

## Responses to the comments of anonymous referee #1

Thank you for your comments that helped to improve our manuscript. Please find below your comments in blue, our responses in black and modifications in the revised manuscript in *italic*.

In this article, the authors apply CAMx to two intensive monitoring periods, one in the cooler season one in the warmer season. CAMx is applied using its particulate source apportionment technology (PSAT). They double the biogenic emissions inventory to test how that impacts the formation of inorganic aerosol. They find that doubling the biogenics reduces inorganic particulate nitrate. This is tied to the reaction of nitrate radicals with terpenes. They also found that sulfate was mainly of foreign origin.

First, such a paper should have a performance evaluation in the main body of the paper. Simply saying that the chemical components are well captured by the model is not sufficient. Actual metrics should be provided. They can show this very economically using soccer or bugle plots, along with some traditional performance metrics. The evaluation should consider the available monitors across the modeling domain. In the supplement, they provide only time series pictures, which can be very deceiving depending upon the scales chosen. They should look at all of the work done as part of the AQMEII and follow that lead. Numerical results for the performance on ozone, aerosol nitrate, sulfate and ammonium, and gaseous precursors should be in the text. (I will note, when I look at the time series, it would appear that the model is not performing well, but showing the numerical evaluation would either confirm or negate that view.. the numerical performance measures should be given either graphically or in a tabular fashion. I think the bugle or soccer plots are best as they can show what is considered reasonable compared to past applications.)

Thank you for this comment. The model performance published by Ciarelli et al., (2016) is very similar to the one in this study- since all the model parameters were the same- except for organics due to the difference in organic aerosol model. However we agree with this comment and added the detailed model performance in the revised manuscript (see section 3.1 Model Evaluation) using soccer plots and tables with statistical parameters as suggested.

Second, while it is good to also consider periods where intensive measurements are available, it would be good, here, to use annual simulations to limit the bias in interpretation that may be derived from using such short periods. If they were using the detailed measurements to make some process changes in the model, that would be different. Here, the measurements are used in a rather limited fashion. It is also a problem when they only show detailed results for one day (in this case, 14 June). How does this compare to other days. Provide a longer time series or provide a summer and winter average. The limited time period is also of concern when suggesting so much sulfate is coming from the boundaries. This brings up a real concern: is this article meant to support policy decisions or for science (this should be answered in the response to review, not the article). If it is to support policy-making, definitely a longer set of simulations are required. If it is for science, deeper investigation is required (in addition to a longer simulation to show how the period used for more intense investigation represents a typical period). If the period is atypical, that is fine. It just needs to be known.

This study is not meant for policy decisions for which we have performed annual

simulations in the past (e.g. Aksoyoglu et al., 2014). Here, after showing the significant contribution of various sources to SIA concentrations in Europe, we aim to attract the attention to the role of BVOC emissions in chemical processes leading to formation of SIA, especially ammonium nitrate. For this purpose, short periods with PM component measurements are very useful. Sensitivity tests aim to analyze the changes in the production of OH radical and HNO<sub>3</sub> from various chemical reactions in the model and therefore they are shown at one point and one day, as an example. As suggested however, we replaced the figures of sensitivity tests on 14 June with those using monthly averages. These results show the model's response to changes in BVOC emissions and chemical reactions. The periods were chosen based on the availability of AMS measurements of the PM components. These measurements are very valuable for the evaluation of model performance because using only PM<sub>2.5</sub> measurements for model evaluation might result in a good performance due to compensation of over- and under estimations of PM components. We inserted a table in the revised manuscript showing the model performance evaluation for the PM components.

High sulfate at the eastern boundary is seen mainly during the February-March 2009 period and it affects only the eastern part of the domain (Russia and Ukraine), the rest of Europe doesn't seem to be affected. There are detailed evaluations of MACC reanalysis data (e.g. Inness et al., 2013, Giordano et al., 2015). Evaluations during the AQMEII-2 exercise showed a positive bias for sulfate and suggested that it was because MACC aerosol model does not contain a representation of ammonium nitrate aerosol which represents a large component of the European aerosol loading (Giordano et al., 2015). Therefore the assimilation of satellite AOD will tend to increase the other aerosol components to give the correct AOD overall.

They used CAMx with PSAT. It should be made clear that PSAT shows where the species (Nitrate, ammonium, sulfate) originates, but it is not a source impact. If all of the reduced N is removed, most of the oxidized N will also go away. Given the nonlinearities in the system, they should also run a series of zero-out simulations, where they zero out the major source categories of interest. These can be compared. This should be computationally quite reasonable.

PSAT is a widely used source apportionment model and has already been compared with other methods (e.g. Pirovano et al., 2015, Koo et al., 2009). Studies comparing PSAT which is a reactive tracer method, with sensitivity analysis methods such as brute-force, zero-out and decoupled direct methods pointed out that source apportionment and source sensitivity are not the same thing for nonlinear systems (Yarwood et al., 2007). In PSAT, a single tracer can track primary PM species, whereas secondary PM species require several tracers to track the relationship between gaseous precursors and the resulting PM - for example, in case of nitrogen, PSAT uses tracers such as NO<sub>x</sub>, NO<sub>3</sub> radical, HONO, N<sub>2</sub>O<sub>5</sub>, PAN, PNA, HNO<sub>3</sub>, organic nitrates, particulate nitrate. Yarwood et al. (2007) compared PSAT and zero-out method results for secondary inorganic aerosols and concluded that PSAT was much more efficient and it was a better approach to source apportionment than zero-out method because it was better able to deal with the nonlinear chemistry. It was recently used to identify source-sector contributions to European fine PM during the Phase 3 of the Air Quality Model Evaluation International Initiative (AQMEII) (Karamchandani et al., 2016).

How do their estimates of nitric acid formation from N<sub>2</sub>O<sub>5</sub> s. OH compare with other

historical estimates?

Brown et al. (2004) and Vrekoussis et al. (2006) confirmed the role of  $\text{NO}_3$  and  $\text{N}_2\text{O}_5$  in producing  $\text{HNO}_3$  with an efficiency similar to daytime production off the East Coast of the United States and in eastern Mediterranean, respectively. Estimated daytime  $\text{HNO}_3$  production rate of 2.76 ppb/d and nighttime production (by  $\text{N}_2\text{O}_5$ ) of 0.21 ppb/d by Minejima (2008) in California are similar to our estimates shown in Fig. 6 in the revised manuscript.

When I go on line, I do not see the “Rest” on their map in the supplement.

“Rest” is shown by the yellow color and it covers all the other countries except those indicated by other colors. Perhaps the tonality of yellow color in the map and the legend were slightly different. We adjusted the legend color and it looks better now.

Given the huge uncertainties in the  $\text{NO}_3$ -organic and  $\text{NO}_2$ -organic radical and sulfate- BVOC reactions, the finding that doubling the biogenics reduces SIA should be accompanied, quite prominently, this uncertainty. How well does the model reproduce BSOA (biogenic SOA) formation, particularly from terpenes and via the IEPOX pathways? How was this assessed or addressed?

We use the Carbon Bond gas-phase mechanism in CAMx which has been developed and updated for EPA atmospheric modeling studies (Yarwood et al., 2005). The CB05 mechanism was evaluated against smog chamber data from the Universities of North Carolina and California at Riverside. Gas-phase reactions of isoprene and its oxidation products as well as reactions of terpenes and SOA precursor reactions are given in the Supplement Tables S1, S2. Isoprene mechanism was revised by the CAMx developers based on Paulot et al. (2009a, b) and Peeters et al. (2009). As seen in Figure S8, BSOA is formed mostly by mono and sesquiterpenes, much less from isoprene. Since SOA is formed mainly from biogenic emissions in Europe, large uncertainties in biogenic VOC emissions are very important (Steinbrecher et al., 2009), might even be more important than the uncertainties in the reactions. As reported by Sartelet et al., (2012), SOA concentrations differ by a factor of 2 using two different biogenic emission inventories. More information was added in the revised introduction.

The discussion of  $\text{NO}_3$  nighttime dynamics lacks context and references, e.g., work done by Seinfeld and co-workers as well as a variety of articles by Platt and coworkers starting, in the early 1980s. They should detail what is new here.

Nighttime chemistry of  $\text{NO}_3$  has of course been studied extensively and we added some more references in the Section 3.5 of the revised manuscript as suggested (*Platt et al., 1981; Russell et al., 1986; Platt and Heintz, 1994; Seinfeld and Pandis, 2012*). Although there is nothing new about the nighttime reactions, this study aims to attract the attention to the consequences of these reactions not only on the formation of organic nitrates and aerosols but also on the inorganic ones. More specifically, we try to show how BVOC reactions play a role on inorganic nitrate formation by consuming nitrate radical. Model studies have so far assumed that other factors such as  $\text{NO}_x$  and  $\text{NH}_3$  emissions, deposition and gas-particle partitioning might be responsible for not well capturing ammonium nitrate. We believe that BVOC emissions might also have an important contribution to the model performance of inorganic nitrates. Several studies so far have emphasized the significance of BVOC reactions with nitrate radicals as leading to “anthropogenically influenced biogenic SOA” (Ng et al., 2016). In this study we aim to show another consequence –although

with smaller influence- of such reactions leading to “biogenic influence on anthropogenic ammonium nitrate”. Our sensitivity tests with doubled BVOC emissions suggest that terpene reactions reduce the amount of nitrate radical available for nighttime HNO<sub>3</sub> formation and consequently, cause a reduction in ammonium nitrate formation.

This section could also benefit from tracing the HNO<sub>3</sub> formed by each reaction. Specifically, while nitric acid is efficiently deposited, the average deposition rate is about 1 cm/s, leading to a lifetime of about a day. It appears more HNO<sub>3</sub> is formed during the day, so there is plenty still around at night formed during the day. Keep in mind, the HNO<sub>3</sub> formed in the afternoon has little time to deposit. Note how quickly the NO<sub>3</sub> raises when the air gets cool enough? The HNO<sub>3</sub> is only being formed at a rate of 0.04 ppb/hr, which is likely not fast enough to supply the nitrate shown to be formed. Isn't much of this left over from during the day?

In Figure 6 of the revised manuscript, formation rate of HNO<sub>3</sub> during the day and night are shown together with the concentration of PNO<sub>3</sub> (not the formation rate). Daytime rate of HNO<sub>3</sub> formation is faster than nighttime. It is true that some of the HNO<sub>3</sub> produced during the day might be left after deposition at night. However, PNO<sub>3</sub> concentration shown in Fig. 6, is the result of several processes such as formation from all pathways, transport, deposition, gas-particle partitioning in addition to the nitrate which was already there before.

In summary, at present there are a number of items that need to be conducted and/or addressed before the paper should be accepted for publication. First, the model evaluation should be brought forward and discussed, and should include numerical overall performance measures, potentially shown as soccer and/or bugle charts in the text and a more detailed set of statistics (not just some time series plots) in the supplemental. In particular, the ammonium and nitrate simulations across the domain should be evaluated and considered closely, and the ability of the model to capture BSOA should be brought out. The model should be run to examine how levels respond to removing a few major sources to show how those results compare with the PSAT results. There can be major nonlinearities that are not found when just using PSAT. It would also be advisable to run full year simulations. They need to put their results in context with past studies, e.g., look at the review by Platt and Heinz (1994) and the early work by Seinfeld and co-workers (as well as the recent work, e.g. by Nga et al. 2015). If these items are done in the revision, it would be acceptable for publication.

Thanks for your suggestions. We revised the manuscript with all the points as addressed above individually.

## References

Aksoyoglu, S., Keller, J., Ciarelli, G., Prévôt, A. S. H., and Baltensperger, U.: A model study on changes of European and Swiss particulate matter, ozone and nitrogen deposition between 1990 and 2020 due to the revised Gothenburg protocol, *Atmos. Chem. Phys.*, 14, 13081-13095, 10.5194/acp-14-13081-2014, 2014.

Brown, S. S., Dibb, J. E., Stark, H., Aldener, M., Vozella, M., Whitlow, S., Williams, E. J., Lerner, B. M., Jakoubek, R., Middlebrook, A. M., DeGouw, J. A., Warneke, C., Goldan, P. D., Kuster, W. C., Angevine, W. M., Sueper, D. T., Quinn, P. K., Bates, T. S., Meagher, J. F., Fehsenfeld, F. C., and Ravishankara, A. R.: Nighttime removal of NO<sub>x</sub> in the summer marine boundary layer, *Geophysical Research Letters*, 31, n/a-

n/a, 10.1029/2004GL019412, 2004.

Ciarelli, G., Aksoyoglu, S., Crippa, M., Jimenez, J. L., Nemitz, E., Sellegri, K., Äijälä, M., Carbone, S., Mohr, C., O'Dowd, C., Poulain, L., Baltensperger, U., and Prévôt, A. S. H.: Evaluation of European air quality modelled by CAMx including the volatility basis set scheme, *Atmos. Chem. Phys.*, 16, 10313-10332, 10.5194/acp-16-10313-2016, 2016.

Giordano, L., Brunner, D., Flemming, J., Hogrefe, C., Im, U., Bianconi, R., Badia, A., Balzarini, A., Baró, R., Chemel, C., Curci, G., Forkel, R., Jiménez-Guerrero, P., Hirtl, M., Hodzic, A., Honzak, L., Jorba, O., Knote, C., Kuenen, J. J. P., Makar, P. A., Manders-Groot, A., Neal, L., Pérez, J. L., Pirovano, G., Pouliot, G., San José, R., Savage, N., Schröder, W., Sokhi, R. S., Syrakov, D., Torian, A., Tuccella, P., Werhahn, J., Wolke, R., Yahya, K., Žabkar, R., Zhang, Y., and Galmarini, S.: Assessment of the MACC reanalysis and its influence as chemical boundary conditions for regional air quality modeling in AQMEII-2, *Atmospheric Environment*, 115, 371-388, <http://dx.doi.org/10.1016/j.atmosenv.2015.02.034>, 2015.

Inness, A., Baier, F., Benedetti, A., Bouarar, I., Chabrillat, S., Clark, H., Clerbaux, C., Coheur, P., Engelen, R. J., Errera, Q., Flemming, J., George, M., Granier, C., Hadji-Lazaro, J., Huijnen, V., Hurtmans, D., Jones, L., Kaiser, J. W., Kapsomenakis, J., Lefever, K., Leitão, J., Razinger, M., Richter, A., Schultz, M. G., Simmons, A. J., Suttie, M., Stein, O., Thépaut, J. N., Thouret, V., Vrekoussis, M., Zerefos, C., and the M. t.: The MACC reanalysis: an 8 yr data set of atmospheric composition, *Atmos. Chem. Phys.*, 13, 4073-4109, 10.5194/acp-13-4073-2013, 2013.

Karamchandani, P., Long, Y., Pirovano, G., Balzarini, A., and Yarwood, G.: Source-sector contributions to European ozone and fine PM in 2010 using AQMEII modeling data, *Atmos. Chem. Phys. Discuss.*, 2016, 1-26, 10.5194/acp-2016-973, 2016.

Koo, B., Wilson, G. M., Morris, R. E., Dunker, A. M., and Yarwood, G.: Comparison of Source Apportionment and Sensitivity Analysis in a Particulate Matter Air Quality Model, *Environmental Science & Technology*, 43, 6669-6675, 10.1021/es9008129, 2009.

Minejima, C.: Nitrogen Oxide Chemistry at Night: Novel Instrumentation Applied to Field Measurements in California, Ph.D. thesis, Department of Chemistry, University of California, Berkeley, CA, USA, 2008.

Ng, N. L., Brown, S. S., Archibald, A. T., Atlas, E., Cohen, R. C., Crowley, J. N., Day, D. A., Donahue, N. M., Fry, J. L., Fuchs, H., Griffin, R. J., Guzman, M. I., Hermann, H., Hodzic, A., Iinuma, Y., Jimenez, J. L., Kiendler-Scharr, A., Lee, B. H., Luecken, D. J., Mao, J., McLaren, R., Mutzel, A., Osthoff, H. D., Ouyang, B., Picquet-Varrault, B., Platt, U., Pye, H. O. T., Rudich, Y., Schwantes, R. H., Shiraiwa, M., Stutz, J., Thornton, J. A., Tilgner, A., Williams, B. J., and Zaveri, R. A.: Nitrate radicals and biogenic volatile organic compounds: oxidation, mechanisms and organic aerosol, *Atmos. Chem. Phys. Discuss.*, 2016, 1-111, 10.5194/acp-2016-734, 2016.

Paulot, F., Crounse, J. D., Kjaergaard, H. G., Kroll, J. H., Seinfeld, J. H., and Wennberg, P. O.: Isoprene photooxidation: new insights into the production of acids and organic nitrates, *Atmos. Chem. Phys.*, 9, 1479-1501, 10.5194/acp-9-1479-2009, 2009a.

Paulot, F., Crounse, J. D., Kjaergaard, H. G., Kürten, A., St. Clair, J. M., Seinfeld, J. H., and Wennberg, P. O.: Unexpected Epoxide Formation in the Gas-Phase

- Photooxidation of Isoprene, *Science*, 325, 730-733, 10.1126/science.1172910, 2009b.
- Peeters, J., Nguyen, T. L., and Vereecken, L.: HOx radical regeneration in the oxidation of isoprene, *Physical Chemistry Chemical Physics*, 11, 5935-5939, 10.1039/B908511D, 2009.
- Pirovano, G., Colombi, C., Balzarini, A., Riva, G. M., Gianelle, V., and Lonati, G.: PM2.5 source apportionment in Lombardy (Italy): Comparison of receptor and chemistry-transport modelling results, *Atmospheric Environment*, 106, 56-70, <http://dx.doi.org/10.1016/j.atmosenv.2015.01.073>, 2015.
- Platt, U., Perner, D., Schröder, J., Kessler, C., and Toennissen, A.: The diurnal variation of NO<sub>3</sub>, *Journal of Geophysical Research: Oceans*, 86, 11965-11970, 10.1029/JC086iC12p11965, 1981.
- Platt, U., and Heintz, F.: Nitrate Radicals in Tropospheric Chemistry, *Israel Journal of Chemistry*, 34, 289-300, 10.1002/ijch.199400033, 1994.
- Russell, A. G., Cass, G. R., and Seinfeld, J. H.: On some aspects of nighttime atmospheric chemistry, *Environmental Science & Technology*, 20, 1167-1172, 10.1021/es00153a013, 1986.
- Sartelet, K. N., Couvidat, F., Seigneur, C., and Roustan, Y.: Impact of biogenic emissions on air quality over Europe and North America, *Atmospheric Environment*, 53, 131-141, <http://dx.doi.org/10.1016/j.atmosenv.2011.10.046>, 2012.
- Seinfeld, John H. and Pandis, Spyros N.: *Atmospheric Chemistry and Physics: From Air Pollution to Climate Change*, 2nd Edition. ISBN: 978-0-471-72018-8, 2012
- Steinbrecher, R., Smiatek, G., Köble, R., Seufert, G., Theloke, J., Hauff, K., Ciccioli, P., Vautard, R., and Curci, G.: Intra- and inter-annual variability of VOC emissions from natural and semi-natural vegetation in Europe and neighbouring countries, *Atmospheric Environment*, 43, 1380-1391, 2009.
- Vrekoussis, M., Liakakou, E., Mihalopoulos, N., Kanakidou, M., Crutzen, P. J., and Lelieveld, J.: Formation of HNO<sub>3</sub> and NO<sub>3</sub><sup>-</sup> in the anthropogenically-influenced eastern Mediterranean marine boundary layer, *Geophysical Research Letters*, 33, n/a-n/a, 10.1029/2005GL025069, 2006.
- Yarwood, G., Rao, S., Yocke, M., and Whitten, G. Z.: *Updates to the Carbon Bond chemical mechanism: CB05* Yocke & Company, Novato, CA 94945RT-04-00675, 2005.
- Yarwood, G., Morris, R. E., and Wilson, G. M.: Particulate Matter Source Apportionment Technology (PSAT) in the CAMx Photochemical Grid Model, in: *Air Pollution Modeling and Its Application XVII*, edited by: Borrego, C., and Norman, A.-L., Springer US, Boston, MA, 478-492, 2007.