

ANSWERS TO REFEREE #2

We thank the referee for his numerous remarks that will allow to greatly improve the paper.

REFEREE #2: 1) The authors use the terminology “urban background” throughout the manuscript. It is suggested that the observational information (Section 2) analyzed is representative of this urban background. Yet the data is from locations within the city center or urban core (“heart of Paris”) – how is this site then representative of the urban background? The use of the terminology is somewhat nebulous – the authors should clearly state what they imply by urban background and how a location in the center of the city is representative of this.

AUTHOR: The terminology « urban background » used in this study is related to the fact that our stations are not directly impacted by local anthropogenic sources (e.g. traffic, industry) as it would be the case for instance at the street level. As indicated in Sect. 2, both stations in PARTICULES and FRANCIPOL campaigns are located on a rooftop, which gives confidence on the fact that measured concentrations are not predominantly influenced by very local pollution sources (cars at the street level). At the scale of a megacity like the Paris agglomeration (2 845 km²), the « urban background » is likely not strictly homogeneous. Thus, our observations are likely more representative of the urban background within the center of Paris than the whole agglomeration. The information is given in the added Sect. 2.4 (see the answer to question 2).

REFEREE #2: 2) Section 2 describes the measurement data analyzed in this study. If I understand this discussion correctly, the locations where the aerosol composition, the gas-phase concentrations, and the meteorological data are collected are not exactly co-located – in fact it appears that they are separated by a few kilometers. Information on the characteristics of these locations should be included. It is not apparent what the local influences are at these locations, how similar or different these influences may be and how they impact the variability in the data collected at these locations. The authors assume that the atmosphere across these locations is relatively homogeneous so that gas-phase measurements at one location can be combined with aerosol composition measurements at another location for prevalent meteorological conditions from a third location to examine gas-particle partitioning of airborne nitrogen compounds – how does one ascertain if this assumption holds? What is the spatial representativeness of each of these locations? Could one site be influenced by local conditions (emission sources, urban morphology) more than the other? It may be reasonable to combine these data from different locations, but this needs to be more clearly justified.

AUTHOR: We agree with the referee that this is an important question. We thus propose to include this discussion in a dedicated section. The first sentence in Sect. 2.2 is simplified as follows: « As part of the PRIMEQUAL « FRANCIPOL » project, gaseous precursors (NH₃, HNO₃, SO₂) were monitored in near real-time on the roof platform (14 m a.g.l.) at the Laboratoire d’Hygiène de la Ville de Paris (LHVP) in the heart of Paris (13th district). » And we add a Sect. 2.4 entitled « Representativeness and datasets combination » with the following text: « The purpose of this study is to investigate the relation of ammonium nitrate with its

gaseous precursors, which ideally requires co-located measurements of all compounds in both phases. This was not the initial purpose of PARTICULES and FRANCIPOL projects, and thus, no such co-located observations are available in Paris. However, we argue here that the two datasets (inorganic aerosols measured in the 4th district of Paris, and gaseous precursors measured in the 13th district) can be reasonably considered as co-located and representative of the urban background of at least the southern half of the Paris city.

Several elements support this hypothesis. First, both sites are only ~3 km away. Second, both sites are located on the rooftop of rather high buildings (20 and 14 m a.g.l.), thus quite far from direct influence of local pollution sources (e.g. traffic) and at a height where the venting of pollution is favored by the absence of obstacles and likely stronger winds (compared to the street level). The height of the LHVP roof site is slightly lower compared to the other site, but the building is located in a public garden, which further limits the possibility of local contamination by surrounding pollution sources. Third, based on the PM_{2.5} chemical speciation measurements performed both inside Paris and at several rural sites all around the Paris region during a whole year, the PARTICULES project has allowed to demonstrate that secondary inorganic aerosols in the Paris urban background are mostly imported from outside the city (Petetin et al., 2014). At the annual scale, the contribution of imports was estimated to 78% for nitrate, 90% for ammonium and 98% for sulfates (see Table 6 in Petetin et al., 2014). This is mostly explained by (i) the presence of strong pollution reservoirs in Europe (e.g. Benelux, eastern Europe) from where large plumes can be advected toward Paris in specific meteorological conditions, (ii) the time necessary for the formation of inorganic aerosols (including the oxidation of NO_x and SO₂) is too low to allow a strong local production that thus preferentially occurs downwind in the Paris plume, as observed during the MEGAPOLI campaign (Freney et al., 2014), and (iii) the limited occurrence of stagnant conditions in Paris (that would let enough time to gaseous precursors to produce inorganic aerosols). The high contribution of imports is confirmed by the comparison of daily inorganic aerosol concentrations between the 4th district site and a traffic site located along the Paris ring 8 km westward, that shows a very good accordance for all inorganic aerosols during the whole year (ammonium: $y=0.95x+0.02$, $R=0.97$, $N=325$; nitrate: $y=0.99x-0.09$, $R=0.98$, $N=325$; sulfate: $y=1.04x+0.01$, $R=0.98$, $N=325$). Thus, concerning secondary inorganic aerosols, the urban background can be considered as rather homogeneous at the scale of the whole Paris agglomeration. And observations in the 4th district of Paris can be reasonably combined to gaseous precursors observations at the other site.

In terms of spatial representativeness for HNO₃ and NH₃, no other measurements are available to quantitatively assess the homogeneity of their urban background. In particular, some NO_x emitted within the center of the city may be already converted into HNO₃ in the borders of the Paris agglomeration, leading to higher concentrations compared to the center of Paris. Thus, one cannot a priori consider that these measurements are representative of the urban background at the scale of the whole Paris agglomeration. However, as we already discussed, considering the morphology and the geographical location of this LHVP site, one can reasonably consider that it is representative of the urban background of at least the southern half of Paris city. »

REFEREE #2: 3a) The description of the measurement locations and its spatial and temporal representativeness is also important for better understanding the discrepancies between the measurements and model predictions. For instance, in

section 2 it is mentioned that six sampling sites were implemented – were model predictions also compared at these locations? Were the error/bias characteristics similar to the city center site?

AUTHOR: Details on the representativeness of sites are previously given in our answer to question 2. Concerning the comparisons of the CHIMERE model with the measurements of PM_{2.5} chemical constituents (no observations of gaseous precursors were available) performed during the PARTICULES campaign, results have been analyzed in Petetin et al. (2014). We propose to add a few sentences on the results in Sect. 4.4.1: “As previously mentioned, in the framework of the PARTICULES campaign, PM_{2.5} chemical constituents have also been measured at 3 rural sites all around the Paris region. Results have been analyzed in terms of local and imported contributions by Petetin et al. (2014). In a few words, concerning sulfates, imports were slightly underestimated by CHIMERE (-17%) while the (low) local production was overestimated (+32%), leading at the end to a moderate negative bias (-17%). For nitrates, a similar but stronger error compensation was underlined between imports and local production (bias of +63 and -109%, respectively), leading to a reasonable bias on concentrations in Paris (+23%). For more details, the reader is invited to look at this previous paper (e.g. statistical results in Table 7).”

REFeree #2: 3b) Based on measurements alone at a city center site it is not readily apparent how one could apportion the role of local versus “imported” pollution to the city. In principle, a model such as CHIMERE could help with such interpretations, but the bias characteristics of the model for reduced and oxidized nitrogen are so large that such inferences are not apparent. This aspect of the discussion needs to be explained more clearly. If the variability in the measurements is indeed influenced by local sources (e.g., Figure 7 shows strong correlation between peak NH₃ and BC, suggestive of influence of local emissions at least on several days), how does one discern this from the import?

AUTHOR: Assessing the contribution of local versus imported pollution ideally requires measurements inside and upwind the city. This has been made possible for secondary inorganic aerosols during the PARTICULES campaign (see answer to question 3a), but concerning HNO₃ and NH₃, no other measurements are available. A chemistry-transport model can theoretically provide useful information on this point. But as you mentioned, strong errors have been found on the urban background concentrations simulated by CHIMERE, which prevents us to use the model for discriminating the local and advected contributions. In this context, no strong conclusion can be derived on this point.

This is particularly true for HNO₃ for which we adopted in the revised version of the manuscript a more cautious approach in our discussion. To our opinion, some episodes suggest a substantial local formation. However, imports remain possible, and it does not appear possible to quantitatively assess their importance in the HNO₃ budget. Therefore, we removed the discussion about local and advected contributions in the CHIMERE simulations, as they are not of major interest for this paper as we do not trust the simulated HNO₃ fields as said before (too strong bias).

However, concerning NH₃, to our opinion, several elements strongly suggest a major contribution of agricultural emissions to the NH₃ levels observed in Paris. Following the remarks of all referees, the Sect. 4.2.1 and 4.3.1 of the revised manuscript were substantially modified. In particular, dedicated sections are created to discuss the influence of temperature (Sect. 4.2.1.1), traffic (Sect. 4.2.1.2) and agriculture (Sect. 4.2.1.3).

REFeree #2: 4) The sensitivity analysis presented in section 4.4.3 is interesting and can potentially be insightful. However, in its current form the discussion is a bit confusing - it was difficult for me to understand how the sensitivities were estimated for the model and the observations. I would think that the ISORROPIA estimated change in NO₃ (S_x) to a perturbation in a parameter (x) would be the same irrespective of the model or measurements. Instead the differences in ratio x/NO_3 between the model and the measurements drive the differences in S_x . The differences in x as discussed in the manuscript however could arise from several factors other than the representation of the thermodynamic partitioning and influence the resultant inferred NO₃ response. How does one infer if the lack of responsiveness in the model is due to uncertainties in the process representation (e.g. gas-particle partitioning) or input data (e.g., emission inventory) or other reasons?

AUTHOR: If we consider for instance the sensitivity to a change of TNH₃, there is no reasons for the change of NO₃ in response to a perturbation of TNH₃ to be the same in the model and in the measurements since this change not only depends on the TNH₃ concentrations but also on the values of all the other parameters of the system - i.e. temperature, RH, TNO₃ (total nitrate HNO₃+NO₃⁻) and TS (total sulfate H₂SO₄+HSO₄⁻+SO₄²⁻) - that are not the same in the model and observations. In this section, we simply intend to quantify how all the model errors affecting the different parameters (temperature, RH, TNO₃, TNH₃, TS) impact the sensitivity of nitrates to a change in one of these input parameters. Potential errors of responsiveness in the model are necessarily related to errors in the simulation of the five inputs. Please also note that the analysis is local, it is performed for the observed and simulated set of parameters at the urban background site. We propose to give more details in the text: «The ISORROPIA thermodynamic model is used here to compute this sensitivity coefficient S_x as a function of various decreases (-10, -25, -50 and -90%) in TNH₃ and TNO₃ concentrations. This 0-dimension model requires five inputs - temperature, RH, and TNO₃, TNH₃ and TS concentrations - and computes the gas-aerosol partitioning coefficient of both TNO₃ and TNH₃ compounds. Please also note that the analysis is local, it is performed for the observed and simulated set of parameters at the urban background site. Decreasing the concentration of a family species - TNO₃ or TNH₃ in our case - leads to a change in its partitioning between both gaseous and aerosol phases. This change not only depends on the concentration of the family species which is altered but also on the value of all the other parameters of the system. Thus, the CHIMERE errors in the different input parameters propagate to the gas-aerosol partitioning coefficient, which can potentially lead to an erroneous sensitivity of nitrates to a change of TNO₃ or TNH₃. Calculations are performed for both the measurements and the model, i.e. all inputs are taken from the observations and the model, respectively, at the

urban background site. In each case, the (observed or simulated) concentrations of TNH_3 or TNO_3 are decreased and the sensitivity coefficient is computed to quantify the impact of this change on the nitrate concentrations. Sensitivity coefficient results and corresponding GR are shown as box plots in Fig. 13. »

REFeree #2: 5) At several places in the manuscript the authors discuss the NH_3 rich conditions in Paris, in spite of NO_x emissions, and attribute this to low HNO_3 . Again, this characteristic could simply be due to the location of the monitoring site. One would expect relatively lower amounts of NO_x oxidation products (like HNO_3) in urban cores and the reverse downwind. Thus a better description of the site characteristics is needed to put the results in context.

AUTHOR: Yes, we agree with the referee. Please see the answer to question 2, where this point of low HNO_3 close to highest NO_x emissions is mentioned (last paragraph of the new Sect. 2.4 in the revised manuscript).

REFeree #2: 6) Pg 23734, line 10: the sentence is awkward – increasing ammonium nitrate should result in increasing PM, not the reverse as implied – the sentence should be reworded.

AUTHOR: The sentence refers to the relative contribution (in %) of ammonium nitrate in PM total mass that increases when the PM mass concentration increases, which is not straightforward. We added the word « relative » to avoid any misunderstanding: « Several studies have reported increasing ammonium nitrate relative contributions with increasing PM mass concentrations in urban sites, thus underlying their importance in exceedances of PM European standards (Putaud et al., 2010; Yin and Harrison, 2008). »

REFeree #2: 7) Pg 23744, line 10: it would be useful to state emissions of which species were impacted the most when anthropogenic emissions were shut-off. For instance it is not clear what the magnitude of NH_3 emissions were in the base case, how these may have got perturbed in the sensitivity, and what their impact was?

AUTHOR: We do not clearly understand the point raised by the referee. The page and line refer to Sect. 4.1 (Sulfate and SO_2) where there is no discussion about shutting-off anthropogenic emissions. Concerning the NH_3 emissions, detailed information on emissions both the Paris region and in France are already given in Table S2 in the Supplement. The magnitude of NH_3 emissions in the Paris region are $4\,994\text{ t yr}^{-1}$, which represents less than 1% of the total emissions in France.

REFeree #2: 8) Pg 23746, line 15-20: defining the S ratio based on molar concentration will be more meaningful for inferring rate of conversion of S(IV) to S(VI) .

AUTHOR: The units were chosen accordingly to the usage in the literature (Pay et al., 2012).

REFeree #2: 9) Fig 3 and associated discussion: It would be useful to also show total S for the two simulations. The results conveyed in Figure 3 are not adequately discussed.

AUTHOR: The discussion of the S-ratio is relatively short in the text, and we do not think that it is useful to show the total S as it brings only minimal

additional information. We still added the figure in the Supplement. Concerning the discussion, without any information on what exactly is not adequately discussed in this paragraph, we do not understand what would expect the referee.

REFeree #2: 10) Pg 23746, line 13: "enrichment in NH₃ of air masses" should perhaps read "enrichment of NH₃ in air masses".

AUTHOR: This part was greatly modified in the revised manuscript.

REFeree #2: 11) What do "daily concentrations" in the left panel of Figure 2 represent – daily averages?

AUTHOR: Yes, we modified the legend to avoid misinterpretation.

REFeree #2: 12a) Pg 23748: it is suggested here that NH₃ in Paris is associated with transport events and not to a specific source region – what does this mean? Is there not a dominant flow pattern associated with the anti-cyclonic regime? If so, is there a predominant source upwind of Paris along this flow?

AUTHOR: Yes, to our opinion, observations suggest that a major part of the NH₃ measured in Paris come from agricultural activities in the rural areas outside Paris. However, back-trajectories during the days of highest concentrations do not highlight any particular source region. There is no clear flow pattern when an anticyclonic regime prevails over the Paris region. Highest NH₃ episodes are associated to highest temperatures (Fig. 4), but not to a particular wind direction (Fig. 5a). The discussion was modified as follows: "Most NH₃ episodes are associated to moderate winds in altitude, air masses at D-1 (one day before reaching Paris) being located in a radius of 50-400 km from Paris. A noticeable exception is found on 9 July in the morning (around 6 UTC) when the wind suddenly changes direction (from Southeast to Southwest) and speed (getting much stronger, with air masses originating from Spain at D-1) while NH₃ concentrations increase. Interestingly, some of the highest NH₃ episodes (e.g. 10 July) are associated to oceanic air masses (excepted to be relatively clean) that have spent only a limited time above land, which suggests the presence of intense NH₃ emissions in the corresponding regions (Normandy). As an overall result of this trajectory analysis, air masses with high NH₃ concentrations do not appear to originate from a particular geographical sector. Instead, the highest episodes appear linked to more diffuse NH₃ emissions in the northern part of France, associated to anticyclonic conditions with high temperature and moderate winds. This is in accordance with Petit et al. (2015) that suggest, based on NH₃ measurements at the SIRTA suburban site (south-west of Paris), a diffuse regional NH₃ source, in particular during summer (in spring, some high NH₃ episodes associated to E/NE/SE winds are also noticed, but without any clear pattern)."

REFeree #2: 12b) Is the suggestion that there are no local sources of NH₃ in Paris (though Figure 7 does not necessarily suggest that)? How are the model sensitivity results used here? This discussion on this page needs to be clarified.

AUTHOR: Yes, there are local sources of NH₃ in Paris, we do not claim the contrary, but we argue here that (i) they are likely not dominant (NH₃ concentrations being mainly driven by agricultural emissions; see answer

to question 3b and the Sect. 4.2.1.1, 4.2.1.2 and 4.2.1.3 in the revised manuscript) but (ii) that it would require further studies to precisely assess their importance. As explained in the text, the situation shown in Fig. 7 (with peaks of BC and NH₃) occurs only during a few days and is not observed during the rest of the campaign. However, from a general point of view, there is no strong evidence of large traffic emissions in Paris (as suggested by the low correlation between BC and NH₃ and the absence of traffic peaks in the diurnal profile). As explained in Sect. 4.2.2, adding some NH₃ traffic emissions in the model has a clear impact on the simulated diurnal profile, which is not in accordance with the observations.

REFeree #2: 13) Pg 23749, line 14: should dry deposition not remove NH3 in the stable layer where emissions are also injected? Or are the authors suggesting that there are no nocturnal NH3 emissions?

AUTHOR: There are NH₃ emissions during both day and night. The sentence refers to the study of Saylor et al. (2010) that tried to understand the diurnal variability of NH₃ concentrations in several locations in and outside NH₃ source regions. Downwind of source regions, NH₃ is available in the whole convective BL. During the night, NH₃ in the nocturnal BL is depleted by dry deposition (that depletion being favored by the reduced volume of the boundary layer) but not enough compensated by local emissions. Conversely, the NH₃ available in the residual BL is not affected by dry deposition, and concentrations are thus expected to be higher than in the nocturnal stable BL. This allows an enrichment in NH₃ of the emerging convective BL during the morning when air masses of the residual BL start to be entrained by turbulent exchanges. There was a mistake in the initial text, the diurnal profile does not peak at 9-10 UTC but 10-13 UTC. The discussion in the initial text has thus been removed, as it does not provide a satisfactory explanation of our diurnal variability.

REFeree #2: 14) Pg 23748, line 22: the increasing background line in Figure 7 is not apparent.

AUTHOR: No, we do not agree. In Fig. 7, the increasing background is obvious, with the lowest NH₃ concentrations increasing from less than 2 ppb the 21st of June to more than 5 ppb the 25th of June (and the 6 following days).

REFeree #2: 15) Pg 23749, line 15: "out" should be "our"

AUTHOR: Modification applied.

REFeree #2: 16) Pg 23750, line 25: While the model sensitivity runs do indeed indicate that most of the NH3 originates from outside, there is also a systematic low bias. How does one then rule out missing local emissions? Is the lack of diurnal variation in both the base and the noIDF runs and their dissimilarity with the observed diurnal variation indicative of a possible local source?

AUTHOR: The results from these two simulations are not used to support our conclusion that most of the NH₃ comes from agricultural emissions since, indeed there is a strong systematic bias. As already mentioned, a dedicated section has been added to explain the reasons that suggest a

major contribution from agricultural activities (e.g. the strong seasonal pattern). Missing (or underestimated) local emission sources may indeed partly explain the lack of diurnal variability. But the most important point here is that this diurnal variability is very limited (increase of 0.5 ppb at mid-day and decrease of 0.5 in the evening relatively to a baseline of 4 ppb), which rules out a major contribution from traffic emissions.

REFeree #2: 17) Pg 23753, line 10-20: there appears to be a sizeable impact of dry deposition even during the day and not just at night as suggested. Also, it would be useful to get a sense of magnitude of the modeled NH₃ deposition velocities.

AUTHOR: We added the following sentence: “Daytime concentrations are also affected but approximately 2 times less than night-time ones. Note that typical deposition velocities simulated by CHIMERE are around 0.3 cm s⁻¹, although it can substantially vary in time and space.”

REFeree #2: 18) Pg 23754, line 20-25: what is the connection between black carbon episodes and HNO₃ peaks? Please clarify.

AUTHOR: Black carbon is mentioned here as a proxy for low-dispersive conditions. As the day-to-day variability of BC emissions in Paris is limited, BC episodes in the city are often due to stagnant conditions that allow its accumulation. We modified the text as follows: « In Paris, the highest HNO₃ episodes are associated with high temperatures and low-to-moderate wind speeds at ground. These conditions increase the atmospheric stratification and the residence time of NO_x emissions over the agglomeration and allow for a more efficient HNO₃ formation via the NO₂+OH reaction. This is confirmed by the fact that many HNO₃ peaks follow BC episodes, these episodes being most of time due to stagnant conditions allowing the accumulation of the BC emitted by the traffic. »

REFeree #2: 19) Pg 23755, line 1: “are sufficient the 4 and 5 June” is awkward.

AUTHOR: We modified this paragraph as follows: « This is illustrated during the first days of June in Fig. 8. The 1st of June is characterized by low wind speed but cloudy conditions that decrease the photooxidation rate of NO_x. During the next 2 days, a strong wind speed (above 3 m s⁻¹) and increasing temperatures are observed, associated to a moderate increase of HNO₃ concentrations. A much higher increase of HNO₃ concentrations is observed the 4th and 5th of June concomitantly with high temperatures (up to 30°C) and low winds. Such stagnant conditions during the night allow the accumulation of NO₂, as shown by the NO₂ measurements at an AIRPARIF station located right next to the LHVP site (not shown). In the early morning, NO₂ concentrations reaches 83 (110) ppb the 4th (5th) of June, and fall below 20 ppb during the afternoon. »

REFeree #2: 20) Pg 23755, line 5-10: this sentence is too long and awkwardly worded.

AUTHOR: We removed this part of the text, and added the following sentences: « As for NH₃, no additional HNO₃ measurements are available upwind of Paris, which prevents us to quantitatively assess the importance of local formation versus imports. But this specific situation of early June supports the idea of a strong local formation of HNO₃. Some HNO₃ is also probably

(slowly) advected by north-easterly winds but the strong photochemically driven diurnal variation observed during these days (where concentrations reach 1.5 ppb in the afternoon) suggests that this contribution is minor in comparison to the local formation. The episode ends concomitantly with a significant decrease of temperature and more dispersive conditions. »

REFEREE #2: 21) Pg 23756, line 1-5: Given that HNO₃ is efficiently removed from the atmosphere via dry deposition, can import of HNO₃ be a dominant source for the Paris metro area?

AUTHOR: We agree on the fact that HNO₃ can be efficiently depleted by dry deposition. However, some major pollution sources (e.g. Benelux, Rhine-Rhur region in Germany) are located only a few hundreds of kilometers away from Paris, which allows a transport at the scale of less than a day. And in addition, some of the HNO₃ may be produced within the pollution plume along its transport.

REFEREE #2: 22) Pg 23757, line 1-5: Is N₂O₅ hydrolysis as a source of HNO₃ represented in CHIMERE?

AUTHOR: Yes, this source is included in the model. We added more clearly the information in Sect. 3.1: “[...]heterogeneous (e.g. HNO₃ formation on existing particles and fog droplets, including the conversion of N₂O₅) reactions [...]”

REFEREE #2: 23) Pg 23757, line 10: it is suggested that dry deposition rate of HNO₃ may be too low in CHIMERE. What are typical deposition velocities for HNO₃ in CHIMERE? How do they compare with those reported in literature?

AUTHOR: Yes, this is a possible source of error in the CHIMERE model. We added more details on this point in Sect. 4.3.2: “Dry deposition plays an important role in the HNO₃ budget, and corresponding parameterizations incorporated in the CHIMERE model have been poorly evaluated so far. In fact, a too low deposition rate modelled by CHIMERE may partly explain the positive bias on HNO₃. In CHIMERE, HNO₃ deposition velocities are typically below 1.5 cm s⁻¹, which appears on the lower end of the values reported in the literature (Brook et al., 1999). However, due to a lack of appropriate data, this hypothesis remains difficult to assess.”

Brook, J. R., Zhang, L., Li, Y. and Johnson, D.: Description and evaluation of a model of deposition velocities for routine estimates of dry deposition over North America. Part II: review of past measurements and model results, Atmos. Environ., 33(30), 5053–5070, doi:10.1016/S1352-2310(99)00251-4, 1999.

REFEREE #2: 24) Pg 23757, line 15-20: what is a quadratic error?

AUTHOR: It is a mistake; we mean the RMSE. We modified the sentence as follows: « Bias and RMSE are much lower for total nitrate »

REFEREE #2: 25) Pg 23758, line 5-10: “poor contribution” should perhaps be “low contribution”

AUTHOR: Modification applied.

REFEREE #2: 26) Pg 23759, line 10: “uncertainties on daytime” should perhaps be “uncertainties in daytime”.

AUTHOR: Modification applied.

REFEREE #2: 27) Pg 23760, line 1-5: Uncertainties in predicted OH are speculated to contribute to errors in modeled HNO₃. If the OH concentrations are significantly off, it should also be reflected in other secondary species – did the authors see similar discrepancies in other secondary species. Biases in dry deposition of HNO₃ could likely drive the model biases and it seems some more quantitative analysis of the modeled dry deposition rates vs chemical production rates will be useful.

AUTHOR: We did not investigate the ability of the CHIMERE model to simulate other secondary species. Satisfactory agreements are generally found for daytime ozone, but error compensations cannot be excluded. We agree with the referee that it would be interesting to investigate more quantitatively the deposition and the chemical production, but it is beyond the scope of this paper. The sensitivity test is only used to illustrate how strong can be the impact of erroneous OH fields in the CHIMERE model.

REFEREE #2: 28) Pg 23760, line 20-25: why would flat terrain result in more dispersive conditions?

AUTHOR: To our sense, the absence of important orographic obstacles favors stronger winds, and is thus expected to result in more dispersive conditions.

REFEREE #2: 29) Pg 23762, line 5-10: Given that the model has a high HNO₃ bias and a low NH₃ bias may be the reason it produces reasonable aerosol NO₃ – is that plausible?

AUTHOR: To begin, it is important to keep in mind that, as explained in the text, there is an uncertainty on the exact value of the positive CHIMERE bias on nitrates due to the possible negative artefact in measurements. We agree with the referee that it is somewhat counter-intuitive to understand how such strong biases on gaseous precursors may lead to a still reasonable bias on nitrate. We added an illustration of how the different biases can compensate: “As a conclusion, the either positive or negative bias on simulated nitrates and ammonium remains relatively small in comparison with the biases reported previously for precursor species. Such a result is not intuitive, and cannot be trivially explained. An interesting point to illustrate the possible error compensations concerns the saturation condition that needs to be achieved to allow the formation of nitrates. This condition is defined as (Ansari and Pandis, 1998):

$$[TNO_3] * ([TNH_3] - 2[TS]) > K$$

(6)

with K the equilibrium constant that depends on various parameters, including temperature and RH. It is obvious here that the errors on TNO₃ and TNH₃ can thus (partly) compensate each other. On average, the left-hand term is 3.6 and 2.5 ppb² based on observations and simulation, respectively. It corresponds to a NMB of -31%, thus much lower than the NMB affecting the different species (+71%, -56% and +48% for TNO₃, TNH₃ and TS). This result thus suggests that the formation of nitrates is slightly more difficult in the model than in the reality,

which would be consistent with a moderate negative bias on nitrates. Due to the possible artefacts, our dataset does not allow a complete assessment of the nitrate formation. It would be useful in the near future to evaluate the CHIMERE model with artefact-free measurements (for instance with aerosol mass spectrometer (AMS) or aerosol chemical speciation monitor (ACSM)).”

REFEREE #2: 30) Pg 23767, line 5-10: How do the wind regimes dictate local HNO₃ formation? This needs to be more clearly explained.

AUTHOR: The meteorological conditions dictate the residence time of air masses within the city, and thus the possibility for HNO₃ to be produced within the urban area (rather than downwind the city, in the Paris plume). However, concerning the importance of HNO₃ local formation versus imports, we decided to be more cautious in our conclusions. We modify the text as follows: « Some strong HNO₃ episodes are observed during anticyclonic conditions (high temperature, low-to-moderate wind) and suggest a substantial local formation from the NO_x emitted within Paris. However, our dataset does not allow quantitatively assessing the relative contributions of this local formation as compared to imports. »

REFEREE #2: 31) Pg 23767, line 10-15: the conclusions should state more specifically what new light this study has shed on debate on contributions of agricultural emissions.

AUTHOR: We modified the text as follows: “Considering the size of the Paris megacity and the intensity of NO_x emissions, one would have primarily expected higher HNO₃ and lower NH₃ in the Paris center. This work thus sheds a new light on the topical debate relative to the respective responsibility of traffic and agriculture in the formation of ammonium nitrate, by highlighting substantial amounts of agricultural NH₃ and relatively low concentrations of HNO₃ in the city.”