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Atmospheric Chemistry and Physics
Discussions

Interactive comment on "Measurements of nitric oxide and ammonia soil fluxes from a wet savanna ecosystem site in West Africa during the DACCIWA field campaign" *by* Federica Pacifico et al.

Anonymous Referee #1

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1. General comments:

The manuscript by Pacifico et al. presents a study of nitric oxide (NO) and ammonia (NH3) soil fluxes form four different land cover types within a wet savanna ecosystem in West Africa. The biogeochemical cycles of both NO and NH3 are strongly altered by anthropogenic activity and their surface-atmosphere exchange has important impacts on atmospheric chemistry and air quality. With a strong increase of anthropogenic emissions and only little or no observations in this region of the world, the presented study is an important contribution.

The manuscript is structured well and the research is presented in a scientifically sound way. However, there are some main aspects which are lacking clarification and have to be improved:

The interpretation of presented fluxes largely depends on the quality of the flux measurements. For the determination of fluxes using the closed-dynamic chamber technique the authors use several assumptions without discussing their validity. For example, it cannot be assumed that there are no interactions of NH3 with the chamber walls without adequate test experiments. While I highly acknowledge the fact that measurements in the present study region are challenging, I believe the validity of the used assumptions has to be tested. An accurate flux error assessment is especially necessary for NH3, which is subject to bi-directional exchange, and might explain some of the strong variability of the presented results.

The authors use the measured NO and NH3 fluxes for a stepwise linear multiple regression analysis, upscaling to country-wide soil fluxes, and comparison with soil emission estimates from the GEOS-Chem model. These analyses give valuable information on the importance of soil NO and NH3 exchange and our current knowledge about them. However, while the authors state that a process understanding of the NO and NH3 fluxes is not within the scope of the presented study, in my opinion it is important to understand the underlying processes of the measured fluxes. For example, the estimated emissions from soil characteristics only poorly agree with the measured fluxes in some parts, which indicates that a more detailed process understanding is necessary.

The study focuses on soil fluxes, which is why the authors do not discuss the impact of vegetation on the NO and NH3 fluxes. Especially for NH3, a present canopy may significantly alter the net ecosystem flux and I suggest to add a note including this aspect in the discussion of the manuscript.

2. Specific comments:

L. 50: The study by Oswald et al. (2013) is on soil HONO emissions. Please cite here the original publication for NO emissions (IPCC or other original source).

L. 159: Active charcoal is mainly suitable for medium to high molecular weight compounds and compounds with low volatility. Hence, I am surprised that the active charcoal was enough to remove all ambient air NH3. Was the quality of zero air source also tested against other methods? If so, please state this in the manuscript.

L. 180: The assumption that the concentration in the chamber is equal to the concentration leaving the chamber to the analyzer is questionable. Due to the low flow rate required for the practical use of the closed-dynamic chamber technique, the residence time within the chamber is substantial (17-18 min). As no active mixing (e.g. with fan) is used, the chamber geometry in relation to the positioning of the ambient air inlet and sample outlet is of importance.

L. 181-182: Especially NH3 is known to be a very sticky molecules and it cannot necessarily be assumed that it does not adsorb to Teflon material. E.g. from online NH3 measurements there is strong evidence that NH3 significantly interacts with the walls of used inlet Teflon tubing, already on a short time scale. The adsorption strength is thought to depend mainly on temperature, presence of NH3 and particulate matter on the Teflon surface, or relative humidity. Likewise, there could be a substantial effect depending on whether the manual chamber was cleaned before each measurement or not. Potential wall effects on NH3 fluxes are an important issue and should be addressed, e.g. by performing a field blank test or adequate laboratory test experiments.

L. 190-193: Both the dilution effect and the detection limit are directly linked to the considered time interval. To my understanding, with longer time intervals the dilution effect increases and the detection limit decreases. As stated in the manuscript, for NO a shorter time interval (120s) was chosen than for NH3 (180-300s) (note here: in Delon et al. (2017), the time intervals for NO and NH3 were the opposite). According to this, the dilution effect is larger for NH3 than for NO, however, the stated detection limit is smaller for an NO than NH3, which should be the opposite. Please correct these

inconsistencies or explain the differences in the revised manuscript.

L. 202-203: Please state if a 1-sigma or 3-sigma detection limit is given here.

L. 227-228: Key for the quality of the closed-dynamic chamber technique is the accurate determination of the initial concentration slope after the chamber installation. For this reason, the authors correctly omit fluxes where the slope is below a threshold correlation coefficient and the measured concentration difference is low. However, especially for NH3, where a R2 threshold value of 0.4 was chosen, the knowledge of the flux error is important for the further interpretation and might explain some of the presented flux variations. Therefore, the authors should include an estimate of the flux error associated with the linear regression and take that into account for the discussion of results.

L. 248-250: This assumptions seems brave if it was not tested with a set of test experiments. Although the microbial activity is reduced due to the dry conditions, there is a chance that NH3 volatilizes with the drying of the soil sample material.

L. 368-439: Presentation of NO and NH3 flux results: The flux at the soil-atmosphere interface is governed next to processes in the soil by the ambient trace gas concentration above the soil surface. The authors report relevant soil properties, while the atmospheric NO and NH3 mixing ratios from the chamber measurement are not reported. As they might significantly impact the magnitude and sign of the fluxes, the authors should include this information in the figures and the manuscript. This is especially important for the interpretation of the NH3 fluxes which are subject to bi-directional exchange and might explain some of the large flux variations observed.

L. 385-387: Why are the underground roots especially important for bare soil and the maize field? Are they more dominant than roots at the grassland and forest site?

L. 431-434: I agree with the authors in addressing the issue of the NH4+ adsorption capacity of soil particles when interpreting the results from the soil measurements.

However, in this context it is also important what method was chosen to determine the soil NH_4^+. E.g. some common methods use a potassium chloride solution, to extract the soil NH_4^+. As a consequence, using a strong extraction solution might result in an overestimation of the emission potential.

L. 435-436: The authors bring up the potential of NH_3 deposition on water film on vegetation surfaces, although the study focuses on soil emissions. Hence, it is important to mention (e.g. in method section) in case the chamber measurements also incorporated lower growing plant species (e.g. for grassland site) and include that in the interpretation of the results (i.e, stomatal emission potential).

3. Technical comments:

L. 109: Use capital in “Guinean”

L. 122: Use “next to” instead of “next”

L. 124: Use “next to the grassland site” instead of “next to grassland site”

L. 304-306: It is common to use the past tense for reporting on measurement results. Also, total rainfall should be added for completeness.

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