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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.

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Please see the Supplement for better editing of the same text and figures

The authors greatly thank the reviewer for the interesting and constructive comments on the manuscript. We will try below to answer the questions and propose solutions. The reviewer’s question is in italic, while the author’s answer is below. The line numbers where the modifications are made correspond to the new version of the manuscript. General comments: 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 referee is totally right in stating that experimental tests are lacking on ammonia adsorption on Teflon chamber walls, in comparison with other surfaces. However, we have trusted the literature on that specific question. Vaittinen et al. (2013, and references therein), have systematically assessed the adsorption of gas phase NH3 on various surface materials. They have stated that polymers generally adsorb less NH3 than stainless steel surfaces (giving that adsorption is the difference between the inlet and outlet mixing ratio). 12 molecules.cm on PFA. The surface of our chamber is 2700 cm , which gives a value of As an example, in their Table 2, they assess that the adsorption of ammonia is 13.9.10 -2 2 12 concentrationsmeasuredonthefield).Thevolumeofthechamberis12300cm (12.3liters).One 37530.10 molecules adsorbed (for a given concentration of 8.5 ppb, which is in the upper range of 3 23 23 12 -5 3.3.10 molecules compared to 37530.10 gives an amount of 1.14.10 % adsorbed on the surface of the chamber. The surface of the Teflon tubing is 2π*0.22*400 cm2 = 553 cm2, i.e. it may adsorb 553*13.9.1012 = mole of gas occupies 22.4 liters, therefore the chamber contains 0.55 moles of gas, i.e. 3.3.10 molecules. 12 -7 7685.10 We therefore suggest that the flux error, relative to ammonia adsorption on Teflon walls, is negligible. The following text has been added line 178: (Vaittinen et al. (2013, and references therein), have demonstrated that the adsorption of ammonia on Teflon walls is negligible) 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, molecules (2.3.10 %). 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 authors agree that a close understanding of the underlying processes of NO and NH3 exchanges is important. There is a misunderstanding of what we wanted to state by writing that the understanding of these processes is not in the scope of this study. Indeed, in our study, we could not find any strong correlation between soil moisture and fluxes, or soil temperature and fluxes, because of the spatial set up of the experiment (with 4 types of soil described). However, this set up is useful to represent the spatial variability of fluxes. This may justify why we did not present any plot of flux magnitude vs environmental variable, but rather temporal evolution of fluxes and comparison with modeling results. Line 520, we have removed the sentence “which is not in the scope of this study” 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. Yes indeed, the role of vegetation in regulating NH3 and NO fluxes from soils is of prime importance. Line 419 we added the following paragraph: The NO flux estimated in this study takes into account the ground flux only. Indeed, the net emission to the atmosphere should take into account the oxidation of NO in NO2 and the eventual re-deposition of NO2 on the vegetation called the Canopy Reduction Factor, assumed to be a linear function of Leaf Area Index (defined for example in Yienger and Levy (1995) and Ganzeveld et al.(2002)). Line 457 we added the following paragraph: Our measurements were conducted without vegetation inside the chambers, but vegetation was present in the fields. It is important to mention that the role of vegetation on NH3 bidirectional fluxes is essential, especially during the wet

season (time of the experiment), when deposition on the vegetation through stomata and cuticles dominate the exchange (during rain events, the cuticular resistance becomes small and cuticular deposition dominates), due to an increase of the deposition velocity of NH3 (consecutive to the humidity response of the surface) and a decrease of the canopy compensation point, sensitive to the surface temperature and the surface wetness (Wichink-Kruit et al., 2007). 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). The reference will be changed by the IPCC reference. 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.

Line 157, the following explanations have been added: “....and a second one to validate the efficiency of the NH3 converter with a NH3/N2 mixture diluted in pure air (Alphagaz 1, Airliquide). The zero air for NO, NO2 calibration was obtained by filtering ambient air, previously passed on charcoal and desiccant cartridges.” 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. As described in Delon et al. (2017): The external volume of the chamber was 40 cm × 20 cm × 20 cm. The useful volume was 18 ×38 ×18 cm3 (12.3l or 0.0123m3), due to the thickness of the Teflonwalls. The air inlet is on one side of the chamber (a small vent of 4 mm in diameter provided the pressure equilibrium between the inside and outside of the chamber). The air outlet on the other side (40 cm away) is connected to the analyzer with a 4 m Teflon tube. These specifications are not recalled in the manuscript, we just added: Line 181: the details of the calculation “and chamber design” are given in Delon et al. (2017). 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. This point was mentioned in the general comments, and considering the literature, we propose to neglect the adsorption of NH3 on Teflon walls and Teflon tubing (for particular temperature, humidity and concentration conditions). Of course, the temperature and humidity conditions in our experiment are different, but even if the number of adsorbed molecules increases, it may not bring discredit on our results A sentence has been added in the manuscript line 181. During this experiment, unfortunately no field blank test has been made. Line 173 we added the following text: The Teflon chamber was cleaned at the beginning of each day of measurement, and during the day when the deposition of sand was considered too important in it. Line 221 we added the following text: The measurements have not been corrected from a possible interaction with particulate matter. 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. Thanks for mentioning this inconsistency.

Actually, the considered time interval varies in a range between 100 and 300s both for NH3 and NO (this is different from Delon et al., 2017). The dilution effect is calculated

separately for each flux and the correction is 7.7 (±1.7) % in average for NH3 fluxes, and 6.7 (±1.6) % in average for NO fluxes. The minimum flux measurable is calculated from the precision of the instrument (and not from the detection limit), which is ±0.4 ppbv f, for a 10s time interval. It does not depend on the time interval used for the calculation of the linear regression. The minimum flux detected by this device would -2 -1 therefore be 0.4 ngN m s for NH3 and for NO. Line 190 the paragraph has been changed into: The linear regression is calculated over a 100 to 300 s time interval after the installation of the chamber on soil for both NO and NH3. Based on the methodology developed in Delon et al. (2017), the dilution effect due to mixing of outside air in the chamber is calculated for each flux separately and is in average 6.7(±1.6) % for NO and 7.7(±1.7) % for NH3. Considering the precision of the analyzer (±0.4 ppbv), the detection limit is 0.4 ngN m-2 s-1 for NO and NH3 fluxes (different from Delon et al., 2017, but fluxes were anyway superior to this value). L. 202-203: Please state if a 1-sigma or 3-sigma detection limit is given here. A 2-sigma detection limit is given, added line 201 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. Line 226, the following point was added: A flux error was estimated, by calculating the dispersion of points around the linear regression line used to calculate the slope. According to this method, the dispersion for NO flux calculation is comprised between 5 and 12%, and the dispersion for NH3 flux calculation is comprised between 15 and 20%.. L. 248-250: This assumption 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. The authors are aware of this particular problem of NH3 volatilization. The analyses have been made as soon as possible after the field campaign. A direct analysis was not possible, due to missing infrastructure. Freezing the samples would have been the best solution, but considering the difficulty of organizing the campaign in a place where the minimum material was installed, we could not afford to bring a freezer. Line 255, new references have been added in the text: Some authors have also published results of ammonium concentrations measured in soils that were dried in ambient air (Bai et al., 2010, Dick et al., 2006, Cassity-Duffrey et al., 2015).

Very few values of ammonium concentrations in African soils are available in the literature, it is therefore very difficult to compare. Line 360, the following references have been added: + -1 Dick et al. (2006) have found NH4 concentrations between 2 and 8 mgN.kg in Senegalese soils, which is very close from our results. Vanlauwe et al. (2002) have found values between 0.8 and 1.4 -1 mgN.kg in West African moist savanna soils (in Togo and Nigeria).. 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. Figure 2 to 5 have been modified and concentrations have been added (see new figures at the end of this document) In section 3.4 line 391 we have added the following paragraph: Daily means of NO concentrations are measured close to the soil (0.1m, half height of the chamber) and reported in fig. 2 to 5. Daily means of NO concentration vary from 1.28 to 5.40 ppb for all sites. The average concentration during the whole campaign on all sites is 2.70 ± 1.03 ppb. Average concentration on bare soil is 2.97 ± 1.49 ppb, it is 2.57 ± 0.96 ppb on grassland, 2.55 ± 0.83 on maize, and 2.76 ± 0.65 ppb on forest soils. The concentrations are quasi equivalent for all

sites. As these concentrations are low, they do not lead to NO deposition on the soil, the NO flux keeps being positive. Indeed, NO deposition has already been measured but only in the case of high NO concentrations (>60ppb, Laville et al., 2011). In section 3.5 line 437 we have added the following paragraph: As for NO concentrations, NH3 concentrations are reported in fig. 2 to 5. Daily means of NH3 concentration vary from 0 to 12.46 ppb for all sites, and the average concentration is 4.42 ± 3.23 ppb during the whole campaign. Average NH3 concentration for bare soils is 6.28 ± 3.90 ppb, it is 3.28 ± 1.79 ppb for grassland, 4.36 ± 3.99 for maize field, and 3.68 ± 2.13 ppb for forest. The largest deposition fluxes are found on bare soils, where the largest concentrations are measured. 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? Line 397 the paragraph has been modified: The spatial variability of NO fluxes is high, for bare soil, forest and the maize field where underground roots (not visible at the surface) are heterogeneously distributed. These roots are likely to influence the ammonium content of the soil and the subsequent NO flux measurement. Standard th th deviation is generally smaller for grassland (except for two days, July 9 and 13) , where the vegetation (and the root distribution) is more homogeneous. The repartition of the vegetation is more homogeneous in grassland. Roots are present everywhere, and their presence is less variable in grassland plots, whereas bare soil and maize plots present a larger heterogeneity. 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 NH4+. E.g. some

common methods use a potassium chloride solution, to extract the soil NH4+. As a consequence, using a strong extraction solution might result in an overestimation of the emission potential. Material and Method section mentions that mineral and organic nitrogen are determined following norm NF ISO 13878. There is an error in the text. NF ISO 13878 is used for Total N. This has been corrected. Line 263 the following text has been added: Mineral nitrogen is determined following an internal method MT-

AZM adapted from norm NF ISO 14256-2. This method uses a potassium chloride solution and is COFRAC certified. PS: the concentration is unknown because the lab does not want to communicate on it. L. 435-436: The authors bring up the potential of NH3 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). All the measurements were made on direct soil without vegetation, even in the grassland field (the grass was too high to be included in the chamber). However, some short stems or leaves sometimes subsist within the chamber and were not removed to avoid any disturbance of the soil condition, but does not justify to take into account stomatal emission potential (because in too low quantity). The hypothesis of a water film on the vegetation is removed from the sentence; the hypothesis of a water film on the soil surface is left. Technical comments: corrections have been done. The following references were added: Bai Junhong, Haifeng Gao, Wei Deng, Zhifeng Yang, Baoshan Cui, Rong Xiao, Nitrification potential of marsh soils from two natural saline–alkaline wetlands, Biol Fertil Soils (2010) 46:525–529. Cassity-Duffey Kate, Miguel Cabrera, John Rema, Ammonia Volatilization from Broiler Litter: Effect of Soil Water Content and Humidity, Soil Sci. Soc. Am. J. 79:543–550, 2014. Dick Jan, Ute Skiba, Robert Munro and Douglas Deans, Effect of N-fixing and non N-fixing trees and crops on NO and N2O emissions from Senegalese soils, Journal of Biogeography (J. Biogeogr.) (2006) 33, 416–423. Ganzeveld L.N., J. Lelieveld, F. J. Dentener, M. C. Krol, A. J. Bouwman, and G.-J. Roelofs, Global soil-biogenic NOx emissions and the role of canopy processes, JOURNAL OF GEOPHYSICAL RESEARCH, VOL. 107, NO. D16, 10.1029/2001JD001289, 2002. Vaittinen O., M. Metsa ÌĹla, S. Persijn, M. Vainio, L. Halonen, Adsorption of ammonia on treated stainless steel and polymer surfaces, Appl. Phys. B, DOI 10.1007/s00340-013-5590-3, 2013. Vanlauwe B., J. Diels, O. Lyasse, K. Aihou, E.N.O. Iwuafor, N. Sanginga, R. Merckx & J. Deckers, Fertility status of soils of the derived savanna and northern guinea savanna and response to major plant nutrients, as influenced by soil type and land use management, Nutrient Cycling in Agroecosystems 62: 139–150, 2002. Wichink Kruit, R. J., van Pul, W. A. J., Otjes, R. P., Hofschreuder, P., Jacobs, A. F. G., and Holtslag, A. A. M (2007), Ammonia fluxes and derived canopy compensation points over non-fertilized agricultural grassland in the Netherlands using the new gradient ammonia – high accuracy – monitor (GRAHAM), Atmos. Environ., 41, 1275–1287. Yienger, J. J., and H. Levy II, Global inventory of soil-biogenic NOx emissions, J. Geophys. Res., 100, 11,447– 11,464, 1995.

Please also note the supplement to this comment:
https://www.atmos-chem-phys-discuss.net/acp-2017-1198/acp-2017-1198-AC1-supplement.pdf

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