. NOx analyzers equipped with non-specific NO2-converters (like the HORIBA APOA-360) convert also other nitrogen compounds, like PAN, NH3, HONO (already mentioned by the authors), but also HNO3, aerosol ammonium, nitrate and nitrite. But as long as a quantitative estimate of the expected interference(s) is missing, the authors could not assess their "NO2" flux measurements to the true NO2 flux. Quantification of expected interferences is not obvious; however, a "worst case" estimate based on appropriate/adopted concentration data of interfering compounds might help in this direction (e.g. below-canopy HONO measurements of Kleffmann et al., 2005). In this context, the authors should re-consider their argumentation (p 1404, line 12-16) to explain upward NO2 fluxes by positive HONO interference of the HORIBA analyzer. Since heterogeneous HONO production (from NO2) at soil, leaf, stem, litter surfaces is most likely working any time (see Kleffmann et al., Geophys. Res. Lett., 32, L05818, doi:10.1029/2005GL022524, 2005 and references therein) :

how can the authors then rule out a positive bias of (omnipresent) HONO to all their NO2 flux measurements ?

p 1387, line 23 ff The authors are right to argue that the loss of NO and NO2 to inner chamber walls is small (referencing Ludwig 1994); but for the "blank" flux of O3 this is definitely not the case (up to 30% loss, if (perspex) chambers are not pre-conditioned with high O3 concentrations; see Ludwig, 1994). Since the in-chamber O3 mixing ratio (particularly when in-chamber O3 mixing ratio is low (nighttimes)) is a crucial quantity for the correction procedure of (at least) the NO flux (see Remde et al, 1993; Ludwig 1994; Meixner et al. 1997; Butterbach-Bahl, 1997; Horvath et al. 2005), the authors should consider and comment that problem.

p 1389, line 5 ff. " Dry deposition of nitrogen dioxide (NO2) and ammonia (NH3) was captured by three passive diffusion tubes and three CEH ALPHA samplers (Tang, 2001) Ě". It is hard to understand why diffusion devices should measure/capture dry deposition (at best concentrations can be "captured"). As reported by Tang et al (2001), there exist, specifically for NO2, unavoidable positive (and negative) artifacts for NO2 measurements using passive diffusion tubes (e.g. due to "in-tube" chemical reactions (NO+O3), effects of exposure time). The error might be in the order of tens of percent, if enhanced ambient NO concentrations (several ppb) might be present (like close to the forest floor). There is no information in the present manuscript addressing these problems. However, as stated by Tang et al (2001) in their conclusions: "Passive diffusion samplers can be used successfully to monitor NO2 and NH3 concentrations, provided that the methods used have been rigorously tested, validated, and, where necessary, calibrated against recognised reference methods." Since the authors might have measured ambient NO2 concentrations (part of the dynamic chamber system), a comparison of NO2 concentrations (diffusion tube vs. chemiluminescence analyzer) will help in this direction. While it is stated, that samplers have been changed monthly, there is no information, how frequent (who many months) the three passive diffusion tubes and three CEH ALPHA samplers have been exposed at both forest sites. By

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the way: what was the purpose to expose passive samplers not only "in the forest", but also "at open sites nearby"? For the sake of completeness: dry deposition as one component of the N budget (even at forest floor) comprises not only NH3 and NO2, but also dry deposition of (NO, if soil compensation mixing ratio is exceeded), HONO, HNO3, PAN, aerosol ammonium, nitrate and nitrite.

p 1389, line 7-10 Since the amount of NO2 and NH3 dry deposition, one of the considered components of N exchange in both forests (see Tab. 2), is derived by the product of NO2 and NH3 concentration and the corresponding deposition velocity : the justification for using (constant) deposition velocities of 1.5mm s-1 for NO2 and 3mm s-1 for NH3 just by citing "Duyzer, pers. comm." is certainly not appropriate with respect to the complexity of the in-canopy dry deposition process.

If there will be convincing arguments for the reported NO2 dry deposition estimates by diffusion tubes, dynamic chamber derived NO2-fluxes may be compared to dry deposition values from the passive samplers. Using the numbers given in the present manuscript, a back-on-the-envelope calculation yields :

SW: 14.8 ug/(m2h) NO2 dry deposition, passive samplers (from Table 2) SW: 2.7 ug/(m2h) NO2 dry deposition, chambers (from section 3.4.3) KL: 7.1 ug/(m2h) NO2 dry deposition, passive samplers (from Table 2) KL: 2.4 ug/(m2h) NO2 dry deposition, chambers (from section 3.4.3, upscaled to 12 months).

p 1394, line 2-15 p 1395, line 21 p 1396, line 6 p 1398, line 11-13 Does it make sense to present and discuss (linear) correlations of N2O emission (as well as NO emission) vs. soil moisture considering the state-of-the-art knowledge about highly non-linear relation of N2O and NO fluxes vs. soil moisture (see Davidson 1993, Otter et al. 1999, Ludwig et al, 2001 and stated (for NO) by the authors on p 1400, line 20)?

p 1395, line 11 versus p 1395, line 18 Before discussing this difference, it may be meaningful to consider the following:

NO, once emitted from the forest floor is (at least partly) oxidized to NO2 still in the trunk space by ozone, which is transported from above the canopy by turbulence. (At most forests floors, the back-reaction, namely the photolysis of NO2 (forming NO) is low or even negligible due to low available short wave radiation). Part of the NO2 (oxidized NO from soil) could be deposited to soil (and plant) surfaces. As has been shown by Gut et al. (2002), some ten percent of the soil emitted NO, oxidized by O3 (originating from above the canopy) to NO2, could be "immediately" deposited to the forest soil. However, there remains the question whether the NO2, which is deposited to the soil (a) is oxidized NO2 (from soil emitted NO) or (b) is originating from above the canopy (by advection and subsequent vertical turbulent diffusion into the forest canopy) ? (see Jacob and Bakwin (1992), Rummel et al. (2002); Meixner et al. (2003)). In other words, in the present manuscript, the origin of the NO2 (deposited to the forest floor of both forests) seems to be the NO2, which is advected from above canopy. If so, what about the oxidized NO2 (from soil emitted NO)? Discussion of this issue (at least mentioning the described problem in the final version of the manuscript) is necessary.

p 1400, line 16 0.2 (year 1) and 0.7 (year 2) kg ha-1 are compared with 0.24 (year 1) and 0.49 (year 2) kg ha-1yr-1 in Table 4 ?

p 1403, line 13 there is already (at least) one publication about topographic variability of N2O fluxes (Corre et al., 1996)

Table 3 & manuscript vs. Table 4, Fig 5-7 & manuscript is there any reason why to call upward fluxes of N2O and NO "losses" (when in kg ha-1 yr-1 ?) and "emissions" (when in ug m-2 h-1) ?

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literature:

Corre, M.D., C. van Kessel, and D.J. Pennock (1996), Landscape and seasonal patterns of nitrous oxide emissions in a semiarid region, Soil Science Society of America

Journal 60:1806-1815.

Galbally, I.E. and Roy, C.R. (1980). Destruction of ozone at the earth's surface.Quart. J. Roy. Meteor. Soc., 106, 599-620.

Horvath et al. (2005), Biogeochemistry Discussions, 2(3), Nitric oxide and nitrous oxide emission from Hungarian forest soils; link with atmospheric N-deposition, 703-723.

Jacob, D.J., Bakwin, P.S. (1992), Cycling of NO in tropical forest canopies. In: W.B. Whitman (Editor), Microbial Production and Consumption of Greenhouse Gases. American Society of Microbiology, Washington, D.C., pp. 237-253

Meixner, F.X., Andreae, M.O., van Dijk, S.M., Gut, U.A., Rummel, U.K., Scheibe, M., Welling, M. (2003), Biosphere-atmosphere exchange of reactive trace gases in a primary rainforest ecosystem : studies on interlinking scales, Report Series in Aerosol Science, 62A, 269-274.

Meixner, F.X., Fickinger, Th., Marufu, L., Serca, D. Nathaus, F.J., Makina, E., Mukurumbira, L., Andreae, M.O. (1997), Preliminary results on nitric oxide emission from a southern African savanna ecosystem, Nutrient Cycling in Agroecosystems, 48, 123-138.

Remde, A., Ludwig, J., Meixner, F.X., and Conrad, R. (1993). A study to explain the emission of nitric oxide from a marsh soil. Journal of Atmospheric Chemistry, 17, 249-275.

Rummel, U., Ammann, C., Gut, A., Meixner, F.X., Andreae, M.O. (2002), Eddy covariance measurements of nitric oxide flux within an Amazonian rain forest, Journal of Geophysical Research, 107 (D20), 8050, doi:10.1029/2001JD000520

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