

## Responses to the comments of anonymous referee #1

Thank you for your comments which 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.)

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 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 by those with 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 highly 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 the 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 the 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 the eastern Mediterranean, respectively. The estimated daytime  $\text{HNO}_3$  production rate of 2.76 ppb/d as well as the nighttime production rate (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. The 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, the large uncertainties in biogenic VOC emissions are very important (Steinbrecher et al., 2009), and 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 the corresponding aerosol but also on the inorganic nitrates. More specifically, we try to show how BVOC reactions play a role in 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  $\text{HNO}_3$  formation and consequently, cause a reduction in the ammonium nitrate formation.

This section could also benefit from tracing the  $\text{HNO}_3$  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  $\text{HNO}_3$  is formed during the day, so there is plenty still around at night formed during the day. Keep in mind, the  $\text{HNO}_3$  formed in the afternoon has little time to deposit. Note how quickly the  $\text{NO}_3$  raises when the air gets cool enough? The  $\text{HNO}_3$  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, the formation rates of  $\text{HNO}_3$  during the day and night are shown together with the concentration of  $\text{PNO}_3$  (not the formation rate). The daytime rate of  $\text{HNO}_3$  formation is faster than the nighttime rate. It is true that some of the  $\text{HNO}_3$  produced during the day might be left after deposition at night. However, the  $\text{PNO}_3$  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 that 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  $\text{NO}_x$  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.: PM<sub>2.5</sub> 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.

## 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<sub>3</sub> 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<sub>2.5</sub> ( $d < 2.5 \mu\text{m}$ ) 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<sub>2.5</sub> 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<sub>3</sub> emissions (Aan de Brugh et al., 2011; Wang et al., 2013) while the effect of uncertainties in NO<sub>x</sub> 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, Giardano 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 (Giardano 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  $\text{NO}_2$  and  $\text{NO}_3$  and terpene (TERP) reactions with  $\text{NO}_3$  (see reactions in Table S1). Organic nitrates may serve as either a  $\text{NO}_x$  reservoir or a  $\text{NO}_x$  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  $\text{NO}_3$  radical were switched off, organic nitrate production decreased significantly, especially at night due to reduced production from terpene +  $\text{NO}_3$  reactions.

The overall effect on total  $\text{PM}_{2.5}$  (up to  $5 \mu\text{g m}^{-3}$ , ~65%) is dominated by the increase in SOA (see Figure S9 in the Supplement). A small negative change in  $\text{PM}_{2.5}$  was predicted around the Benelux area and northern Italy due to the decrease in  $\text{PNO}_3$  of about  $1 - 1.4 \mu\text{g m}^{-3}$  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

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.

Gibson, M. D., Haelssig, J., Pierce, J. R., Parrington, M., Franklin, J. E., Hopper, J. T., Li, Z., and Ward, T. J.: A comparison of four receptor models used to quantify the

boreal wildfire smoke contribution to surface PM<sub>2.5</sub> in Halifax, Nova Scotia during the BORTAS-B experiment, *Atmos. Chem. Phys.*, 15, 815-827, 10.5194/acp-15-815-2015, 2015.

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 MACC team: The MACC reanalysis: an 8 yr data set of atmospheric composition, *Atmos. Chem. Phys.*, 13, 4073-4109, 10.5194/acp-13-4073-2013, 2013.

Kiendler-Scharr, A., Mensah, A. A., Friese, E., Topping, D., Nemitz, E., Prévôt, A. S. H., Äijälä, M., Allan, J., Canonaco, F., Canagaratna, M., Carbone, S., Crippa, M., Dall'Osto, M., Day, D. A., De Carlo, P., Di Marco, C. F., Elbern, H., Eriksson, A., Freney, E., Hao, L., Herrmann, H., Hildebrandt, L., Hillamo, R., Jimenez, J. L., Laaksonen, A., McFiggans, G., Mohr, C., O'Dowd, C., Otjes, R., Ovadnevaite, J., Pandis, S. N., Poulain, L., Schlag, P., Sellegri, K., Swietlicki, E., Tiitta, P., Vermeulen, A., Wahner, A., Worsnop, D., and Wu, H. C.: Ubiquity of organic nitrates from nighttime chemistry in the European submicron aerosol, *Geophysical Research Letters*, 2016GL069239, 10.1002/2016GL069239, 2016.

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.

# **Secondary inorganic aerosols in Europe: sources and the significant influence of biogenic VOC emissions especially on ammonium nitrate**

Sebnem Aksoyoglu, Giancarlo Ciarelli, Imad El-Haddad, Urs Baltensperger and André S. H. Prévôt  
Laboratory of Atmospheric Chemistry, Paul Scherrer Institute, 5232 Villigen PSI, Switzerland

5 *Correspondence to:* Sebnem Aksoyoglu (sebnem.aksoyoglu@psi.ch)

**Abstract** Contributions of various anthropogenic sources to the secondary inorganic aerosol (SIA) in Europe as well as the role of biogenic emissions on SIA formation were investigated using the three-dimensional regional model CAMx (Comprehensive air quality model with extensions). Simulations were carried out for two periods of EMEP field campaigns (February-March 2009 and June 2006), which are representative of cold and warm seasons, respectively. Biogenic volatile organic compounds (BVOCs) are known mainly as precursors of ozone and secondary organic aerosol (SOA), but their role on inorganic aerosol formation has not attracted much attention so far. In this study, we showed the importance of the chemical reactions of BVOCs and how they affect the oxidant concentrations leading to significant changes especially in the formation of ammonium nitrate. A sensitivity test with doubled BVOC emissions in Europe during the warm season showed a large increase in secondary organic aerosol (SOA) concentrations (by about a factor of two) while particulate inorganic nitrate concentrations decreased by up to 35% leading to a better agreement between the model results and measurements. Sulfate concentrations decreased as well, the change, however, was smaller. The changes in inorganic nitrate and sulfate concentrations occurred at different locations in Europe indicating the importance of precursor gases and biogenic emission types for the negative correlation between BVOCs and SIA. Further analysis of the data suggested that reactions of the additional terpenes with nitrate radicals at night were responsible for the decline in inorganic nitrate formation, whereas oxidation of BVOCs with OH radicals led to a decrease in sulfate. Source apportionment results suggest that the main anthropogenic source of precursors leading to formation of particulate inorganic nitrate is road transport (SNAP7), whereas combustion in energy and transformation industries (SNAP1) was the most important contributor to sulfate particulate mass. Emissions from international shipping were also found to be very important for both nitrate and sulfate formation in Europe. In addition, we examined also contributions from the geographical source regions to SIA concentrations in the most densely populated region of Switzerland, the Swiss Plateau.

## 1 Introduction

Particulate matter (PM) is known to have adverse effects on human health and climate, and is still a problematic pollutant in Europe in spite of considerable improvements in the last decades (Barmpadimos et al., 2012; EEA, 2014). The sources and evolution of PM in the atmosphere are among the most extensively investigated topics in current atmospheric research (Fuzzi et al., 2015; Denier van der Gon et al., 2015). PM is either directly emitted or formed in the atmosphere as secondary inorganic (SIA) and organic aerosols (SOA). The main precursor gases for SIA are SO<sub>2</sub>, NO<sub>x</sub> and NH<sub>3</sub>, which react in the atmosphere to form ammonium sulfate and nitrate compounds. Observations from the EMEP network show that SIA concentrations in Europe increase from north to south, with an average contribution of 34% to PM<sub>10</sub> (particles with an aerodynamic diameter  $d < 10 \mu\text{m}$ ) mass (Aas et al., 2012). Earlier studies suggest that SIA constitutes more than half of PM<sub>2.5</sub> ( $d < 2.5 \mu\text{m}$ ) 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<sub>2.5</sub> 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<sub>3</sub> emissions (Aan de Brugh et al., 2011; Wang et al., 2013) while the effect of uncertainties in NO<sub>x</sub> 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.

25

## 2 Modeling Methods

### 2.1 Air quality model CAMx

In this study, we used the regional air quality model CAMx-v5.40 with its PSAT (Particulate Source Apportionment Technology) tool (ENVIRON, 2011). The model domain covered Europe using latitude-longitude geographical coordinates with a horizontal resolution of  $0.25^\circ \times 0.25^\circ$ . We used 33 terrain-following  $\sigma$ -levels up to about 350 hPa. The Carbon Bond (CB05) gas phase mechanism (Yarwood et al., 2005) was used and partitioning of inorganic aerosols (sulfate, nitrate, ammonium, sodium and chloride) was performed using the ISORROPIA thermodynamic model (Nenes et al., 1998). Aqueous sulfate and nitrate formation in cloud water was simulated using the RADM aqueous chemistry algorithm (Chang et al., 1987). Partitioning of condensable organic gases to secondary organic aerosols (SOA) was calculated using the semi-volatile equilibrium scheme called SOAP (Strader et al., 1999). SOA precursor species and reactions are given elsewhere (Aksoyoglu et al., 2011). Removal processes including dry and wet deposition were simulated using the Zhang resistance model (Zhang et al., 2003) and a scavenging model approach for both gases and aerosols (ENVIRON, 2011).

Input parameters for CAMx were provided by INERIS within the EURODELTA III project (Bessagnet et al., 2016). Hourly three-dimensional meteorological fields for wind speed and direction, pressure, temperature, specific humidity, cloud cover and rain were calculated from ECMWF IFS (Integrated Forecast System) data at  $0.2^\circ$  resolution within the EURODELTA III exercise. MACC (Monitoring Atmospheric Composition and Climate) reanalysis data were used to generate initial and boundary condition fields (Benedetti et al., 2009; Inness et al., 2013). Photolysis rates were calculated using the Tropospheric Ultraviolet and Visible (TUV) Radiation Model (<https://www2.acom.ucar.edu/modeling/tropospheric-ultraviolet-and-visible-tuv-radiation-model>). The ozone column densities to determine the spatial and temporal variation of the photolysis rates were extracted from TOMS data (<https://ozoneaq.gsfc.nasa.gov/data/omi/>). Anthropogenic emissions were prepared by merging different emission databases such as TNO-MACC (Kuenen et al., 2011), EMEP (Vestreng et al., 2007) and GAINS (<http://gains.iiasa.ac.at/gains>) as described in Bessagnet et al. (2016). We calculated the gridded biogenic VOC emissions using the Model of Emissions of Gases and Aerosols from Nature (MEGAN v2.1) (Guenther et al., 2012) driven by the meteorological variables.

We ran CAMx with PSAT for the two EMEP intensive measurement campaign periods: 25 February-26 March 2009 (cold season) and 1-30 June 2006 (warm season) with a 14-day spin-up before each period. The model results for aerosols in this study refer to PM<sub>2.5</sub> fraction. In order to investigate the role of biogenic emissions on the SIA formation, we doubled the BVOC emissions in June 2006 in the model domain and repeated the simulations. We analyzed the model results by means of the Chemical Process Analysis (CPA) tool of CAMx, which provides detailed reaction rate information for selected species from various chemical reactions.

## 2.2 Particulate Source Apportionment Technology (PSAT)

Source apportionment techniques are used to identify the sources of atmospheric pollutants (Viana et al., 2008). It is relatively simple to apportion primary PM among its sources using any pollution model because their source-receptor relationships are linear. On the other hand, Eulerian models are better suited to model secondary PM because they account for chemical interactions among sources. The CAMx tool PSAT was used to assess the contribution of different geographic regions and source categories to modeled concentrations of SIA. PSAT uses reactive tracers to apportion primary and secondary PM as well as the gaseous precursors among different source categories and regions. A single tracer can track primary PM species, whereas secondary PM species require several tracers because of the more complex relationship between gaseous precursors and the resulting particles. PSAT assumes that PM should be apportioned to the primary precursor for each type of particle. Thus particulate sulfate (PSO<sub>4</sub>) is apportioned to SO<sub>x</sub> emissions, particulate nitrate (PNO<sub>3</sub>) is apportioned to NO<sub>x</sub> emissions, and particulate ammonium (PNH<sub>4</sub>) is apportioned to NH<sub>3</sub> emissions (ENVIRON, 2011). We defined source categories (Table 1) based on the SNAP codes given by Kuenen et al. (2011). We also modeled the contribution from the boundaries of the domain as a non-European source.

In addition to source categories, we also investigated in a case study the contribution from various source regions to SIA concentrations in the Swiss Plateau, which is the most densely populated part of Switzerland, comprising the area between the Jura Mountains and the Swiss Alps (Fig. S1). The selected source regions were identified as Switzerland (domestic), France, Germany, Italy and Austria



(surrounding countries), Poland and Benelux countries (polluted regions), Sea (marine areas), Rest (rest of the domain), and BC (boundary conditions) (see Fig. S2).

Measurements with the high resolution AMS (Aerosol Mass Spectrometer) are available at 11 European sites for the February-March 2009 period (Crippa et al., 2014). A detailed evaluation of CAMx model performance for the two periods simulated in this study can be found elsewhere (Ciarelli et al., 2016). Since AMS data are only available at Payerne for the summer June 2006 period, we evaluated meteorological parameters and SIA concentrations at that site in both cold and warm seasons.

### 3 Results and discussion

#### 3.1 Model evaluation

10 Model performance was evaluated using methods implemented in the Atmospheric Model Evaluation Tool (AMET; Appel et al., 2011). The modeled concentrations of the gas phase species and PM<sub>2.5</sub> were compared with the measurements from the AirBase database (see soccer-goal plots in Fig. 1). Only rural-background stations with at least 80% daily average observations available were considered for the evaluation. The model performance for the gaseous species in June 2006 was similar to another study performed during the AQMEII exercise in July 2006 using the CAMx model (Nopmongkol et al., 15 2011). Although NO<sub>2</sub> was underestimated in both cases, fractional bias (FB) and fractional error (FE) were smaller in our study (AQMEII: FB -62, FE 73; this study; FB -42, FE 60). The positive bias for SO<sub>2</sub> in both studies is likely due to vertical distribution of emissions as reported by Nopmongkol et al. (2011). The performance for NO<sub>2</sub> in February-March 2009 was better than in summer. The tendency to 20 underestimate NO<sub>2</sub> in summer was reported in other modeling studies as well (Bessagnet et al., 2016, Knote et al., 2011) and may result from either insufficient NO<sub>x</sub> emissions or from too high measurements (very close to sources or by artefacts from other oxidized nitrogen compounds in the NO<sub>2</sub> measurements) (Steinbacher et al., 2007; Vaughan et al., 2016). Ozone concentrations were captured well in the cold season while there was a slight overestimation in June 2006.

25 The model performance for PM<sub>2.5</sub> was very good; recommended model performance criteria (MFB  $\leq \pm$  60%, MFE:  $\leq +75\%$ ) as well as the performance goal (MFB  $\leq \pm$  30%, MFE  $\leq +50\%$ ) by Boylan and

Russell (2006) were achieved in both periods (see Fig. 1). The components of PM<sub>2.5</sub> were further evaluated for the period in February-March 2009 where high-resolution AMS measurements at 11 European sites were available (Table 2). In general, there is a tendency to overestimate the inorganic aerosols and underestimate the organic aerosols. The detailed discussion for the evaluation of nitrate, sulfate and ammonium at all sites can be found in Ciarelli et al. (2016) where the input parameters and the model were the same except the VBS (Volatility Basis Set) approach used to model organic aerosols.

The components of PM<sub>2.5</sub> were also evaluated for the period in June 2006 at Payerne (Switzerland) where the AMS measurements were available. Since Payerne is a representative site for the Swiss Plateau, evaluation of model performance at that location is also important for the case study discussed in Section 3.6. The temporal variations of both meteorological parameters and chemical components were captured quite well by the model in both periods (Figs. S3-S4). There is a clear correlation between the SIA concentrations and wind speed. In the cold season, agreement between modeled and measured wind speed is very good (Fig. S3); concentrations are higher when the wind speed is low (25 February-5 March, 18-19 March, and 22-23 March). The modeled SIA concentrations are very close to the measured ones, except for a few days (3 and 23 March). As part of the EURODELTA III project, Bessagnet et al. (2016) analyzed measured and modeled meteorological variables such as PBL height and wind speed at several sites in Paris. The study suggested that observations were well reproduced by ECMWF IFS in general except for a few days when the PBL height was overestimated (Bessagnet et al., 2016). The modeled SIA concentrations during the warm season were also very close to measurements except for an overestimation during the first week when temperatures were relatively lower (Fig. S4, right panel). Underestimated wind speed and PBL height might be some of the reasons of this discrepancy. A slight underestimation of temperature might also have caused more partitioning on the particle phase.

### 3.2 Particulate Nitrate (PNO<sub>3</sub>)

The modeled PNO<sub>3</sub> concentrations were higher in the cold season with a monthly average of up to 14 µg m<sup>-3</sup> over northern Italy (Fig. 2, top left). In the warm season, highest concentrations (7-8 µg m<sup>-3</sup>)

were predicted mainly around the English Channel and Benelux area (Fig. 2, top right). The largest contribution to nitrate was from road transport, followed by ships and combustion in energy and transformation industries while the contribution from the boundaries was very small (Fig. 2). The relative contribution from road traffic was higher in Eastern Europe (Fig. S5). The contribution of SNAP 1 sources to PNO<sub>3</sub> was higher in East European countries during the cold season (Fig. 2). The relative contribution from offshore petroleum activities in the North Sea to PNO<sub>3</sub> was quite high as seen in Fig. S5. Emissions from the petroleum sector are generally exhaust gases from combustion of natural gas in turbines, flaring of natural gas and combustion of diesel. Ship emissions (SNAP8) in the warm season led to PNO<sub>3</sub> formation mainly along the English Channel, whereas their contribution in the cold season was predicted throughout the whole of Central Europe, most likely because of higher NH<sub>3</sub> emissions in this area in the early spring. This agrees with the results of previous simulations (Aksoyoglu et al., 2016). On the other hand, the relative contribution from ship emissions to PNO<sub>3</sub> was clearly higher over the Mediterranean in both seasons (Fig. S5).

### 3.3 Particulate Sulfate (PSO<sub>4</sub>)

The modeled particulate sulfate concentrations were relatively low over central Europe during the cold season (Fig. 3). A significant contribution, however, was detected from the eastern boundaries of the model domain (for relative contributions see Fig. S6). The effect of boundary inflows on sulfate levels in the warm season was much lower. MACC reanalysis data have already been evaluated in detail (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. In our study, high sulfate at the eastern boundary was mainly during the February-March 2009 period and affected only the eastern part of the domain while the rest of Europe was not affected.

Emissions from the combustion in energy and transformation industries are the main sources for particulate sulfate in Eastern Europe, while shipping contributes mainly in the Mediterranean and along

other shipping routes around Europe (Fig. 3). Significant contributions from SNAP1 sources in June were predicted over the Balkan countries as well as in northwest Spain (Fig. S6) where large facilities are grouped (Guevara et al., 2014). The contribution from ships to  $\text{PSO}_4$  was predicted to be larger during the warm season. Although ship emissions are only slightly higher in summer, their larger contribution to sulfate is mainly due to higher oxidation potential in the warm season (Aksoyoglu et al., 2016).

### 3.4 Particulate Ammonium ( $\text{PNH}_4$ )

The modeled  $\text{PNH}_4$  concentrations were relatively higher during the period of February-March 2009 since its main source is agriculture with largest emissions occurring in early spring (Fig. 4, see Fig. S7 for relative contributions). The highest  $\text{PNH}_4$  concentrations were predicted in central Europe. A small contribution (2-10%) from road transport could be seen around the urban areas (Fig. 4, Fig.S7).

### 3.5 Role of biogenic VOC emissions

Biogenic VOC emissions are known as effective SOA precursors. There are large uncertainties associated with BVOC emission estimates due to the substantial number of compounds and biological sources (Guenther, 2013; Oderbolz et al., 2013). The gas-phase reactions of biogenic species used in the chemical mechanism CB05 in CAMx are given in Table S1. Some of the oxidation reactions produce condensable gases (CG) that might lead to formation of SOA particles (Table S2). The monthly average emissions of isoprene, monoterpenes and sesquiterpenes and their contributions to SOA concentrations in the warm season are shown in Fig. S8. Although isoprene emissions were larger (especially in southern Europe), more SOA was produced by sesquiterpenes and monoterpenes due to their higher SOA yields (Lee et al., 2006; Hallquist et al., 2009; ENVIRON, 2011). SOA was predominantly produced by biogenic precursors and oligomerization processes; the contribution of anthropogenic precursors to SOA was very small.

The model results showed a large increase in SOA (Fig. S9) when BVOC emissions were doubled while  $\text{PNO}_3$  and  $\text{PSO}_4$  concentrations decreased (Fig. 5). Since the positive correlation between biogenic emissions and SOA is relatively well known, we focused on the role of BVOCs on SIA formation.

Increased BVOC emissions led to greater decreases in PNO<sub>3</sub> (up to 35%, Fig. S10, left panel) than in PSO<sub>4</sub> (<12%, Fig. S10, right panel). The largest decrease in PNO<sub>3</sub> occurred around the Benelux area and northern Italy where concentrations were highest (Fig. 5). PSO<sub>4</sub> decreased mostly in Eastern Europe where SO<sub>2</sub> concentrations were relatively higher. In a study in the eastern U.S, Karambelas (2013) also reported a negative correlation between BVOC emissions and SIA. From the comparison of the base case and no-biogenic emission simulations, the author attributed the increase in SIA concentrations to the increased availability of OH radicals (as a result of elimination of SOA in the absence of BVOC emissions) for oxidation of precursor gases such as NO<sub>2</sub> and SO<sub>2</sub>.

We analyzed our results in June 2006 further by investigating the changes in OH radical and production rate of organic nitrates and nitric acid (HNO<sub>3</sub>) from the two main reaction pathways: NO<sub>2</sub> + OH (daytime) and N<sub>2</sub>O<sub>5</sub> + H<sub>2</sub>O (nighttime) in one grid cell (Payerne, Switzerland) for three different cases: 1) with standard BVOC emissions, 2) with doubled BVOC emissions, 3) with doubled BVOC emissions and without BVOC+NO<sub>3</sub> reactions (see Table S1 for the reactions of BVOCs used in CAMx). OH radical consumption increased when BVOC emissions were doubled, mainly during the daytime (Fig. S11) due to OH oxidation reactions of BVOCs. The decrease in OH radicals most likely caused a reduction in SO<sub>2</sub> oxidation leading to a decrease in PSO<sub>4</sub> concentrations (see Fig. 5, right panel). On the other hand, HNO<sub>3</sub> production from daytime (Fig. 6a) and nighttime (Fig. 6b) reactions as well as PNO<sub>3</sub> concentrations (Fig. 6d) decreased with increasing BVOC emissions. Although most of the HNO<sub>3</sub> comes from the daytime reaction of OH with NO<sub>2</sub>, since the deposition rate of HNO<sub>3</sub> is very high, the main pathway leading to the formation of PNO<sub>3</sub> is the hydrolysis of N<sub>2</sub>O<sub>5</sub> at night, when the temperature is sufficiently low for partitioning to the particle phase. The decrease in HNO<sub>3</sub> production via daytime reaction indicates a decrease in available OH radicals due to BVOC+OH reactions (Table S1 and Fig. S11). Switching off the reactions with NO<sub>3</sub> radical did not affect the daytime production further (Fig. 6a) as expected since NO<sub>3</sub> is a nocturnal oxidant (e.g. Platt et al., 1981; Russell et al., 1986; Platt and Heintz, 1994; Seinfeld and Pandis, 2012). On the other hand, HNO<sub>3</sub> production at night decreased with increased BVOC emissions suggesting that the available NO<sub>3</sub> radicals decreased due to BVOC + NO<sub>3</sub> reactions (Fig. 6b). The fact that HNO<sub>3</sub> formation at night increased significantly when BVOC + NO<sub>3</sub> reactions were switched off presents further evidence that BVOC+NO<sub>3</sub> reactions were

responsible for the changes in  $\text{PNO}_3$  concentrations (Fig. 6b, d). Organic nitrates may serve as either a  $\text{NO}_x$  reservoir or a  $\text{NO}_x$  sink (Kiendler-Scharr et al., 2016). Their production increased with doubled BVOC emissions (Fig. 6c) because of isoprene (ISOP) and isoprene oxidation product (ISPD) reactions with  $\text{NO}_2$  and  $\text{NO}_3$  and terpene (TERP) reactions with  $\text{NO}_3$  (see reactions in Table S1). On the other hand, when BVOC reactions with  $\text{NO}_3$  radical were switched off, organic nitrate production decreased significantly, especially at night due to reduced production from terpene + $\text{NO}_3$  reactions. Steinbacher et al (2005) showed that isoprene emissions vanish after sunset and isoprene mixing ratios decline quickly due to chemical reactions with  $\text{NO}_3$ ,  $\text{O}_3$  and OH, leaving no isoprene for further reactions during the night. In addition, isoprene oxidation with  $\text{NO}_3$  radical produces not only organic nitrates (NTR) but  $\text{HNO}_3$  as well (see Table S1). It is therefore more likely that oxidation of terpenes with  $\text{NO}_3$  is the main driver for the BVOC effect on  $\text{PNO}_3$ . Comparison of modeled and measured diurnal variation of  $\text{PNO}_3$  concentrations shows that increasing BVOC emissions brought modeled results closer to the observations especially at night (Fig. 7). The results of these sensitivity tests suggest that the overestimation of particulate inorganic nitrate might be partly due to too low biogenic VOC emissions.

### 3.6 A case study: The Swiss Plateau

#### 3.6.1 Cold Season (February-March 2009)

The modeled SIA concentrations were relatively high during the first few days in March and during the second half of the period (Fig. 8). Low winds from southwest at the beginning of March (Fig. S3, left panel) led to relatively larger contribution from sources in France as well as from domestic sources to SIA concentrations in the Swiss Plateau. Then, when the wind direction shifted towards the northeast between 16 and 22 March (see Fig. S3), the contribution from Germany became larger.

Domestic sources contribute to  $\text{PNO}_3$  concentrations (21%) in the Swiss Plateau as much as sources in Germany (18%) and France (24%) during the whole period of February-March 2009 (Fig. 8, top-middle panel). A large fraction of  $\text{PNO}_3$  originates from road transport (40%), while 22% is from shipping emissions in the coastal areas (Fig. 8, top-right panel). Sources from non-industrial combustion (SNAP2) and combustion in energy and transformation industries (SNAP1) contribute 16% and 12%, respectively.

Boundary conditions are predicted to have the largest contribution to  $\text{PSO}_4$  in the Swiss Plateau (24%) followed by sources in France (17%), Germany (13%) and the sea areas (13%) (Fig. 8, middle panels). The Swiss sources contribute only to 11%. The main source categories are combustion in energy and transformation industries (SNAP1) and non-industrial combustion (SNAP2) contributing 33% and 23% of total sulfate, respectively.

In the case of  $\text{PNH}_4$ , domestic sources are clearly the main contributor (73%) followed by the two neighboring countries France (11%) and Germany (10%). These mainly originate from agricultural activities with a small contribution (3%) from road transport (Fig. 8, lower panels).

### 3.6.2 Warm Season (June 2006)

The magnitude of  $\text{PNO}_3$  and  $\text{PNH}_4$  concentrations shown in Fig. 9 reflects the temporal evolution of air temperature in June 2006 (Fig. S3, right panel). During the first half of the month, maximum daily temperatures increased from  $10^\circ\text{C}$  to about  $30^\circ\text{C}$ , while both  $\text{PNO}_3$  and  $\text{PNH}_4$  concentrations decreased. Then both temperatures and nitrate concentrations remained almost the same until the end of June. The wind was blowing from northeast and northwest during the first half of June leading to relatively high contributions to  $\text{PNO}_3$  concentrations in the Swiss Plateau from Germany, France and the Benelux countries. Over the whole period, the largest contribution to nitrate was predicted to be from Germany (30%) followed by Switzerland (18%) and France (14%) (Fig. 9). A significant amount was also predicted from marine areas (13%) and the Benelux countries (10%). Our results also suggest that nearly half of  $\text{PNO}_3$  originated from road transport (47%), while ship emissions also contributed significantly (about 22%). On the other hand, Switzerland itself was predicted to be the main source for  $\text{PNH}_4$  concentrations (71%) with some contribution from Germany (13%) in the first half of June due to northerly winds. Almost all of  $\text{PNH}_4$  (96%) originated from agricultural activities.

Time series and pie charts for  $\text{PSO}_4$  in Fig. 9 indicate a large contribution to sulfate concentrations from remote areas – boundary conditions (34%), marine areas (16%) and the rest of the domain (17%) – especially in the second half of the month, which experienced various wind directions. The contribution of domestic sources to  $\text{PSO}_4$  concentrations was very small (3%); the largest contribution among the emission sources was from SNAP1 (45%), followed by SNAP8 (22%).

## 4 Conclusions

In this study, sources of secondary inorganic aerosols in Europe and the role of biogenic emissions on their formation were investigated. Model simulations with CAMx including its PSAT tool were used to estimate the contributions from 10 anthropogenic emission sources as well as from boundary conditions to the concentrations of particulate inorganic nitrate, sulfate and ammonium in Europe during two periods of EMEP measurement campaigns; February-March 2009 (cold season) and June 2006 (warm season).

Road transport (SNAP7) was predicted to be the most important source for  $\text{PNO}_3$  with the largest contribution during the cold season over northern Italy. Other important sources were ship emissions (SNAP8), which contributed to particulate inorganic nitrate along the English Channel and Benelux area, and combustion in energy and transformation industries (SNAP1) in Central and Eastern Europe. The model results suggested that  $\text{PSO}_4$  in Europe originated from SNAP 1 sources especially in Eastern Europe. The contribution of ship emissions in the Mediterranean and along busy shipping routes was larger during the warm season. A large contribution to sulfate in the eastern part of the domain during the cold season was attributed to inflow from the boundary. Agricultural activities were the dominant source for  $\text{PNH}_4$ , with a small (2-10%) contribution from road transport.

A case study with the Swiss Plateau as receptor, showed how wind speed and direction affected the contribution from various source areas to the particulate nitrate, sulfate and ammonium concentrations in the area. These results suggested that the contribution from the domestic sources to  $\text{PNO}_3$  concentrations in the Swiss Plateau was similar to those from Germany and France during the cold season and almost half of it was from road transport. The sources of  $\text{PSO}_4$  were mostly of foreign origin from combustion in energy and transformation industries with the domestic contributions of 11% and 3% in winter and summer, respectively. The local agricultural activities were the main source of  $\text{PNH}_4$ .

An important outcome of this study was the significant role of biogenic VOC emissions on the SIA formation, especially on particulate inorganic nitrate. The sensitivity tests carried out during the warm season showed a negative correlation between BVOC emissions and SIA concentrations. Increasing BVOC emissions by a factor of two led to a decrease by 35% and 12% in  $\text{PNO}_3$  and  $\text{PSO}_4$ , respectively.

Overestimation of particulate nitrate at night was reduced as a result of increased BVOC emissions.



leading to a better agreement with observations. Further investigations using the Chemical Process Analysis tool of CAMx suggested that reactions of terpenes with nitrate radical at night led to a decrease in PNO<sub>3</sub> formation (by reducing HNO<sub>3</sub>) when BVOC emissions were doubled. Although OH radical concentration was reduced by oxidation reactions of BVOCs, decreased daytime oxidation of NO<sub>2</sub> with OH did not affect PNO<sub>3</sub> concentrations. On the other hand, reduced availability of OH radical for gas-phase oxidation of SO<sub>2</sub> caused a decrease in PSO<sub>4</sub> concentrations especially over the Aegean and Mediterranean Sea. These results indicated the importance of BVOC emissions not only for secondary organic aerosol formation but also for inorganic aerosols. Considering the challenges in BVOC emission estimates in addition to uncertainties in NH<sub>3</sub> and NO<sub>x</sub> emissions, modeled particulate inorganic nitrate concentrations might have larger uncertainties than assumed so far.

### Acknowledgements

We acknowledge INERIS for providing various model input data within the EURODELTA III exercise. Anthropogenic emissions were based on TNO and EMEP inventories and data from the GAINS database of IIASA. We thank the European Centre for Medium-Range Weather Forecasts (ECMWF) for the access to the meteorological and the global air quality model data. Calculations of land use data were performed at the Swiss National Supercomputing Centre (CSCS). We appreciate the availability of CAMx model with PSAT and support of RAMBOLL ENVIRON. This work was financially supported by the Swiss Federal Office of Environment (FOEN).

### References

- Aan de Brugh, J. M. J., Schaap, M., Vignati, E., Dentener, F., Kahnert, M., Sofiev, M., Huijnen, V., and Krol, M. C.: The European aerosol budget in 2006, *Atmos. Chem. Phys.*, 11, 1117-1139, doi:10.5194/acp-11-1117-2011, 2011.
- Aas, W., Tsyro, S., Bieber, E., Bergström, R., Ceburnis, D., Ellermann, T., Fagerli, H., Frölich, M., Gehrig, R., Makkonen, U., Nemitz, E., Otjes, R., Perez, N., Perrino, C., Prévôt, A. S. H., Putaud, J. P., Simpson, D., Spindler, G., Vana, M., and Yttri, K. E.: Lessons learnt from the first EMEP intensive measurement periods, *Atmos. Chem. Phys.*, 12, 8073-8094, 10.5194/acp-12-8073-2012, 2012.

- Aksoyoglu, S., Keller, J., Barmpadimos, I., Oderbolz, D., Lanz, V. A., Prévôt, A. S. H., and Baltensperger, U.: Aerosol modelling in Europe with a focus on Switzerland during summer and winter episodes, *Atmos. Chem. Phys.*, 11 doi:10.5194/acp-5111-7355-2011, 7355-7373, 2011.
- Aksoyoglu, S., Keller, J., Oderbolz, D. C., Barmpadimos, I., Prévôt, A. S. H., and Baltensperger, U.:  
 5 Sensitivity of ozone and aerosols to precursor emissions in Europe, *Int. J. Environ. Pollut.*, 50 451-459, 10.1504/ijep.2012.051215, 2012.
- Aksoyoglu, S., Baltensperger, U., and Prévôt, A. S. H.: Contribution of ship emissions to the concentration and deposition of air pollutants in Europe, *Atmos. Chem. Phys.*, 16, 1895-1906, 10.5194/acp-16-1895-2016, 2016.
- 10 Appel, K. W., Gilliam, R. C., Davis, N., Zubrow, A., and Howard, S. C.: Overview of the Atmospheric Model Evaluation Tool (AMET) v1.1 for evaluating meteorological and air quality models, *Environ. Modell. Softw.*, 26, 434–443, 2011.
- Ayres, B. R., Allen, H. M., Draper, D. C., Brown, S. S., Wild, R. J., Jimenez, J. L., Day, D. A., Campuzano-Jost, P., Hu, W., de Gouw, J., Koss, A., Cohen, R. C., Duffey, K. C., Romer, P., Baumann,  
 15 K., Edgerton, E., Takahama, S., Thornton, J. A., Lee, B. H., Lopez-Hilfiker, F. D., Mohr, C., Wennberg, P. O., Nguyen, T. B., Teng, A., Goldstein, A. H., Olson, K., and Fry, J. L.: Organic nitrate aerosol formation via  $\text{NO}_3$  + biogenic volatile organic compounds in the southeastern United States, *Atmos. Chem. Phys.*, 15, 13377-13392, 10.5194/acp-15-13377-2015, 2015.
- Barmpadimos, I., Keller, J., Oderbolz, D., Hueglin, C., and Prévôt, A. S. H.: One decade of parallel fine  
 20 ( $\text{PM}_{2.5}$ ) and coarse ( $\text{PM}_{10}$ – $\text{PM}_{2.5}$ ) particulate matter measurements in Europe: trends and variability, *Atmos. Chem. Phys.*, 12, 3189-3203, 10.5194/acp-12-3189-2012, 2012.
- Benedetti, A., Morcrette, J. J., Boucher, O., Dethof, A., Engelen, R. J., Fisher, M., Flentje, H., Huneus, N., Jones, L., Kaiser, J. W., Kinne, S., Mangold, A., Razinger, M., Simmons, A. J., and Suttie, M.: Aerosol analysis and forecast in the European Centre for Medium-Range Weather Forecasts Integrated  
 25 Forecast System: 2. Data assimilation, *J. Geophys. Res.*, 114, D1325 10.1029/2008JD011115, 2009.
- Bessagnet, B., Pirovano, G., Mircea, M., Cuvelier, C., Aulinger, A., Calori, G., Ciarelli, G., Manders, A., Stern, R., Tsyro, S., García Vivanco, M., Thunis, P., Pay, M. T., Colette, A., Couvidat, F., Meleux, F., Rouïl, L., Ung, A., Aksoyoglu, S., Baldasano, J. M., Bieser, J., Briganti, G., Cappelletti, A.,

- D'Isidoro, M., Finardi, S., Kranenburg, R., Silibello, C., Carnevale, C., Aas, W., Dupont, J. C., Fagerli, H., Gonzalez, L., Menut, L., Prévôt, A. S. H., Roberts, P., and White, L.: Presentation of the EURODELTA III intercomparison exercise – evaluation of the chemistry transport models' performance on criteria pollutants and joint analysis with meteorology, *Atmos. Chem. Phys.*, 16, 12667-12701, 10.5194/acp-16-12667-2016, 2016.
- 5
- Boyd, C. M., Sanchez, J., Xu, L., Eugene, A. J., Nah, T., Tuet, W. Y., Guzman, M. I., and Ng, N. L.: Secondary organic aerosol formation from the  $\beta$ -pinene+NO<sub>3</sub> system: effect of humidity and peroxy radical fate, *Atmos. Chem. Phys.*, 15, 7497-7522, 10.5194/acp-15-7497-2015, 2015.
- Boylan, J. W., and Russell, A. G.: PM and light extinction model performance metrics, goals, and criteria for three-dimensional air quality models, *Atmospheric Environment*, 40, 4946-4959, 2006.
- 10
- Carlton, A. G., Wiedinmyer, C., and Kroll, J. H.: A review of Secondary Organic Aerosol (SOA) formation from isoprene, *Atmos. Chem. Phys.*, 9, 4987-5005, 2009.
- Chang, J. S., Brost, R. A., Isaksen, I. S. A., Madronich, S., Middleton, P., Stockwell, W. R., and Walcek, C. J.: A three-dimensional eulerian acid deposition model : Physical concepts and formulation, *J. Geophys. Res.*, 92, 14681-14700, 10.1029/JD092iD12p14681,1987.
- 15
- 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.
- 20
- Colette, A., Granier, C., Hodnebrog, O., Jakobs, H., Maurizi, A., Nyiri, A., Bessagnet, B., D'Angiola, A., D'Isidoro, M., Gauss, M., Meleux, F., Memmesheimer, M., Mieville, A., Rouil, L., Russo, F., Solberg, S., Stordal, F., and Tampieri, F.: Air quality trends in Europe over the past decade: a first multi-model assessment, *Atmos. Chem. Phys.*, 11 11657-11678, 2011.
- Crippa, M., Canonaco, F., Lanz, V. A., Äijälä, M., Allan, J. D., Carbone, S., Capes, G., Ceburnis, D., Dall'Osto, M., Day, D. A., DeCarlo, P. F., Ehn, M., Eriksson, A., Freney, E., Hildebrandt Ruiz, L., Hillamo, R., Jimenez, J. L., Junninen, H., Kiendler-Scharr, A., Kortelainen, A. M., Kulmala, M., Laaksonen, A., Mensah, A. A., Mohr, C., Nemitz, E., O'Dowd, C., Ovadnevaite, J., Pandis, S. N., Petäjä, T., Poulain, L., Saarikoski, S., Sellegri, K., Swietlicki, E., Tiitta, P., Worsnop, D. R.,
- 25

- Baltensperger, U., and Prévôt, A. S. H.: Organic aerosol components derived from 25 AMS data sets across Europe using a consistent ME-2 based source apportionment approach, *Atmos. Chem. Phys.*, 14, 6159-6176, 10.5194/acp-14-6159-2014, 2014.
- de Meij, A., Krol, M., Dentener, F., Vignati, E., Cuvelier, C., and Thunis, P.: The sensitivity of aerosol  
5 in Europe to two different emission inventories and temporal distribution of emissions, *Atmos. Chem. Phys.*, 6, 4287-4309, 10.5194/acp-6-4287-2006, 2006.
- Denier van der Gon, H. A. C., Bergström, R., Fountoukis, C., Johansson, C., Pandis, S. N., Simpson, D., and Visschedijk, A. J. H.: Particulate emissions from residential wood combustion in Europe – revised estimates and an evaluation, *Atmos. Chem. Phys.*, 15, 6503-6519, 10.5194/acp-15-6503-2015, 2015.
- 10 EEA: Air Quality in Europe, 2014 Report, doi:10.2800/22847, 2014
- Emmerson, K. M., Galbally, I. E., Guenther, A. B., Paton-Walsh, C., Guerette, E. A., Cope, M. E., Keywood, M. D., Lawson, S. J., Molloy, S. B., Dunne, E., Thatcher, M., Karl, T., and Maleknia, S. D.: Current estimates of biogenic emissions from eucalypts uncertain for southeast Australia, *Atmos. Chem. Phys.*, 16, 6997-7011, 10.5194/acp-16-6997-2016, 2016.
- 15 ENVIRON: User's Guide, Comprehensive Air Quality Model with Extensions (CAMx), Version 5.40, Environ International Corporation, California., 2011.
- Fry, J. L., Kiendler-Scharr, A., Rollins, A. W., Brauers, T., Brown, S. S., Dorn, H. P., Dubé, W. P., Fuchs, H., Mensah, A., Rohrer, F., Tillmann, R., Wahner, A., Wooldridge, P. J., and Cohen, R. C.: SOA from limonene: role of NO<sub>3</sub> in its generation and degradation, *Atmos. Chem. Phys.*, 11, 3879-3894,  
20 10.5194/acp-11-3879-2011, 2011.
- Fuzzi, S., Baltensperger, U., Carslaw, K., Decesari, S., Denier van der Gon, H., Facchini, M. C., Fowler, D., Koren, I., Langford, B., Lohmann, U., Nemitz, E., Pandis, S., Riipinen, I., Rudich, Y., Schaap, M., Slowik, J. G., Spracklen, D. V., Vignati, E., Wild, M., Williams, M., and Gilardoni, S.: Particulate matter, air quality and climate: lessons learned and future needs, *Atmos. Chem. Phys.*, 15,  
25 8217-8299, 10.5194/acp-15-8217-2015, 2015.
- 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.
- 5 Guenther, A. B., Jiang, X., Heald, C. L., Sakulyanontvittaya, T., Duhl, T., Emmons, L. K., and Wang, X.: The Model of Emissions of Gases and Aerosols from Nature version 2.1 (MEGAN2.1): an extended and updated framework for modeling biogenic emissions, *Geosci. Model Dev.*, 5, 1471-1492, 10.5194/gmd-5-1471-2012, 2012.
- 10 Guenther, A.: Biological and Chemical Diversity of Biogenic Volatile Organic Emissions into the Atmosphere, *ISRN Atmos. Sci.*, 2013, 27, 10.1155/2013/786290, 2013.
- Guevara, M., Pay, M. T., Martínez, F., Soret, A., Denier van der Gon, H., and Baldasano, J. M.: Inter-comparison between HERMESv2.0 and TNO-MACC-II emission data using the CALIOPE air quality system (Spain), *Atmos. Environ.*, 98, 134-145, <http://dx.doi.org/10.1016/j.atmosenv.2014.08.067>, 2014.
- 15 Hallquist, M., Wenger, J. C., Baltensperger, U., Rudich, Y., Simpson, D., Claeys, M., Dommen, J., Donahue, N. M., George, C., Goldstein, A. H., Hamilton, J. F., Herrmann, H., Hoffmann, T., Iinuma, Y., Jang, M., Jenkin, M. E., Jimenez, J. L., Kiendler-Scharr, A., Maenhaut, W., McFiggans, G., Mentel, T. F., Monod, A., Prévôt, A. S. H., Seinfeld, J. H., Surratt, J. D., Szmigielski, R., and Wildt, J.: The formation, properties and impact of secondary organic aerosol: current and emerging issues, *Atmos. Chem. Phys.*, 9 5155-5235, 2009.
- 20 Huang, L., McDonald-Buller, E., McGaughey, G., Kimura, Y. & Allen, D.T. (2015) Comparison of regional and global land cover products and the implications for biogenic emission modeling, *Journal of the Air & Waste Management Association*, 65:10, 1194-1205, DOI: 10.1080/10962247.2015.1057302.
- 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 MACC team: The MACC reanalysis: an 8 yr data set of atmospheric composition, *Atmos. Chem. Phys.*, 13, 4073-4109, 10.5194/acp-13-4073-2013, 2013.
- Kanakidou, M., Seinfeld, J. H., Pandis, S. N., Barnes, I., Dentener, F. J., Facchini, M. C., Van Dingenen, R., Ervens, B., Nenes, A., Nielsen, C. J., Swietlicki, E., Putaud, J. P., Balkanski, Y., Fuzzi, S., Horth, J., Moortgat, G. K., Winterhalter, R., Myhre, C. E. L., Tsigaridis, K., Vignati, E., Stephanou, E. G., and Wilson, J.: Organic aerosol and global climate modelling: a review, *Atmos. Chem. Phys.*, 5, 1053-1123, 2005.
- Karambelas, A.: The Interactions of Biogenic and Anthropogenic Gaseous Emissions with Respect to Aerosol Formation in the United States, Master of Science, Department of Atmospheric and Oceanic Sciences, University of Wisconsin, Madison, 2013.
- Kiendler-Scharr, A., Mensah, A. A., Friese, E., Topping, D., Nemitz, E., Prévôt, A. S. H., Äijälä, M., Allan, J., Canonaco, F., Canagaratna, M., Carbone, S., Crippa, M., Dall'Osto, M., Day, D. A., De Carlo, P., Di Marco, C. F., Elbern, H., Eriksson, A., Freney, E., Hao, L., Herrmann, H., Hildebrandt, L., Hillamo, R., Jimenez, J. L., Laaksonen, A., McFiggans, G., Mohr, C., O'Dowd, C., Otjes, R., Ovadnevaite, J., Pandis, S. N., Poulain, L., Schlag, P., Sellegri, K., Swietlicki, E., Tiitta, P., Vermeulen, A., Wahner, A., Worsnop, D., and Wu, H. C.: Ubiquity of organic nitrates from nighttime chemistry in the European submicron aerosol, *Geophysical Research Letters*, 2016GL069239, 10.1002/2016GL069239, 2016.
- Knote, C., Brunner, D., Vogel, H., Allan, J., Asmi, A., Äijälä, M., Carbone, S., van der Gon, H. D., Jimenez, J. L., Kiendler-Scharr, A., Mohr, C., Poulain, L., Prévôt, A. S. H., Swietlicki, E., and Vogel, B.: Towards an online-coupled chemistry-climate model: evaluation of trace gases and aerosols in COSMO-ART, *Geosci. Model Dev.*, 4, 1077-1102, 2011.
- Kuenen, J., Denier van der Gon, H., Visschedijk, A., van der Brugh, H., and van Gijlswijk, R.: MACC European emission inventory for the years 2003-2007, The Netherlands, TNO-060-UT-2011-00588, 2011.
- Lee, A., Goldstein, A. H., Kroll, J. H., Ng, N. L., Varutbangkul, V., Flagan, R. C., and Seinfeld, J. H.: Gas-phase products and secondary aerosol yields from the photooxidation of 16 different terpenes, *J. Geophys. Res.*, 111, D17305, 10.1029/2006JD007050, 2006.

- Nenes, A., Pandis, S. N., and Pilinis, C.: ISORROPIA: A new thermodynamic equilibrium model for multiphase multicomponent inorganic aerosols, *Aquat. Geochem.*, 4, 123-152, 1998.
- 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.,  
5 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.
- 10 Nopmongkol, U., Koo, B., Tai, E., Jung, J., Piyachaturawat, P., Emery, C., Yarwood, G., Pirovano, G., Mitsakou, C., and Kallos, G.: Modeling Europe with CAMx for the Air Quality Model Evaluation International Initiative (AQMEII), *Atmos. Environ.*, 2011.
- Oderbolz, D. C., Aksoyoglu, S., Keller, J., Barmpadimos, I., Steinbrecher, R., Skjøth, C. A., Plaß-Dülmer, C., and Prévôt, A. S. H.: A comprehensive emission inventory of biogenic volatile organic  
15 compounds in Europe: improved seasonality and land-cover, *Atmos. Chem. Phys.*, 13 1689-1712, 10.5194/acp-13-1689-2013, 2013.
- 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,  
20 289-300, 10.1002/ijch.199400033, 1994.
- Prank, M., Sofiev, M., Tsyro, S., Hendriks, C., Semeena, V., Vazhappilly Francis, X., Butler, T., Denier van der Gon, H., Friedrich, R., Hendricks, J., Kong, X., Lawrence, M., Righi, M., Samaras, Z., Sausen, R., Kukkonen, J., and Sokhi, R.: Evaluation of the performance of four chemical transport models in predicting the aerosol chemical composition in Europe in 2005, *Atmos. Chem. Phys.*, 16,  
25 6041-6070, 10.5194/acp-16-6041-2016, 2016.
- Revuelta, M. A., Harrison, R. M., Núñez, L., Gomez-Moreno, F. J., Pujadas, M., and Artíñano, B.: Comparison of temporal features of sulphate and nitrate at urban and rural sites in Spain and the UK, *Atmos. Environ.*, 60, 383-391, <http://dx.doi.org/10.1016/j.atmosenv.2012.07.004>, 2012.

- 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, *Atmos. Environ.*, 53, 131-141, <http://dx.doi.org/10.1016/j.atmosenv.2011.10.046>, 2012.
- Schaap, M., van Loon, M., ten Brink, H. M., Dentener, F. J., and Builtjes, P. J. H.: Secondary inorganic aerosol simulations for Europe with special attention to nitrate, *Atmos. Chem. Phys.*, 4, 857-874, 10.5194/acp-4-857-2004, 2004.
- Sciare, J., d'Argouges, O., Zhang, Q. J., Sarda-Estève, R., Gaimoz, C., Gros, V., Beekmann, M., and Sanchez, O.: Comparison between simulated and observed chemical composition of fine aerosols in Paris (France) during springtime: contribution of regional versus continental emissions, *Atmos. Chem. Phys.*, 10, 11987-12004, 10.5194/acp-10-11987-2010, 2010.
- 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
- 15 Simpson, D., Winiwarter, W., Börjesson, G., Cinderby, S., Ferreira, A., Guenther, A., Hewitt, N. C., Janson, R., Khalil, M. A. K., Owen, S., Pierce, T. E., Puxbaum, H., Shearer, M., Skiba, U., Steinbrecher, R., Tarrasón, L., and Öquist, M. G.: Inventorying emissions from nature in Europe, *Journal of Geophysical Research*, 104 8113-8152, 1999.
- Sindelarova, K., Granier, C., Bouarar, I., Guenther, A., Tilmes, S., Stavrou, T., Müller, J. F., Kuhn, U., Stefani, P., and Knorr, W.: Global data set of biogenic VOC emissions calculated by the MEGAN model over the last 30 years, *Atmos. Chem. Phys.*, 14, 9317-9341, 10.5194/acp-14-9317-2014, 2014.
- Squizzato, S., Masiol, M., Brunelli, A., Pistollato, S., Tarabotti, E., Rampazzo, G., and Pavoni, B.: Factors determining the formation of secondary inorganic aerosol: a case study in the Po Valley (Italy), *Atmos. Chem. Phys.*, 13, 1927-1939, 10.5194/acp-13-1927-2013, 2013.
- 25 Steinbacher, M., Dommen, J., Ordonez, C., Reimann, S., Gruebler, F. C., Staehelin, J., Andreani-Aksoyoglu, S., and Prévôt, A. S. H.: Volatile Organic Compounds in the Po Basin. Part B: Biogenic VOCs, *J. Atmos. Chem.*, 51, 293-315, DOI: 10.1007/s10874-005-3577-0, 2005.
- Steinbacher, M., Zellweger, C., Schwarzenbach, B., Bugmann, S., Buchmann, B., Ordóñez, C., Prevot,



- A. S. H., and Hueglin, C.: Nitrogen oxide measurements at rural sites in Switzerland: Bias of conventional measurement techniques, *Journal of Geophysical Research*, 112 doi:10.1029/2006JD007971, 2007.
- Steinbrecher, R., Smiatek, G., Köble, R., Seufert, G., Theloke, J., Hauff, K., Ciccioli, P., Vautard, R.,  
5 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.
- Strader, R., Lurmann, F., and Pandis, S. N.: Evaluation of secondary organic aerosol formation in winter, *Atmos. Environ.*, 33, 4849-4863, 1999.
- Vaughan, A. R., Lee, J. D., Misztal, P. K., Metzger, S., Shaw, M. D., Lewis, A. C., Purvis, R. M.,  
10 Carslaw, D. C., Goldstein, A. H., Hewitt, C. N., Davison, B., Beevers, S. D., and Karl, T. G.: Spatially resolved flux measurements of NO<sub>x</sub> from London suggest significantly higher emissions than predicted by inventories, *Faraday Discussions*, 189, 455-472, 10.1039/C5FD00170F, 2016.
- Vestreng, V., Myhre, G., Fagerli, H., Reis, S., and Tarrasón, L.: Twenty-five years of continuous sulphur dioxide emission reduction in Europe, *Atmos. Chem. Phys.*, 7, 3663-3681, 10.5194/acp-7-3663-  
15 2007, 2007.
- Viana, M., Kuhlbusch, T. A. J., Querol, X., Alastuey, A., Harrison, R. M., Hopke, P. K., Winiwarter, W., Vallius, M., Szidat, S., Prévôt, A. S. H., Hueglin, C., Bloemen, H., Wählin, P., Vecchi, R., Miranda, A. I., Kasper-Giebl, A., Maenhaut, W., and Hitzenberger, R.: Source apportionment of particulate matter in Europe: A review of methods and results, *J. Aerosol Sci.*, 39, 827-849, 2008.
- 20 Wang, Y., Zhang, Q. Q., He, K., Zhang, Q., and Chai, L.: Sulfate-nitrate-ammonium aerosols over China: response to 2000–2015 emission changes of sulfur dioxide, nitrogen oxides, and ammonia, *Atmos. Chem. Phys.*, 13, 2635-2652, 10.5194/acp-13-2635-2013, 2013.
- Xu, L., Guo, H., Boyd, C. M., Klein, M., Bougiatioti, A., Cerully, K. M., Hite, J. R., Isaacman-VanWertz, G., Kreisberg, N. M., Knote, C., Olson, K., Koss, A., Goldstein, A. H., Hering, S. V., de  
25 Gouw, J., Baumann, K., Lee, S.-H., Nenes, A., Weber, R. J., and Ng, N. L.: Effects of anthropogenic emissions on aerosol formation from isoprene and monoterpenes in the southeastern United States, *Proceedings of the National Academy of Sciences*, 112, 37-42, 10.1073/pnas.1417609112, 2015.

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.

Zhang, L., Brook, J. R., and Vet, R.: A revised parameterization for gaseous dry deposition in air-quality models, *Atmos. Chem. Phys.*, 3 2067-2082, 10.5194/acp-3-2067-2003, 2003.

5

Table 1: Source categories used in this study

---

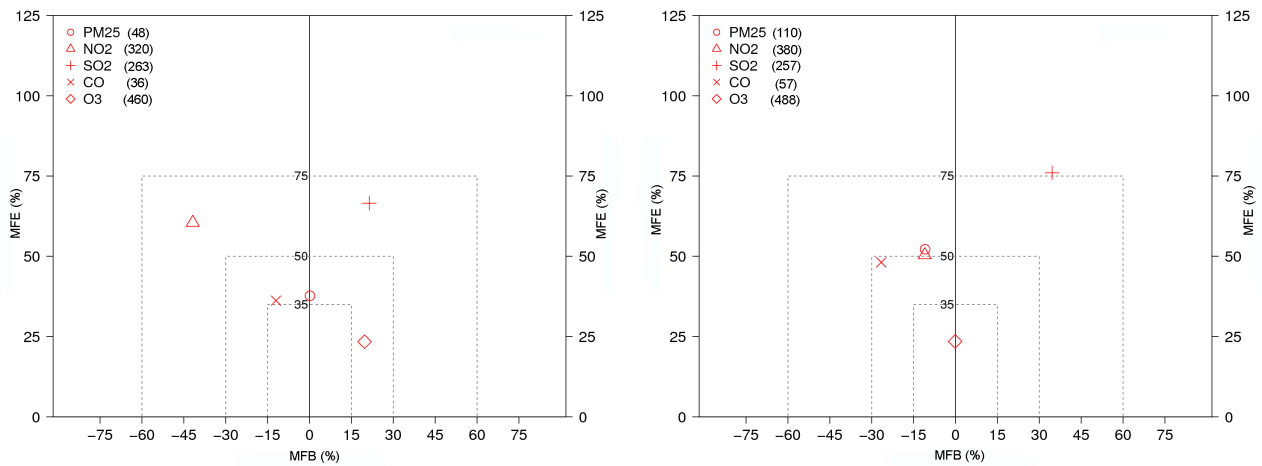
Source categories	
SNAP1	Combustion in energy and transformation industries
SNAP2	Non-industrial combustion
SNAP3	Combustion in manufacturing industry
SNAP4	Production processes
SNAP5	Extraction and distribution of fossil fuels and geothermal energy
SNAP6	Solvent and other product use
SNAP7	Road transport
SNAP8	Other mobile sources and machinery
SNAP9	Waste treatment and disposal
SNAP10	Agriculture
Boundary conditions (concentrations on the lateral model boundaries)	

---

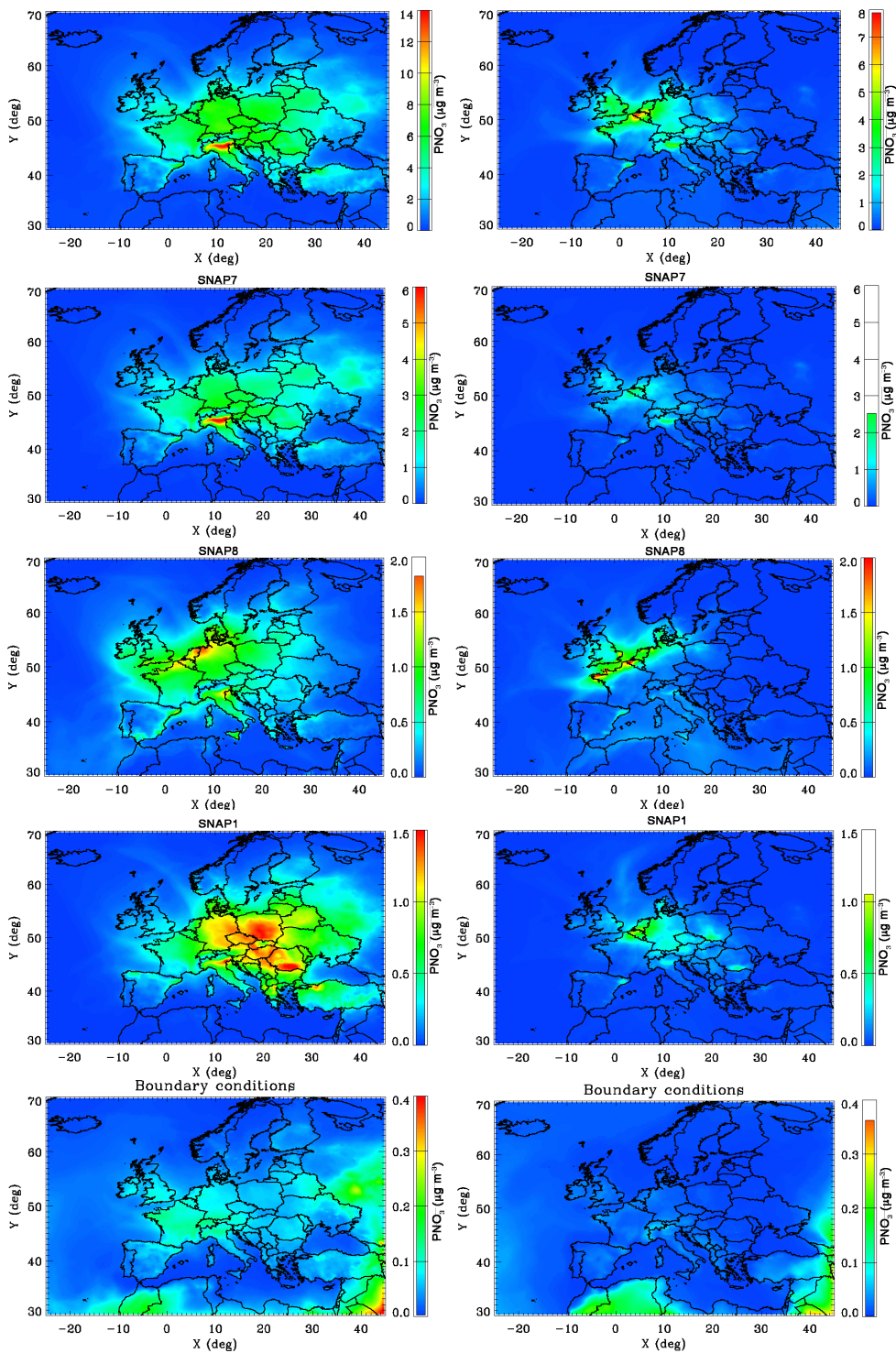
Table 2: Statistical analysis of PNO<sub>3</sub>, PNH<sub>4</sub>, PSO<sub>4</sub> and OA for February-March 2009 at different AMS sites. (MB: mean bias, ME: mean error, MFB: mean fractional bias, MFE: mean fractional error)

Site	observed ( $\mu\text{g m}^{-3}$ )	modeled ( $\mu\text{g m}^{-3}$ )	MB ( $\mu\text{g m}^{-3}$ )	ME ( $\mu\text{g m}^{-3}$ )	MFB (-)	MFE (-)
PNO <sub>3</sub>						
Barcelona	3.6	6.0	2.4	4.1	0.43	0.95
Cabauw	2.2	6.5	4.3	4.4	0.85	0.98
Chilbolton	2.7	3.9	1.2	2.1	0.01	0.75
Helsinki	1.0	2.3	1.3	1.6	0.48	0.94
Hyytiälä	0.2	1.3	1.1	1.2	0.49	1.11
Mace Head	0.6	1.7	1.1	1.1	0.26	0.70
Melpitz	3.1	4.9	1.8	2.7	0.47	0.72
Montseny	3.1	6.2	3.1	4.5	0.47	1.00
Payerne	3.9	6.3	2.4	3.2	0.47	0.66
Puy de Dôme	0.9	2.8	1.9	2.3	1.19	1.31
Vavihill	2.8	4.3	1.5	2.5	0.27	0.79
PNH <sub>4</sub>						
Barcelona	1.6	2.6	1.0	1.4	0.48	0.70
Cabauw	1.0	2.6	1.6	1.6	0.92	0.94
Chilbolton	1.3	1.9	0.5	0.9	0.34	0.59
Helsinki	0.8	1.5	0.8	0.8	0.66	0.73
Hyytiälä	0.4	1.0	0.6	0.7	0.61	0.77
Melpitz	1.4	2.4	1.0	1.3	0.52	0.72
Montseny	1.7	2.7	1.0	1.6	0.45	0.75
Payerne	1.7	2.6	0.9	1.3	0.42	0.62
Puy de Dôme	0.7	1.2	0.6	0.9	0.88	1.11
Vavihill	1.6	2.2	0.7	1.0	0.29	0.57
PSO <sub>4</sub>						
Barcelona	2.7	2.3	-0.4	1.2	-0.15	0.44
Cabauw	1.0	1.9	0.9	1.2	0.65	0.78
Chilbolton	1.3	2.0	0.6	1.1	0.36	0.68
Helsinki	2.4	2.8	0.4	0.9	0.17	0.41
Hyytiälä	1.4	2.2	0.7	1.0	0.19	0.71
Mace Head	0.4	1.2	0.9	0.9	1.10	1.17
Melpitz	1.1	2.5	1.4	1.7	0.53	0.82
Montseny	1.4	2.3	1.0	1.2	0.57	0.68
Payerne	1.1	2.0	1.0	1.2	0.57	0.77
Puy de Dôme	0.4	1.2	0.8	0.9	1.13	1.23
Vavihill	1.6	2.6	1.0	1.2	0.27	0.57
OA						
Barcelona	8.2	2.0	-6.3	6.3	-1.08	1.1

Cabauw	1.2	1.0	-0.3	0.5	-0.18	0.49
Chilbolton	2.4	0.6	-1.8	1.8	-1.14	1.15
Helsinki	2.7	2.0	-0.7	1.5	-0.21	0.64
Hyytiälä	1.3	0.7	-0.7	0.7	-0.69	0.72
Mace Head	0.8	0.2	-0.6	0.6	-0.71	0.90
Melpitz	1.5	0.5	-1.0	1.0	-0.86	0.88
Montseny	3.1	2.5	-0.5	1.7	-0.05	0.62
Payerne	4.1	1.1	-3.0	3.0	-1.03	1.07
Puy de Dôme	0.6	1.0	0.4	0.7	0.56	0.92
Vavihill	3.9	1.1	-2.8	2.8	-1.06	1.07



5 Fig. 1: Soccer-goal plots for hourly concentrations of PM<sub>2.5</sub>, NO<sub>2</sub>, SO<sub>2</sub>, CO and O<sub>3</sub> in June 2006 (left) and February-March 2009 (right). The number of measurement stations (AirBase) is indicated in the legend for each species.



**Figure 2: Average concentrations of PNO<sub>3</sub> and contributions from road transport (SNAP7), ships (SNAP8), combustion in energy and transformation industries (SNAP1) and boundary conditions in February-March 2009 (left) and in June 2006 (right).**

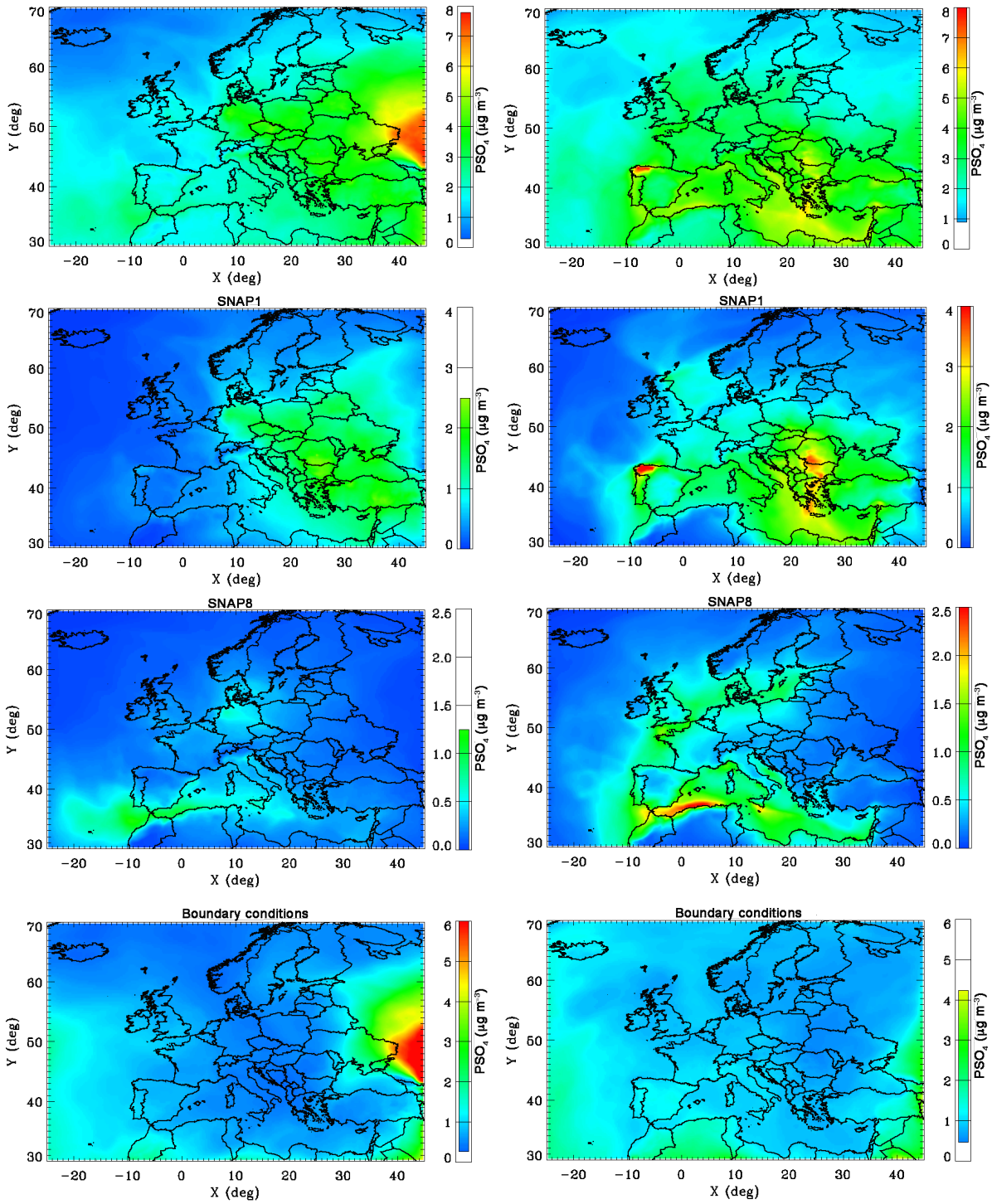


Figure 3: Average concentrations of  $\text{PSO}_4$  and contributions from combustion in energy and transformation industries (SNAP1), ships (SNAP8) and boundary conditions in February-March 2009 (left) and in June 2006 (right).

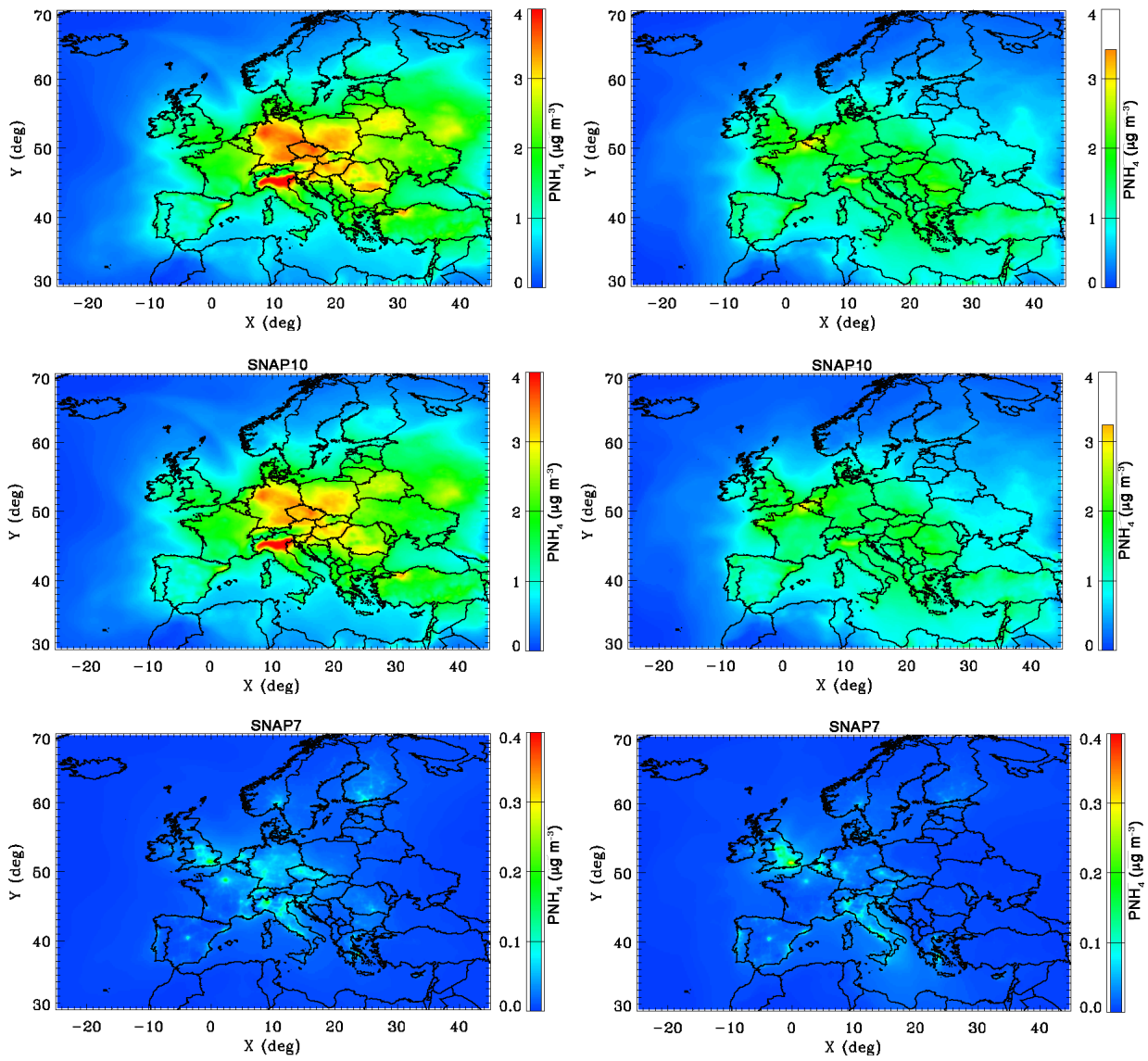


Figure 4: Average concentrations of  $\text{PNH}_4$  and contributions from agriculture (SNAP10) and road transport (SNAP7) in February-March 2009 (left) and in June 2006 (right).



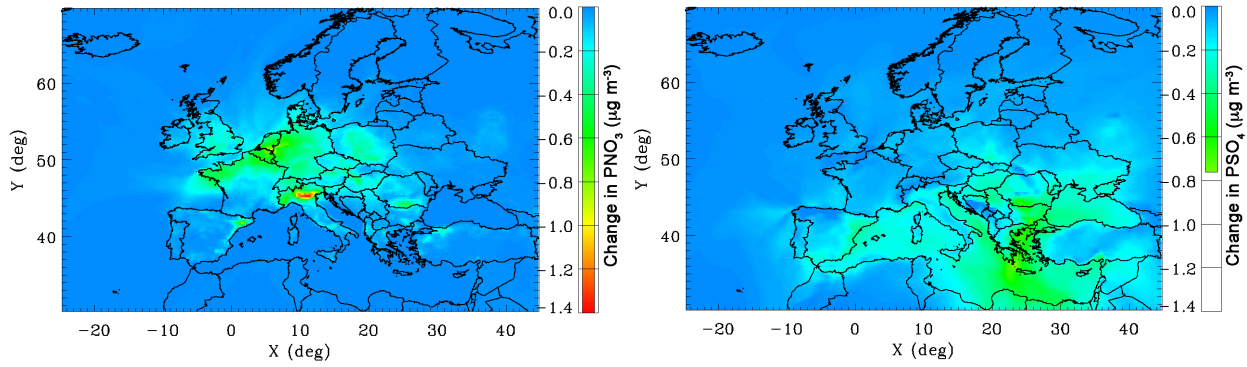
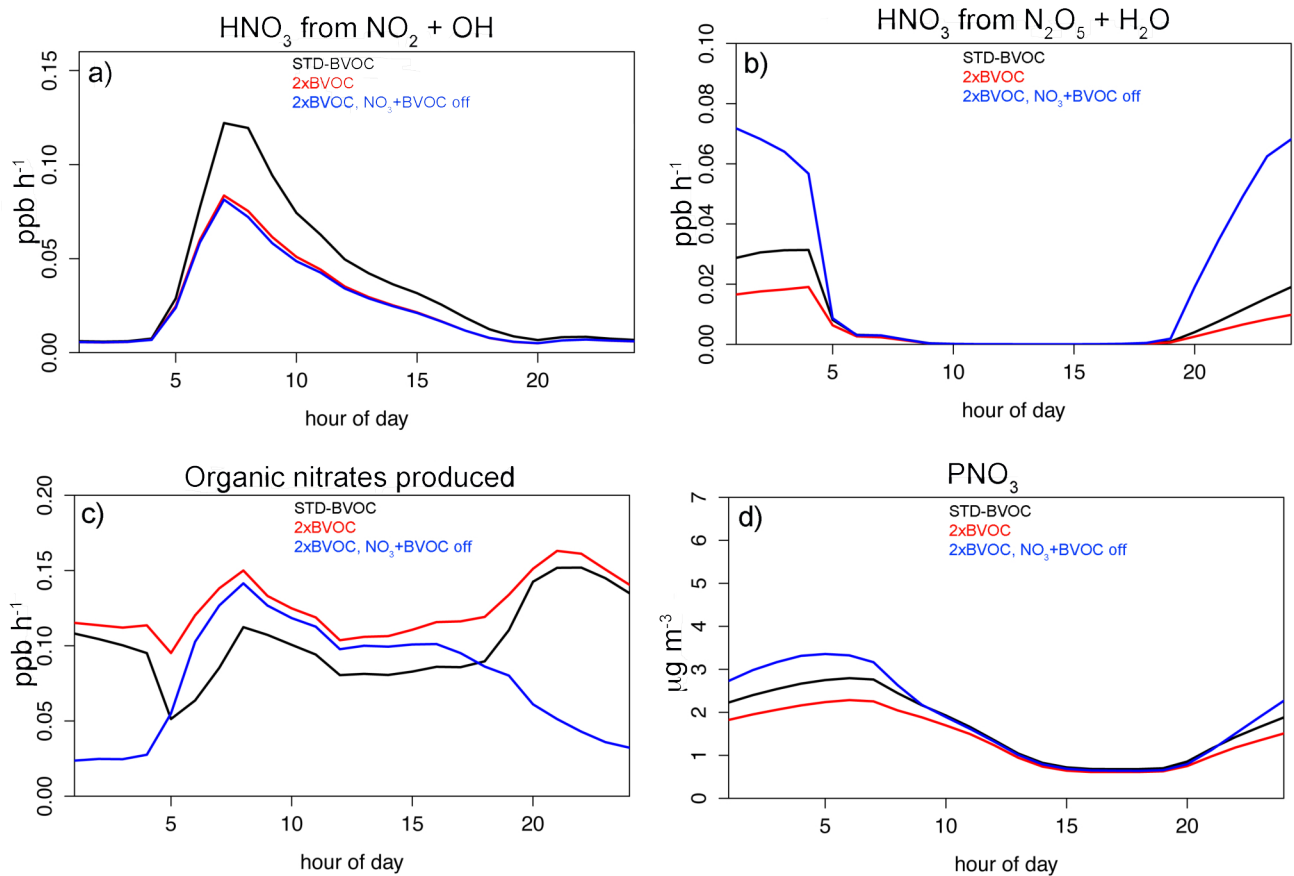


Figure 5: Change in  $\text{PNO}_3$  (left) and  $\text{PSO}_4$  (right) concentrations in June 2006 when BVOC emissions were doubled.



5 Figure 6: Changes in diurnal cycle of a) production rate of  $\text{HNO}_3$  from daytime reaction, b) production rate of  $\text{HNO}_3$  from nighttime reaction, c) production rate of organic nitrates d) particulate nitrate concentrations. Black: with standard BVOC emissions, red: with doubled BVOC emissions, blue: with doubled BVOC emissions and without  $\text{BVOC}+\text{NO}_3$  reactions (Payerne, average June 2006).

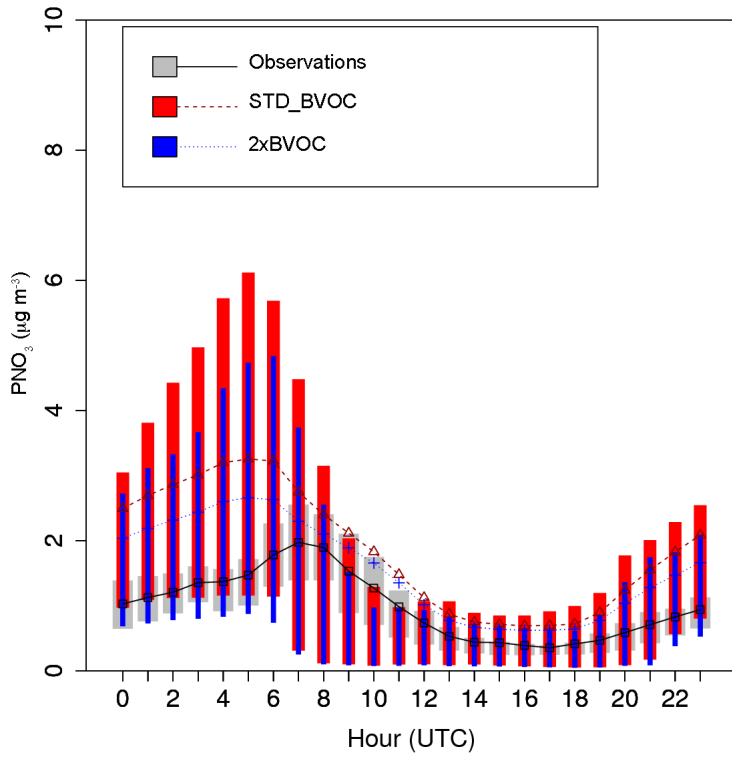


Fig. 7: Hourly box plots showing the diurnal cycle of observed (grey) and modelled particulate nitrate concentrations with standard BVOC emissions (red) and with doubled BVOC emissions (blue) in June 2006 at Payerne. Bars show the 25<sup>th</sup> and 75<sup>th</sup> quantiles while the mean is displayed by the line.

5

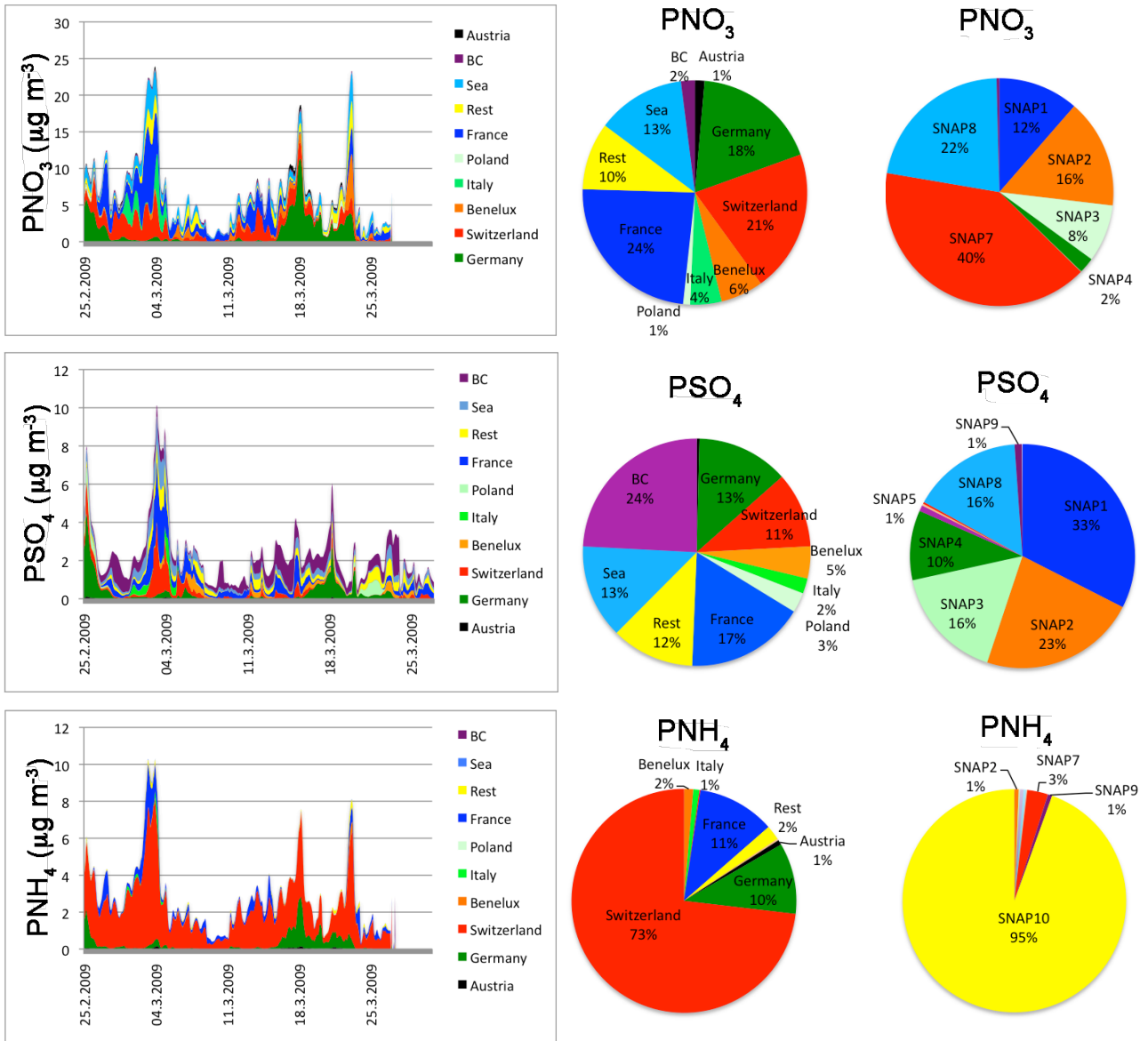


Figure 8: Contributions from various source regions (time series on the left, pie-charts in the middle) and categories (pie-charts on the right) to the concentrations of  $\text{PNO}_3$  (top),  $\text{PSO}_4$  (middle) and  $\text{PNH}_4$  (bottom) in the Swiss Plateau during February-March 2009.

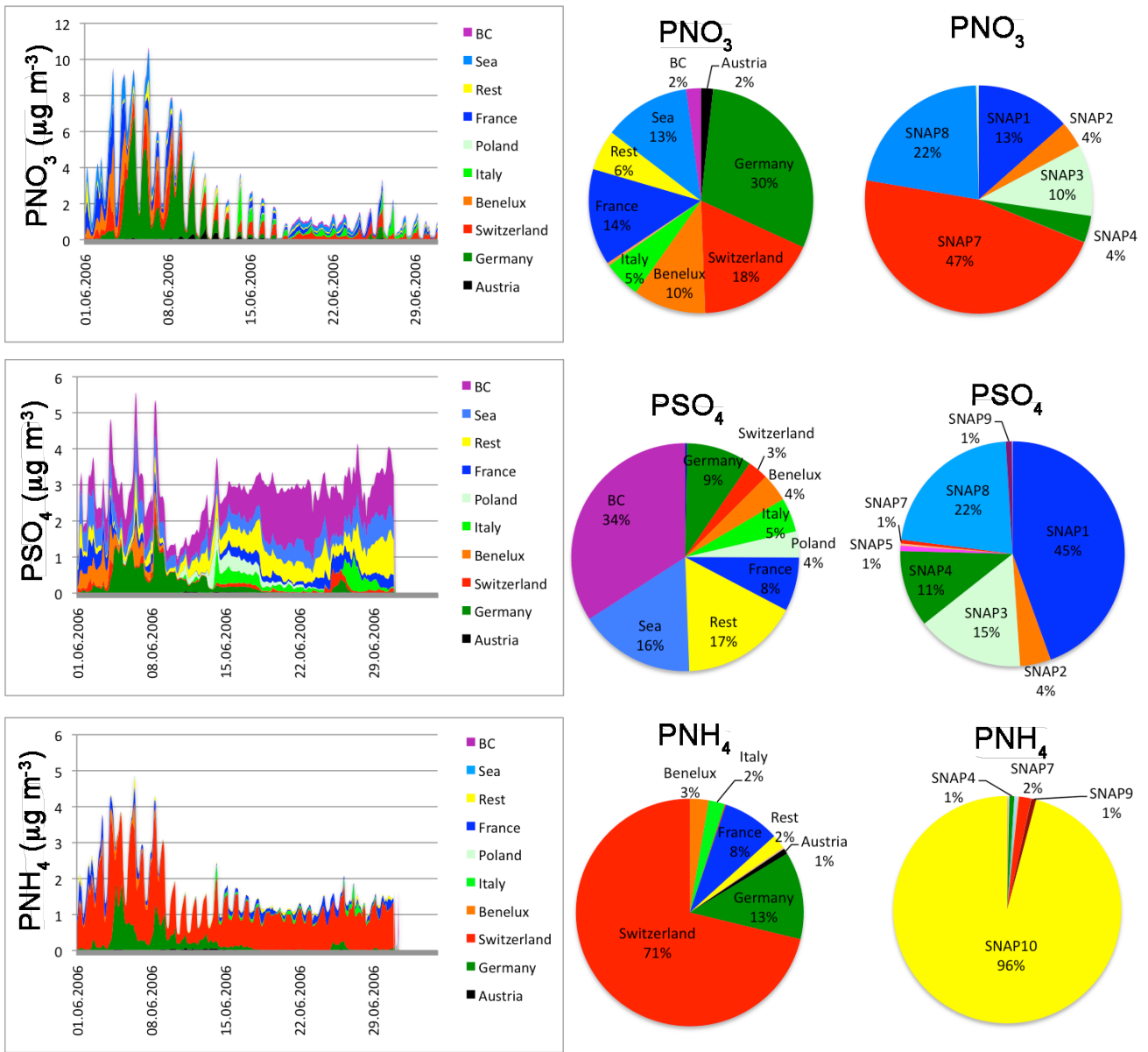


Figure 9: Contributions from various source regions (time series on the left, pie-charts in the middle) and categories (pie-charts on the right) to concentrations of  $\text{PNO}_3$  (top),  $\text{PSO}_4$  (middle) and  $\text{PNH}_4$  (bottom) in the Swiss Plateau during June 2006.

## Supplementary Material

Table S1: Reactions and rate constants for biogenic BVOC in the CB05 mechanism (ENVIRON, 2011)

Isoprene reactions	Reaction products	$k_{298}$ ( $\text{ppm}^{-n}\text{min}^{-1}$ )
ISOP + O	0.75 ISPD + 0.5 FORM + 0.25 XO2 + 0.25 HO2 + 0.25 CXO3 + 0.25 PAR	5.318E+04
ISOP+OH	0.912 ISPD + 0.629 FORM + 0.991 XO2 + 0.912 HO2 + 0.088 XO2N	1.473E+05
ISOP + O3	0.65 ISPD + 0.6 FORM + 0.2 XO2 + 0.066 HO2 + 0.266 OH + 0.2 CXO3 + 0.15 ALDX + 0.35 PAR + 0.066 CO	1.898E-02
ISOP+NO3	0.2 ISPD + 0.8 NTR + XO2 + 0.8 HO2 + 0.2 NO2 + 0.8 ALDX + 2.4 PAR	9.954E+02
ISOP + NO2	0.2 ISPD + 0.8 NTR + XO2 + 0.8 HO2 + 0.2 NO + 0.8 ALDX + 2.4 PAR	2.216E-04
ISPD+OH	1.565 PAR + 0.167 FORM + 0.713 XO2 + 0.503 HO2 + 0.334 CO + 0.168 MGLY + 0.252 ALD2 + 0.21 C2O3 + 0.25 CXO3 + 0.12 ALDX	4.963E+04
ISPD + O3	0.114 C2O3 + 0.15 FORM + 0.85 MGLY + 0.154 HO2 + 0.268 OH + 0.064 XO2 + 0.02 ALD2 + 0.36 PAR + 0.225 CO	1.049E-02
ISPD+NO3	0.357 ALDX + 0.282 FORM + 1.282 PAR + 0.925 HO2 + 0.643 CO + 0.85 NTR + 0.075 CXO3 + 0.075 XO2 + 0.15 HNO3	1.477E+00
ISPD	0.333 CO + 0.067 ALD2 + 0.9 FORM + 0.832 PAR + 1.033 HO2 + 0.7 XO2 + 0.967 C2O3	photolysis
<b>Terpene reactions</b>		
TERP + O	0.15 ALDX + 5.12 PAR	5.318E+04
TERP+OH	0.75 HO2 + 1.25 XO2 + 0.25 XO2N + 0.28 FORM + 1.66 PAR + 0.47 ALDX	9.997E+04
TERP + O3	0.57 OH + 0.07 HO2 + 0.76 XO2 + 0.18 XO2N + 0.24 FORM + 0.001 CO + 7 PAR + 0.21 ALDX + 0.39 CXO3	1.128E-01
TERP+NO3	0.47 NO2 + 0.28 HO2 + 1.03 XO2 + 0.25 XO2N + 0.47 ALDX + 0.53 NTR	9.833E+03

OH	Hydroxyl radical
HO2	Hydroperoxy radical
NO2	Nitrogen dioxide
NO3	Nitrate radical
HNO3	Nitric acid
NTR	Organic nitrate (RNO <sub>3</sub> )
CO	Carbon monoxide
FORM	Formaldehyde
ALD2	Acetaldehyde
ALDX	Propionaldehyde and higher aldehydes
PAR	Paraffin carbon bond (C-C)
XO2	NO to NO2 conversion from alkylperoxy (RO2) radical
XO2N	NO to organic nitrate conversion from alkylperoxy (RO2) radical
MGLY	Methylglyoxal and other aromatic products
C2O3	Acetylperoxy radical
CXO3	C3 and higher acylperoxy radicals
ISOP	Isoprene
ISPD	Isoprene product (lumped methacrolein, methyl vinyl ketone, etc.)
TERP	Terpene

**Table S2: Biogenic SOA precursor reactions included in CAMx (ENVIRON, 2011)**

Precursor	Reaction	CG (condensable gas) products	$k_{298}$ (ppm <sup>-n</sup> min <sup>-1</sup> )
Isoprene	ISP + O	none	5.32E+04
	ISP + OH	0.015 CG3 + 0.12 CG4	1.47E+05
	ISP + O3	none	1.90E-02
	ISP + NO3	none	9.96E+02
Terpenes	TRP + O	0.065 CG5 + 0.29 CG6	4.12E+04
	TRP + OH	0.065 CG5 + 0.29 CG6	7.76E+04
	TRP + O3	0.065 CG5 + 0.29 CG6	1.33E-01
	TRP + NO3	0.065 CG5 + 0.29 CG6	9.18E+03
Sesquiterpenes	SQT + OH	0.85 CG7	2.91E+05
	SQT + O3	0.85 CG7	1.71E+01
	SQT + NO3	0.85 CG7	2.81E+04

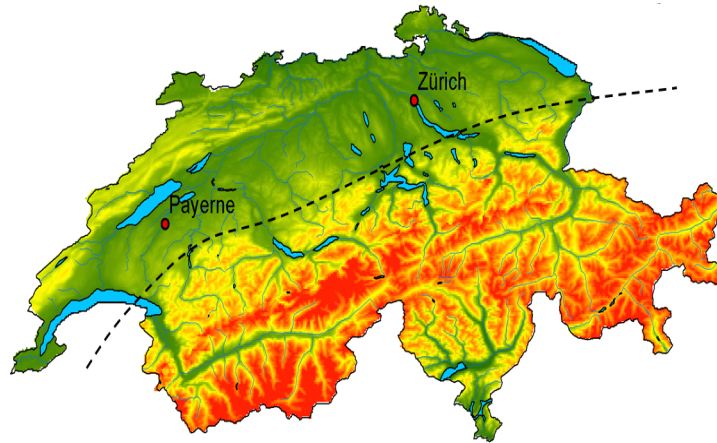


Figure S1: The Swiss Plateau (the region above the dashed line) used as receptor in PSAT calculations.

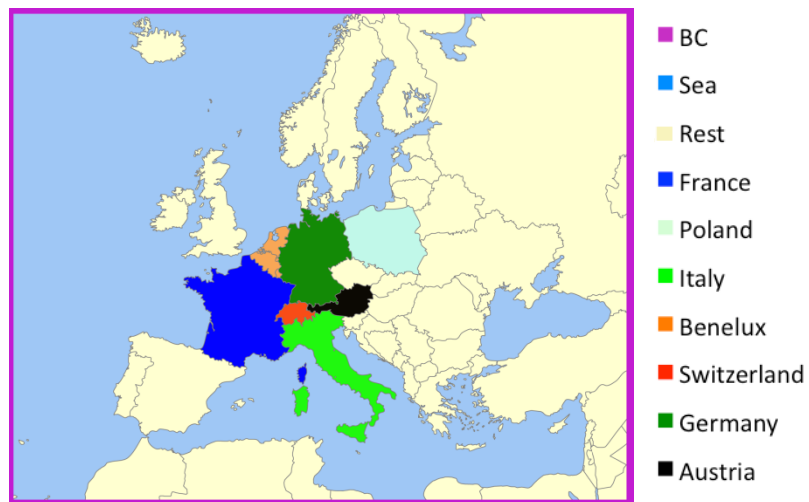
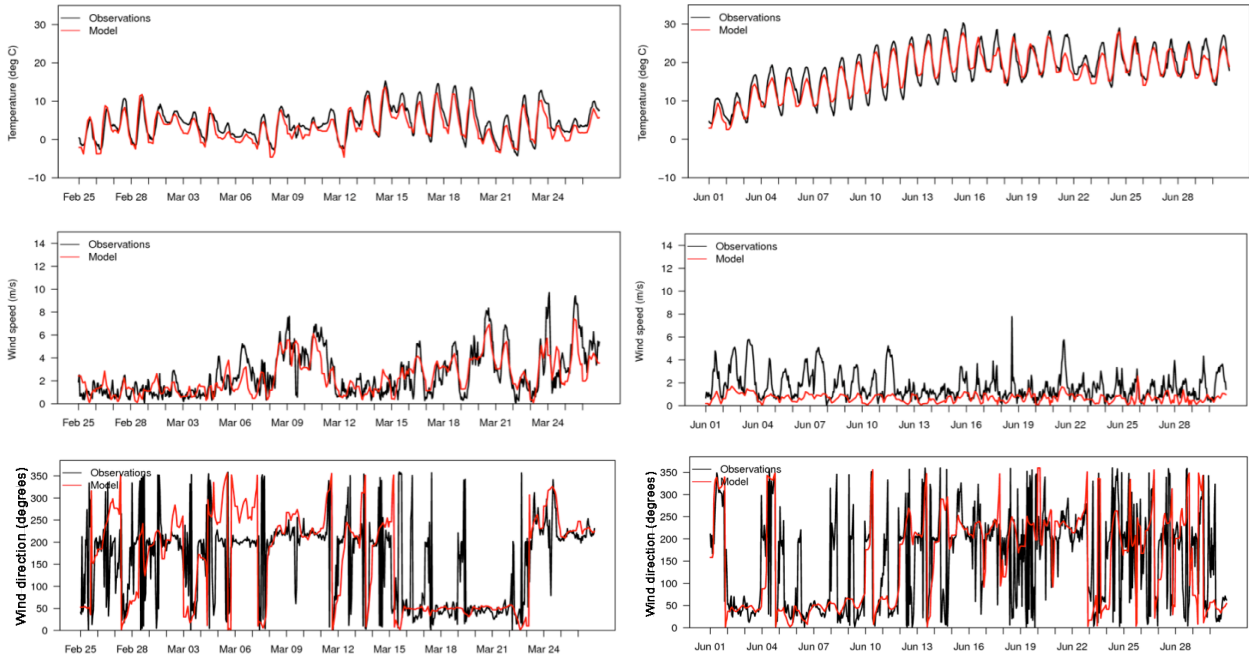
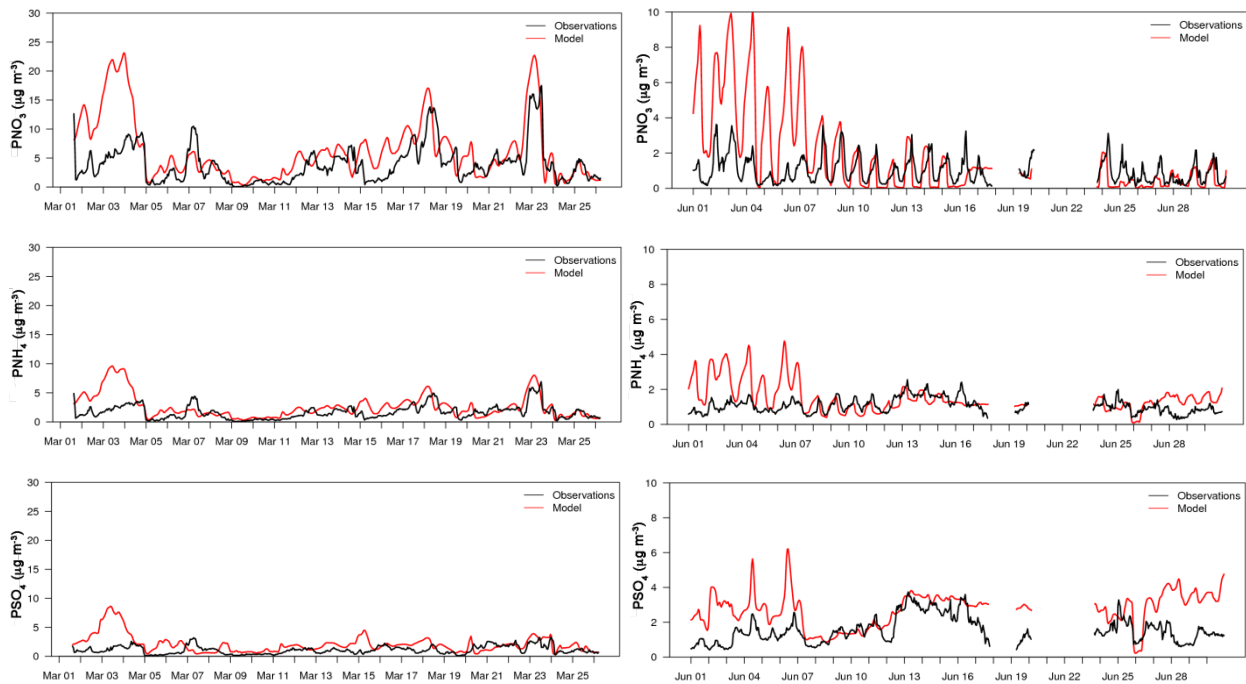


Figure S2: Source regions used in PSAT calculations. Note that this map was only used for illustration of the regions and their colors and it doesn't have the same projection used in the model simulations.

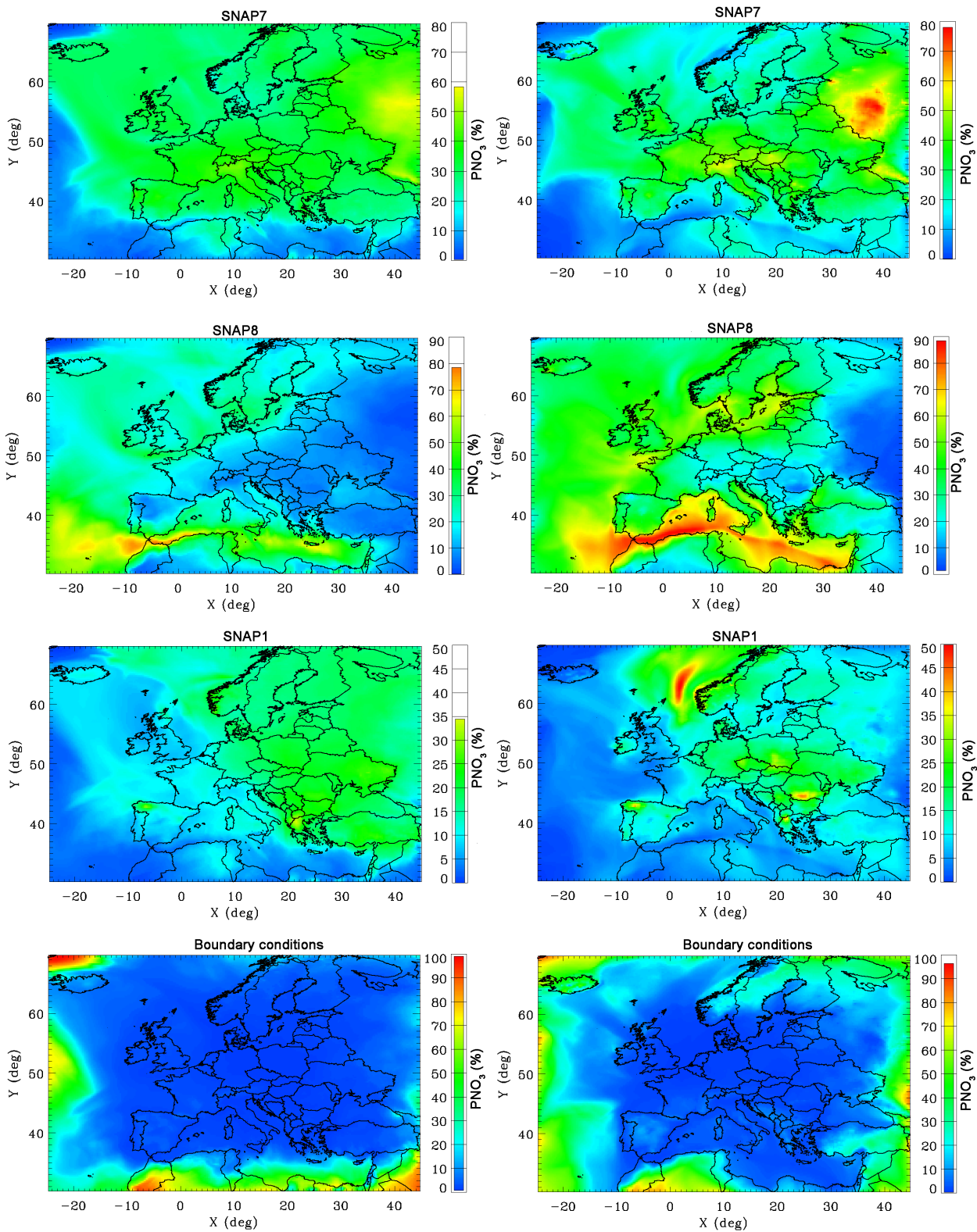


**Figure S3: Modelled (red) and measured (black) temperature, wind speed and wind direction for the cold season in Feb-Mar 2009 (left) and the warm season in June 2006 (right) in Payerne, Switzerland.**

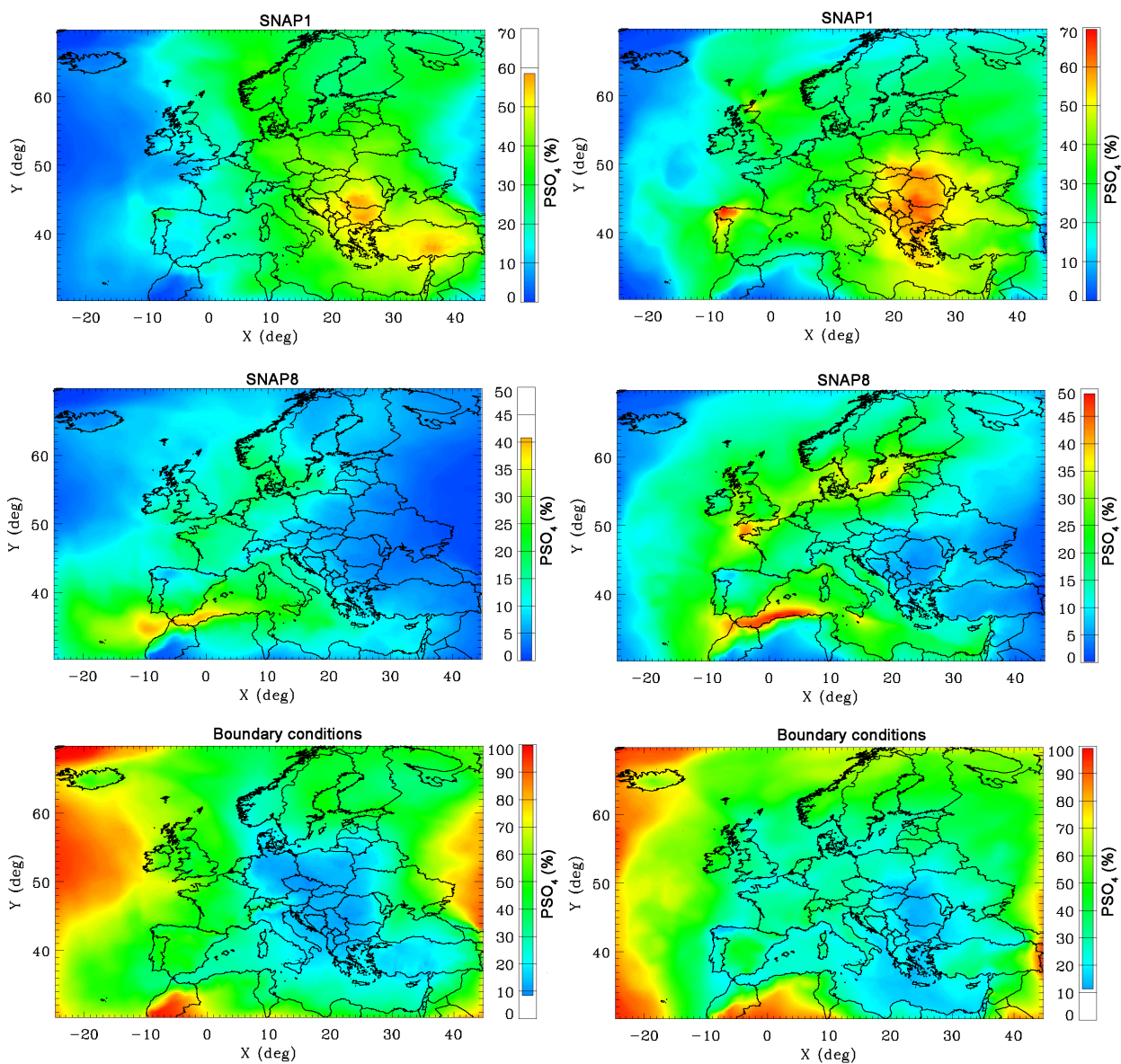


**Figure S4: Modelled (red) and measured (black) nitrate (PNO<sub>3</sub>), ammonium (PNH<sub>4</sub>) and sulfate (PSO<sub>4</sub>) for the cold season in Mar 2009 (left) and the warm season in June 2006 (right) in Payerne, Switzerland.**

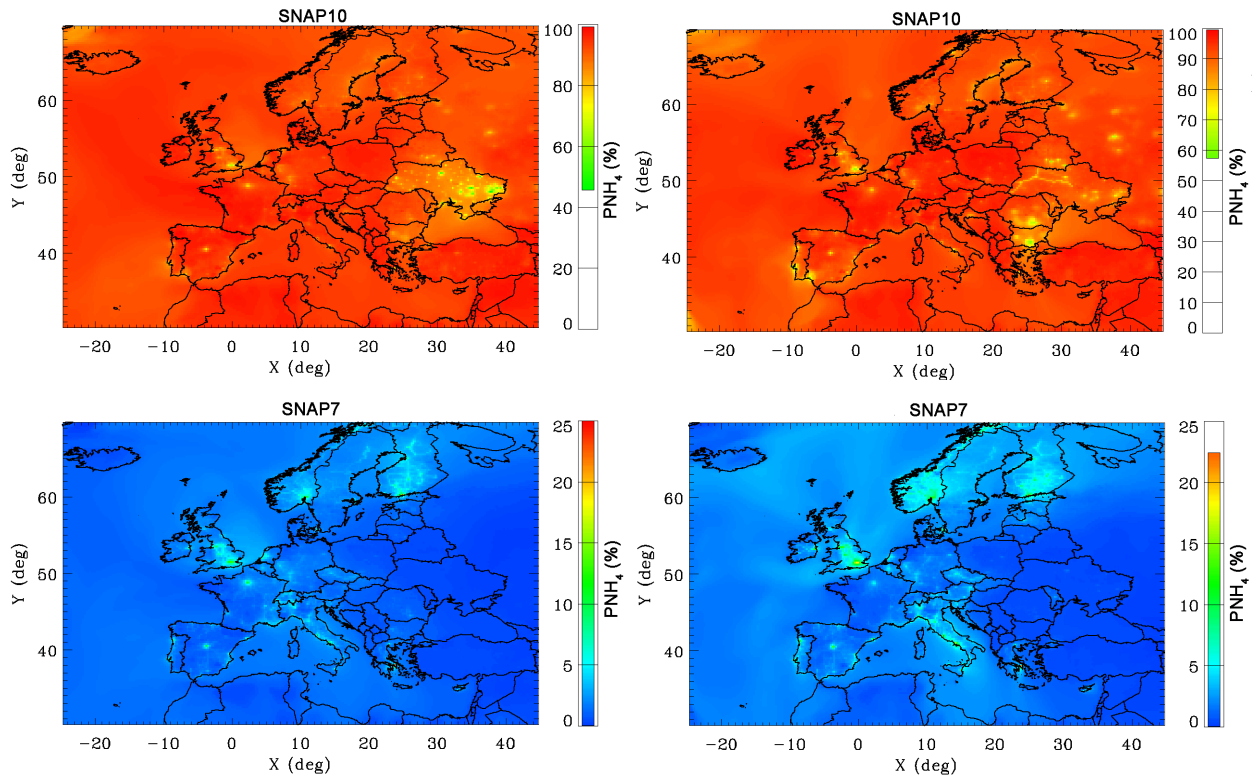




**Figure S5: Relative contributions to PNO<sub>3</sub> from road transport (SNAP7), ships (SNAP8), combustion in energy and transformation industries (SNAP1) and boundary conditions in February-March 2009 (left) and in June 2006 (right).**



**Figure S6: Relative contributions to  $\text{PSO}_4$  from combustion in energy and transformation industries (SNAP1), ships (SNAP8) and boundary conditions in February-March 2009 (left) and in June 2006 (right).**



**Figure S7: Relative contributions to  $\text{PNH}_4$  from agriculture (SNAP10) and road transport (SNAP7) in February-March 2009 (left) and in June 2006 (right).**

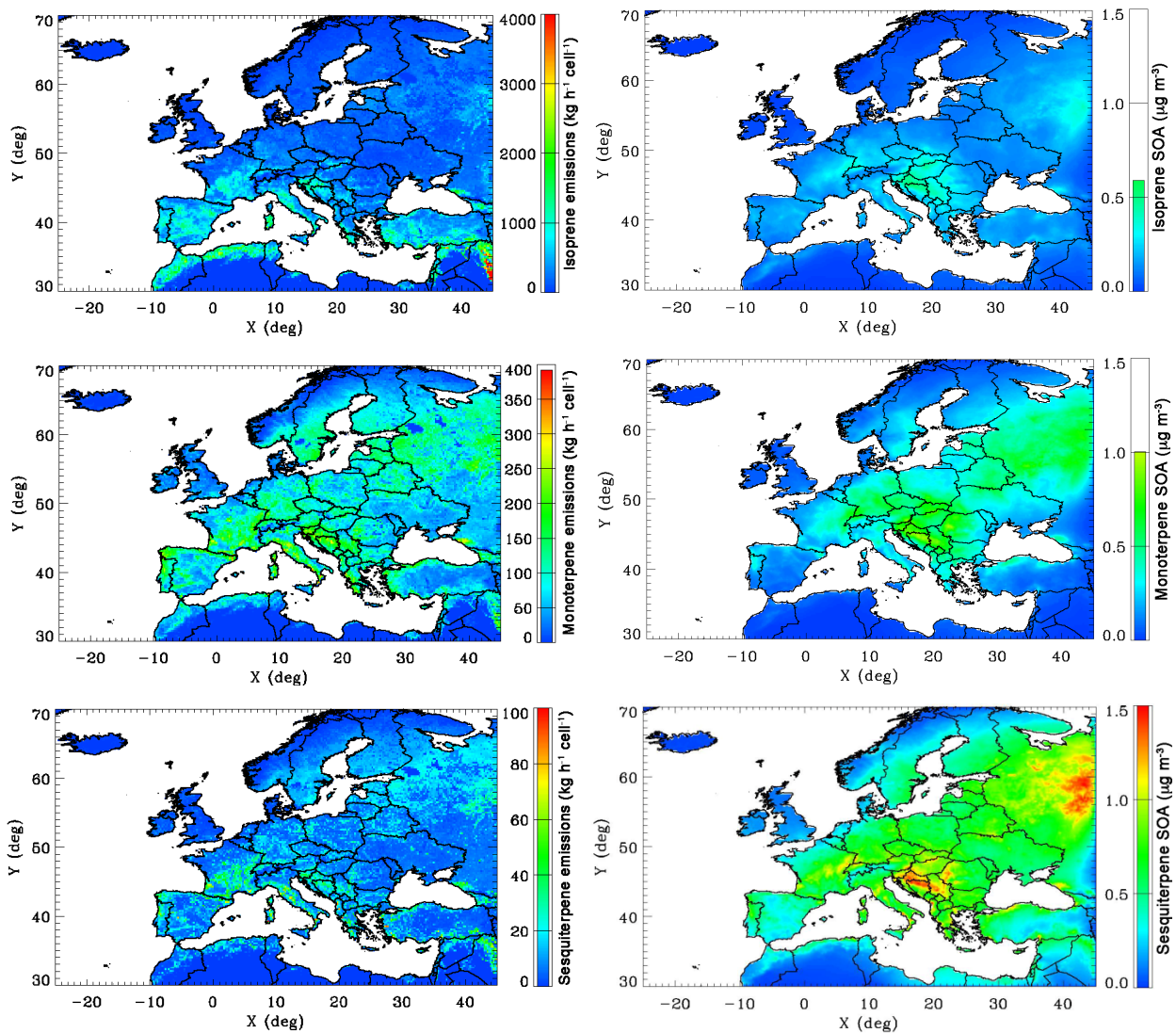


Figure S8: Monthly average emissions of biogenic species (left) and their SOA products (right); isoprene (top), monoterpenes (middle) and sesquiterpenes (bottom) in June 2006.

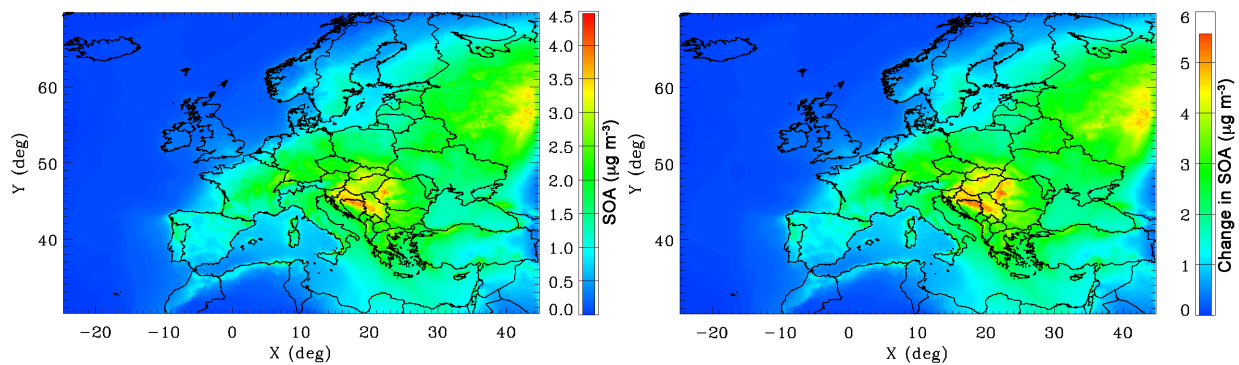


Figure S9: Total SOA concentrations in the base case (left) and changes in SOA when BVOC emissions were doubled (right) in June 2006.

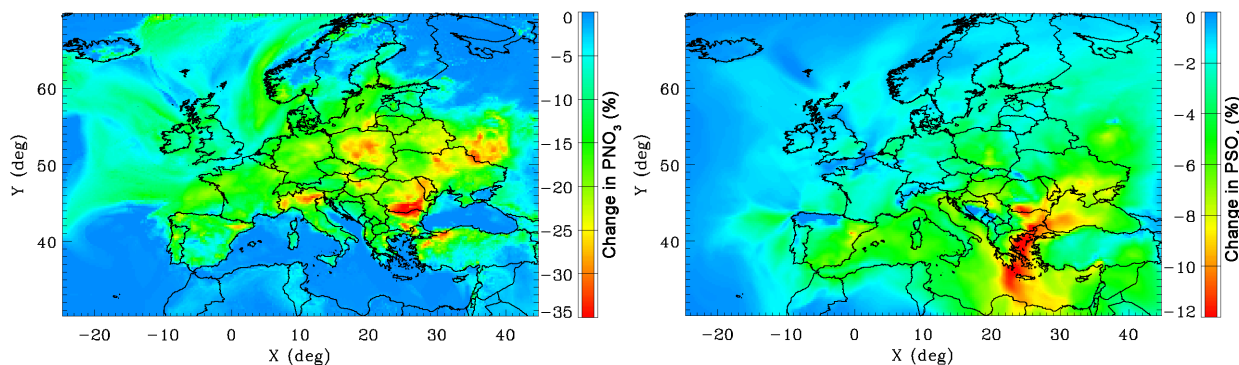


Figure S10: Relative changes in PNO<sub>3</sub> (left) and PSO<sub>4</sub> (right) concentrations in June 2006 when BVOC emissions were doubled.

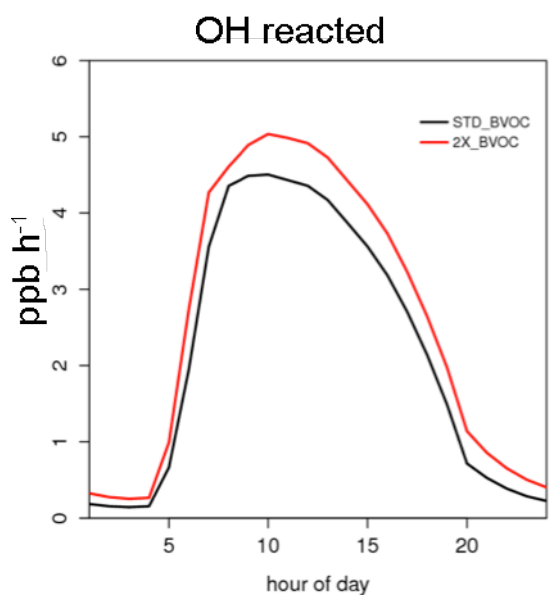


Figure S11: Changes in diurnal variation of reacted OH radical (June 2006, Payerne). Black: with standard BVOC emissions, red: with doubled BVOC emissions.