

Reviewer #2

We wish to thank the referee for his/her helpful comments. The full reviews are copied hereafter and our responses are inserted. The comments of the reviewer are in normal black and our answers in bold.

The authors present an inter-comparison of two alternative inventories with the European reference inventory (TNO) to quantify the French NH₃ emissions during spring 2011; (i) NH₃SAT inventory which is based on a top-down approach of correcting TNO-NH₃ emissions based on total column observations and (ii) CADASTRE-CIT inventory which is built from the bottom-up based on modeled NH₃ emissions related to fertilizer application and animal husbandry. There is a thorough comparison of inventories based on different regions of France with known anthropogenic NH₃ emitting activities. The work specifies which regions in France, represented in the European reference inventory, need to be improved upon and highlights the general conclusion of improving NH₃ emissions inventories based on measurements and process knowledge is required. Inventories are key inputs in forecasting air quality, so the goal of this study to build a more representative inventory over France is important work. Building NH₃ inventories is very challenging because of its varied lifetime in the atmosphere and complex exchange mechanisms making its spatial distribution and temporal behavior difficult to predict. Atmospheric NH₃ is an important precursor to PM and can also damage N-sensitive ecosystems, therefore, refined emissions inventories are needed for air quality modeling and monitoring emissions reductions. This study details methods to refine inventories, therefore, I would recommend publishing this manuscript after some revisions.

Major Comments

There have been other global inventories built by the atmospheric community using similar methods that have not been mentioned and would add to the discussion of the authors' work. Work from Zhang et al. (ACP, 18, 339-355, 2018), who reconcile bottom-up and top-down inventories, also show including more detailed information on crop-specific fertilizer application practices and met factors does a better job at reproducing spatial and seasonal variations in China, which seems to be similar in this study, but in France.

We agree, we now mention the work of Zhang et al. [2018] in the introduction.

How do the two alternative inventories compare to currently available inventories, aside from TNO? How does CADASTRE-CIT compare with the MASAGE_NH₃ inventory? and other global inventories that represent France, such as EDGAR?

First, a reference to the interesting study of Paulot et al., [2014] is now done in the introduction.

We have found a comparison of NH₃ European annual emissions between various inventories in Riddick et al., [2016]. Nevertheless, this comparison for annual budgets could be not relevant as we only focused on spring period. Nevertheless, we have added a sentence about the MASAGE_NH₃ inventory in Section 3.2: "The northeastern part of France presents the largest difference with the TNO-GEN inventory (48 ktNH₃) for both NH₃SAT and CADASTRE-CIT inventories (65 and 135 ktNH₃, respectively). The high emissions in the northeastern part of France are in agreement with the MASAGE_NH₃ inventory [Paulot et al., 2014], the magnitude of annual NH₃ emissions from mineral fertilizer being calculated by combining an inventory of crop

acreages, crop- and country-specific fertilizer application rates and fertilizer-, crop-, and application-specific emission factors.”

Riddick, S., Ward, D., Hess, P., Mahowald, N., Massad, R., and Holland, E.: Estimate of changes in agricultural terrestrial nitrogen pathways and ammonia emissions from 1850 to present in the Community Earth System Model, *Biogeosciences*, 13, 3397–3426, <https://doi.org/10.5194/bg-13-3397-2016>, 2016.

Is TNO built upon any of these inventories already?

TNO is built upon official reported emissions by country under the Convention for Long-Range Transboundary Air Pollution (CLRTAP) from the Centre for Emission Inventories and Projections (CEIP, <http://www.ceip.at/webdab-emission-database/officially-reported-emission-data/>). If these data were not available or not of sufficient quality, emissions data were replaced by emissions from the IIASA GAINS model (http://gains.iiasa.ac.at/models/gains_models.html). This especially applies to countries outside of the EU but that are part of the United Nations Economic Commission for Europe (UNECE) domain. In addition, JRC EDGAR data (<http://edgar.jrc.ec.europa.eu/>) have been used for gapfilling for countries that are part of the domain but not part of UNECE (i.e., Armenia, Azerbaijan, Georgia).

The full overview of the choices made per country by the TNO team can be seen in the supplementary materials of Kuenen et al. [2014].

Kuenen, J. J. P., Visschedijk, A. J. H., Jozwicka, M., and Denier van der Gon, H. A. C.: TNO-GEN-MACC_II emission inventory; a multi-year (2003–2009) consistent high-resolution European emission inventory for air quality modelling, *Atmos. Chem. Phys.*, 14, 10963-10976, <https://doi.org/10.5194/acp-14-10963-2014>, 2014.

Atmospheric NH₃ is known to undergo bi-directional exchange with surfaces and this aspect is not discussed. The NH₃SAT is generated based on chemical transport modeling of TNO, however, the CHIMERE model parameterizes NH₃ dry deposition uni-directionally. Is this a limit of the model? If NH₃ dry deposition is assumed to be a net sink, then in most cases that would underestimate atmospheric concentrations. How does this impact NH₃ estimates? and to what degree?

Indeed, the misrepresentation of deposition could have impact on our simulated NH₃ columns. We have added the following discussion in the CHIMERE description: « As most of the models in the world, the parameterization of NH₃ dry deposition is unidirectional in CHIMERE. The parameterization of a bidirectional exchange with surfaces in Wichink Kruit et al. [2012] increased their yearly mean modeled LOTOS-EUROS European ammonia concentrations almost everywhere, and particularly over agricultural source areas. However, Zhu et al. [2015], with the Goddard Earth Observing System-Chemistry (GEOS-Chem) global CTM, estimated decrease of NH₃ European concentrations in April, when the inclusion of a compensation point for vegetation is included. Further work needs to be done to better investigate the sensitivity of NH₃ concentrations to the bi-directional exchange for dry deposition. Nevertheless, without such parameterization for bi-directional exchange, Azouz et al. [2019] assessed that regional models such as CHIMERE usually operating with large grid cell sizes simulate quite well the average NH₃ dry deposition flux over a large domain of simulation. »

Wichink Kruit, R. J., M. Schaap, F. J. Sauter, M. C. van Zanten, and W. A. J. van Pul: Modeling the distribution of ammonia across Europe including bi-directional surface-atmosphere exchange, *Biogeosciences*, 9, 5261–5277, doi:10.5194/bg-9-5261-2012, 2012.

Zhu, L., D. Henze, J. Bash, G.-R. Jeong, K. Cady-Pereira, M. Shephard, M. Luo, F. Paulot, and S. Capps: Global evaluation of ammonia bidirectional exchange and livestock diurnal variation schemes, *Atmos. Chem. Phys.*, 15, 12,823–12,843, doi:10.5194/acp-15-12823-2015, 2015.

Azouz, N. et al: Comparison of spatial patterns of ammonia concentration and dry deposition flux between a regional Eulerian chemistry-transport model and a local Gaussian plume model, *Air Quality, Atmosphere & Health* (2019) 12:719–729 <https://doi.org/10.1007/s11869-019-00691-y>, 2019.

Can the authors comment on how well CHIMERE can predict particulate NH₄⁺? How much does that influence NH₃ estimates?

We wanted to evaluate the different sets of emissions by comparison with independent ammonium NH₄⁺ surface measurements. Among the nine available stations presenting NH₄⁺ measurements during the spring 2011, only one site is exploitable, as it presents a significant number of measurements for each month in the spring 2011. This station is located at Rouen (FR25048), in the northeastern part of France (e.g., in the region Haute-Normandie). To our knowledge, there is no additional interpretable NH₄⁺ surface measurements for the focused period here, making the interpretation of the results difficult and this is the reason why we did not add this evaluation in the study. In Rouen, the ammonium measurements presented a strong maximum in March, and a decrease in April and May. The daily variability was well reproduced by simulations with all three inventories, even if the simulations often underestimate the NH₄⁺ maximums.

NH₄⁺ comparisons during other periods are scarce also. For instance, Tuccella et al., [2019] compared CHIMERE simulated and observed NH₄⁺ at the Cabaux supersite and found average concentrations for May 2008 of 1.3 µg/m³ for both, with a correlation coefficient of 0.52. For the Paris agglomeration between September 2009 and 2010, the modelled regional NH₄⁺ burden was 1.8 µg/m³ while the modelled one was 1.6 µg/m³ [Petetin et al., 2016]. From June to September 2010, 83% of modelled total NH_x was gaseous, while in the model, it was only 50%, coherent with this NH₃ was underestimated especially during warmer days. Thus, it is concluded for one site and season, that particulate NH₄⁺ has a low to medium impact on NH₃.

We have added the following text in the CHIMERE description in Section 2.2.1: “The evaluation of CHIMERE NH₃ and NH₄⁺ concentrations should be done against NH₃ (as done in Fortems-Cheiney et al., [2016]) and NH₄⁺ measurements. Nevertheless, to our knowledge, there is no available NH₃ measurement over France for the focused period here. There is interpretable NH₄⁺ surface measurements at only one site, making the interpretation of the results difficult. NH₃ and NH₄⁺ comparisons during other periods are scarce also. For instance, Tuccella et al., [2019] compared CHIMERE simulated and observed NH₄⁺ at the Cabaux supersite and found average concentrations for May 2008 of 1.3 µg/m³ for both, with a correlation coefficient of 0.52. For the Paris agglomeration between September 2009 and 2010, the modelled regional NH₄⁺ burden was 1.8 µg/m³ while the modelled one was 1.6 µg/m³ [Petetin et al., 2016]. From June to September 2010,

83% of modelled total NH_x was gaseous, while in the model, it was only 50%, coherent with this NH_3 was underestimated especially during warmer days. Thus, it is concluded for one site and season, that particulate NH_4^+ has a low to medium impact on NH_3 .”

Petetin, H., Sciare, J., Bressi, M., Gros, V., Rosso, A., Sanchez, O., Sarda-Estève, R., Petit, J.-E., and Beekmann, M.: Assessing the ammonium nitrate formation regime in the Paris megacity and its representation in the CHIMERE model, *Atmos. Chem. Phys.*, 16, 10419–10440, <https://doi.org/10.5194/acp-16-10419-2016>, 2016.

Tuccella, P.; Menut, L.; Briant, R.; Deroubaix, A.; Khvorostyanov, D.; Mailler, S.; Siour, G.; Turquety, S. Implementation of Aerosol-Cloud Interaction within WRF-CHIMERE Online Coupled Model: Evaluation and Investigation of the Indirect Radiative Effect from Anthropogenic Emission Reduction on the Benelux Union. *Atmosphere* 2019, 10, 20, 2019.

What are the limits of the Volt’air model? It is usually used to predict emissions from slurry applications, so it doesn’t account for a crop canopy. Does that matter? Are there any fast-growing crops that would sprout in the first month in which the model was run?

Volt’Air indeed does not account for the canopy effect on NH_3 volatilization. Well-developed canopies reduce soil surface temperature and wind speed in the canopy i.e., the rate of vertical NH_3 transport from the soil surface. Growing canopies also absorb the NH_3 gas emitted by the mineral fertilizer or manure, in large quantities for well-developed canopies. In the case of applications to the soil surface beneath the crop canopy, the use of Volt’Air would lead to an overestimation of emissions for fertilizations occurring during plant growth, depending on the type, the height or the leaf area index, and the phenological stage of the crop. This would be mainly the case for slurry applied using either trailing hose or trailing shoe. But, in France in 2010-11, (i) manure applications on arable crops occurred mainly before sowing, i.e., on bare soils; (ii) band spreading techniques were not of wide use, and anyway; (iii) in practice, grassland fertilization is most often carried out immediately after the grass is cut when it is in need of mineral N i.e., when the canopy has no effect on ammonia volatilization. Furthermore, when fertilizers and manure are applied on well-developed canopies, part of them may coat the crop or grass leaves, partially enhancing exchange surface with air. Volatilization is not that much reduced in this case. That is why in a first approach, we used Volt’Air for bare soils.

What is the availability of ground-based NH_3 measurements in regions which have the most variation? If so, how do they compare with IASI observations if we assume the total column of NH_3 is all at the surface? Were ground-based NH_3 concentrations used as an a priori for IASI total column calculations?

To our knowledge, there is no ground-based NH_3 measurements available that could have allowed an independent evaluation of our results in regions with highest and most variable NH_3 concentrations. Nevertheless, we have added a reference to the study of Tournadre et al, [2020] in Section 3.3: “This maximum in March is also noticed by Tournadre et al. [2020], providing nine years of total column observations from ground-based infrared remote sensing over the Paris megacity.”

Tournadre, B., Chelin, P., Ray, M., Cuesta, J., Kutzner, R. D., Landsheere, X., Fortems-Cheiney, A., Flaud, J.-M., Hase, F., Blumenstock, T., Orphal, J., Viatte, C., and Camy-

Peyret, C.: Atmospheric ammonia (NH₃) over the Paris megacity: 9 years of total column observations from ground-based infrared remote sensing, Atmos. Meas. Tech., 13, 3923–3937, <https://doi.org/10.5194/amt-13-3923-2020>, 2020.

Ground-based NH₃ measurements are not used as an a priori for IASI total column calculations.

Minor Edits

Line 401 is missing a parenthesis - (68, 73, and 71 ktNH₃, respectively).

It has been corrected.

I am not sure if there is something funky with the text editor file that messes with the spacing in the pdf, but there are some words that have been compounded throughout the article.

We apologized for the inconvenience. It has been corrected.

IASI reference should also include Clarisse, L., Clerbaux, C., Dentener, F., Hurtmans, D., and Coheur, P.: Global ammonia distribution derived from infrared satellite observations, Nat. Geosci., 2, 479–483, 2009.

The reference has been added.