**Biogeosciences
Discussions**

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

B. Kitzler et al.

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We are grateful for the comments of the reviewer and did our best to answer the questions. For easy reading we wrote the questions and suggestions of the reviewers in boxes, answered directly beneath and wrote the changes in the manuscript in "cursive".

General comments:

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

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

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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.

For better understanding of data coverage we inserted now a new Figure (Fig. 1) showing the measurement frequency from N2O, CO2, NOx, emissions, throughfall and stemflow, dry deposition and litterfall.

Static chambers:

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)

Closing time:

Preinvestigations have shown that for low N2O fluxes as in our forests 2 hours closing time give more reliable results than shorter closing times. We never observed a flattening of the N2O increase in our chambers, which would indicate that we approach the compensation point for N2O.

"Duplicate air samples were taken from the chambers with 60\,ml polypropylene gastight syringes at an interval of 0, 1 and 2\,h. Linearity of emission was always tested. We never observed a flattening of the N2O increase in our chambers, which would indicate that we approach the compensation point for N2O. Additional measurements every 15 minutes showed that the increase in N2O concentrations remained linear for

up to 4 hours (Zechmeister-Boltenstern et al., 2002)."

Pre-investigations were also conducted for the AGPS system, where 3 samples were taken. The first sample was taken after 10min., the second after 55min. and the third after 100min. These investigations showed also a linearity of concentrations over time. Because of these control measurements and the small difference (120 vs. 100min) in incubation time is unlikely to be the cause for differences between manual and AGPS measurements.

Dynamic chambers:

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 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).

General information:

We reformulated the mentioned section and included information about chamber type, material, volume, enclosed area, rate of through-flow and dimensions.

"Air samples were taken from six stainless steel chambers (Area: 0,03m2; Vol: 3,27l;

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flow rate 1l min-1) connected to the NOx-analyzer via PTFE tubing (inner diameter: 4mm; length: 10m). The closing (Plexiglas lid) of the dynamic chambers is initiated by a motor. One of the six dynamic chambers was used as a reference chamber by sealing the opening to the soil through a Plexiglas pane. The chambers were closed for 5min within which steady state was reached."

Mixing and pressure:

The volume of our chambers is small (Vol: 3,27l), and turbulent mixing is reached more easily than with larger chambers. We used the method suggested by the editor (Ludwig 1994) to test turbulent mixing in the dynamic chamber in an experiment carried out in Garmisch-Partenkirchen. A chamber was placed on sand and under artificial ozone gassing of 73.66 ppbv we measured an ozone concentration at the outlet of 10.16 ppbv resulting in a deposition velocity of 0.0164 m s-1 and an upper estimate for the resistance in the chamber of 61 s m-1. This value is accordance to published values by (Meixner et al., 1997; Gut et al., 2002) (55 and 60, respectively). The concentrations and area of KJ container are as follows (O3 in: 73.66 ppbv, O3 out: 10.16 ppbv, A(KJ): 63.62 cm-2).

Detection limits and error analyses:

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 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.

N2O:

Regarding the N2O flux we made an error analysis with all possible sources of errors (gas analysis, temperature) and inserted the detection limit of N2O flux.

P 1368, line 5. "We quantified a minimum detectable N2O flux of 0.04 μg Nm-2 h-1 and the relative error falls below <17% with a median of 5%."

NO:

We also made a comprehensive error analysis for NO flux and inserted the following data into section 2.3.

"The detection limit of the NOx-analyzer (HORIBA APNA-360) was 1ppbv NO or 0.6 μg NO m-2 h-1. The calculated error was high for fluxes near the detection limit ˜130%, whereas it was low for high NO fluxes ˜3%. A median error was calculated to be ˜15% and ˜35% for NO and NO2, respectively."

NOx fluxes:

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"?

We inserted in section 2.3.

"Considering the basically bi-directional nature of NO exchange, the operation of dynamic chambers under "zero-gas" conditions (NO free air) can lead to an overestimation of NO fluxes due to exposing the enclosed soil to low NO concentrations (Ludwig et al. 2001). As the NO fluxes measured from our chambers are very low and NO concentrations are far under calculated compensation points of 50 ppbv (SW) and 24 ppbv (KL) (at 15°C) determined in a laboratory experiment the error by using "zero-gas" was neglible in our case."

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 ?

We agree with the editor regarding the upward flux of NO2. As our NOx analyser is not specifically constructed to separate NO2 from other oxidised nitrogen compounds, we changed our argumentation at page 1401, line 12-16.

"As our NOx analyzer doesn't measure NO2 specifically (see 2.3), the upward flux of NO2 could be explained by the conversion of other nitrogen compounds. HONO

for example might be abundant in substantial amounts in forest atmospheres, but as HONO production (from NO2) is most likely working any time (Kleffmann et al., 2005) also other nitrogen compounds may contribute to an upward flux."

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.

We agree with the editor, that an O3 loss can not be excluded although our chambers consist of a stainless steel frame and a 20cm2 Perspex lid. Therefore we performed an error analysis and revealed that when the ozone concentration is underestimated by 30%, what is unlikely to occur in our chambers (only the lid is made of Perspex) , as published by Ludwig (1994), the calculated NO flux would be less than 0.2 μg N m-2 h-1. This value is smaller than the detection limit and we therefore suppose that the error is of minor importance.

We inserted in section 2.3:

An error analyses revealed that O3 loss to chamber walls is not source of concern. If O3 would be lost by as much as 30%, as reported by Ludwig (1994) for full Perspex chambers, the change of NO flux is less than 0.2 μg N m-2 h-1 which is smaller than the detection limit.

Dry deposition:

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) Eˇ ". 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 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.

Use of passive diffusion samplers:

We inserted in section 2.6.

Passive diffusion samplers are widely used to monitor atmospheric concentrations of trace gases such as NH3 and NO2 (Krupa and Legge, 2000; Brown, 2000). The am-

monia ALPHA sampler method (used by CEH, Edinburgh) is rigorously tested against a reference active diffusion denuder method (Sutton et al, 2001). A modification of the GRADKO diffusion tube, which is widely used in the UK was used for monitoring NO2 (Stevenson et al, 2001). This diffusion tube was modified by adding a turbulence damping membrane across the inlet. It was extensively validated (Bush et al, 2001) and has been rigorously tested against measurements by continuous chemiluminescence analyzers (Cape et al, 2004).

The open site was used to show that the presence of trees changes the deposition rates, i.e. it acts as a control. Ideally one would measure NH3 and NO2 concentrations above the canopy, but this was not possible for 50% of the Nofretete sites, due to the lack of towers.

General comments:

We made several changes to ensure easy reading: p 1389, line 5 ff.

"Dry deposition as one component of the N budget comprises NH3 and NO2, but also dries deposition of NO (if soil compensation mixing ratio is exceeded), HONO, HNO3, PAN, aerosol ammonium, nitrate and nitrite. In this study dry deposition of nitrogen dioxide (NO2) and ammonia (NH3) was measured by three passive diffusion tubes and three CEH ALPHA samplers (Tang, 2001) and were analysed by CEH Edinburgh."

Frequency:

In Table 2 and in Fig. 3 and section 3.3 it is mentioned explicitly that dry deposition was only measured in the first investigation year. But for better understanding we inserted the measuring time under point 2.6.

Dry deposition was measured in the first investigation year, whereas wet deposition was measured throughout the study period (Fig. 1).

Total dry deposition:

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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).

As it was not within the scope of this study to measure atmospheric turbulence, we couldn't calculate deposition velocities. We used however calculated vd's based on very recent research on this matter at CEH and also by applying a standard vd for NH3 used by NETCEN. All methods suggest that our estimate of N deposition rates is a conservative estimate.

We inserted in Section 3.3. Concentration of NH3, NO2 was measured in the first year and amounted to 14.3 and 3.0 μg NH3 m-3 and 115.4 and 54.2 μg NO2 m-3 in SW and KL, respectively. Under the assumption that the above mentioned deposition velocities are correct we estimated a deposition of NH3 and NO2 of 2.38 and 0.85 kg ha-1y-1 in SW and KL, respectively, thus, displaying highly significant differences between the sites (p<0.001). A total of 22.6kg and 13.5kg N ha-1y-1 was deposited from the atmosphere in SW and KL, respectively (year 1) and it has to be emphasized that N-deposition is dominated by wet deposition at our sites.

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NO2 deposition of passive samplers and NO2 deposition from chambers can only be compared for the period when the ambient air was not cleaned before it was introduced to the chambers. This is year 2003. We measured NO2 deposition with passive samplers from May 2002 until April 2003. NO and NO2 from chambers in KL was only measured from August to October 2003. A comparison of NO2 fluxes from chambers with NO2 deposition measured with passive samplers over such short time periods would be not valid.

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.

We inserted in the discussion in part 4.3.

"In the trunkspace part of the NO emitted from the soil may be converted by reactions with ozone vented into the trunkspace from the atmosphere. NO2 is formed in this reac-

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tion. As a result of this the NO emitted from the forest floor may reach the atmosphere. It will be converted to NO2 in the trunkspace and may be related to NO recently emitted from the soil and not from the atmosphere. This NO2 can be partly deposited to the forest soil. NO2 which is deposited to the soil can also originate from above the canopy (by advection and subsequent vertical turbulent diffusion into the forest canopy) (Jacob and Bakwin (1992); Rummel et al. (2002); Meixner et al. (2003). The deposition flux observed in our chambers may be therefore related to atmospheric NO2 as the amount of NO2 measured from the passive samplers is higher than NO2 deposition measured in the chambers. As, measuring NO2 in the trunkspace was not within the scope of the work it has to be mentioned that the reported fluxes may consequently not represent the fluxes exchanged at the forest atmosphere interface."

General comments:

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)?

During the vegetation period a positive dependency was of soil moisture on N2O was found. As optimum soil moisture was never reached we neither reached maximum emissions. This explains the positive linear relationship during summer. For better understanding and to avoid confusion, we deleted the presented correlations in the text.

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 ?

There was an editing mistake from an older manuscript version. We corrected the wrong value at page 1400. Thank you for mentioning this.

BGD

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

We considered now existing publications to this topic in the discussion:

Landscape-scale patterns of N2O production/emission are controlled by topography through its influence on fundamental hydrologic and pedologic processes as reported previously by Corre, (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) ?

There is no reason for using emission and losses. In the present manuscript we changed "losses" into "emissions" for better reading.

Interactive comment on Biogeosciences Discussions, 2, 1381, 2005.

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