

Interactive comment on “Controls over N₂O, NO_x and CO₂ fluxes in a calcareous mountain forest soil” by B. Kitzler et al.

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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.

(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).

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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)").

(4) Table 4 and Table 5 make reference to "mean annual rates". However if one at-

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tempts 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".

(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 $0.96 \text{ kg ha}^{-1} \text{ a}^{-1}$, which corresponds to $10.96 \text{ ug m}^{-2} \text{ s}^{-1}$ (in terms of mass of N).

In paragraph 3.3.3 the authors quote NO_2 deposition rates (as measured by the automated chamber system) of 0.4 and $0.3 \text{ ug NO}_2 \text{ m}^{-2} \text{ h}^{-1}$ for 2002 and 2003, respectively (actually, the deposition rate of 2002 is given in units of $\text{ug NO m}^{-2} \text{ h}^{-1}$, but might be a typing error). As already mentioned above, it is not clear whether the authors deliberately expressed here their NO_2 deposition rates in terms of mass of NO_2 , or (consistency suggested) in terms of $\text{NO}_2\text{-N}$. If rates are given in terms of mass of NO_2 , then the reported 0.4 and $0.3 \text{ ug m}^{-2} \text{ h}^{-1}$ (for 2002 and 2003), would be 0.12 and $0.09 \text{ ug m}^{-2} \text{ h}^{-1}$ in terms of mass of N.

Anyway, the dramatic difference between $10.96 \text{ ug m}^{-2} \text{ s}^{-1}$ (by the passive sampler/fixed deposition velocity approach, see 2.6) and 0.4 (0.12) and 0.3 (0.09) $\text{ug m}^{-2} \text{ h}^{-1}$ (by automated chambers) requires convincing elucidation.

(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 NO_2 (and NO). If so, then NO_2 free air has entered the automated chamber system in 2002. Surprisingly, the authors report a NO_2 deposition rate of $0.4 \text{ ug m}^{-2} \text{ h}^{-1}$ (in terms of mass of NO, NO_2 or $\text{NO}_2\text{-N}$?) measured by the dynamic chamber system in 2002 (see 3.3.3). Where is the NO_2 coming from? More surprisingly, the NO_2 deposition rate for 2003 ($0.3 \text{ ug m}^{-2} \text{ h}^{-1}$, in terms of mass of NO_2 or $\text{NO}_2\text{-N}$?), when no filter cylinder has been applied (?) is quite similar to that of 2002.

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(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 3mm s⁻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. 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) 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 must have measured ambient NO₂ (i.e., NO_x minus NO) concentrations (part of the dynamic chamber system), a comparison of NO₂ concentrations

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(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)).

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).

(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.

(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

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chamber derived fluxes. The authors may wonder why the editor strongly recommends the authors 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 artifacts 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)).

(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.

(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

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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.

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2, S830–S837, 2005

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