ANSWERS TO REFEREE #3

We are greatful 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 TNO_3 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 HNO_3/TNO_3 below 40%, HNO_3 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 TNO_3 concentrations, closer to the detection limit (roughly around 0.1 ppb for HNO_3). In August, ratio values below 40% indeed correspond to HNO_3 and TNO_3 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 NH_3 concentrations in Paris (see Sect. 4.2.1.3 in the revised manuscript). Local NH_3 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-nodep simulation is being performed.
AUTHOR: We propose the following modification: « In addition, as NH_3 is strongly impacted by dry deposition which is still poorly constrained in current CTMs, a third simulation (so-called MOD-nodep) is performed without any NH_3 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 SO_2-to-sulfate conversion since SO_2 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 SO_2 over $SO_2+SO_4^{2-}$, 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 SO_2, while low S-ratios are associated to older air masses in which more SO_2 have already been converted into sulfates. The observed and simulated S-ratios are shown in Fig. 3 (the $SO_2+SO_4^{2-}$ 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 SO_2 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), NH_3 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 NH_3.
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 NH3 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 $NH_3/(NH_3+NO_x)$ 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 HNO3 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 NH_3, no additional HNO_3 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 HNO_3. Some HNO_3 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, HNO_3 dry deposition has never been evaluated in the CHIMERE model. Some typical values of HNO_3 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 (NH_4^+, NO_3^-, SO_4^{2-}) are available at the daily scale between the 1 April and the 10 September 2010. NH_3 (HNO_3) 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.