Responses to the comments of anonymous referee #2

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

The manuscript presents a modeling study to investigate source contributions to PM concentrations in Europe. Using a 3-D model and source apportionment analysis, the authors identified major sources that contribute particulate sulfate, nitrate and ammonium in the modeling domain. They also discussed correlation between biogenic VOC emissions and secondary inorganic PM formation using sensitivity simulations and process analysis. The topic should interest atmospheric modeling community as well as policy-makers. However, there are a couple of issues that need to be addressed before the manuscript should be considered for publication.

Detailed and comprehensive source apportionment analysis is valuable and useful in developing effective air quality management plans. However, it is not clear what scientific contribution this study brings: This study used existing model, modeling database, and analysis tools and methodologies. The authors should clarify/emphasize what their unique and noble contributions are.

The new scientific contribution can be summarized as follows: 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 a “biogenic influence on anthropogenic ammonium nitrate”. Our sensitivity tests with doubled BVOC emissions suggest that terpene reactions reduce the available nitrate radical for nighttime HNO_3 formation and consequently, cause a reduction in ammonium nitrate formation.

In the introduction of the revised manuscript we emphasized the main scientific contribution as shown below.

Earlier studies suggest that SIA constitutes more than half of $PM_{2.5}$ ($d < 2.5$ µm) concentrations in Europe, especially in winter, and ammonium nitrate is the dominant component of SIA in western and central Europe (Schaap et al., 2004; Aksoyoglu et al., 2011; 2012; Squizzato et al., 2013). A combination of meteorological conditions and various emission sources led to highly elevated PM concentrations in Europe during early spring episodes in the past, mainly due to high ammonium nitrate concentrations (Sciare et al., 2010; Revuelta et al., 2012). Knowing the location and strength of sources contributing to $PM_{2.5}$ is essential for developing effective control strategies. In spite of the fact that the formation mechanisms of SIA are better understood than those of organic aerosols, chemical transport models (CTMs) still have difficulties to capture measured concentrations. This is usually attributed to uncertainties in NH_3 emissions (Aan de Brugh et al., 2011; Wang et al., 2013) while the effect of uncertainties in NO_x emissions and transformation cannot be ruled out (Vaughan et al., 2016). Modeling the formation of the semi-volatile ammonium nitrate is difficult because it is strongly dependent on the ambient conditions. On the other hand, a lot of effort is being made on understanding the formation of SOA and the role of BVOC emissions on organic nitrates, but the indirect effect of BVOC emissions on the formation of inorganic nitrate (ammonium nitrate) has so far not attracted any attention. Biogenic species such as isoprene, mono- and sesquiterpenes emitted from vegetation are known mainly as precursors of secondary pollutants like ozone and SOA (Kanakidou et al., 2005; Sartelet et al., 2012). The nitrate radical is *an effective nocturnal oxidizer of VOCs and it is especially reactive towards biogenic volatile organic compounds (BVOCs). Laboratory experiments showed a rapid production of SOA with high yields when some monoterpenes were oxidized by nitrate radicals (Fry et al., 2011; Boyd et al., 2015). Reactions of isoprene lead to the formation of SOA mainly during the daytime while nighttime oxidation of monoterpenes by the nitrate radical is responsible for organic nitrate formation (Ayres et al., 2015). Atmospheric reactions of BVOC species might change the oxidant concentrations significantly, affecting the formation of secondary compounds. In many areas in Europe, models overestimate ammonium nitrate concentrations during nighttime while SOA is underestimated especially during daytime hours (Prank et al., 2016; Knote et al., 2011; Colette et al., 2011; de Meij et al., 2006). Among other issues such as uncertainties in anthropogenic precursor emissions, deposition and missing emission sources, one should also consider the sensitivity of the secondary inorganic aerosol formation to BVOC emissions. Biogenic emissions are generated by emission models (e.g. MEGAN, Guenther et al., 2012; BEIS (https://www.epa.gov/air-emissions-modeling/biogenic-emission-inventory-system-beis); Simpson et al., 1999; Steinbrecher et al., 2009) to be used in CTMs and the resulting emissions vary significantly depending on the model used or even on the land cover used within the same model (Huang et al., 2015). BVOC emissions are known to have very large uncertainties (Sindelarova et al., 2014; Emmerson et al., 2016) and therefore, their role in the formation of secondary inorganic aerosols might be quite significant.*

Although there has been extensive research on the formation of SOA from the oxidation of BVOCs (Carlton et al., 2009; Hallquist et al., 2009; Ayres et al., 2015; Xu et al., 2015; Fuzzi et al., 2015), to our knowledge, effects of BVOCs on SIA, especially on ammonium nitrate, have been scarcely investigated (Karambelas, 2013). Several studies so far emphasized the significance of BVOC reactions with nitrate radicals as leading to "anthropogenically influenced biogenic SOA" (Ng et al., 2016). In this study we show another consequence –although with smaller influence- of such reactions leading to "biogenic influence on anthropogenic ammonium nitrate" in Europe.

The model performance section lacks any quantitative performance evaluation. The authors stated that the model performance has been presented in another paper (Ciarelli et al., 2016), but it appears that Ciarelli et al. mainly evaluated CAMx with a VBS approach while this study used a traditional SOA scheme. In any case, at least some basic statistical performance metrics should be provided. Also, I wonder if any sort of evaluation was done for the boundary conditions from MACC: It seems important considering that BC contributes significantly to sulfate. If manuscript length is a concern, these can be included in the supporting material.

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 the 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 statistical parameters as suggested also by the other referee.

MACC reanalysis data have already been evaluated in detail (e.g. Inness et al., 2013, Giardono et al., 2015). Evaluations during the AQMEII-2 exercise showed a positive bias for sulfate and suggested that it was because the MACC aerosol model does not contain a representation of ammonium nitrate aerosol which represents a large component of the European aerosol loading (Giardono et al., 2015). Therefore the assimilation of satellite AOD will tend to increase the other aerosol components to give the correct AOD overall. In our study, high sulfate levels at the eastern boundary were mainly during the February-March 2009 period affecting only the eastern part of the domain (Russia and Ukraine).

And here are some specific questions: 1. It appears Table 1 doesn't include natural sources (biogenic, wildfires, etc.). They were not considered in the source apportionment analysis? Are their contributions minor?

Wildfires were not considered in the source apportionment analysis because they would contribute to carbonaceous aerosols, but not much to secondary inorganic aerosols (Gibson et al., 2015). In addition, emission databases for wildfires have usually very low spatial and temporal resolution leading to very high uncertainty in the model predictions. The contribution of other natural sources to fine secondary inorganic aerosols is negligible compared to the anthropogenic sources in Europe.

2. Increased BVOC reduces inorganic nitrate formation, but will increase organic nitrate.

What is the overall effect on total PM? Does the model adequately model organic nitrate formation?

It is true that increased BVOC increases organic nitrates (NTR) through isoprene (ISOP) and isoprene oxidation product (ISPD) reactions with NO_2 and NO_3 and terpene (TERP) reactions with NO_3 (see reactions in Table S1). Organic nitrates may serve as either a NOx reservoir or a NOx sink (Kiendler-Scharr et al., 2016). We inserted also a figure for the production rate of organic nitrates in the revised manuscript (Fig. 6c). Organic nitrate production increased with doubled BVOC emissions. On the other hand, when BVOC reactions with NO_3 radical were switched off, organic nitrate production decreased significantly, especially at night due to reduced production from terpene $+NO_3$ reactions.

The overall effect on total $PM_{2.5}$ (up to 5 $\mu g\ m^{-3}$, ~65%) is dominated by the increase in SOA (see Figure S9 in the Supplement). A small negative change in $PM_{2.5}$ was predicted around the Benelux area and northern Italy due to the decrease in PNO_3 of about 1 -1.4 $\mu g\ m^{-3}$ in those regions.

3. Figure S10 shows significant nitrate reduction (_15%) over the ocean while SOA increases are mostly confined inland. There should be no BVOC emissions over the ocean. What is causing nitrate reduction there?

This is just due to a small difference in a small number. As seen in Fig.1 (upper left panel), nitrate concentrations over the ocean are very low and the absolute change (Fig. 4, left panel) is small.

References

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