

ANSWERS TO REFEREE #1

We thank the referee for his good appreciation of the paper and his comments.

REFEREE #1: 1) It would be better if the module(s) on deposition processes be explained in more detail since the authors claimed deposition might be one of the important error sources for ammonia.

AUTHOR: We add in Sect. 3.1: « Dry and wet deposition of gaseous and aerosol species is parameterized from three types of sequential resistances following the resistance analogy (Wesely, 1989). An aerodynamical resistance is estimated based on turbulent parameters (e.g. Monin-Obukhov length, friction velocity, dynamical roughness length). A quasi-laminary boundary layer resistance is calculated based on the molecular diffusivity of water and gaseous species and Prandtl number. The surface resistance of vegetation and soils is estimated from several parallel resistances related to plant surfaces via opening of stomata, and related to non-stomatal deposition at plant and soil surfaces (Erisman et al., 1994). The scavenging of gases and particles, both in clouds and rain droplets, is included in CHIMERE. The scavenging of HNO₃ and NH₃ by cloud droplets (in rain droplets) is assumed reversible (irreversible). In clouds, particles can be scavenged by coagulation with cloud droplets or by precipitation, or can act as cloud condensation nuclei to form new droplets. Particles can also be scavenged by raining drops below the clouds. More details can be found in Menut et al. (2013). »

REFEREE #1: 2) The authors claimed that crustal species were minor and I agree with the authors on it. Another point that should be checked for the validity of the gas/particle equilibrium model is the effects of organic acids. Since some organic compounds (gas phase) were measured, a discussion on the effects of organic acids would be possible (though qualitative or semi-qualitative)

AUTHOR: We agree that this is an interesting topic but the ISORROPIA model does not take into account any of these effects. This point is thus beyond the scope of this paper.

REFEREE #1: 3) It would be nice to discuss on the sensitivity of ISORROPIA to the RH near to the deliquescence point of ammonium nitrate.

AUTHOR: The partitioning of inorganic compounds between the gas and the aerosol phase depends on temperature and RH conditions. As mentioned in Sect. 4.2.2, both parameters are slightly biased in the simulation (-1.6°C for temperature, +5.9% for RH) but these errors have a very limited influence for instance on NH₃ that increases by around 7% on average when the errors of RH and temperature are corrected in ISORROPIA. The impact of errors on meteorological parameters may be larger close to the deliquescence point of NH₄NO₃ where the partitioning between both phases is more strongly influenced by RH (and consequently by errors on RH). However, focusing on the days with RH between 60 and 65% (80%), the average increase of NH₃ only reaches +14% (6%). We propose to add the following sentences in Sect. 4.2.2: « Errors may be larger close to the deliquescence point where the influence of RH is stronger. The deliquescent RH (DRH) of NH₄NO₃ and (NH₄)₂SO₄ at 298K are 61.8 and 79.9%, respectively (Seinfeld and Pandis, 2006). A mixture of both salts will have a DRH between these two extreme values. Focusing on days where RH ranges between 60 and 80% (i.e. close to the deliquescent point of the mixture), the average NH₃ increase is

even lower (6%). It reaches 14% when considering RH between 60 and 65%. In any case, the impact remains limited. »

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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 (NH_3 , HNO_3 , SO_2) 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 $\text{PM}_{2.5}$ 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 SO_2) 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 HNO_3 and NH_3 , 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 HNO_3 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 NH_3 , to our opinion, several elements strongly suggest a major contribution of agricultural emissions to the NH_3 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 NO_3 (ΔNO_3) to a perturbation in a parameter (Δx) would be the same irrespective of the model or measurements. Instead the differences in ratio $\Delta x / \Delta \text{NO}_3$ 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 NO_3 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 TNH_3 , there is no reasons for the change of NO_3 in response to a perturbation of TNH_3 to be the same in the model and in the measurements since this change not only depends on the TNH_3 concentrations but also on the values of all the other parameters of the system – i.e. temperature, RH, TNO_3 (total nitrate $\text{HNO}_3 + \text{NO}_3^-$) and TS (total sulfate $\text{H}_2\text{SO}_4 + \text{HSO}_4^- + \text{SO}_4^{2-}$) – 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, TNO_3 , TNH_3 , 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 TNH_3 and TNO_3 concentrations. This 0-dimension model requires five inputs – temperature, RH, and TNO_3 , TNH_3 and TS concentrations – and computes the gas-aerosol partitioning coefficient of both TNO_3 and TNH_3 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 – TNO_3 or TNH_3 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 TNO_3 or TNH_3 . 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 NH₃ rich conditions in Paris, in spite of NO_x emissions, and attribute this to low HNO₃. 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 HNO₃) 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 HNO₃ 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 NH₃ 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 SO₂) where there is no discussion about shutting-off anthropogenic emissions. Concerning the NH₃ emissions, detailed information on emissions both the Paris region and in France are already given in Table S2 in the Supplement. The magnitude of NH₃ emissions in the Paris region are 4 994 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):

$$[TNO_3] * ([TNH_3] - 2[TS]) > K \quad (6)$$

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.”

* * *

ANSWERS TO REFEREE #3

We are grateful for the detailed comments of the referee and his contribution to the improvement of this paper.

REFEREE #3: This manuscript evaluates several aspects of nitrate formation in Paris, including an analysis of ammonia and nitric acid observations from several sites, along with a corresponding analysis of the CHIMERE modeled concentrations for the same locations and time periods. Observations of ammonia and nitric acid are analyzed to determine regions of origin (through back trajectory analyses). CHIMERE model estimates are analyzed and compared to observed concentrations and a number of statistical metrics are calculated to attempt to determine how well the model estimates both the model concentrations of various species and the conditions under which those species pollutants are formed. While I think the scientific methods presented in the manuscript are sound, the manuscript itself would benefit substantially from a great deal of editorial review. I found I often had difficulty understanding what point the authors were trying to make, and had to re-read sentences or entire paragraphs to finally understand the point being made. In addition, the use of chemical abbreviations is lacking, with the authors often switching back-and-forth between chemical names and chemical abbreviations. This also applies to meteorological abbreviations, such as relative humidity (RH). Also, there are a number of spelling errors in the manuscript (e.g. trafic) that need to be addressed. All these issues detract from the message trying to be conveyed in the manuscript. I would like to see these issues addressed before the manuscript is accepted. I also have a number of specific comments/corrections as well.

AUTHOR: Following the numerous comments of the three referees, we made substantial modifications of the manuscript in order to make its message clearer.

General suggestions:

REFEREE #3: It might be useful to look at an inert gas species (e.g. CO) that is well captured in the emission inventory as an indicator of the quality of meteorological simulation, in particular the evolution of the boundary layer throughout the day. The authors do discuss the meteorological performance to some degree, but this type of analysis might be enlightening to the reader, and presumably measurements of CO are available at a number of within the modeling domain.

AUTHOR: Comparisons with inert gases like CO have been performed at the 3 urban background sites available in the Paris megacity. However, to our opinion, they do not allow drawing a very clear picture of how well the boundary layer is simulated because other error sources are likely at stake. Indeed, if CO emissions are expected to be well constrained at a large scale (e.g. national scale), uncertainties are much higher at a finer scale (e.g. an area of Paris). And we indeed found substantial negative biases at several sites (from -15 to -38%) that are likely not only due to errors in the boundary layer height. And concerning the diurnal profiles, correlations appear very contrasted from one site to the other

(from 0.48 to 0.78). Moreover, some uncertainties can arise from the diurnal profile applied in CHIMERE to the traffic emissions. Thus we do not think that such comparisons are useful in our discussion. In addition, in this paper, we are mostly considering daily average data for which uncertainties on the boundary layer diurnal variability are less crucial.

REFeree #3: I'd like to see better support of some of statements in the manuscript. Often the authors will point to an aspect of the meteorology, emissions or model as the cause of a particular deficiency in the model performance, but without what I feel is adequate support or a reference. One example is the last sentence of section 4.3.1, stating "Such a pattern may be due to high measurement uncertainties occurring for low TNO₃ concentrations". I don't recall any discussion of this uncertainty, and there is no reference provided to support this claim.

AUTHOR: Concerning this sentence, we do not have material to investigate more deeply such low HNO₃/TNO₃ values in summer, it is just a hypothesis. A more appropriate formulation would be "Such a pattern may be due to higher measurement uncertainties occurring for low TNO₃ concentrations". To our opinion, measurement uncertainties are higher when the measured quantities are low and close to the limit detection of instruments. In August, during the days with HNO₃/TNO₃ below 40%, HNO₃ concentrations are below 0.2 ppb. We propose to modify the sentence as follows: "Such a pattern may be due to higher measurement uncertainties occurring for low TNO₃ concentrations, closer to the detection limit (roughly around 0.1 ppb for HNO₃). In August, ratio values below 40% indeed correspond to HNO₃ and TNO₃ concentrations below 0.2 and 0.7 ppb, respectively."

REFeree #3: Also, the authors point to errors in agriculture emissions as a large source of error in the model results, however, I don't think this claim is well supported in the manuscript (and if the authors think it is, it should probably have its own section detailing why those emissions are in error).

AUTHOR: A dedicated section has been added on this point. Most of the arguments were already in the initial text, but they are now gathered in a more convincing way. The main argument that allows us to think that agricultural emissions dominate is the seasonal variations of NH₃ concentrations in Paris (see Sect. 4.2.1.3 in the revised manuscript). Local NH₃ sources within the city can also contribute, but none of them can explain such a seasonal pattern with maximum concentrations in spring and early summer, and minimum ones in late autumn and winter (see Sect. 4.2.1.1 and 4.2.1.1 in the revised manuscript).

Specific comments:

REFeree #3: 23736, 13: Define EMEP.

AUTHOR: Definition added.

REFeree #3: 23738, 21: Define PRIMEQUAL FRANCIPOL.

AUTHOR: Definition added for PRIMEQUAL. But FRANCIPOL does not correspond to any acronym.

REFeree #3: 23741, 11: What is an "air quality survey"?

AUTHOR: Survey was replaced by monitoring.

REFeree #3: 23741, 14: Define MELCHIOR2.

AUTHOR: Definition added for MELCHIOR2.

REFeree #3: 23742, 17: MM5 is quite old now. Why was a more up-to-date meteorological model, such as WRF, not used?

AUTHOR: This study follows a previous paper that focused on the evaluation of the CHIMERE aerosol simulations during the PARTICULES campaign (Petetin et al., 2014), which was done with the operational modeling system of AIRPARIF that is still using MM5. We agree with the referee that using WRF would have been more appropriate, in particular for the treatment of the boundary layer.

REFeree #3: 23743, 13: It would be good to explain to the reader here why the MOD-noddep simulation is being performed.

AUTHOR: We propose the following modification: « In addition, as NH₃ is strongly impacted by dry deposition which is still poorly constrained in current CTMs, a third simulation (so-called MOD-noddep) is performed without any NH₃ dry deposition over the entire domain in order to investigate its influence on concentrations within Paris.»

REFeree #3: 23743, 19: Change "field" to "the observed".

AUTHOR: Modification applied.

REFeree #3: 23745, 18: Explain here why the S ratio is being calculated.

AUTHOR: We modified the text as follows: “This does not appear to be related to a too high SO₂-to-sulfate conversion since SO₂ concentrations are significantly overestimated in Paris, by about a factor of 3 (Table 1). This is also suggested by the simulated S-ratio. This indicator – defined as the ratio of SO₂ over SO₂+SO₄²⁻, all concentrations being expressed in µg m⁻³ (Hass et al., 2003; Pay et al., 2012) – allows to assess how fresh is a plume containing sulfur. High S-ratios are found in air masses containing freshly emitted SO₂, while low S-ratios are associated to older air masses in which more SO₂ have already been converted into sulfates. The observed and simulated S-ratios are shown in Fig. 3 (the SO₂+SO₄²⁻ time series is shown in Fig. S4 in the Supplement). In the MOD simulation, CHIMERE clearly overestimates the S-ratio (average value of 0.54 against 0.34 in the observations, i.e. a positive bias of +60%), i.e. the simulated air masses contain too much freshly emitted SO₂ compared to reality.”

REFeree #3: 23746, 13: 4 ppb is not in the middle of the range between 0.4 and 63.6 ppb.

AUTHOR: It is meant here that 4 ppb is roughly in the middle of the logarithmic range between 0.4 and 63.6 ppb. As this range covers more than two orders of magnitude, a logarithmic scale is more appropriate. We modified the sentence as follows: “According to the review of Reche et al. (2012), NH₃ concentrations in worldwide urban environments range between 0.4 and 63.6 ppb, thus spanning over two orders of magnitude. On a logarithmic scale, the average concentration of 4.0 ppb measured in Paris over the whole period is roughly in the middle range of this range.”

REFeree #3: 23747: It would be good to briefly explain here how exactly temperature and relative humidity affect the formation of NH₃.

AUTHOR: We propose to add the following sentence: “Temperature and RH strongly influence the equilibrium constant governing the partitioning of inorganic compounds

between the gas and aerosol phases, with higher NH_3 concentrations expected when the temperature is high and the RH is low due to the volatilization of NH_4^+ contained in NH_4NO_3 .”

REFeree #3: 23749, 26: Change kerbside to curbside (the more common form of this word).

AUTHOR: Modification applied.

REFeree #3: 23751/23752: How exactly were NH_3 emissions from traffic added to the simulation?

AUTHOR: To explain this feature, we added the following details in the text: “Several sensitivity tests were performed with added NH_3 traffic emissions, derived from the NO_x traffic emissions with $\text{NH}_3/(\text{NH}_3+\text{NO}_x)$ conversion factors of 1, 6, 12 and 18% (not shown). Such additional emissions reduce the bias, but do not improve the correlation between model and measurements. In particular, they induce a clear increase of NH_3 concentrations during the morning and evening rush hours, which is not in agreement with the observed diurnal profile. These results thus prevent us from concluding on the importance of these traffic emissions on NH_3 urban background levels.”

REFeree #3: 23754, 1: I don't feel like the statement "in particular the lack of dynamical treatment of agricultural emissions as a function of environmental factors" is well supported. Please add additional support for that statement.

AUTHOR: We refer here to agricultural emissions as they are treated in our CHIMERE model. As explained in the paper, the treatment is far too simplistic as a monthly profile is simply applied to the annual total emissions, without taking into account any environmental factor like the temperature. Many details on this point are already given in the previous Sect. (4.2.2) to support this statement. We simply clarified the text given here as follows: “Thus, the simulated NH_3 concentrations appear mainly affected by uncertainties in emissions, and in particular the lack of dynamical treatment of agricultural emissions as a function of environmental factors (temperature, etc.) in the CHIMERE model (the annual total emissions being simply disaggregated with a monthly profile).”

REFeree #3: 23754, 26: How do you know that high winds are the reason that HNO_3 is not higher for that period?

AUTHOR: High winds are probably not the only reason explaining why HNO_3 is not higher the 2-3 June. However, the wind drives the accumulation of the NO_x emitted locally in Paris, and is thus expected to influence to a substantial part the variability of HNO_3 . This is supported by the NO_2 measurements at an AIRPARIF station near the LHVP site that shows strong enhancements of NO_2 concentrations the 4-5 June during the night when the wind falls below 1 m s^{-1} . We added more details on this point: “During the next 2 days, stronger wind speed (above 3 m s^{-1}) and increasing temperatures are observed, associated to a moderate increase of HNO_3 concentrations. A much higher increase of HNO_3 concentrations is observed the 4th and 5th of June concomitantly with high temperatures (up to 30°C) and slow winds. Such stagnant conditions during the night allow the accumulation of NO_2 , as shown by the NO_2 measurements at an AIRPARIF station located right next to the LHVP site (not shown). In the early morning of the 4th (5th) of June, NO_2 concentrations reach 83 (110)

ppb, and fall below 20 ppb during the afternoon. As for NH₃, no additional HNO₃ measurements are available upwind of Paris, which prevents us from quantitatively assessing 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 #3: 23757, 8: Why is dry deposition of HNO₃ in the model thought to be too low? Is there a reference to support this assertion?

AUTHOR: This is just an assumption. Our model shows a strong positive bias and we are discussing all the possible reasons for that. To our knowledge, HNO₃ dry deposition has never been evaluated in the CHIMERE model. Some typical values of HNO₃ dry deposition velocity in CHIMERE are added in the text (see answer to referee #2, question 23).

REFeree #3: 23763, 16: Since the observations of NH₃ and NH₄ (and HNO₃ and NO₃) are not measured at the same sites, it would be useful to provide some discussion of the heterogeneity of those species in space.

AUTHOR: A section was added to discuss this point (see answer to referee #2, question 2).

REFeree #3: Table 1: Not sure this table is really necessary since it conveys minimal information.

AUTHOR: We replaced the Table by the following sentences: “Measurements of secondary inorganic aerosols (NH₄⁺, NO₃⁻, SO₄²⁻) are available at the daily scale between the 1 April and the 10 September 2010. NH₃ (HNO₃) observations are available at the hourly scale from the 20 May (1 April) to the 31 December 2010.”

REFeree #3: Figure 1: It would be useful to provide the different domain resolutions on the figure.

AUTHOR: Resolutions are already indicated in the text. To our opinion, it does not appear useful to add them on the figure. We just added the information in the legend: “Resolutions are 0.5x0.5° (LAR domain), 9x9 km (MED) and 3x3 (FIN).”

REFeree #3: Figure 3: It's difficult to pick out the different lines since all the colors are similar. Please change to more contrasting colors.

AUTHOR: These same colors are used in the whole paper for the different simulations, and to our opinion, the contrast is strong enough to distinguish the different lines.

REFeree #3: Figure 6: Same suggestion as for figure 3.

AUTHOR: On this figure, the two lines are very similar, which explains that it is not easy to distinguish them.