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Interactive comment on “Controls over N_2O, NO_x and CO_2 fluxes in a calcareous mountain forest soil” *by* B. Kitzler et al.

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Interactive comment on “Controls over N2O, NOx and CO2 fluxes in a calcareous mountain forest soil” by B. Kitzler et al. F. Meixner (Editor)

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The editor still feels, that the wealth of the data presented by Kitzler et al. is important enough to favour publication in Biogeosciences.

But even in the revised manuscript, there are still a number of serious open questions (chamber measurements; deposition estimates), and also a number of confusing information as far as (a) time periods of measurements, calculations and annual estimates, and (b) units of fluxes, emissions, production rates, etc. are concerned.

We thank the editor for the enormous amount of time and effort put into the improvement of our manuscripts. Still, there seem to be some obvious misunderstandings, which we tried to finally clarify in this version. (The responses of the authors to the editor comments are marked as 1A - 11A).

(1) throughout the manuscript there is considerable confusion with respect to the time periods for measurements, time periods for calculation of fluxes and time periods for "annual" estimates (see paragraphs 2.2, 2.3, 2.6, 3.3.1, 3.3.2, 3.3.3, 4.4, as well as Table 2 - 5 & 7, and Figures 1 - 4). Particularly, as far as the terms "year 1" and "year 2" are concerned, there is no indication whether they relate (a) to the full calendar year 2002, 2003, 2004, or (b) to a duration of full 12 month (e.g. April 2002 to April 2003), or (c) to "vegetation periods" of 2002 and 2003, or (c) to June-November 2002 (year 1) and May-November 2003" (Tab. 5). Finally, the reader is finally left confused and unable to judge the results of time-series analysis.

(2) throughout the manuscript the authors make use of a variety of units for their observed rates (emission, deposition, production and throughfall). Rates are given in terms of mass per area per time, however, the reader finds units of "kg ha-1 a-1" as well as "ug m-2 h-1" (which hampers comparison of data, particularly between Table 4 and Table 5). Furthermore, mass is referred to either mass of N, mass of N2, mass of NO, mass of NO2, mass of NO-N, mass of NO2-N, and mass of N2O-N. This is particularly confusing and entertains (unnecessary) doubts on the reported results.

(3) in this context, there is also some confusion about "annual" rates. Table 4 there "mean annual CO2-C, N2O-N and mean NO-N" rates are given in units of "ug m-2 h-1"; however, if there is actually emphasis on "annual" rates they should be related to the temporal unit of a year (i.e. "kg ha-1 a-1" may be used). In Table 4 "mean annual rates" for the "vegetation period" are given (but no information about the duration of the vegetation period). If the presented rates truly relate to the corresponding vegetation periods of year 1 and year 2 (to whatever year 1 and year 2 is relating), then the term "mean annual rates" is wrong; if the authors have upscaled the measured rates for the "vegetation period" to a full year (to whatever the full year is relating), then the upscaling procedure must be described. Table 5 same as for Table 4, but as "annual

rates" for the N2O- and NO measurements with automated chambers are concerned ("annual rates" vs. "June-November 2002 (year 1) and May-November 2003 (year 2)").

(1A, 2A, and 3A) We agree with the editor and tried to avoid confusion in the revised version of the manuscript. We further specified the information about time periods for calculation of fluxes and time periods for "annual" estimates, and units of observed rates and hope that the manuscript can be read more easily now. These changes were made in para. 2.2; 2.3; 2.6; 3.3.1; 3.3.2; 3.3.3; 4.4; Tables 2-5 and Figures 1-4. Additionally, year 1 and year 2 on which the calculations depend are now shown explicitly in all Figures (2nd X axis). Calculations for N2O - N (AGPS) and NO - N are based on shorter time periods and are now clearly mentioned in the text (para. 2.2; 2.3) and figures (4 and 5).

(4) Table 4 and Table 5 make reference to "mean annual rates". However if one attempts to compare the results, he will be surprised by the following: "manual" chambers: year 1: CO2 emission 11.6 mg m-2 h-1 (= 1016 kg ha-1 a-1) from Table 4 year 2: CO2 emission 19.7 mg m-2 h-1 (= 1726 kg ha-1 a-1) from Table 4 year 1: CO2 emission (11.6 mg m-2 h-1) 1020 kg ha-1 a-1 from Table 5 year 2: CO2 emission (18.7 mg m-2 h-1) 1636 kg ha-1 a-1 from Table 5

year 1: N2O emission 4.5 ug m-2 h-1 (= 0.39 kg ha-1 a-1) from Table 4 year 2: N2O emission 4.4 ug m-2 h-1 (= 0.39 kg ha-1 a-1) from Table 4 year 1: N2O emission (3.42 ug m-2 h-1) 0.30 kg ha-1 a-1 from Table 5 year 2: N2O emission (4.68 ug m-2 h-1) 0.41 kg ha-1 a-1 from Table 5

"automated" chambers: year 1: N2O emission (2.51 ug m-2 h-1) 0.22 kg ha-1 a-1 from Table 5 year 2: N2O emission (2.17 ug m-2 h-1) 0.19 kg ha-1 a-1 from Table 5

year 1: NO emission 0.7 ug m-2 h-1 (= 0.06 kg ha-1 a-1) from Table 4 year 2: NO emission 0.5 ug m-2 h-1 (= 0.04 kg ha-1 a-1) from Table 4 year 1: NO emission (0.34 ug m-2 h-1) 0.03 kg ha-1 a-1 from Table 5 year 2: NO emission (0.34 ug m-2 h-1) 0.03 kg ha-1 a-1 from Table 5 In any further revision of their manuscript, the authors should elucidate of the obvious differences of "mean annual rates".

(4A) Differences between hourly flux rates and calculated mean annual rates are inherent to the way of calculation. The measured mean hourly emission rates were multiplied with the days between the manual sampling times that were for example not always exactly 14days but sometimes 12 days or 15 days etc. The same (14, 12, 15 days etc.) period was then used for automatic daily values. By weighting the emissions a more realistic annual rate can be calculated.” Furthermore, N2O from the AGPS and NO emissions are not calculated for the entire year but for a) June - November 2002 and b) May-November 2003 and is now stated explicitly in the tables and in the text.

We wrote in the material and method part: “Annual rates were calculated by weighting hourly emission rates with the exact period between sampling times.”

(5) there is also considerable confusion (doubts) on the given NO2 deposition rates. According to Table 3, the "mean annual" NO2 deposition rate for "study year 1" / "year 1" (actually inferred for May 2002 - 2003, see Figure 2) is 0.96 kg ha-1 a-1, which corresponds to 10.96 ug m-2 s-1 (in terms of mass of N). In paragraph 3.3.3 the authors quote NO2 deposition rates (as measured by the automated chamber system) of 0.4 and 0.3 ug NO2 m-2 h-1 for 2002 and 2003, respectively (actually, the deposition rate of 2002 is given in units of ug NO m-2 h-1, but might be a typing error). As already metioned above, it is not clear whether the authors deliberately expressed here their NO2 deposition rates in terms of mass of NO2, or (consistency suggested) in terms of NO2-N. If rates are given in terms of mass of NO2, then the reported 0.4 and 0.3 ug m-2 h-1 (for 2002 and 2003), would be 0.12 and 0.09 ug m-2 h-1 in terms of mass of N. Anyway, the dramatic difference between 10.96 ug m-2 s-1 (by the passive sampler/fixed deposition velocity approach, see 2.6) and 0.4 (0.12) and 0.3 (0.09) ug m-2 h-1 (by automated chambers) requires convincing elucidation.

(7) also in the context of comment (5), the editor likes to point the authors to paragraph 2.6 ("Deposition measurements"). They state, that "Dry deposition of NO2 and NH3

was captured by three passive diffusion tubes and three CEH ALPHA samplers, respectively (Tang et al., 2001) and were analysed by CEH Edinburgh. They were placed in the canopy at the investigation site and at an open site nearby, at a height of 1.5m and were changed monthly. Dry deposition velocities were assumed to be 1.5mm s-1 for NO2 and 3mms-1 for NH3 (Duyzer, pers. comm.)". Diffusion devices are not able to measure/capture dry deposition : at best, corresponding concentrations can be "captured". As far as the capability of passive samplers to correctly "capture" ambient NO2 concentrations is concerned, the editor likes to cite Tang et al (2001): "For NO2 sampling, positive bias also arises from the reaction of NO with O3 within the sampler. The interference from the chemical reaction is severe close to NO sources, with errors up to 30% for curbside locations when using the ‘tubetype’ sampler.Eˇ . In some implementations, there is also a negative bias over long sampling periods caused by the degradation of trapped NO2." Therefore, there exist, specifically for NO2, unavoidable positive (and negative) artefacts 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 must have measured ambient NO2 (i.e., NOx minus NO) concentrations (part of the dynamic chamber system), a comparison of NO2 concentrations (diffusion tube vs. chemiluminescence analyzer) may help in this direction. However, if NO2 concentrations derived from both systems might agree (even within +-tens of %), then the authors have still to tackle the problem, why the NO2 deposition rates derived (a) by the passive sampler/fixed deposition velocity approach and (b) by automated chambers differ by a factor of at 25 (if not 100, depending of reference to NO2 or NO2-N, see comment (5)).

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By the way: what was the purpose to expose passive samplers not only "in the canopy at the investigation site", but also "at an open site 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. The authors should at least mention that (if not give a zero-order estimate of the missing part of dry deposition, using literature data).

(5A) The dashed line was and is showing a full measuring year (from 1.May 2002-31.April 2003). Concerning the NO2 deposition rates: All mentioned values are referring to NO2-N and the manuscript was corrected accordingly.

(7A, 5A) The diffusion samplers described in Tang et al., 2001 were tested at several urban and rural sites and published as a CEH report to the Scottish funding agency SEERAD in January 2001 (McGowan et al., 2002) which we now have cited instead of Tang et al., 2001.

We agree with the referee and changed information about dry deposition in the material and methods part into:

“Dry N-deposition comprises NH3 and NO2, NO (if soil compensation mixing ratio is exceeded), HONO, HNO3, PAN, aerosol ammonium, nitrate and nitrite. In this study, concentrations of NO2 and NH3 were captured by three passive diffusion tubes and three CEH ALPHA samplers, respectively (McGowan et al., 2002) and were analysed at CEH Edinburgh. Passive diffusion samplers can be used to monitor NO2 and NH3 concentrations. The methods have been rigorously tested, validated, and, calibrated against reference methods. However, there are artefacts for NO2 measurements using passive diffusion tubes. Positive bias can arise from the reaction of NO with O3 within the sampler, a negative bias can arise due to the degradation of trapped NO2 (McGowan et al., 2002). At NO concentrations of several ppb, the concentration can be off by tens of percent. Furthermore, NO once emitted from the forest soil is rapidly converted to NO2 by O3 (Rummel el al., 2002). In this study the samplers were placed in the canopy at the investigation site at a height of 1.5m and were changed monthly. Dry deposition velocities were assumed to be 1.5mm s−1 for NO2 and 3mms−1 for NH3 (Duyzer, pers. comm.). Wet deposition was collected biweekly using 15 crown throughfall collectors. Wet deposition was analysed for NH+4 -N and NO−3 -N (Dionex DX100 and Dionex 120). Concentrations of NO2 and NH3 were measured in the first investigation year (May 02 - April 03), whereas wet deposition was measured in the first and the second investigation year (May 03 - April 04).“

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. As this information was not important for this work we deleted the information about measuring outside the forest canopy.

Nevertheless, there is an obvious difference between NO2 concentrations between ambient air and passive samplers. NO2 concentrations in ambient air varied from 0 ppb to max. 12ppb. We have compared our NO2 concentrations with concentrations measured at the same site in another project (Smidt, personal communication) from 1994-2001 and found similar concentrations. Mean ambient air concentration from October 02 for example was 1.44 ppb. When using a factor of 1.89 (for 20°C and 1bar) we would have 2.7 μg m-3 NO2 in these months. For the same months a concentration of 8.313 μg m-3 was measured with the provided passive samplers. So we have a factor of 6. We can only hypothesize why we have measured different concentrations with the two methods:

NO2 fluxes measured with the NOx analyzer and NO2 deposition measured with passive samplers may differ as: Ţ the measuring height is different Ţ Herbal vegetation (cover at the measuring site ˜90%) may trap NO2 and provide a physical barrier between NO2 from soil and from atmosphere Ţ Water may have condensed in the tubing

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system and as the solubility of NO2 is high in H2O (compared to NO), some NO2 may have been trapped before it reached the analyzer. Ţ our NOx analyzer doesn’t measure NO2 specifically (as now mentioned in the material and method section). Ţ Wind might have played an important role, as wind speed is lower in the diffusion samplers and concentrations are higher. Ţ The detection limits of the two methods are different.

(6) in the context of comment (5), the editor likes to point the authors to paragraph 2.3 ("NO flux measurements"). They state, that "to avoid reactions of NO and O3 in the chambers, a filter cylinder, filled with Purafil and activated charcoal, was used in 2002 as no ozone analyzer was available in this year". Since there is no further information in paragraph 2.3, it is assumed that the "filter cylinder" (a) has been applied in front of the dynamic chamber(s) in 2002, and (b) was no longer applied in 2003 (due to the availability of an O3 analyzer in 2003).

Due to state-of-the-art experience, a filter cylinder, filled with Purafil and activated charcoal removes effectively not only ozone from the ambient air, but also NO2 (and NO). If so, then NO2 free air has entered the automated chamber system in 2002. Surprisingly, the authors report a NO2 deposition rate of 0.4 ug m-2 h-1 (in terms of mass of NO, NO2 or NO2-N?) measured by the dynamic chamber system in 2002 (see 3.3.3). Where is the NO2 coming from? More surprisingly, the NO2 deposition rate for 2003 (0.3 ug m-2 h-1, in terms of mass of NO2 or NO2-N?), when no fliter cylinder has been applied (?) is quite similar to that of 2002.

(6A) You are exactly right in your argument. This discrepancy is a consequence of the following: According to the suggestions of the reviewers in the course of the total revision process of this manuscript (and our beech forest manuscript) we have changed the calculations of the annual fluxes from calendar year (2002, 2003, 2004) to measurement years (year 1: May 2002-April 2003, year 2: May 2003-April 2004) in both manuscripts. Therefore measured NO2 deposition from the second calendar year (measured without filter) now shows up the first measurement year. NO2 deposition listed in year 1 is the mean of April 2003 values. To be more precise we deleted this one month mean NO2 deposition rate.

(8) for CO2, N2O, NO (and most likely also NO2), partially (very) low fluxes and (in case of NO) bi-directional fluxes have been observed (see Fig. 3). Therefore, it would enhance the quality of the manuscript, to quantify the detection limits of CO2-, N2O-, NO-, and NO2-fluxes. Corresponding numbers (and/or discussion of them) are missing in the present manuscript. A precise error analysis should be done including the uncertainty in gas analysis and other possible sources of errors. A graphical representation of each flux detection limit in Fig. 3 a-c (e.g. as grey shaded "deadband" around zero-flux) is recommended. Whereas 1ppb is given as the detection limit for the NO concentration, corresponding detection limits of the NO and NO2 fluxes are entirely missing. 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.

(8A) We agree with the editor and introduced information about the detection limits of CO2-, N2O-, NO-, and NO2-fluxes or made a reference to the second manuscript submitted to the BG as sample analysis was the same.

(9) the editor likes to point the authors to the problem of the pressure difference (dynamic chamber - ambient air) which is most critical for under- and overestimation of chamber derived fluxes. The authors may wonder why the editor strongly recommends the autors to give a finite number of the pressure deficit of their chambers under their mode of operation. For explanation, they may have a intensive look (at least) to the following publications: (a) Reichman, R., Rolston, D.E. (2002) Design and performance of a dynamic gas flux chamber, J. Environ. Qual. 31:1774-1781 (2) Davidson, E.A., Savage, K., Verchot, L.V., Navarro, R. (2002) Minimizing artefacts and biases in chamber-based measurements of soil respiration, Agricultural and Forest Meteorology 113:21-37. Pressure deficits already in the range of a few tenth of Pa to a few Pa have generally been observed to cause flux overestimation in the order of tens of percent

(see also reference lists in (a) and (b)).

(9A) We agree with the editor regarding the need of a finite number of pressure deficit of our chambers.

“The measured pressure deficit (Pressure sensor: PCLA 12X5D Sensor Technics) in our chambers is $<$ than 0.6 Pa and irrelevant for N-fluxes. Turbulence in the chambers was tested as suggested by (Ludwig, 1994). The resistance of O3 in the chamber was 61 s m−1 and is in accordance to published values (55 and 60 s m−1) by (Meixner et al., 1997; Gut et al., 2002).”

10) the editor likes to point the authors to the problem of the considerable underestimation of static chamber derived fluxes when using (a) shallow chambers (in the present case: h = 8 cm) and (b) long closing times (2 h) as described by Rayment (2000): Rayment, M. B.: Closed chamber systems underestimate soil CO efflux 2 , Europ. J. Soil Sci, 51, 107-110, 2000. The authors are recommended to reflect this problem for their measured CO2 as well as for their N2O emission fluxes.

(10A) Compared to many other investigations fluxes in the presented forests are very low and compensation points were not reached. Using higher chambers and/or shorter closing times we would raise our detection limits. Preinvestigations have shown that for the low N2O fluxes in our forest 2 hours closing time gives 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. 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 also showed a linearity of concentrations over time and we are convinced that with our static chamber fluxes were not underestimated.

“Gas measurements were carried out as described in Kitzler et al. (2005). Gas samples of four manually operated chambers (area: 1m2, volume: 80 l) were taken biweekly from May 2002 until July 2004. Duplicate air samples from the chambers were taken after 0, 1 and 2 h and injected into gas tight head-space vials (20 ml). Linearity of emission was always tested. We never observed a flattening of the N2O increase in our chambers, which would indicate an approach of 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)."

(11) The authors have published a companion paper on nitrogen oxides emissions from the Schottenwald- and Klausenleopoldsdorf sites (near Vienna, Austria), see Kitzler, B., Zechmeister-Boltenstern, S., Holtermann, C., Skiba, U., Butterbach-Bahl, K. (2005), Nitrogen oxides emission from two beech forests subjected to different nitrogen loads, Biogeosciences Discussion, 2(5), S1381-S1422. The editor has provided an "editor comment" to this manuscript (see Meixner, F.X. (2005), Interactive comment on "Nitrogen oxides emission from two beech forests subjected to different nitrogen loads" by B. Kitzler et al., Biogeosciences Discussions, 2, S709-S715). Since the authors most likely have applied (presumably very) similar flux instrumentation and methodologies at the Achenkirch site as at both Vienna sites, they are finally recommended to consider these editor's comments also for their present manuscript.

Interactive comment on Biogeosciences Discussions, 2, 1423, 2005.