



Interactive comment on “Diurnal evolution of total column and surface atmospheric ammonia in the megacity of Paris, France, during an intense springtime pollution episode” by Rebecca D. Kutzner et al.

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Received and published: 9 April 2021

General comments This manuscript presents ammonia total column concentration measured above Paris with an FTIR instrument (OASIS) during an intense springtime pollution episode in March 2012. The main object of the manuscript is to discuss the diel cycle of the total column NH₃ concentration observed, which shows a flat profile in the morning and a steady increase in the afternoon, contrary to surface NH₃ concentrations (measured at around 30 km south), that show a rather flat cycle. The

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manuscript provides a large overview analysis making full use of LIDAR, and surface aerosol concentration and composition, measurements as well as meteorological informations, to try explaining the total NH₃ column diel cycle. The manuscript shows clearly that the surface NH₃ and particulate matter concentrations are decoupled from the total column concentrations, which is a clear and important outcome of this work.

The manuscript is well structured and written and make appropriate reference to the literature (some more references are given in the detailed comments). The data presented are of great interest for the community to better understand the relationship between surface concentration and satellite measurements for ammonia, which is a key pollutant in developed countries.

The main conclusion raised by the authors is that the observed total NH₃ column diel cycle may be due to a combination of dilution (linked to the atmospheric boundary layer height cycle), aerosol volatilisation, and ammonia emissions at the regional scale. However, no clear quantitative evidence is shown to strengthen either of these conclusions, but rather qualitative arguments are given. This is the main weakness of the manuscript, which to my view, should be addressed prior to publication.

In particular, I would suggest better quantifying the effect of relative humidity and temperature on the ammonia-to-ammonium-nitrate equilibrium, and showing a graph of these dependencies. I also suggest trying to calculate, if possible, the averaged column concentration of ammonia and particles using the boundary layer height retrieved from the LIDAR measurements. I am not sure this is fully feasible, but even with some uncertainties; this may help comparing the column averaged “concentration” with the surface concentration. Additionally, the authors should bear in mind that the surface concentration of ammonia might be very much influenced by the surface surrounding the measurements, which in this case is probably a mix of forests and crops, and hence would lead to an active sink.

Detailed comments Line 35: vertical dilution is not per se a variable but a process. The

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boundary layer height may be the variable to add here. Lines 58-59: Other effects of particle transport and deposition are acidification and loss of biodiversity (e.g. Sutton et al. 2011). Lin 59-61: This sentence on volatilisation of ammonium nitrate particles may benefit from being moved at the end of this paragraph or maybe even later in the text. Line 65: please provide the year of the evaluation of the total ammonia emission in Europe. Line 67: ammonia volatilization also depends on soil conditions like for instance humidity and pH. Line 71-72: Fires are also probably a significant source of ammonia in South East Asia. Please give a range of significance of this source worldwide. Line 82-83: Although it is true that agricultural activities are one of the key factor, explaining the rise in particle pollution it may be important to stress that other precursors are also essential in the process, like for instance nitrogen oxides emissions. Line 91-94: please consider reading this paper regarding stickiness of ammonia and inlet materials: Whitehead, J. D., Twigg, M., Famulari, D., Nemitz, E., Sutton, M. A., Gallagher, M. W., and Fowler, D.: Evaluation of laser absorption spectroscopic techniques for eddy covariance flux measurements of ammonia, *Environmental Science & Technology*, 42, 2041-2046, 2008. Line 169: please explain what you mean by “co-add 30 scans”. Line 176-177: it would be important here better explaining how the nitric acid HNO₃, in particular, is taken into account since these compound made directly interact with ammonia in the atmosphere. Although it is explained in Trounadre et al. (2020), it would be also important here to quantify the water vapour interference here. Line 182: Retrieval error that is given between 20 and 35% may be dependent on one or two compounds mostly. It would be good to explain the weight of water vapour and of the vertical profile shapes on this error. Line 192: It may be worth precisising here that ammonia is first absorbed in acid solution. Line 208: The word “pre-conditions” is unclear. Could you please rephrase? Line 205-219: Since equilibrium between ammonia and ammonium aerosol is key in this manuscript I would suggest precisising quantitatively this process. Indeed, in the current manuscript, it is said that when RH is much lower than DRH, particulate volatilization is favoured. However, volatilisation depends on the difference between RH and DRH I guess. I would therefore suggest adding a graph

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showing how the equilibrium between ammonia and ammonium nitrate may be dependent on relative humidity. A representation like what is shown by (for instance) Nemitz (Figure 8 of the following paper) would be interesting. Alternatively, the ISORROPIA box model could be used for that. Nemitz, E., Sutton, M. A., Wyers, G. P., Otjes, R. P., Schjoerring, J. K., Gallagher, M. W., Parrington, J., Fowler, D., and Choulaton, T. W.: Surface/atmosphere exchange and chemical interaction of gases and aerosols over oilseed rape, *Agric. For. Meteorol.*, 105, 427-445, Doi 10.1016/S0168-1923(00)00207-0, 2000. Line 220: I would have expected the opposite dependence of evaporation of ammonium nitrate to pH, since water solution a lower pH leads to lower hip operation. However, this may not be true in an aerosol, which is not my domain of expertise. Line 236: Please consider replacing “exist” by “are simulated”. Line 263: Please consider replacing “manually” by “visually”. Line 300: this is very interesting to see that PM₁ is 30% lower and PM_{2.5} during this episode would it be possible to propose some hypothesis ? Line 308: Please consider replacing “denominate these two regimes as ...” by “name these two regimes ...” Line 320 and Figure 4: It would be worth showing the ratio of PM₁ to PM_{2.5} in the Parisian area. Line 355: it is unclear if the Oasis inversion methodology uses this water vapour profile. Would this be of any help to better estimate water vapour interference? Line 372-374: it is a shame that these ISORROPIA model outputs are not shown. As already proposed in an earlier comment it would be worth showing the effect of temperature and relative humidity on the equilibrium between ammonia and ammonium nitrate. Line 377: the meaning of the sentence “vertically decreasing variation of ammonia with increasing altitudes” is unclear. Please rephrase. Line 420: It may be worth looking at the following paper that reported ammonia emissions and concentrations during the very same period in the west of Paris: Personne, E., Tardy, F., Genermont, S., Decuq, C., Gueudet, J. C., MASCHER, N., Durand, B., Masson, S., Lauransot, M., Flechard, C., Burkhardt, J., and Loubet, B.: Investigating sources and sinks for ammonia exchanges between the atmosphere and a wheat canopy following slurry application with trailing hose, *Agric. For. Meteorol.*, 207, 11-23, 10.1016/j.agrformet.2015.03.002, 2015. Lines 422-249:

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The manuscript would benefit a lot if some more quantitative estimation of the effects of the boundary layer height on the concentration of the total ammonia column concentration could be estimated even roughly. Would it be feasible to use the atmospheric boundary layer height as retrieved from the LIDAR measurements shown in figure 9 to estimate an averaged ammonia concentration in the column? Lines 440-445: it should be stressed here that the ammonia concentration measured at the surface is measured in the south of Paris in a mostly forested area that would be a sink for ammonia. Since ammonia concentration varies drastically at the surface depending on the surface itself, the surface concentration used here may not be representative of the average surface concentration of the overall region, while the concentration in the total column is representative of the overall region. Section 3.5: Consider reducing the length by being less descriptive and quantitative: Similarly to what was proposed for ammonia in a previous comment, LIDAR measurements may be used to retrieve boundary layer height that could be used to evaluate an average particle concentration, which could then be compared to the surface particles concentration. Line 567-569: Although vertical dilution is, surely an important process to explain the reduction of surface concentrations, for ammonia the surface interaction is also a key process should be considered. In particular, since surface absorption will be light dependent and temperature-dependent because of the stomatal functioning and the compensation point. See e.g. Flechard, C. R., Massad, R. S., Loubet, B., Personne, E., Simpson, D., Bash, J. O., Cooter, E. J., Nemitz, E., and Sutton, M. A.: Advances in understanding, models and parameterizations of biosphere-atmosphere ammonia exchange, *Biogeosciences*, 10, 5183-5225, 10.5194/bg-10-5183-2013, 2013. Sutton, M. A., Reis, S., Riddick, S. N., Dragosits, U., Nemitz, E., Theobald, M. R., Tang, Y. S., Braban, C. F., Vieno, M., Dore, A. J., Mitchell, R. F., Wanless, S., Daunt, F., Fowler, D., Blackall, T. D., Milford, C., Flechard, C. R., Loubet, B., Massad, R., Cellier, P., Personne, E., Coheur, P. F., Clarisse, L., Van Damme, M., Ngadi, Y., Clerbaux, C., Skjoth, C. A., Geels, C., Hertel, O., Kruit, R. J. W., Pinder, R. W., Bash, J. O., Walker, J. T., Simpson, D., Horvath, L., Misselbrook, T. H., Bleeker, A., Dentener, F., and de Vries, W.: Towards a climate-dependent paradigm

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of ammonia emission and deposition, *Philos. Trans. R. Soc. B-Biol. Sci.*, 368, 10.1098/rstb.2013.0166, 2013. Massad, R. S., Nemitz, E., and Sutton, M. A.: Review and parameterisation of bi-directional ammonia exchange between vegetation and the atmosphere, *Atmospheric Chemistry and Physics*, 10, 10359-10386, 10.5194/acp-10-10359-2010, 2010.

Line 580: I might have missed something but this is the first time I see “enhanced HNO₃ transport in the polluted plume”. Please argue.

Figures Figure 1: please give scale on the maps. Figure 2: please explain what “a.u” means in the legend. Also please use the same units in the x-axis and in the legend text here you use 10 micrometre at once and wavenumber in cm⁻¹. also explain what the arrows are for. Figure 3: The axes and legends are difficult to read please consider increasing the font size. Figure 4: Consider showing a graph joint with Figure 4 with the ratio of PM₁ to PM_{2.5} over the period. This would ease the reader to see the differences and similarities. Figure 5: I would suggest to add a graph with the boundary layer height and another one with the average ammonia concentration in the column and considering ammonia is mainly in the boundary layer. This would allow a better comparison of the concentration at the surface and also withdraw the dilution effect due to BLH changing with time. Figure 6: To interpret Figure 6b it would be important to show the ammonia to ammonium nitrate equilibrium and its dependence on temperature and relative humidity. Figure 9: as explained before I suggest extracting the boundary layer height from these graphs and computing the average concentration over the column. This could be done in figure a and b and also for ammonia.

Interactive comment on *Atmos. Chem. Phys. Discuss.*, <https://doi.org/10.5194/acp-2020-782>, 2020.

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