

***Interactive comment on* “The relationship between ammonia emissions from a poultry farm and soil NO and N₂O fluxes from a downwind source” by U. Skiba et al.**

U. Skiba et al.

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Author's reply to: Biogeosciences Discussions, 2, S843-S847, 2005
www.biogeosciences.net/bgd/2/S843/ Biogeosciences Discussions Interactive comment on “The relationship between ammonia emissions from a poultry farm and soil NO and N₂O fluxes from a downwind source” by U. Skiba et al. F. Meixner (Editor) meixner@mpch-mainz.mpg.de Received and published: 8 January 2006 1) Editors comment: The authors ask referee #1 (in context with referee's #1 comment no.5), why he does not like short papers. The editor feels, that the referee's concern is not with the length of the paper, it is rather with the substance of the paper which referee #1 judges to be not sufficient to merit separate publication. More generally, yes - conventional journals like short papers (for obvious reasons), but as soon as shortness of a paper comes along with the lack of clarity and/or comprehensibility,

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then a recommendation like that of referee #1 becomes serious. 1) Authors reply I have provided additional information to mainly the materials and methods and result sections in order to reduce any lack of clarity.

2) Editors comment: Additionally, the editor likes to put further questions / comments on the manuscript bgd-2005-0045. (1) Have the authors reflected the problem of the considerable underestimation of static chamber derived fluxes when using (shallow?) chambers and long closing times (1 h) as described by Rayment (2000) ? Rayment, M. B.: Closed chamber systems underestimate soil CO efflux, *Europ. J. Soil Sci*, 51, 107-110, 2000. 2) Authors reply: As we are dealing with N₂O and not soil respiration it perhaps may be more appropriate to consult Conen's work rather than Rayment's work on this matter (Conen F, Smith KA, 2000: An explanation of linear increases in gas concentration under closed chambers used to measure gas exchange between soil and the atmosphere *Europ. J. Soil Sci*, (1), 111-117). According to the method described by Conen and Smith (2000) I have calculated the potential underestimation from using static rather than dynamic chambers, and thereby not including any N₂O stored in the soil air, as 9% for the 1 m² auto chamber and 16% for the 40 cm diameter round chambers. Rates of underestimation are less than any spatial and temporal variability. These underestimates are not trivial, but compared to the temporal and spatial variability encountered here and elsewhere in the literature are small. I have included this information in the materials and method section as follows: There are views that the static enclosure method underestimates the real flux by not considering N₂O stored in the surface layers of the soil. The linear model developed by Conen and Smith (2005) to calculate the fraction of N₂O stored in soil air suggests that the potential underestimation by using static rather than dynamic chambers was 9% for the 1 m² autochamber and 16% for the 40 cm diameter round chambers. These underestimates are not trivial and therefore absolute values should be treated with caution. However, as the same static chamber approach was used for all chambers a comparison between sites receiving different rates of deposition is valid. Using shallow chambers and 1-hour closure times are standard procedures for N₂O flux measurements. Employment of

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deeper chambers or shorter closure times is often not possible due to detection limits of the gas chromatograph. The methodology/ detection limits are described in detail by MacDonald et al (as cited in my paper) and have now been also been added to the materials and methods section: The detection limit of the ECD for N₂O was < 20 ppb and the precision was 2%. Concentrations were calculated against an N₂O standard containing 1 ppm N₂O in a 20% O₂, 80% N₂ mix. The ECD response was linear in the range of 0.3 to >10 ppm N₂O. The enclosure time of 1 hour was routinely applied; tests showed that the N₂O concentration inside both chamber types increased linearly with time of closure for at least 2 hours.

3) Editors comment: Since the authors reference their static chamber method to Kitzler et al. (2005), they may also consider the corresponding editor's comments to that manuscript (Biogeosciences Discussions, 2, S1381-S1422, 2005) and to the companion paper of Kitzler et al. (Biogeosciences Discussions, 2, S1423-S1455, 2005). 3) Authors reply: The reference to Kitzler et al. (Biogeosciences Discussions, 2, S1423-S1455, 2005) refers only to the description of the automatic chamber used.

4) Editors comment: (2) Can the authors guarantee (a) complete mixing of their dynamic chambers, and (b) negligible pressure deficit between ambient and chamber atmospheres? ad (a): The "steady state" inside dynamic chambers depends on flow rate and volume, but particularly on the turbulent (complete) mixing of the chamber air (see Ludwig 1994). In this context, it should be mentioned, that the fact to install two small fans in the 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). ad (b): the pressure difference (dynamic chamber - ambient air) is most critical for under- and overestimation of dynamic chamber derived fluxes. 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. For further expla-

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nation, the authors may have an intensive look (at least) to the following publications: Reichman, R., Rolston, D.E. (2002) Design and performance of a dynamic gas flux chamber, *J. Environ. Qual.* 31:1774-1781 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. 4) Authors reply: a) The chamber system is described in detail by Pilegaard et al. (1999) (as referenced in my paper). In his paper Pilegaard et al showed that a high flow rate of 7 l/min for the 22.6 l chamber was sufficient to obtain thorough turbulent mixing. Our flowrate was larger (11 l/min) and once dug into the ground the chamber volume was slightly smaller (18 l). So one can assume that mixing was complete. This assumption has been included in the materials and methods section: Complete mixing of air inside the chambers was not demonstrated here, but was shown by Pilegaard et al (1999) under very similar conditions. b) We checked the atmospheric pressure inside the chamber using a pressure transducer on several occasions. There was always a positive pressure inside the closed dynamic chambers. This has been stated in the materials and methods section: Positive pressure was maintained under these conditions.

5) Editors comment: (3) "Cumulative monthly concentrations of NH₃ and NO₂ were measured by passive diffusion. Triplicate alpha samplers for NH₃ and diffusion tubes for NO₂ were installed at a height of 1.5 m at all sites and were analysed by conductivity within two weeks of collection (Tang et al., 2001)" (page 980, line 14-18 of manuscript bgd-2005- 0045). While there is convincing evidence in Tang et al (2001) that passive samplers correctly capture NH₃ concentrations, there is nothing equivalent for NO₂: "Work is now currently in progress for NO₂ sampling", see page 526 in Tang et al, 2001), and "On the other hand, negative bias reported for longer exposure times can lead to underestimation of NO₂ concentration, and more work is required to address the issue of sample stability", see page page 526 in Tang et al, 2001). As far as the capability of passive samplers to correctly capture ambient NO₂ concentrations is concerned, the editor likes to cite again 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." (page 513 in Tang et al, 2001). 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." (page 526 in Tang et al, 2001) Since the authors must have measured ambient NO₂ concentrations (part of the dynamic chamber system), a comparison of NO₂ concentrations (diffusion tube vs. chemiluminescence analyzer) will definitely help in this direction. 5) Authors reply: I am sorry I provided the incorrect reference for the NO₂ diffusion work. Since the Tang 2001 publication, Sim Tang and her colleagues have carried out extensive tests comparing different diffusion samplers (2 types of tube architecture and 2 types of chemical absorbents) at several rural and urban sites with chemiluminescence measurements. Based on these tests the diffusion tube reported in Tang (2001) was modified and the agreement between chemiluminescence and diffusion tube is excellent ($y= 1.0066x+0.2182$, $r^2 = 0.989$). This work was published as a CEH report to the Scottish funding agency SEERAD in January 2001 (McGowan et al, 2002), Sim Tang is soon preparing an article for peer reviewed publication. The reference to Mc Gowan et al has been included in the manuscript: McGowan, G.M., Palmer, S.C.F., Tang, Y.S., van Dijk, N, Cape, J.N., Sutton, M.A., Love, L. & Storeton-West, R. 2002, Biodiversity in Road Site Verges, 1. Extensive botanical survey, 2. Test and validation of passive diffusion sampling methods for long-term ambient monitoring of NO₂ and NH₃ concentrations. CEH Interim report to SEERAD, project

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C01759, 79 pages Ambient NO₂ was measured 10 cm above the forest floor for 4 min every hour by chemiluminescence. For the period 1.1.04 to 1.6.04 median NO₂ concentrations were: 4.75 $\mu\text{g NO}_2/\text{m}^3$ and ranged from 0 to 32.9 $\mu\text{g NO}_2/\text{m}^3$ (n = 3436). For the same period the median from 5 monthly integrated NO₂ measurements by passive diffusion at a 1.5 m height were 3.97 $\mu\text{g NO}_2/\text{m}^3$ and ranged from 3.19 to 4.15 $\mu\text{g NO}_2/\text{m}^3$ (n=5). These concentrations are similar and this information has been included in the materials and methods section, as the McGowan reference may not be readily available to all readers: The passive samplers, providing integrated monthly concentrations, have been calibrated against recognised reference methods (Tang et al, 2001, MacGowan et al, 2004). In addition the NO₂ concentrations measured from the open dynamic chambers for 4 minutes every hour 10 cm above the forest floor, for the period 1.1.04 to 1.6.04 (median: 4.75 $\mu\text{g NO}_2/\text{m}^3$, range: 0 to 32.9 $\mu\text{g NO}_2/\text{m}^3$ n = 3436) were very similar to the median from 5 monthly integrated NO₂ measurements by passive diffusion at a 1.5 m height (3.97 $\mu\text{g NO}_2/\text{m}^3$, range: 3.19 to 4.15 $\mu\text{g NO}_2/\text{m}^3$, n = 5). NH₃ concentrations were not measured at a more intensive time resolution.

6) Editors comment: Furthermore, NO once being emitted from the forest soil is rather rapidly converted to NO₂ by ozone (turbulent transport from aloft). The conversion can easily reach 100% particularly in the first few meters above the forest floor (e.g. Rummel et al., 2002). So, it is a rather fair assumption, that part of the NO₂ concentration captured by the passive samplers is converted biogenic NO. The authors are kindly asked to consider this fact. 6) Authors reply: The average NO fluxes 15, and 25 m downwind of the farm were 111.2 and 123.3 $\mu\text{g NO}/\text{m}^2/\text{h}$ and declined sharply to 38.3 $\mu\text{g NO}/\text{m}^2/\text{h}$ 45 m downwind. If the NO emitted from the soil would significantly influence the NO₂ captured by passive diffusion, then a good correlation between NO flux and NO₂ deposition should be expected. The data however do not show such correlation. Average NO₂ concentrations measured by monthly diffusion at the three sites closest to the farm were: 3.9, 4.3 and 4.1 $\mu\text{g NO}_2/\text{m}^3$.

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7) Editors comment: (4) in the context of (3), the editor wonders, why the authors have not compared dynamic chamber NO₂ deposition rates (which can be easily be inferred from their dynamic chamber measurements, see Butterbach- Bahl et al., 1997) with those obtained by the passive sampler/fixed deposition velocity approach ("... deposition velocity of 1.5mms⁻¹ was applied for NO₂ (Duyzer, pers. comm.)", see page 982 of manuscript bgd-2005-0045)? 7) Authors reply: The average NO₂ deposition rate calculated from the chambers was 1.15 kg N ha⁻¹ y⁻¹. This suggests a NO₂ deposition velocity of 3 mm s⁻¹. I have adjusted the text and table 1 accordingly: The average NO₂ deposition rate calculated from the continuous NO/NO₂ flux measurements by chambers was 1.15 kg N ha⁻¹ y⁻¹. This deposition rate together with the NO₂ concentrations measured by passive diffusion implies a NO₂ deposition velocity of 3 mm s⁻¹. The wet and dry deposition of oxidised N was of similar magnitude, but much smaller than the deposition of reduced N (Table1).

8) Editors comment: (5) for the estimation of dry deposition NO₂ fluxes, the authors make use of a constant deposition velocity of 1.5mms⁻¹. Considering the rather complex interaction of in-canopy turbulent transport with vegetation uptake processes and chemical reaction of the NO-NO₂-O₃ triad (e.g. Meixner et al, 2003) this is a very crude (and not state of- the-art) approach. By the way, what deposition velocities have been used for NH₃? The editor feels, that any reader would most likely welcome a bit more precise information in this direction than the present statement, namely "Rates of NH₃ deposition to the forest floor were calculated using concentration dependent deposition velocities for NH₃ as described by Fowler et al. (1998)". 8) Authors reply: I realise that the use of standard deposition velocities is a very crude way of calculating fluxes. It obviously would be best to measure the deposition fluxes, and second best to calculate deposition velocities. Neither was possible, as the appropriate measurements were not made. For this reason I felt that the best approximation of deposition fluxes was only achievable by using those published and measured elsewhere. In response to your referees I have already altered my manuscript so that the comparison with fluxes are made with NO₂ and NH₃ concentrations and NOT with deposition fluxes. However, I

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do feel it is helpful to the reader to get a feel of the approximate magnitude of the deposition fluxes in relation to the emission fluxes. I hope the uncertainty of these estimates is obvious in my paper. I furthermore have tried to explain the reason for using the concentration dependent deposition fluxes and have included the following text: Rates of NH₃ deposition to the relatively open forest floor were estimated using deposition velocities calculated elsewhere, because necessary meteorological variables to calculate deposition velocities from first principals were not measured in this forest. The same concentration dependent deposition velocities as used by Fowler et al. (1998) for the same forest a few years earlier were also applied in this study. These NH₃ deposition velocities were based on observations that over a moorland vegetation canopy resistance increased from 20 s m⁻¹ at 0.3 g NH₃ m⁻³ to 50 s m⁻¹ at 2 g NH₃ m⁻³ for example for wet canopy surfaces (Flechard and Fowler, 1998). Average NH₃ deposition rates close to the farm may therefore be 62, 42, 23 kg NH₃-N ha⁻¹ y⁻¹ compared to the background deposition rates of 5 kg NH₃-N ha⁻¹ y⁻¹ (Table 1). The uncertainties in assuming same canopy and aerodynamic resistances for a forest and moorland ecosystem at slightly different locations are high; however in comparison with the wet deposition of NH₄⁺ do show almost identical fractional increases above background deposition rates in rainwater as calculated for dry NH₃ deposition rates (Table 1).

Editors References : Galbally, I.E. and Roy, C.R. (1980). Destruction of ozone at the earth's surface. *Quart. J. Meteor. Soc.*, 106, 599-620. Ludwig J (1994) Untersuchungen zum Austausch von Stickoxiden zwischen Biosphaere und Atmosphaere. Ph.D thesis, University of Bayreuth, Germany (see also Butterbach-Bahl et al. (1997), Fluxes of NO and N₂O from temperate forest soils: impact of forest type, N deposition and of liming on the NO and N₂O emissions, *Nutrient Cycling in Agroecosystems* 48: 79-90) Meixner et al. (1997), Preliminary results on nitric oxide emission from a southern African savanna ecosystem, *Nutrient Cycling in Agroecosystems*, 48, 123-138. 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, Re-

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