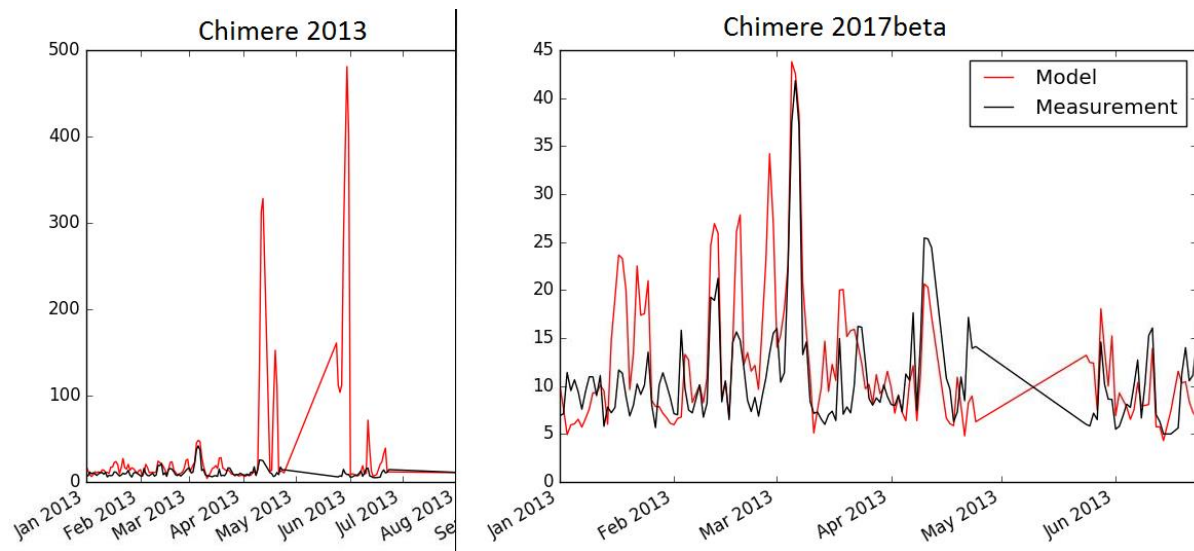


We would like to thank all the reviewer for the interesting comments. Before addressing the specific comments of all the reviewer, we would like to address the common comment on the comparison between the CHIMERE 2013 and CHIMERE 2017 $\beta$  versions. One of the reason that originally motivated this study is the lack of numerical stability of the model in some configurations (illustrated by the following figure obtained over a station), but also problems in the representation of several processes in the model (like coagulation which was based on an old parameterization not taking into account the number of particles or condensation/evaporation routines which has numerical issues and did not represent to our opinion adequately the process). Moreover, a few bugs were present in the Chimere2013 version. The improvements referred inside the text concern all these issues.



Due to this, the aerosol modules (except for the nucleation subroutine) was entirely rewritten.

Comparing the two versions does not have to our opinion any sense as Chimere2013 is not stable in the closest configuration possible. The aim of this study is not to change a few parameterizations and to see their effect but to present the results of a new module. We chose therefore to present the results of this version without referring to the Chimere 2013 because:

1. It is almost impossible to run the Chimere 2013 version without changing the configuration and the code
2. Even if it was the case, differences would be difficult to analyze because of some corrections and bugs present in Chimere 2013.

The aim of this study was therefore only to present the new module without referring on how these parameterizations differ from Chimere 2013. Presenting the differences between the two versions was done in the first version of the paper and it was found to be mainly confusing and deserving the quality of the paper. Moreover, presenting the changes between the Chimere 2013 and Chimere 2017beta versions gave the wrong idea that only a few modifications were done, whereas it is indeed a new module. A few references to the Chimere 2013 were however still present and may have been confusing. The references to the Chimere 2013 version were limited and the text was modified to emphasize the fact the results of a new aerosol module is presented. However, a table presenting the differences between the two versions is added in Supplementary Materials.

*Anonymous Referee #1*

*The paper describes a series of developments in the chemical transport model Chimere and the evaluation of the model against aerosol measurements in several stations in Europe during 2013. The changes include new biogenic VOC emissions, replacements of the inorganic aerosol model ISORROPIA with that of ISORROPIA-II, update of the secondary organic aerosol module and better description of wet deposition. The description of the changes and the evaluation of the model are satisfactory. The scientific content of the paper could be improved by better connection of the changes made with the predictions and also the performance of the model. Overall, the paper is suitable for publication in GMD after some improvements and corrections are made. These are described below.*

#### *General Comments*

*(1) One of the major weaknesses of the work is that there is very little about the effect of the various changes on the predictions of the CTM. I understand that repeating these simulations with the previous version of Chimere requires significant work and may not be worthwhile. However, some discussion of the results of previous evaluations of the model is necessary.*

Addressed in the general reply.

*(2) Abstract. The use of the terms “good performance”, “good seasonal evolution”, “performs well”, etc., should be avoided or at least the quantitative metrics should be presented instead.*

The abstract was modified.

*(3) Abstract and rest of the paper. Most of the work focuses on PM10 with some analysis performed for PM2.5. However, it is not clear in most of the paper if the concentrations refer to the former or the latter. I think that the size-range should be mentioned everywhere in the paper to avoid confusion.*

To prevent weighting down the paper by specifying every time the fraction, the following sentence was added at the beginning of the section “Results”:

“When not mentioned otherwise, concentrations of components used for the comparison are in the PM10 fraction.”

*(4) Abstract. The conclusion that the model “strongly underestimates SOA concentrations” is not supported by the evaluation which is based on the comparison with total OC concentrations. The same applies to the explanation that “this underestimation could be due to a lack of anthropogenic SOA in the model*

*“strongly underestimates SOA concentrations”. replaced by “strongly underestimates summer organic aerosol concentrations”. More discussions were added into the text and the conclusions was nuanced by arguing that the underestimation could also be due to a lack of biogenic emissions*

*“For the northern half of Europe, except for stations DE0003, CH0005R in Switzerland and PL0005R in Poland which have strong concentrations of modeled biogenic SOA, summer concentrations of organic aerosol are underestimated. Only a peak of organic aerosol (due to biogenic aerosols in the model) at the end of August for several stations (CZ0003R, DE0002R, DE0007R, DE0008R, DE0044R) is reproduced by the model. These stations correspond to areas with strong anthropogenic emissions. A lack of anthropogenic SOA could therefore explain this pattern. However, this underestimation could be also due to a lack of biogenic emissions over these areas.”*

#### *Model description*

*(5) It is not clear if the composition of dust is taken into account in the calculation of cloud pH.*

The following sentence is added into the text:

“The effect of dust on pH is not taken into account as composition of dusts is not represented within Chimere.”

*(6) The volatilities of the three POA components should be mentioned. Also despite the corresponding discussion it is not clear to me how their emissions are calculated from the OA emissions in the corresponding inventory for the various sources. A table with the corresponding volatility-resolved emission rates for the various sources would be helpful.*

The partitioning constant are added into the text. Properties were already shown in Table 3.

The SVOC split is added into the text: “For each sector, emissions of SVOC are splitted into emissions of POAIP (25% of emissions), POAmP (32% of emissions) and POAhP (43% of emissions) to follow the dilution curve of POA in Robinson et al. (2007).

*(7) The POA aging reactions (1)-(3) are a net sink of OH. In the rest of the SOA reactions it is assumed that the OH is recycled. Why are these treated differently?*

It was not treated differently (OH is recycled). The text and the equations are modified.

*(8) If my understanding is correct the authors assume that the primary OA emissions in the inventory that they are using represent 20 percent of the organic compounds emitted in a certain volatility range (less or equal than 100  $\mu\text{g m}^{-3}$  as IVOCs are neglected). So the corresponding emissions are multiplied by a factor of 5. Given that a lot of these emissions have been measured at high OA levels this increase appears to be too high. It appears that the emissions used set the IVOC emissions to zero and at the same time add a lot of organic emissions to the more volatile SVOCs. This is an important issue for the model so some additional analysis of what exactly is done and why is necessary.*

As discussed in section “Anthropogenic emissions”, it was already demonstrated by van der Gon et al. (2015) that biomass burning OA emissions are strongly underestimated. More discussions are added into the text:

“van der Gon et al. (2015) has shown that POA emissions are greatly underestimated due to a strong underestimation of residential wood burning emissions by a factor 3 over Europe (between 1 and 10 depending on the countries) if SVOC emissions are included. This strong underestimation of emissions is due to the use of filter at high temperature (for which SVOC are mainly present as vapors) for emission factor measurement. This result is confirmed by May et al. (2013) who found that 80% of SVOC evaporate at high temperature.”

“A sensitivity analysis of the SVOC/POA ratio was already performed by Couvidat et al. (2012).”

Moreover, the importance of SVOC emissions is already discussed in the discussions.

*(9) The use of ISORROPIA-II is rather confusing. Its major advantage compared to ISORROPIA is its ability to simulate the thermodynamics of calcium, magnesium, etc., compounds. However, the authors state in Section 2.1.4 (page 5, lines 22-24) that the crustal elements are not taken into account for the partitioning. This counterintuitive choice requires some justification.*

As written in the text, the composition of dusts is not simulated by the model and therefore composition of dusts cannot be used into ISORROPIA and therefore simple hypothesis were used to

simulate coarse nitrate formation. However, we agree that taking properly dusts into account could be a major improvement.

The following text is added into discussions:

“Interactions of dust with inorganic aerosols could be better represented in the model. The interactions could for example be simulated by taking into account the mineralogy of dusts within Chimere, by emitting dusts with different composition depending on the location of emissions.”

*(10) Some discussion of the aerosol size resolution used in the model is needed.*

Added at the beginning of the method section:

“The model uses a sectional approach where particles are separated into several diameter bins. In this study, particles were separated into 10 bins from 10 nm to 10 μm. “

*(11) Section 2.1.8. The way that the mass transfer is between the gas and particulate phases is simulated is not entirely clear. If my understanding is correct, bulk equilibrium is assumed for both inorganics and organics for sizes below 1.25 micrometers. However, it is not clear what happens for coarse particles for compounds like ammonia, hydrochloric acid, organics, etc. Also is the formation of calcium nitrate the only way that nitrate can be transferred to the coarse particles? What about sodium nitrate?*

Explanations are added into the text:

“For particle with a diameter above the cutting diameter, absorption/evaporation is represented by solving the equation of condensation/evaporation (Seinfeld and Pandis, 1998):

$$\frac{dA_{p,i}^{bin}}{dt} = k_i^{bin} (p_i - p_{eq,i}^{bin})$$

with  $p_i$  the vapor pressure of  $i$  and  $p_{eq,i}^{bin}$  the vapor pressure of  $i$  at equilibrium with the particle-phase concentration of  $i$  inside the bin.  $p_{eq,i}^{bin}$  is computed with the reverse mode of ISORROPIA for inorganics. However, the condensation of SVOC onto coarse particle is not taken into account.”

As detailed in section 2.1.8, the condensation of HNO<sub>3</sub> into sea salt leading to the evaporation of HCl is taken into account.

*(12) Tables 1-3. A list of the species names probably in the Supplementary Information is needed to understand the information in these tables.*

We don't think that a list of species would improve the quality of the study. Table 2 provides a list of the main species.

The list of SOA precursors was added to the caption of Table 1. The reference is added to the caption

*(13) The Henry's law constants of a number of organic species are both in Tables 2 and 4 and in quite different units. These important parameters should be in one table with some explanation about their source. Also the fact that they appear to be known quite accurately (three significant digits in Table 2) is problematic.*

The units are harmonized. As said in the text, SOA is formed with the H<sub>2</sub>O mechanism [Couvidat et al., 2012] and therefore parameters come from H<sub>2</sub>O. Reference is added to Table 2.

Table 3 presents effective Henry's law parameters (contrary to Table 2). Therefore, values can be different. The following explanation is added to the text:

"For SVOC, Henry's law parameters for wet and dry deposition were computed for a pH of 5.6 (pH of water in presence of CO<sub>2</sub>)."

*(14) The authors mention that they use the EMEP inventory published in 2003. Are they using any emissions updates for 2013 or the emissions used are that old? A table summarizing the anthropogenic emissions used for each major source category would be helpful together with additional information about the origins of these estimates. The biomass emission rates should be mentioned.*

2003 corresponds to the year of the paper describing the methodology. The EMEP inventory for 2013 have been published in 2015 and provides national official data.

The EMEP inventory is widely used in the modeling of air quality over Europe.

We don't see how it could be possible to summarize emissions and biomass emission rates into a single table as emissions vary spatially with different emissions according to official estimations for each country. Moreover, describing emissions is outside the scope of this paper.

For additional information, please report to the ceip website (<http://www.ceip.at/>) where all the information of the 2013 inventory can be found.

*(15) How are the sea-salt emissions calculated? What is the assumed composition and size distribution? This scheme appears to perform quite well based on the Chimere evaluation presented here.*

Sea salt emissions are computed as in Chimere 2013 with the parameterization of Monahan. Reference added into the text.

*(16) Some additional discussion of the ammonia emissions used would be helpful. Is there a diurnal variation of the emissions? Is the monthly variation (shown in Fig. 10 for six countries) similar for all areas in the domain? What are the total emissions?*

Total emissions come from the EMEP inventory.

The following precision is added into the text:

"Temporalization of emissions is done according temporal factors for each country provided by GENEMIS [Ebel et al., 1997]."

*(17) A short description of the various stations used in the paper is needed. This could be part of the Supplementary Information. My understanding is that all of them are regional background stations. Is this correct? Are there any exceptions?*

The stations are regional background. Description of the stations are present in the text when necessary to the understanding of results. Due to the great number of stations, they will not be described in this publication as lot of information are available in <http://www.nilu.no/projects/ccc/sitedescriptions/index.html>

*(18) There appear to be around 20 stations measuring sodium in Figure 2. However, 38 stations are mentioned in Table 5. What is causing this discrepancy? There are similar issues with other PM components.*

The number of stations was checked. The right number of stations is plotted in Figures. The figure are modified to make figures more readable.

*(19) A number of urban background stations (e.g., in Paris) could have also been used in the evaluation. Is there a reason why they have been excluded? Also there should be PM1 measurements from the ACTRIS network available for the same period.*

Only open access data available in ebas were used for the comparison. Moreover, due to the huge amount of work that was necessary for this study, not all type of comparison could be done. Moreover, the resolution of the model is not enough (20km) for comparison to urban background stations to be meaningful.

*(20) How well did the measured PM mass concentrations compare to the sum of the components? Could some of the measured PM mass be water as previous studies have indicated for Europe but also for the US?*

Very few stations provide a lot of components. As explained in the text, we try to close the mass balance for station DE0044R (Melplitz) and based on measurements it was not possible to reproduce PM. However, even at this station, more information would be needed on primary components.

The presence of water in measurements is indeed a possibility, but it should depend on the method and the conditions of measurements.

*(21) The number of measurements used in the evaluation should be mentioned in Table 5.*

The number of measurements is added into the text.

*(22) A brief summary of the boundary condition values (or ranges) provided by Mozart for the various sides of the domain would be helpful. It appears that these boundary conditions may be partially responsible for some of the discrepancies between model predictions and observations in areas like Northern Europe.*

Boundary conditions are hourly, vary spatially and are therefore to be summarized in a single range. The impact of boundary conditions are however illustrated in the maps at the limit of the domain.

*(23) The authors discuss the potential errors in the comparison of model-predicted OM values with OC measurements. However, they never discuss the actual values of the OM/OC ratios that they use. I understand that these vary temporally, but the average values for each station for at least the summer and winter could be presented. Given that there are now a lot of measurements of this ratio by High-Resolution Aerosol Mass Spectrometers in locations around Europe a more informed comparison could be made.*

The OM/OC ratios and the method used to estimate those ratios are already discussed in the section "Organic Aerosol". OC is evaluated according to the method of Couvidat et al. (2012) and the uncertainties were already investigated in this study:

"Organic Aerosol concentration measurements are not available in the database. However, measurements for organic carbon (OC) concentrations are available. OC is the mass of carbon inside the organic aerosols. For the comparison, OM/OC ratios (that depend on the composition of organic aerosols, especially the degree of oxidation of compounds) have to be assumed to estimate OC concentrations from modeled OM concentrations. Turpin and Lim (2001) measured the OM/OC ratios at different 25 locations and found ratios between 1.2 and 2.5 and recommended to use a ratio of 2.1 for rural areas. Following Couvidat et al. (2012), OC concentrations were calculated directly from the concentrations of each organic surrogate compounds using their molecular structure to estimate the OM/OC ratio of the surrogate compounds. Several sensitivity tests were conducted by Couvidat et al. (2012) and has shown that the OM/OC simulated by the H<sub>2</sub>O mechanism is generally quite low

compared to the OM/OC ratio recommended by Turpin and Lim (2001). An overestimation of OC concentrations by the model could therefore be due to an underestimation of the OM/OC ratio.”

OM data were not used for the comparison as they are not freely accessible on the ebase database and were therefore not used in this study. OM and OC refer to very different techniques that are not directly comparable. Moreover, OM is often measured in the PM<sub>1</sub> fraction and OC in the PM<sub>2.5</sub> or PM<sub>10</sub> fraction. Based on this, it will be difficult to evaluate the OM/OC ratio.

*(24) The study focuses on daily average measurements. However, some discussion of the diurnal variations of components like OM would have been welcome. There are measurements of these variations in stations like Melpitz that could be useful.*

OM measurements at the Melpitz station are not available for 2013 in the ebas database at the Melpitz station and were therefore not used for the comparison in this study.

Moreover, hourly measurements are scarce and the analysis would not be representative.

*(25) The predicted high levels of OC in parts of central and eastern Europe during the winter appear to be too high. I am assuming that these are due to biomass burning. Is this an indication of emissions that are too high? May be atmospheric mixing that is too weak? Some discussion is needed here because other authors have argued that the biomass burning emissions in the European inventory is too low. Could it also be a problem due to the high SVOC emissions used by the model that become particles under low temperatures?*

“During winter, OC is overestimated over a few stations: ES1778R, IT0004R, CH0005R and DE0003R. These 4 stations are under meteorological conditions difficult to simulate at such a low resolution (25 km). They are often close to cities: ES1778R is close to Barcelona (60 km), IT0004R (Ispra) is in the Po valley (an area with strong anthropogenic emissions) not far from Milan, CH0005 is at less than 20 km of Lucerne (with 205 000 inhabitants) and DE0003R is at 12 km from Freiburg (a city of 206 000 inhabitants). Moreover, these stations are in mountainous regions with high variations of altitude that are difficult to represent at such a resolution. Except for these 4 stations, concentrations of organic aerosol in winter simulated by the model tend to be underestimated although reasonable performances could be attained for numerous stations emphasizing the need to better represent anthropogenic emissions in winter.”

*(26) There is no discussion regarding the predictions of EC by Chimere.*

As EC measurements are scarce and therefore difficult to generalize, they were not included in the analysis. Moreover, concentrations are low and will not have a significant impact on PM concentrations.

*(27) Some discussion of the evaluation of coarse nitrate predictions by Chimere are needed at least in Cyprus but also in other areas where PM<sub>2.5</sub> and PM<sub>10</sub> nitrate measurements may be available. A plot of this coarse nitrate in Figure 18 would be useful. Could some of the nitrate prediction problems be due to the challenges in predicting coarse nitrate? (28) The model predicts high nitrate levels in the southeastern Mediterranean (Figure 6). This is rather unexpected due to the relatively low NO<sub>x</sub> levels and high sulfate concentrations. The values appear to be quite high compared to what has been observed (there are available measurements in Crete). Is this due to dust? How does the model produce so much nitric acid in that area?*

High concentrations of HNO<sub>3</sub> are typically simulated over the Mediterranean Sea due to high emissions of NO<sub>x</sub> and high concentrations of OH. HNO<sub>3</sub> can condense onto both the sea salts and the dusts. As shown in section 3.3.3, total concentrations of nitrate is well represented into the model with high concentrations of nitrate measured at the stations whereas concentrations of ammonium are low.

A coarse nitrate evaluation is added on the ammonium and nitrate section.

*(29) Figures 3, 5, 7, 8, and 9 are quite confusing because they contain too much information and do not have legends. One solution would be to show just the predicted and measured concentrations in these figures and then show the evaluation metrics in the supplementary information. It would be nice to also indicate the number of stations in each area in these figures.*

The big interest of these figures is that they summarize all the results of the models and provide a lot of information on monthly and regional performance. Just putting the mean model and the mean observation would oversimplify the figures. The legend was described in the caption. However, these figures were put in the supplementary materials.

The number of stations in each area is now indicated in Table 6.

*(30) The axes of Figure 10 do not have titles.*

The caption was modified:

“Seasonal factors used in CHIMERE to compute the evolution of NH<sub>3</sub> emissions for several countries. The factors originate from GENEMIS”

*(31) There are several cases with missing data in the time series of Figures 12, 13, etc. These are replaced by lines connecting the existing measurements. This is confusing and may be misleading. There should be gaps in the corresponding lines. Even better symbols could be used instead of lines for the measurements.*

Measurements were intentionally chosen to be represented as lines. Representing measurements as lines make the figure more readable as it can be very difficult to compare lines to lines. Figures were done to be as readable as possible.

*(32) An explanation of what is shown in the QQ scatter plot (Figure 16) is needed.*

An explanation was already present in the text:

“A Quantile-Quantile (QQ) scatter plot of modeling results against measurements for PM<sub>10</sub> and PM<sub>2.5</sub> is shown in Figure 16. QQ plots can be used to assess the similarity of the distribution of two compared datasets.”

The following sentence was added to provide more explanation:

“Fig. 16 shows the quantile of modeled concentrations against the corresponding quantile of measured concentrations.”

*Other issues*

*(33) The use of Na instead of Na<sup>+</sup>, SO<sub>4</sub> instead of SO<sub>4</sub><sup>2-</sup>, etc., throughout the manuscript is problematic and should be avoided.*

Changed.



(34) There are a number of typos that should be corrected. Some of them: Page 7, line 18. NH3 Page 7, line 26, Henr's Page 11, lines 29-20, with strong observed of Na Page 20, line 24, S. et al. (2016) Page 26, lines 4-5. Missing author names. Figure 3, 5, 7, 8, 9 captions. monyhly. Page 46, line 1. PM2.5

Corrected

Anonymous Referee #2 Received and published: 2 August 2017

*The manuscript describes an updated aerosol module for the CHIMERE regional air quality model, along with evaluation of these changes against surface concentration measurements over Europe. The updates cover a number of different processes within the model: emissions, wet deposition, evaporation and condensation of both organic and inorganic semi-volatile components and hygroscopic growth. A set of performance criteria from the literature are adopted and the model is shown to perform well against these. However, while the work itself is a worthy contribution to the field of aerosol modelling for air quality applications, there are a number of deficiencies in the presentation such that I would recommend major revisions before the manuscript is suitable for publication in GMD.*

#### *General comments*

*1. There are a very large number of figures (21), many of them with multiple panels and similar in nature and with dense high-frequency time series that are hard to interpret. This makes it difficult for the reader to discern what are the important results being presented. If this level of detail is necessary for completeness, it would be better placed in supplementary material, and a smaller number of clearer figures used to (i) exemplify the raw data, and (ii) summarise its meaning statistically in a visual form.*

Some figures were moved to the supplementary materials to simplify the document. These figures already summarize statistically the spatial and temporal evolution of the concentrations.

*2. The manuscript presents an updated version of an existing model; however it is frequently unclear how the new schemes described here compare to those used in the reference/baseline version of CHIMERE (Menut et al., 2013) in their formulation and complexity. Corresponding results for the reference version should also be included, in order to assess not only the absolute performance of the revised model, but to what extent the changes described in this manuscript produce improvements in these performance metrics.*

Addressed in the general reply.

*3. In several places in the manuscript, positive and negative biases and larger or smaller errors and correlations are shown at individual stations and over various regions. These may very well be statistically significant variations, however the analysis presented does not adequately demonstrate this.*

The statistics compute here are based on the results of several stations. Mathematically, several stations will have a larger bias and some a lower bias. When statistics differ significantly from the average statistics over a region, the specific results are discussed in the text. That is why every time, the map of MFB for each station was shown along to the seasonal and regional statistics.

Generally, air quality model evaluation studies present statistics over the whole domain without entering into much details.

*Specific comments*

4. Page 1, line 1. This describes a “new” aerosol module, although elsewhere it is clear that this is in fact an update to an existing module; the introductory text should be re-worded accordingly.

It is really a new module has everything has been rewritten (except for the nucleation routine). The text was modified to emphasize on that.

5. Page 1, lines 1–17. It would be good to see some quantitative results quoted in the abstract about the performance of the updated model and how that compares to the reference/baseline version.

Addressed in the general reply.

6. Page 1, line 19–page 2, line 3. The introductory paragraph is quite vague on the subject of why such models are useful, despite the list of model references. A little more background on the motivation for such modelling would be welcome.

The sentence was modified:

“The development of models is necessary to simulate the formation of particles in order to study processes leading to particle formation, to produce air quality forecasting, to evaluate the efficiency of air pollution mitigation strategies and to study the impact of emissions sources on air quality.”

7. Page 2, line 10. What definition of “fine” is being used in this context?

PM2.5. Added.

8. Page 3, line 19–21. An overview of the reference/baseline model version here would be very useful – overall approach and assumptions, what are the tracers used, does it represent the particle size distribution or is it a bulk scheme etc.? This would also make it easier to clarify in the rest of the section how the updated schemes relate to this baseline.

“The model uses a sectional approach where particles are separated into several diameter bins. In this study, particles were separated into 10 bins from 10 nm to 10  $\mu\text{m}$ .”

There is no tracers simulated in this study.

9. Page 3, line 24–page 4, line 10. How does this compare to the chemical mechanism in the baseline version?

Addressed in the general reply.

10. Page 4, lines 13–22. How does this compare to the treatment of biogenic emissions in the baseline version?

Addressed in the general reply.

11. Page 4, line 25. A brief discussion of what these emissions are would be helpful, even if further detail is to be found in the reference.

“VOC emissions (based on the EMEP inventory in this study) are used as in Menut et al. (2013), COV are split into CHIMERE model species according to a speciation database depending on the emission sector.”

12. Page 4, line 25–page 5, line 17. This subsection cites various conflicting studies, but leaves the reader unclear as to what conclusion is drawn for the purposes of this work.

The subsection was reformulated for further clarity. The conflicting works are a justification for why IVOC emissions are not taken into account (contradicting results from various studies).

13. Page 5, line 20–page 6, line 14. How does this compare to the treatment of aerosol thermodynamics in the baseline version?

Addressed in the general reply.

14. Page 6, line 10. A description and/or reference should be provided for the “H<sub>2</sub>O mechanism”.

“As in Couvidat et al. (2012)” replaced by “As in the Hydrophilic/Hydrophobic Organic H<sub>2</sub>O mechanism [Couvidat et al., 2012]”

15. Page 8, line 1–page 9, line 1. How does this compare to the treatment of wet deposition in the baseline version?

Addressed in the general reply.

16. Page 9, lines 3–28. How does this compare to the treatment of condensation/evaporation in the baseline version?

Addressed in the general reply.

17. Page 10, lines 1–8. How does this compare to the treatment of coagulation in the baseline version?

Addressed in the general reply.

18. Page 10, lines 11–12. There are several IFS-based products from ECMWF. Please clarify whether this refers to operational analyses or forecasts, or to one of one of the reanalyses (e.g. ERA-Interim).

Operational analyses. Added.

19. Page 11, lines 7–11. The description of the observations is very brief, and would benefit from being extended – e.g. what type of instruments to these measurements come from, and how extensive is its coverage in space and time? Also, a reference and acronym expansion should be provided for EBAS if possible.

No acronym was found on the website or the publication.

Reference was already present. It is moved for better presentation.

A few details were added:

“Results of the model are compared to various measurements (NO<sub>3</sub><sup>-</sup>, NH<sub>4</sub><sup>+</sup>, SO<sub>2</sub>, Na<sup>+</sup>, Cl<sup>-</sup>, OC, PM<sub>1</sub>, PM<sub>2.5</sub> and PM<sub>10</sub>) available in the EBAS database (Tørseth et al., 2012) from various instruments (i.e. filters, Tapered Element Oscillating Microbalances, beta ray absorption) for regional background stations. The stations cover most of Europe with the first measurements available beginning in the seventies. EBAS is a database hosting observation data of atmospheric chemical composition and physical properties in support of a number of national and international programs ranging from monitoring activities to research projects. EBAS is developed and operated by the Norwegian Institute for Air Research (NILU). This database is mostly populated by the EMEP (European Monitoring and Evaluation Program) measurements”

20. Page 11, lines 23–24. Please explain why this is a likely explanation for the Na and Cl results.

This sentence was removed as this result is not clear enough.

21. Page 13, lines 23–25. *It could also be that a third factor which is poorly captured in the model affects both sulfates and nitrates.*

Indeed nitrate could be a source of error too. The following sentence was added in the text:

“Part of the errors may be also due to errors on  $\text{NO}_3^-$  and  $\text{HNO}_3$  concentrations.”

22. Page 14, line 20. *Please describe and/or give a reference for MELCHIOR 2.*

A reference for Melchior 2 was added.

23. Page 15, line 9. *It is not clear whether “OC concentrations were calculated directly” from the model or from observations. Please clarify.*

Clarified: “modeled OC concentrations were calculated directly from the modeled concentrations of each organic surrogate compounds”

24. Page 16, line 6. *MFB for PM10 is still positive, suggesting coarse particles are still overestimated, just less so than smaller particles.*

No coarse particles are underestimated but PM10 remains overestimated due to the overestimation of PM2.5. We modify the text to compare model PM coarse concentrations directly to the differences between PM10 and PM2.5.

25. Page 17, line 26. *This sounds like the measurements are overestimated, but presumably is intended to say that the model overestimates  $\text{NO}_3$  compared to the measurements?*

Corrected. “Measured” was used instead of “modeled”

26. Page 17, line 34–page 18, line 1. *Please explain why a lack of  $\text{HNO}_3$  condensation is likely to explain this.*

An explanation was added: “with more  $\text{HNO}_3$  condensing onto dust and sea salt, less  $\text{HNO}_3$  will be available to form ammonium nitrate”

27. Page 20, line 23. *A reference to the data referred to here would be good.*

A reference was added.

*Technical corrections*

28. Page 1, line 8 (and elsewhere): *Performances were* → *Performance was*. 29. Page 1, lines 8 and 10 (and elsewhere): *sea salts* → *sea salt*. 30. Page 1, line 15: *most of stations* → *most of the stations*.

Corrected

31. Page 2, line 18: *dusts* → *dust*.

Corrected

32. Page 2, line 24: *aerosols thermodynamics* → *aerosol thermodynamics*.

Corrected

33. Page 3, line 15: *described in which part of the paper?*

Corrected

34. Page 3, lines 25–26: “ $\alpha$ ” should be before “function”, not “partitioning”.

Corrected

35. Page 3, line 28: insert “and” before “equilibrium constants”.

Corrected

36. Page 4, line 14: “temperature” and “solar” should not be capitalised.

Corrected

37. Page 4, lines 16–17: “wilting point” should not be capitalised.

Corrected

38. Page 4, line 20: landuse → land-use.

Corrected

39. Page 5, line 14: vehicle → vehicles.

Corrected

40. Page 5, line 15: aromatics compounds → aromatic compounds.

Corrected

41. Page 9, line 13: Delta →  $\Delta$ .

Corrected

42. Page 9, lines 15 and 17: what is Kn?

The Knudsen number. Description added.

43. Page 9, line 21: insert “in” before “computed with”.

Sentence corrected.

44. Page 9, line 25: CaCO<sub>3</sub> of dusts → CaCO<sub>3</sub> in dust.

Corrected

45. Page 10, lines 12 and 15: “temperature” should not be capitalised.

Corrected

46. Page 10, line 15: “wind speed” should not be capitalised.

Corrected

47. Page 10, line 16: underestimation of the PBL around. . . → underestimation of the PBL height of around. . .

Corrected

48. Page 10, lines 17–18: “boundary conditions” should not be capitalised.

Corrected

49. Page 10, lines 21–22 (and elsewhere): *performances* → *performance*.

Corrected

50. Page 11, line 25: *than* → *as*.

Corrected

51. Page 11, lines 29–30: *observed of Na* → *observed Na*.

Corrected

52. Page 14, line 3: “*summer*” should not be capitalised.

Corrected

53. Page 15, line 19: *criteria is* → *criteria are*.

Corrected

54. Page 15, lines 19–20: *overestimation. . . do not correspond* → *overestimation. . . does not correspond*.

Corrected

55. Page 16, line 18: delete “*the*” before “*Southern Europe*”.

Corrected

56. Page 16, line 24: *PM2.5 are* → *PM2.5 is*.

Corrected

57. Page 16, lines 25, 31–32: “*winter*”, “*spring*”, “*summer*” and “*fall*” should not be capitalised. Also, please use either “*fall*” or “*autumn*” consistently throughout – both appear in the manuscript.

Corrected

58. Page 16, line 32: *due to mostly to* → *due mostly to*.

Corrected.

59. Page 17, lines 20–23. This sentence is confusing, with two consecutive “*but*” clauses and multiple parentheses. Consider breaking it up to clarify the meaning.

Corrected

60. Page 17, line 27: *faction* → *fraction*.

Corrected

61. Page 18, line 14: “*April*” and “*August*” should be capitalised.

Corrected

62. Page 18, line 31: *could be explain* → *could be explained*.

Corrected

63. Page 19, line 4: *emissions is* → *emissions are*.

Corrected

64. Page 20, line 13: *inorganics aerosol* → *inorganic aerosol*.

Corrected

65. Page 20, line 24: the “*S. et al*” citation should have a full surname, not just an initial. (The same applies to all authors in the corresponding bibliography entry.)

Corrected.

66. Page 21, line 9: *dynamic* → *dynamics*.

Corrected

67. Page 21, line 14: “*CHIMERE*” should be capitalised as elsewhere in the manuscript.

Corrected

*Anonymous Referee #3*

*Received and published: 22 August 2017*

*This manuscript presents an update of the CHIMERE’s aerosol module. The chemical mechanism was modified for the formation of the secondary organic aerosol precursors. The equilibrium between the aerosol and the gas phase is then treated using the module SOAP. For the secondary inorganic aerosols, the thermodynamic equilibrium is computed using ISORROPIA, which has been updated to the version 2.1 here. Biogenic emissions have been updated and are now computed using MEGAN 2.1. Belowcloud scavenging has also been updated. After a presentation of the model CHIMERE and the aerosol module, the developments are validated over the year 2013 using surface measurements from the EBAS database by separating Europe into 5 coherent sub-regions based on country borders. The authors give some recommendations for paper future development. Finally the manuscript ends with a conclusion. This manuscript is interesting for the aerosol community as it presents recent features in aerosol modelling. However, it presents some serious issues for a publication as it is. The manuscript presents a new aerosol module (cf. abstract), but otherwise in the text it is treated as an update of the existing module. It is sometimes difficult to differentiate the parametrization and developments related to the 2013 version from the new 2017 version. The authors need to be clearer about this point that highlights the important development work done here. I would recommend to present the 2013 version of the parametrizations before introducing the new features. Following this remark, there is no comparison between the 2013 and 2017 versions over the year 2013. It would be very interesting to see the evolution in the performance of the model between the two versions.*

It is indeed a new module. This point is addressed in the general comments.

*The comparison to the observation set is very interesting as it uses a lot of collocated information on several measuring stations. It is then possible to evaluate the aerosol load, but also the aerosol composition and the seasonality. All these pieces of information could point out easily the strengths and the weaknesses of the model. However the authors only use ground based stations. It would have been interesting to compare the simulation to vertically integrated measurements such as aerosol optical depths, especially to evaluate the impact of the changes on wet deposition.*

Ongoing works are carried out on deposition which will have its specific evaluation. Indeed, comparing to aerosol optical depths present many interests and coupling this to the analysis of wet deposition

could be very useful. However, it was chosen in this study to concentrate on ground based stations (because of the huge amount of work) to evaluate the capacity of the model to simulate composition of particle.

*Also, almost all the mathematical formulations need to be reviewed. There are for example undefined variables used in equations or discrepancies between the name of a variable in the text and in an equation. I would then recommend major revisions before publication.*

Equations were revised.

*General comments:*

*1. The use of paragraph breaks is sometimes puzzling, for example on page 13. This sentence might make think that the next paragraph does not refer to the figures 7 and 8, which is not the case.*

Corrected.

*2. Page 2 line 2: I do not understand the presence of the "Vestreng, 2003" reference for the air quality model.*

Bug inside bibtex. Corrected.

*3. Section 2.1.1: Maybe a table that summarizes the reaction rate for the oxidation of SO<sub>2</sub> in clouds could be useful.*

The reactions were added in the text.

*4. Section 2.1.3: I didn't understand how are the anthropogenic emissions managed for the POA and SVOC. You use POA emissions from an emission inventory. These POA are emitted into the species POAIP, POAmP and POAhP. Then you use the quantity of POA emitted to emit the SVOC by saying that SVOC = 5 \* POA and say that you don't take into account the IVOC. Is this right? How are then the SVOC emitted into the MELCHIOR species?*

POA are transformed into SVOC and the SVOC are splitted into POAIP, POAmP and POAhP. POA emissions are transformed into POAIP, POAmP, POAhP emissions. The text is modified to improve clarity:

"In this study, POA are transformed into SVOC emissions: a SVOC/POA of 5 is used for residential emissions (without adding IVOC emissions and assuming that POA emissions only account for 20% of emissions) and 1 for the other sectors (assuming therefore that no SVOC emissions from other sectors are missing).

For each sector, emissions of SVOC are splitted into emissions of POAIP (25% of emissions), POAmP (32% of emissions) and POAhP (43% of emissions) to follow the dilution curve of POA in Robinson et al., 2007."

These species do not correspond to MELCHIOR species. They are added and are assumed to not impact OH radical and therefore the gas chemistry. The text is modified to emphasize on that.

*5. Page 6 line 4: I understand the dynamic method requires a lot of computation time explaining you choices. But did you run a test to know the impact it could have on a specific test-case for example?*



This is undergoing work that should be published soon. This particular method requires a lot of CPU time (increase of a factor 10) and the effect of such a method on concentrations is a study in itself.

6. Page 7, line 1: *pleas also add "the mass fraction of respectively the solid phase, the aqueous phase and the organic phase in the particle" for a better understanding.*

Added.

7. Section 2.1.6: *The title is "Dry deposition of particles and semi-volatile organic species" but you talk about other gaseous species such as O<sub>3</sub>, SO<sub>2</sub>, etc. Please change the text to be consistent.*

Corrected.

8. Section 2.2: *When talking about the simulation set-up, you don't talk about the vertical resolution of the simulation made. Please add these informations.*

Corrected.

9. Page 10, line 18: *You wrote "Boundary Conditions were generated from [...]". Could you explain how they were generated?*

The text is modified:

"Boundary conditions were generated from the results of the Model for OZone And Related Tracers (MOZART v4.0) available online on <https://www.acom.ucar.edu/wrf-chem/mozart.shtml>."

10. Section 2.3: *This part is too small. Could you please add a table with the total number of stations and the number of stations in each of the regions you defined. According to Fig. 1 there are no stations for western Europe. Could you please explain why? Also, please add the link to the EBAS database in the text.*

A link for EBAS and some information were added.

Fig 1. Shows only the stations that are referred in the text. These stations are mostly stations with measurements of OC. No particular station in western Europe was discussed in text (mostly because there are no OC measurements).

The number of stations in each area in now indicated in Table 6.

11. Page 11, line 19: *You wrote "Only one station in Spain underestimates [...] concentrations for Na." while on Fig. 1 there are three blue triangles.*

Corrected. "Concentrations for Na<sup>+</sup> are underestimated significantly for only one station in Spain (along the Bay of Biscay)"

12. Page 11, line 29: *You talk about the station ES0008R, but without showing any figures. Also this sentence is hard to understand.*

The sentence was reformulating. A figure was added in supplementary Materials.

13. Page 12 line 2: *"The other stations [...] the opposite trend". I do not understand which other stations? All the stations or the other stations from southern Europe? Could you please make this part clearer?*

The sentence was reformulated:

"Except from ES0008R, the stations of Southern Europe share the same pattern shown"

14. Section 3.2: You are talking about sulfate observations. But are you using "total sulfate" or "corrected sulfate" (or non sea salt sulfate) measurements?

We use non-corrected measurements (so the "true" sulfate measurements) as sea salt sulfate is taken into account in the model.

15. Page 14, line 23: I do not understand how an overestimation of NH<sub>3</sub> emissions could induce an overestimation of TNO<sub>3</sub>. Could you please explain it with more details?

"because the deposition velocities of these gases are generally higher than those of particles" was added to the explanation.

16. Section 3.3.1: How many measurements do you have for each stations in Table 6? it seems that some stations have very few measurements points, e.g. CH0002R looks like to have around 10 points. What is the confidence in the statistics you can have in this case?

Statistics are weighted by the number of measurements points. A station with a low number of point will a low weight and therefore has a low impact on the statistics.

17. Page 16, line 16: "especially in the Alps". How is the relief represented in the model in this area? Can it explain the overestimation of the PM by the model? Maybe you could try to interpolate the model at the altitude of the stations to improve the comparison made.

The model doesn't really take into account the relief. That is a classic problem for 3D air quality models that runs at such a coarse resolution and yes it should be one of the main reason explaining the overestimation.

We try to interpolate according to the altitude but it didn't really improve the results. The best way to handle this problem would be run the model with a high resolution.

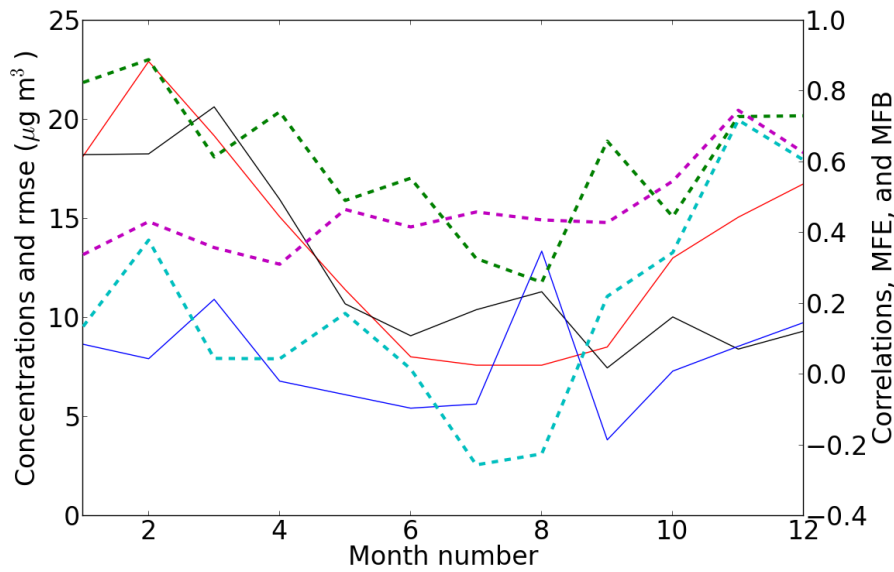
The following sentence was added to the text:

"The overestimation over the Alps is probably due to difficulties in reproducing the complexity of mountainous meteorology for a model with such a coarse resolution."

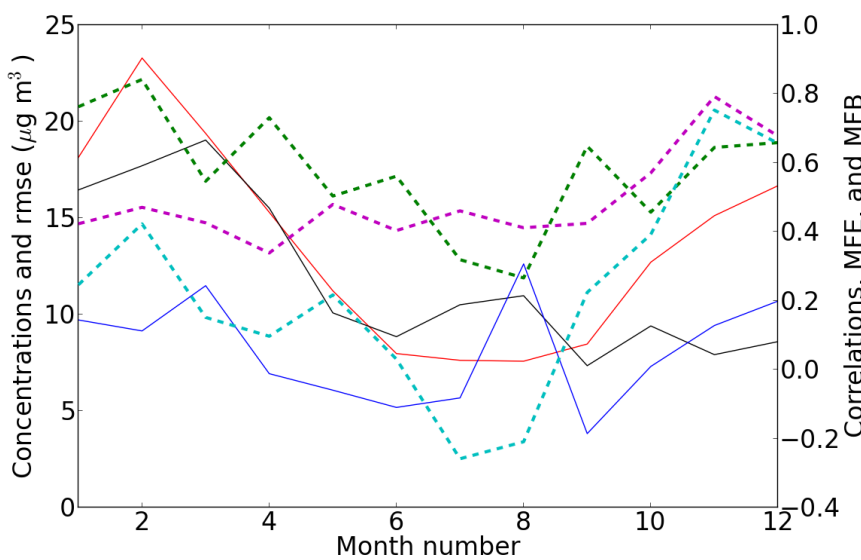
18. Page, line 30: What is the effect of the strong overestimation over the Alps on the results of Fig. 15 and 17 for central Europe?

The effect is quite low. For example, we removed the 3 stations for PM<sub>2.5</sub> over Alp that are overestimated. The results are illustrated below. The RMSE and the MFB are a bit lower but the results are similar.

Without the 3 stations



With the stations



19. Section 3.3.3: You talk about Ca and NO<sub>3</sub> in PM<sub>10</sub>, but in Fig. 18 there is "total Ca" and "total NO<sub>3</sub>". Are these two quantities supposed to be the same? Please change the text to be clearer.

Total replaced by "in PM<sub>10</sub>"

Figure related comments:

1. The manuscript preparation guidelines for authors claims that: The abbreviation "Fig." should be used when it appears in running text and should be followed by a number unless it comes at the beginning of a sentence, e.g.: "The results are depicted in Fig. 5. Figure 9 reveals that...". Please check that the right word is used in the text.

Corrected.

2. Also the authors should check the legend of their figures that are not always satisfactory. For example, the legend of the first figure does not mention what are the measuring station marked by dots.

Corrected.

3. Concerning the time series, it seems that there are missing values in the observations linked by a segment in the figures (e.g. On Fig. 12 between Feb and Mar 2013 for GR0002R). This can be misleading for the interpretation of the figure. Could you please change this? Maybe you could use symbol for the measurements and have continuous line for the simulation results.

Measurements were intentionally chosen to be represented as lines. Representing measurements as lines make the figure more readable as it can be very difficult to compare lines to plots. Figures were done to be as readable as possible.

4. Figure 2, 4, 6, 11 and 14: These figures does not seem to be complete on the right side for negative numbers. What represent the squares on these figures?

Corrected.

Squares were modified by triangles.

5. Figure 3, 5, 7, 8, 9, 15, 17: Is it possible to have slightly thicker lines? Is it possible to draw a line for 0 in order to read more easily some quantities such as the MFB.

Based on the other reviews, these figures were moved to the Supplementary because they are quite difficult to read.

6. Figure 3: All your sub figures does not have the same size or position.

Corrected

7. Figure 12 and 13: All your sub figures does not have the same size.

Corrected

8. Figure 13: There seems to be a mistake. I think "CH0005R" should be "CY0002R".

The Cyprus station was missing. Corrected.

9. Figure 16: The figure for PM2.5 is very small. Is it possible to enlarge it?

Changed.

Table related comments:

1. Table 2, line "BiDer": hydrohilic -> hydrophilic.

Corrected.

2. Table 2: for the type you mention type A, B and C, but in the table you only write hydrophilic or hydrophobic. Please explain this a little more.

Removed.

3. Table 4: What are the Henry's law constant used for the other species such as HNO3?

"High numerical values were used for HNO<sub>3</sub> and for gaseous H<sub>2</sub>SO<sub>4</sub> to take into account their hydrophilic properties." Was added in the caption of the table.

4. Page 14, line 8: Please add a reference to Table 5 when talking about TNO<sub>3</sub> and TNH<sub>4</sub>.

Added

5. Table 5 presents results for O<sub>3</sub> and NO<sub>2</sub> but you never talk about them in the text.

Removed from the table.

*Technical comments (when a letter or a word is missing, it is in bold in the comment):*

1. Page 3, line 15: I guess the word "first" is missing in the sentence.

Corrected.

2. Page 5, line 19: "Thermodynamic of Secondary organic and [...]" -> "Thermodynamic of secondary organic and [...]"

Corrected.

3. Section 2.1.5: the symbols *w* are different but refers to the same quantity. So are *d* and *d*. There is also a discrepancy between *dsol* and *dsolid*.

Corrected.

4. Page 7, line 9-12: *F<sub>d, i</sub>* is different from *F<sub>dry, i</sub>*. Same for *v<sub>d, i</sub>*, *v<sub>d</sub>* and *v<sub>d, i</sub>*. What represents *C<sub>i</sub>*?

Corrected.

5. Page 7, line 25: *peau* and *ρ*. What is *Meau*? Does *H<sub>i</sub>* stand for the Henry's law constant?

Corrected.

6. Page 7, line 26: Henry's law.

Corrected

7. Page 9, line 12: there is no verb in the sentence.

Corrected

8. Page 9, Eq. 18: What is *P*?

Added. Precipitation rate in mm/h.

9. Page 9, Eq. 19: Delta ->  $\Delta$ , *k bin* -> *k bin i*

Corrected

10. page 9, Eq. 20: What is *R* and *T*?

Added

11. Page 9, Eq. 21: Delta ->  $\Delta$

Corrected

12. Page 10, line 2: *J bin coag, i* and *J b coag, i*

Corrected

13. page 10, Eq. 23:  $K_{j,k}$  instead of  $K_{j,l}$ . What is  $A_{p,i}$ ? The second sum symbol does not have attribute. Is the sum going from 1 to b over j?

Corrected

14. Page 10, line 13: Wind Speed -> wind speed (also line 15).

Corrected

15. Page 10, line 13: Planetary Boundary Layer (PBL) -> planetary boundary layer (PBL).

Corrected.

16. Page 10, line 15: Temperature -> temperature.

Corrected

17. Page 10, line 18: Mozart -> MOZART.

Corrected.

18. Page 10, line 18: "Boundary Conditions" -> "boundary conditions"

Corrected

19. Page 11, line 5: Figure 1 -> Fig. 1.

Corrected.

20. Page 12 line 17: Tsyro et al. (2011) and Neumann et al. (2016).

Corrected.

21. Page 15, line 11: "OM/OC simulated" -> "OM/OC ratio simulated".

Corrected

22. Page 15, line 29: "summer concentrations are underestimated in summer". Summer is written twice.

Corrected

23. Page 16, line 18: "PM2.5 and PM10, respectively" -> "PM2.5 and PM10 respectively", no comma.

Corrected

24. Page 18, line 9: "Figure 12" -> "Fig. 13".

Corrected.

25. Page 19, line 9: "to take into IVOC emissions", it seems that a word is missing here.

Corrected.

# Development of an inorganic and organic aerosol model (CHIMERE 2017 $\beta$ v1.0): seasonal and spatial evaluation over Europe

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## Abstract.

A new aerosol module was developed and integrated in the air quality model CHIMERE. Developments include ~~an update of biogenic emissions and the use of MEGAN 2.1 for biogenic emissions, the implementation~~ of the inorganic thermodynamic model ISORROPIA 2.1, revision of wet deposition processes and of the algorithms of condensation/evaporation and coagulation and the implementation of the SOA mechanism H<sup>2</sup>O and the thermodynamic model SOAP.

Concentrations of particles over Europe were simulated by the model for the year 2013. Model concentrations were compared to the EMEP program observations and other observations available in the EBAS database to evaluate the ~~performances~~ performance of the model. Performances were determined for several components of particles (sea ~~salts~~salt, sulfate, ammonium, nitrate, organic aerosol) with a seasonal and regional analysis of results.

The model gives ~~good performances~~ satisfactory performance in general. For sea ~~salts~~salt, the model succeeds in reproducing the seasonal evolution of concentrations for Western and Central Europe. For sulfate, except for an overestimation of sulfate in Northern Europe, modeled concentrations are close to observations ~~with a good~~ and the model succeeds in reproducing the seasonal evolution of concentrations. For organic aerosol, the model ~~performs well~~ reproduces with satisfactory results concentrations for stations with strong modeled biogenic SOA concentrations.

However, the model strongly overestimates ammonium nitrate concentrations during late autumn (possibly due to problems in the temporal evolution of emissions) and strongly underestimates ~~SOA~~ summer organic aerosol concentrations over most of ~~the~~ stations (especially in the Northern half of Europe). This underestimation could be due to a lack of anthropogenic SOA ~~in the model~~ or biogenic emissions in northern Europe.

A list of recommended tests and developments to improve the model is also given.

## 1 Introduction

Atmospheric Particulate Matter (PM) contributes to adverse effects on health and ecosystems. The development of models is necessary to ~~predict the formation of particles estimate exposure~~ in order to ~~evaluate their concentrations and to evaluate mitigation strategies~~ produce air quality forecasting (Rouil et al., 2009), to evaluate the efficiency of air pollution mitigation strategies (Schucht et al., 2015) and to study the impact of emissions sources on air quality. However, developing models with enough precision is quite challenging due to the complexity and variety of phenomena and the great number of chemical species involved. Numerous air quality models have been developed to simulate PM concentrations (~~Emmons et al., 2010; Pozzoli et al., 2011; Zhang et al., 2010; Simpson et al., 2012; Carlton et al., 2010; Menut et al., 2013; Sartelet et al., 2010; Pozzoli et al., 2011; Zhang et al., 2010; Simpson et al., 2012; Carlton et al., 2010; Menut et al., 2013; Sartelet et al., 2010~~).

PM is constituted of various chemical species: organic matter (OM), elemental carbon (EC) mainly originating from anthropogenic sources, major inorganic components (ammonium, nitrate and sulfate), sea salt, mineral dust and other crustal compounds. These species originate from numerous emission sources which can be natural (biogenic emissions from vegetation, sea-salt emissions, dust emissions) or anthropogenic (for example emissions from residential biomass burning, road traffic, agriculture, industrial sources). Particles can be primarily emitted in the atmosphere or secondary formed from chemical reactions.

OM typically represents between 20 and 60% (Kanakidou et al., 2005; Yu et al., 2007; Zhang et al., 2007) of the fine particulate mass ( $\text{NH}_3$ ) and is formed via the partitioning of Semi-Volatile Organic Compounds (SVOC) between the gas and particle phases. These SVOCs can be primary in origin but OM is often considered to be mainly constituted of secondary organic compounds formed via the oxidation in the atmosphere of Volatile Organic Compounds (VOC) which can be biogenic (like isoprene, monoterpenes and sesquiterpenes) or anthropogenic (for example long-chain alkanes, toluene and other aromatics). The oxidation (in the gas phase or in the aqueous phase) of sulfur dioxide  $\text{SO}_2$  produces sulfuric acid  $\text{H}_2\text{SO}_4$  which leads to sulfate formation via condensation or nucleation processes. If ammonia  $\text{NH}_3$  is present in the atmosphere, it will neutralize sulfate and form ammonium. If there is still  $\text{NH}_3$  available in the gas phase, it can lead to the formation of ammonium nitrate in the presence of nitric acid  $\text{HNO}_3$  (formed via the oxidation of nitrogen oxides  $\text{NO}_x$ ). Sea ~~salts and natural dusts~~ salt and natural dust are primary natural particles and can interact with atmospheric pollutants. For example,  $\text{HNO}_3$  can condense onto sea salts salt and leads to sodium nitrate and then to the volatilization of chloride acid (HCl). Similarly,  $\text{HNO}_3$  can condense onto dust particles and leads to the formation of calcium nitrate. As dust and sea salts salt are mainly coarse particles, these two processes can lead to the formation of coarse nitrate whereas ammonium nitrate will mainly remain in fine particles.

To simulate PM concentrations, models have to take into account the microphysics of particles (condensation/evaporation, coagulation, nucleation), chemical mechanisms for the gas-phase chemistry, aerosols aerosol thermodynamics, emissions and deposition processes. In the scope of this study, a new aerosol module has been developed in a modified version of the CHIMERE model. ~~These modifications include an update of biogenic emissions and microphysics parameterizations, the implementation of thermodynamics model ISORROPIA v2.1 (Fountoukis and Nenes, 2007) and SOAP (Couvidat and Sartelet, 2015), the SOA mechanism of Couvidat et al. (2012) and modifications of deposition parameterizations. This new model version is~~



referred hereafter as CHIMERE 2017 $\beta$ . The results of the model were evaluated by comparison to measurements of PM<sub>2.5</sub> and PM<sub>10</sub> concentrations but also of composition (Cl, Na<sup>+</sup>, SO<sub>4</sub><sup>2-</sup>, NO<sub>3</sub><sup>-</sup>, NH<sub>4</sub><sup>+</sup>, SO<sub>4</sub>, NO<sub>3</sub>, NH<sub>4</sub>, organic carbon).

~~The representation of several processes was revised to improve the results of the model~~ The aerosol module include the following processes:

- 5     – Biogenic emissions are computed with the MEGAN 2.1 algorithm (Guenther et al., 2012) with ~~updated~~ high resolution emission factors and Leaf Area Index (LAI) data.
- Below-cloud scavenging is represented as in Henzing et al. (2006) with a polydispersed distribution of cloud droplets (providing a distribution of droplet diameter as a function of rainfall). In-cloud scavenging is represented with the algorithm of Croft et al. (2010).
- 10    – Evaporation/condensation of semi-volatile species is represented with the algorithm of Pandis et al. (1993) using thermodynamic equilibria. Coagulation of particles is represented as in Debry et al. (2007). Thermodynamic equilibria are computed with the ISORROPIA II model (Fountoukis and Nenes, 2007) for inorganic compounds and with the Secondary Organic Aerosol Processor SOAP (Couvidat and Sartelet, 2015) for organic compounds. ~~The CHIMERE 2013 version used an older version of ISORROPIA 2.1 and a model for organic aerosol based on Pun et al. (2002).~~ H<sub>2</sub>SO<sub>4</sub> nucleation is based on Kulmala and Pirjola (1998) for sulfuric acid nucleation is used.
- 15    – The SOA formation mechanism of Couvidat et al. (2012) is used for toluene, xylene and biogenic VOC. ~~The CHIMERE 2013 version used the mechanism of Bessagnet et al. (2008).~~
- The amount of water in particles is calculated as a function of humidity and the composition of particles using ISORROPIA. This amount is used to calculate the wet density of particles (with water) and the wet diameter of particles which are used to compute the kinetics of absorption, coagulation and deposition ~~instead of the dry values as in Menut et al. (2013).~~
- 20

The aerosol module is described in the part “Model development” of the paper. The second part focuses on the comparison of modeled concentrations with observations for Cl<sup>-</sup>, Na<sup>+</sup>, SO<sub>4</sub><sup>2-</sup>, NO<sub>3</sub><sup>-</sup>, NH<sub>4</sub><sup>+</sup>, Na, SO<sub>4</sub>, NO<sub>3</sub>, NH<sub>4</sub>, organic carbon, PM<sub>2.5</sub> and PM<sub>10</sub> with a regional and seasonal ~~analyses~~ analysis of results.

## 25    **2 Method**

The CHIMERE 2017 $\beta$  is based on the CHIMERE 2013 version (Menut et al., 2013) ~~was modified to update some parameterizations which is modified by implementing the new aerosol module~~ and chemical mechanisms. ~~The modified version of CHIMERE Table S1 in Supplementary Materials provide a comparison of algorithms between Chimere 2017 $\beta$  with Chimere 2013 to illustrate the differences between the two versions.~~ CHIMERE2017 $\beta$  was then evaluated for the simulation of PM concentration and composition over Europe in 2013.

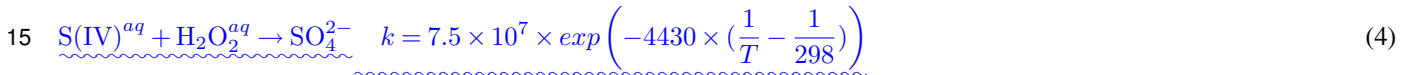
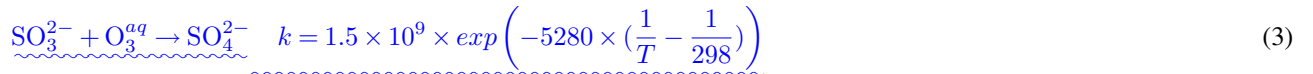
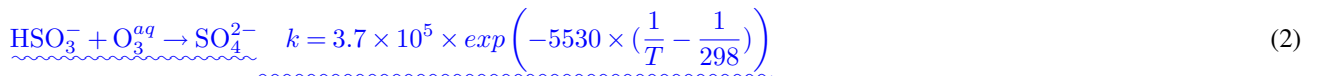
30

The model uses a sectional approach where particles are separated into several diameter bins. In this study, particles were separated into 10 bins from 10 nm to 10  $\mu\text{m}$ .

## 2.1 Model development

### 2.1.1 Chemical mechanisms

- 5 A simple aqueous-phase chemical mechanism is used for sulfate formation from the oxidation of  $\text{SO}_2$  in clouds. This mechanism assumes that the aqueous-phase concentrations of  $\text{SO}_2$ ,  $\text{H}_2\text{O}_2$  and  $\text{O}_3$  are at equilibrium with the gas phase with a partitioning being a function of pH for  $\text{SO}_2$ . The pH of clouds is computed by taking into account the absorption and dissociation of various acids ( $\text{H}_2\text{SO}_4$ ,  $\text{HCl}$ ,  $\text{HNO}_3$  and  $\text{H}_2\text{CO}_3$ ) and the formation of  $\text{NH}_4^+$ . The effect of dust on pH is not taken into account as composition of dust is not represented within CHIMERE. The electroneutrality equation is solved with the Newton-Raphson method. Henry's law constants and equilibrium constants are taken from Seinfeld and Pandis (1998). The following reactions are taken into account:



with  $\text{O}_3^{aq}$  the concentration of  $\text{O}_3$  in the aqueous-phase,  $\text{H}_2\text{O}_2^{aq}$  the concentration of  $\text{H}_2\text{O}_2$  in the aqueous-phase,  $\text{SO}_2^{aq}$  the concentration of  $\text{SO}_2$  in the aqueous-phase,  $\text{HSO}_3^-$  and  $\text{SO}_3^{2-}$  are respectively the concentration of the bisulfite and sulfite ions (at equilibrium with  $\text{SO}_2^{aq}$ ),  $\text{S(IV)}^{aq}$  corresponds to the total of  $\text{SO}_2^{aq}$ ,  $\text{HSO}_3^-$  and  $\text{SO}_3^{2-}$ ,  $T$  the temperature and the kinetic rate parameter in  $\text{M}^{-1} \text{s}^{-1}$ .

- 20 For SVOC formation that leads to the formation of SOA compounds after partitioning, the mechanism of Couvidat et al. (2012) is used. The mechanism is shown in Table 1. It takes into account the formation of SVOC from biogenic (isoprene, monoterpenes, sesquiterpenes) and anthropogenic precursors (toluene, xylenes) under high- $\text{NO}_x$  and low- $\text{NO}_x$  conditions.

- In Following Couvidat et al. (2012), Primary Organic Aerosols (POA) are assumed to be SVOC and are split into three compounds POAIP, POAmP ( $K_p = 1.1 \text{ m}^3/\mu\text{g}$ ), POAhP ( $K_p = 0.00031 \text{ m}^3/\mu\text{g}$ ) having respectively a low, medium and high volatility to follow the dilution curve of POA in Robinson et al. (2007). The aging of these compounds is also taken into account with a reaction with OH which leads to less volatile compounds SOAIP, SOAmP and SOAhP via the following reactions:





with  $k$  the kinetic rate constant equal to  $2 \times 10^{-11}$  molecules<sup>-1</sup>.cm<sup>3</sup>.s<sup>-1</sup>. Oxidants are present as both reactants and products so that a reaction added to the mechanism will not affect the original photochemical oxidant concentrations. Following Grieshop et al. (2009), aging was-is assumed to lead to a decrease of volatility by a factor 100 (SOAIP, SOAmP and SOAhP are respectively less volatile by a factor 100 than POAIP, POAmP and POAhP). Properties of these species are summarized in Table 3.

### 2.1.2 Biogenic emissions

Biogenic emissions are computed with the Model of Emissions and Gases and Aerosols from Nature MEGAN 2.1 algorithm (Guenther et al., 2012), which was-is implemented in CHIMERE. It uses meteorological conditions (Temperature, Solar temperature, solar radiation and soil moisture), the Leaf Area Index and the Plant Functional Type (PFT) to compute biogenic emissions. In this study, the above-canopy model is used. The effect of soil moisture on isoprene emissions is-are not taken into account because of no Wilting-Point-wilting point (i.e. the soil moisture level below which plants cannot extract water from soil) database are available over Europe. Therefore, isoprene emissions may be overestimated during dry periods.

High spatiotemporal data (30 arc-seconds every 8 days) generated from MODIS (Yuan et al., 2011) were-are used for LAI inputs. The 30 arc-seconds USGS (US Geophysical Survey) landuse-database-was-land-use database is used to provide information on the plant functional type. The PFT was-is then combined with the emissions factors for each functional type of Guenther et al. (2012) to compute the landscape average emissions factors.

### 2.1.3 Anthropogenic emissions

VOC emissions (based on the EMEP inventory in this study) are used as in Menut et al. (2013) except-for-, volatile organic compounds are split into CHIMERE model species according to a speciation database depending on the emission sector.

For primary SVOC emissions, a SVOC/POA factor is applied to convert POA emissions into SVOC emissions. In Couvidat et al. (2012), a SVOC/POA factor of 5 was used on the basis that SVOC primary emissions were-are underestimated. With this factor, the model was able to simulate the strong concentrations of organic aerosols in winter and to give satisfactory results over most of Europe. Denier van der Gon et al. (2015) has shown that POA emissions are greatly underestimated due to a strong underestimation of residential wood burning emissions by a factor 3 over Europe (between 1 and 10 depending on the countries) if SVOC emissions are included. This strong underestimation of emissions is due to the use of filter at high temperature (for which SVOC are mainly present as vapors) for emission factor measurement. This result is confirmed by

May et al. (2013) who found that 80% of SVOC evaporate at high temperature. By correcting POA emissions and assuming that Intermediate-Volatility Organic Compounds (IVOC) are missing from the inventory (with the assumption that IVOC emissions are equal to 1.5 POA emissions), ~~the authors~~ Denier van der Gon et al. (2015) obtained satisfactory results in winter but still with an underestimation of OM from biomass burning. The authors used therefore a total (IVOC+SVOC)/POA factor of 5 7.5.

In this study, POA are transformed into SVOC emissions: a SVOC/POA of 5 is used for residential emissions (without adding IVOC emissions and assuming that POA emissions only account for 20% of emissions) and 1 for the other sectors (assuming therefore that no SVOC emissions from other sectors are missing). For each sector, emissions of SVOC are split into emissions of POAIP (25% of emissions), POAmP (32% of emissions) and POAhP (43% of emissions) to follow the dilution curve of POA in Robinson et al. (2007). A sensitivity analysis of the SVOC/POA ratio was already performed by Couvidat et al. (2012)

However, IVOCs are not taken into account because of the large uncertainties on their emissions and their oxidation mechanism. Pye and Seinfeld (2010) used naphthalene as a surrogate for IVOC and used the yields from smog chamber experiments (Chan et al., 2009; Kautzman et al., 2010) to develop a mechanism of IVOC oxidation. The authors found that only minor concentrations of SOA are formed from IVOC (only 5% of total OM) whereas Zhao et al. (2016a) simulated strong concentrations of SOA from IVOC contributing to half the ~~OA-OM~~ over China. However, Pye and Seinfeld (2010) argued that naphthalene may not be an appropriate choice for the surrogate species. Platt et al. (2013) investigated the SOA formation from gasoline ~~vehicle-vehicles~~ in an environmental reaction chamber and found that only a small part of SOA could be explained by the oxidation of ~~aromatics-aromatic~~ compounds and therefore most of the SOA formation could be attributed to the oxidation of IVOC. This result is however contradicted by Nordin et al. (2013) who found that most of the SOA formation is due to the oxidation of ~~aromatics-aromatic~~ compounds.

#### 2.1.4 Thermodynamic of ~~Secondary-secondary~~ organic and inorganic aerosol

Two thermodynamic modules ~~were-are~~ implemented inside CHIMERE to take into account the formation of secondary aerosols: ISORROPIA v2.1 (Fountoukis and Nenes, 2007) for inorganic aerosols and the Secondary Organic Aerosol Processor (SOAP) (Couvidat and Sartelet, 2015) for organic aerosols. Due to the lack of information on the dust composition, crustal elements are not taken into account for the partitioning whereas it can strongly impact the formation of ammonium nitrate (Ansari and Pandis, 1999; Moya et al., 2002). However, a simple reaction (described in section "Condensation/evaporation") is added to CHIMERE to take into account the formation of calcium nitrate as done by Hodzic et al. (2006).

SOAP computes the partitioning of organic compounds between the gas and particle phases according to the complexity required by the user. It uses the molecular surrogate approach in which surrogate compounds are associated with molecular structures to estimate several properties and parameters (hygroscopicity, absorption into the aqueous phase of particles, activity coefficients and phase separation). Each surrogate can be hydrophilic (condenses only into the aqueous phase of particles), hydrophobic (condenses only into the organic phases of particles) or both. Activity coefficients are computed with the UNIFAC

(UNIversal Functional group Activity Coefficient; Fredenslund et al. (1975)) thermodynamic model for short-range interactions and with the Aerosol Inorganic-Organic Mixtures Functional groups Activity Coefficients (AIOMFAC) parameterization for medium- and long-range interactions between electrolytes and organic compounds (Zuend et al., 2008, 2011; Zuend and Seinfeld, 2012; Ganbavale et al., 2015).

5 SOAP can simulate SOA formation with either an equilibrium representation or a dynamic representation of organic aerosol condensation processes. The dynamic representation takes into account the condensation/evaporation kinetic of organic compounds and their diffusion in the particle by dividing the organic particle into several layers. However, this method requires a lot of computing time. Therefore, in a first approach, the equilibrium approach of SOAP is used.

As in [Couvidat et al. \(2012\)](#) the [Hydrophilic/Hydrophobic Organic H<sup>2</sup>O mechanism \(Couvidat et al., 2012\)](#), SOA surrogate  
 10 compounds are assumed to be either hydrophilic or hydrophobic and the impact of medium-range and long-range interactions on activity coefficients are not taken into account. For hydrophilic acids, SOAP takes into ~~accounts for~~ [account](#) the dissociation of organic acids at high pH as a function of their dissociation constant. Moreover, Pun and Seigneur (2007) developed a parameterization to take into account the impact of pH on the oligomerization of aldehyde compounds by computing an effective Henry's law constant:

$$H_{eff} = H \left( 1 + 0.1 \left( \frac{a(H^+)}{10^{-6}} \right)^{1.91} \right) \quad (8)$$

15 where  $H_{eff}$  is the effective Henry's law constant of BiA0D (surrogate species of the H<sup>2</sup>O mechanism for aldehydes formed from the oxidation of monoterpenes),  $H$  is the monomer Henry's law constant of BiA0D, and  $a(H^+)$  is the activity of protons in the aqueous phase.

Thermodynamic properties of biogenic and anthropogenic species are shown in Tables 2. Table 3 shows the properties of primary SVOC compounds (POAIP, POAmP, POAhP) and their aging products.

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### 2.1.5 Computation of the wet diameter and the wet density of particles

Several parameterizations (condensation/evaporation, coagulation, particle deposition) depend on the particle diameter  $D_{p,wet}$  which is different from the dry diameter (without water)  $D_{p,dry}$ . Similarly, dry deposition of particles depends on the wet density  $d_w$  of particles.

25 To compute the wet diameter  $D_{p,wet}$  and the wet density  $d_w$ , ISORROPIA is used to compute the amount of water absorbed by each size bin as a function of the composition and the relative humidity. The method of Semmler et al. (2006) is used to compute the density of the liquid aqueous phase  $d_l$ . The volume of the whole particle is computed with:

$$V_{tot} = V_{solid} + V_{liq,inorg} + V_{org} \quad (9)$$

With  $V_{tot}$  the volume of the whole particle,  $V_{solid}$  the volume of the solid part of the particle (including dust, black carbon),  
 30  $V_{liq,inorg}$  the volume of the aqueous phase (including ~~Na, Cl, SO<sub>4</sub>, NH<sub>4</sub>, NO<sub>3</sub>~~ [+, Cl<sup>-</sup>, SO<sub>4</sub><sup>2-</sup>, NH<sub>4</sub><sup>+</sup>, NO<sub>3</sub><sup>-</sup>](#) and H<sub>2</sub>O) and  $V_{org}$

the volume of the organic phase of particles. For simplification purposes, the organic phase density is assumed to be equal to 1300 kg/m<sup>3</sup> and the density of the aqueous phase is assumed to be not influenced by hydrophilic organic compounds.

Using the density of the solid phase  $d_{solid}$  (assumed to be equal to 2200 kg/m<sup>3</sup>), the density of the liquid aqueous phase  $d_l$  and the density of the organic phase  $d_{org}$ , Eq. 9 leads to:

$$5 \quad \frac{d_w}{d} = \left( \frac{w_{solid} \frac{w_{solid}}{d_{solid}}}{\frac{d_{solid}}{d_{solid}}} + \frac{w_{liq,inorg} \frac{w_{liq,inorg}}{d_l}}{\frac{d_l}{d_l}} + \frac{w_{org} \frac{w_{org}}{d_{org}}}{\frac{d_{org}}{d_{org}}} \right)^{-1} \quad (10)$$

With  $w_{solid}$ ,  $w_{liq,inorg}$  and  $w_{org}$  the mass fraction inside the particle of respectively the solid phase, the aqueous phase and the organic phase.

The wet diameter can be computed with the following equation given by the ratio of the volume of the wet particle to the volume of the dry particle:

$$10 \quad \frac{D_{p,wet}^3}{D_{p,dry}^3} = \frac{1}{1 - w_{H_2O}} \frac{d_{dry}}{d_{wet}} \frac{1}{1 - w_{H_2O}} \frac{d_{dry}}{d_{wet}} \quad (11)$$

with  $w_{H_2O}$  the mass fraction of water in the particle and  $d_{dry}$  the dry density of the particle which can be computed with Semmler et al. (2006) and Eq. 9 without taking into account the mass of water.

### 2.1.6 Dry deposition of particles and semi-volatile organic species

15 Dry deposition is parameterized via a downward flux  $F_{dry,i}$  such as:

$$F_{d,i} = -v_{d,i} * C_i \quad (12)$$

with  $v_d$  the deposition velocity and  $C_i$  the concentration. The deposition velocity is represented via the resistance analogy of Wesely (1989). For each gaseous species  $i$ ,  $v_{d,i}$  is calculated with:

$$v_{d,i} = \frac{1}{R_a + R_{b,i} + R_{c,i}} \quad (13)$$

20 with  $R_a$  the aerodynamic resistance associated with turbulent transport in the atmosphere,  $R_{b,i}$  the quasi-laminar resistance and  $R_{c,i}$  the surface resistance.

The surface resistance depends on the nature of the surface and is generally divided into three categories: water, ground and vegetation. For the deposition of gases to water and vegetation, the parameterizations depend on the Henry's law constants of compounds  $i$ . ~~For  $O_3$ ,  $SO_2$ ,  $NO_2$ ,  $NO$  and  $NH_3$ , the values of Menut et al. (2013) are used.~~

25 For SVOC, Bessagnet et al. (2010) showed that without not taking into account dry deposition of gas-phase SVOC could lead to an overestimation of SOA by 50 %. As done by Bessagnet et al. (2010), Henry's law constants  $H_i$  of SVOC are used to take into account their deposition. The Henry's law constants of hydrophilic species are taken from Couvidat et al. (2012). For hydrophobic species, they ~~were~~ are calculated using the activity coefficients at infinite dilution as in Couvidat and Seigneur

(2011), by using the saturation ~~vapour~~vapor pressure  $P^0$  and the activity coefficient of compound  $i$  at infinite dilution computed with UNIFAC  $\gamma_i^\infty$  such as:

$$H_i = \lim_{C_i \rightarrow 0} \left( \frac{C_i}{P_i} \right) = \frac{\rho_{\text{water}}}{M_{\text{water}} \times \gamma_i^\infty \times P_i^0} \quad (14)$$

with  ~~$\rho_{\text{water}}$~~  the density of water,  ~~$M_{\text{water}}$~~  the molar mass of water,  $M$  For primary SVOC (POAIP, POAmP and POAhP), a Henry's law constant of 0.01 mol/L/atm is used (similar to the ~~Henr~~Henry's law constant of alkanes). For their aging products, a Henry's law constant of 3000 mol/L/atm is used (for a slightly oxidized molecule). Table 4 shows the effective Henry's law constants used in this study. For SVOC, Henry's law parameters for wet and dry deposition are computed for a pH of 5.6 (pH of water in presence of CO<sub>2</sub>).

For dry deposition of particles, the parameterizations of Menuet et al. (2013) are used. However, the wet diameter and the wet density are used instead of the dry values.

### 2.1.7 Wet deposition of particles and semi-volatile species

In-cloud scavenging for both gases and aerosols is represented by the parameterization of Croft et al. (2010), assuming that wet deposition by in-cloud scavenging is proportional to the amount of cloud water lost by precipitations, such as:

$$15 \quad \frac{dC}{dt}_{\text{incl}} = \frac{\zeta_l f_l p_r}{w_l h} C \quad (15)$$

with  $p_r$  the precipitation rate (in  $\text{g cm}^{-2} \text{s}^{-1}$ ),  $w_l$  the liquid water content of clouds (in  $\text{g cm}^{-3}$ ),  $C$  the concentration and  $h$  the height of the cell (in cm)  $f_l$  is the fraction of the compound present in the cloud and  $\zeta_l$  an empirical uptake coefficient chosen equal to 1.

For gases,  $f_l$  is computed with the effective Henry's law constant and the liquid water content. For particles,  $f_l$  is taken as 1 except for particles with a diameter lower than a dry critical radius (chosen equal to  $0.1 \mu\text{m}$ ) which are assumed to be too small to form clouds due to the Kelvin effect.

For the below-cloud scavenging of gases and particles, deposition is described by a scavenging coefficient  $\lambda$  (in  $\text{s}^{-1}$ ) such as:

$$\frac{dC}{dt} = -\lambda C \quad (16)$$

25 For gases, the scavenging coefficient  $\lambda_g$  can be calculated with the following equation assuming an irreversible scavenging (Seinfeld and Pandis, 1998):

$$\lambda_g = \int_0^\infty 2\pi D_{dif} Sh RN(R) dR \quad (17)$$

with  $R$  the radius of the droplet colliding with the gas,  $D_{dif}$  the molecular diffusion coefficient of the deposited compound,  $Sh$  is the Sherwood number describing the transfer of gases from air towards a raindrop and  $N(R)$  is the number of rain droplets

distribution function.

For particles, the scavenging coefficient is expressed by (Seinfeld and Pandis, 1998):

$$\lambda_g = \int_0^{\infty} \pi R^2 U_t E(R, R_p) N(R) dR \quad (18)$$

with where  $U_t$  is the terminal velocity of the droplet (in m/s) and  $E(R, R_p)$  is the collision efficiency between a droplet of radius

5  $R$  and a particle of radius  $R_p$ .

Following Henzing et al. (2006), the rain droplet velocity parameterization of Mätzler (2002) and the rain droplet size distribution parameterizations of de Wolf (1999) are used:

$$U_t = 0 \quad R < 0.015mm \quad (19)$$

$$10 \quad = 4.323(R - 0.015) \quad 0.015 \leq R \leq 0.3mm \quad (20)$$

$$= 9.65 - 10.3 \exp(-0.3R) \quad R > 0.3mm \quad (21)$$

$$N(R) = (1.047 - 0.0436 * \ln(P) + 0.00734 * (\ln P)^2) \times 1.98 \times 10^{-5} P^{-0.384} R^{2.93} \exp(-5.38 P^{-0.186} R) \quad (22)$$

with  $P$  the precipitation rate in mm/h.

## 15 2.1.8 Condensation/evaporation

Absorption is described by the "bulk equilibrium" approach of Pandis et al. (1993) Pandis et al. (1993). In this approach, all the bins for which condensation is very fast are merged into a "bulk particulate phase". Following Debry et al. (2007), a cutting diameter of 1.25  $\mu\text{m}$  is used to separate bins which are inside the "bulk particle" (with a diameter lower than the cutting diameter) from bins for which condensation/evaporation is represented with a dynamic method. Thermodynamic models are used to compute the partitioning between the gas and particle phases and estimate the gas-phase concentrations at equilibrium. The equilibrium concentration  $G_{eq}$  is calculated by the thermodynamic module ISORROPIA for inorganic semi-volatile compounds and by SOAP for SVOC.

The mass of compounds condensing onto particles  $\Delta A_p$  is redistributed over bins according to the kinetic of condensation into each bin whereas the mass of compounds evaporating from each bin is proportional to the amount of the compounds in the bins. If the variation of particulate bulk concentration of compound  $i$   $\Delta A_{p,i} > 0$ :

$$\Delta A_{p,i}^{bin} = \frac{k_i^{bin} \Delta A_p}{\sum_j k_i^j} \frac{k_i^{bin}}{\sum_j k_i^j} \Delta A_{p,i} \quad (23)$$

with  $k_i^{bin}$  the kinetic of condensation of compound  $i$  onto the bin and  $\Delta A_{p,i}^{bin}$  the concentration of compound  $i$  inside the bin. The kinetic is given by Seinfeld and Pandis (1998):

$$k_i^{bin} = \text{Number}^{bin} \frac{2\pi D_{p,wet}^{bin} D_i M_i}{RT} f(Kn, \alpha) \quad (24)$$



with  $Number^{bin}$  the number of particles inside the bin,  $D_p^{bin}$  the mean diameter of the bin,  $D_i$  the diffusion coefficient for species  $i$  in air,  $M_i$  its molecular weight,  $R$  the gas constant,  $T$  the temperature and  $f(Kn, \alpha)$  is the correction due to non-continuum effects and imperfect surface accommodation with  $Kn$  the Knudsen number and  $\alpha$  the accommodation coefficient.

- 5 If the variation of particulate bulk concentration of compound  $i$   $\Delta A_{p,i} < 0$ :

$$\Delta A_{p,i}^{bin} = \frac{A_{p,i}^{bin}}{\sum_j A_{p,i}^j} \Delta A_{p,i} \quad (25)$$

The absorption flux  $J$  ( $\mu g m^{-3} s^{-1}$ ) of a semi-volatile inorganic or organic species onto a bin is computed with:

$$J = \frac{1}{\tau} \Delta A_{p,i}^{bin} \quad (26)$$

with  $\tau$  the time to reach equilibrium (chosen equal to the time step of integration).

- 10 For particle with a diameter above the cutting diameter, absorption/evaporation is represented by solving the equation of condensation/evaporation (Seinfeld and Pandis, 1998):

$$\frac{dA_{p,i}^{bin}}{dt} = k_i^{bin} (p_i - p_{eq,i}^{bin}) \quad (27)$$

with  $p_i$  the vapor pressure of  $i$  and  $p_{eq,i}^{bin}$  the vapor pressure of  $i$  at equilibrium with the particle-phase concentration of  $i$  inside the bin.  $p_{eq,i}^{bin}$  is computed with the reverse mode of ISORROPIA for inorganics. However, the condensation of SVOC onto coarse particle is not taken into account.

- 15 The gas to particle conversion of  $HNO_3$  onto dust and sea salts-salt is also taken into account.  $HNO_3$  can indeed react with calcite  $CaCO_3$  of dusts-in dust to form calcium nitrate  $Ca(NO_3)_2$ .  $HNO_3$  can also react with dolomite ( $MgCa(CO_3)_2$ ) but only the reaction with calcite is taken into account. Formenti et al. (2008) found a mass fraction of  $Ca$  in dusts-2+ in dust between 4% and 9%. A calcium fraction of 6% is used. In sea salt-salt,  $HNO_3$  can replace the  $Cl^-$  present in sea salt and leads to the volatilization of  $HCl$ . Both reactions were-are assumed to be limited by the condensation kinetic of  $HNO_3$  onto particles as in Hodzic et al. (2006).

### 2.1.9 Coagulation

- 25 The flux of coagulation  $J_{coag,i}^{bin}$  of a compound  $i$  inside a bin  $b$  is computed with the size binning method of Jacobson and Turco (1994):

$$J_{coag,i}^b = \sum_{j=1}^b \sum_{k=1}^b f_{j,k}^b K_{j,i} A_{p,i}^j Number^k - A_{p,i}^b \sum_{j=1}^{Nbins} K_{bin,j} Number^k \quad (28)$$

with  $K_{j,i}$  the coagulation kernel coefficient between bins  $i$  and  $j$ ,  $A_{p,i}^j$  the particle-phase concentration of compound  $i$  into bins  $j$ ,  $Nbins$  the number of bins and  $f_{j,k}^b$  the partition coefficient (the fraction of the particle created from the coagulation of

bins j and k which is redistributed inside bin b). The coagulation kernel and the partition coefficient are calculated as in Debry et al. (2007).

## 2.2 Nucleation

5 Following Menut et al. (2013), the parameterization of Kulmala and Pirjola (1998) for sulfuric acid nucleation is used. This process, favored by cold humid atmospheric conditions, affects the number of ultrafine particles. The nucleated flux is added to the smallest bin in the sectional distribution. Since the sulfuric acid nucleation process competes with absorption processes, it is expected to occur in weakly particle polluted conditions.

## 2.3 Simulation set-up

~~The new model~~ CHIMERE 2017 $\beta$  was run to simulate the concentrations of particles and their composition in 2013 over Europe with a resolution of  $0.25^\circ \times 0.25^\circ$  and 9  $\sigma$ -levels up to 500 hPa. Meteorology was obtained from the operational analysis of the Integrated Forecasting System (IFS) model of the European Centre for Medium-Range Weather Forecasts (ECMWF). The meteorology was evaluated in Bessagnet et al. (2016) for 2-meter ~~Temperature~~ temperature, 10-meter ~~Wind Speed and the Planetary Boundary Layer~~ wind speed and the planetary boundary layer (PBL) for the model intercomparison project Eurodelta III. The authors reported high correlations for temperature (between 0.88 and 0.94) over the whole domain and a slight underestimation of ~~Temperature~~ temperature (between -0.3K and -0.7K), an overestimation of the Wind Speed from 0.1 to 0.9 m/s and an underestimation of the PBL height of around -100 m (although ECMWF in the Eurodelta III project was shown to be one of model with the lowest RMSE). ~~Anthropogenic~~ Annual anthropogenic emissions of gases and particles were taken from the EMEP inventory (~~Vestreng, 2003~~) and Boundary Conditions. Methodology is described by Vestreng (2003). Temporalization of emissions is done according temporal factors for each country provided by GENEMIS (Ebel et al., 1997)

20 Boundary conditions were generated from the results of the Model for OZone And Related Tracers (~~Mozart~~ MOZART v4.0 (Emmons et al., 2010)) available online on <https://www.acom.ucar.edu/wrf-chem/mozart.shtml>. Sea salt emissions were computed according to Monahan et al. (1986). The Melchior 2 (Derognat et al., 2003) mechanism was used to simulate the gas-phase chemistry.

For  $PM_{2.5}$ ,  $PM_{10}$  and each component of PM, several statistics were computed: Root Mean Square Error (RMSE), the correlation coefficient, the Mean Fractional Error (MFE) and the Mean Fractional Bias (MFB). Boylan and Russell (2006) defined two criteria to estimate the ~~performances~~ performance of the model. The model performance criteria (described as the level of accuracy that is considered to be acceptable for modeling applications) is reached when  $MFE \leq 75\%$  and when  $MFB \leq \pm 50\%$  whereas the performance goal (described as the level of accuracy that is considered to be close to the best a model can be expected to achieve) is reached when  $MFE \leq 50\%$  and when  $MFB \leq \pm 30\%$ . Although these criteria are not recent,

30 they provide a useful basis to evaluate models.

The seasonal evolution of statistics was examined to study the ~~performances~~ performance of the model for different seasons and to separate ~~performances~~ the performance over a month from ~~annual performances~~ the annual performance. The statistics were also computed by "regions" gathering countries having similar features. 5 regions were selected:

- Southern Europe gathering Spain, Portugal and Italy
- Western Europe gathering Ireland, Great Britain and France
- Central Europe gathering Germany, Belgium, Netherlands, Switzerland, Denmark and Austria
- Northern Europe gathering Norway, Sweden and Finland (characterized by low temperatures and low concentrations of particles)
- Eastern Europe gathering the other countries at the east of Europe

Figures S2 to S7 in Supplementary Materials show the seasonal evolution of the various statistics (correlation, RMSE, MFB, MFE) for each region.

A map of regions and ~~stations referred hereafter~~ of the specific stations that are referred hereafter in the text (mostly stations with measurements of OC) is shown in ~~Figure 1~~. Fig. 1.

## 2.4 Observations

Results of the model are compared to various measurements ( $\text{NO}_3$ ,  $\text{NH}_4$ ,  $\text{SO}_4$ ,  $\text{Na}_3^-$ ,  $\text{NH}_4^+$ ,  $\text{SO}_4^{2-}$ ,  $\text{Na}^+$ ,  $\text{Cl}^-$ ,  $\text{Cl}$ , OC,  $\text{PM}_{10}$ ,  $\text{PM}_{2.5}$  and  $\text{PM}_{10}$ ) available in the EBAS database. ~~EBAS is~~ (Tørseth et al., 2012) from various instruments (i.e. filters, Tapered Element Oscillating Microbalances, beta ray absorption) for regional background stations. The stations cover most of Europe with the first measurements available beginning in the seventies. EBAS (<http://ebas.nilu.no/is>) a database hosting observation data of atmospheric chemical composition and physical properties in support of a number of national and international programs ranging from monitoring activities to research projects. EBAS is developed and operated by the Norwegian Institute for Air Research (NILU). This database is mostly populated by the EMEP (European Monitoring and Evaluation Programme) measurements (Tørseth et al., 2012) Program) measurements.

## 3 Results

### 3.1 Sea salts

When not mentioned otherwise, concentrations of components used for the comparison are in the  $\text{PM}_{10}$  fraction.

#### 3.1 Sea salt

Annual scores for sodium (Na) and chloride (Cl) are given in Table 5. Comparisons are carried out over 38 stations for  $\text{Na}^+$  and 35 stations for  $\text{Cl}^-$ . Scores are very similar between Na and  $\text{Cl}^+$  and  $\text{Cl}^-$ . The simulated mean concentrations are close ( $0.67 \mu\text{g m}^{-3}$  for  $\text{Na}^+$  and  $1.28 \mu\text{g m}^{-3}$  for  $\text{Cl}^-$ ) to the measured mean concentrations ( $0.69 \mu\text{g m}^{-3}$  for  $\text{Na}^+$  and  $1.17 \mu\text{g m}^{-3}$  for  $\text{Cl}^-$ ) and the spatiotemporal correlations are high (0.66 for  $\text{Na}^+$  and 0.67 for  $\text{Cl}^-$ ). MFB are low (6% for  $\text{Na}^+$  and

9% for  $\text{Cl}^-$ ) and MFE (52% for  $\text{Na}^+$  and 49% for  $\text{Cl}^-$ ) are close to the goal criteria of Boylan and Russell (2006) (MFE  $\leq$  50% and MFB  $\leq \pm 30\%$ ). ~~Figure Fig. 2 shows the annual concentrations and MFB of Na and  $\text{Cl}^+$  and  $\text{Cl}^-$  at each station. Only Concentrations for  $\text{Na}^+$  are underestimated significantly for only one station in Spain underestimates (along the Bay of Biscay) concentrations for Na. Most stations in Spain, Central Europe and Western Europe have a low annual bias for  $\text{Na}^+$  whereas most stations in Northern and Eastern Europe seem to have a high MFB with overestimated concentrations. Results are similar for  $\text{Cl}^-$  except in Spain with overestimations-observed-overestimated concentrations near the Mediterranean Sea and in some stations in Central Europe far from the seas. This may indicate that the kinetic of  $\text{HNO}_3$  condensation onto sea salts and the evaporation of HCl is not important enough.~~

~~Figure ?? Fig. S2 shows the seasonal evolution of the statistics by regions. The same behavior was found for  $\text{Cl}^-$  concentrations as for  $\text{Na}^+$  concentrations.  $\text{Na}^+$  concentrations than-for-Na concentrations. Na concentrations seem to be underestimated for the stations in the Southern Europe (only stations in Spain for Na and  $\text{Cl}^+$  and  $\text{Cl}^-$ ) from April to October with MFB reaching -60% and the MFE is between 60% to 80% throughout all the year. The temporal correlation is high but the spatial correlation is low. However, for the station ES0008R along the Bay of Biscay with strong observed of Na, the model underestimates the concentrations of  $\text{Na}^+$  while strong concentrations are measured at this station (with several peaks higher than  $6 \mu\text{g m}^{-3}$ ), the model underestimates the concentrations. Temporal evolutions of measured and modeled concentrations are shown in Fig. S1 in Supplementary Materials. It could then be possible that  $\text{Na}^+$  concentrations at this station cannot be reproduced due to the low resolution of the model and the strong evolution of concentrations between the sea and the land. The other stations have all a similar Except from ES0008R, the stations of Southern Europe share the same pattern shown in Figure ?? Fig. S2. Concentrations of  $\text{Na}^+$  are overestimated by the model in late Autumn and Winter autumn and winter (with a MFB from 30% to 60%) whereas concentrations are underestimated from June to October with a MFB of -60%. Measurements give higher concentrations of  $\text{Na}^+$  in summer and lower concentrations in winter whereas the model simulate the opposite trend.~~

For the stations in Western Europe and Central Europe, the model gives satisfactory results and is able to reproduce the seasonal evolution of  $\text{Na}^+$  concentrations with MFE around 40 % and MFB between +20% and -20% except for February in Central Europe. Correlations are high (between 50% and 80% in Western Europe around 80% in Central Europe). RMSE are relatively low for Western Europe (between 0.6 and  $1.1 \mu\text{g m}^{-3}$  for concentrations between 0.8 and  $1.7 \mu\text{g m}^{-3}$ ) whereas RMSE for Central Europe are of the same range than measured and modeled concentrations (between 0.4 and  $1.6 \mu\text{g m}^{-3}$ ).

For Eastern and Northern Europe, the model overestimates concentrations throughout the year with MFB often higher than 50% for Eastern Europe and often higher than 30% for Northern Europe and with high MFE (often higher than 50% and even exceeding 100% for some months in Eastern Europe). However, if relative errors are high in Eastern Europe, absolute errors are low (RMSE lower than  $0.35 \mu\text{g m}^{-3}$ ) because concentrations in Eastern Europe are very low (mean concentrations lower than  $0.12 \mu\text{g m}^{-3}$  and modeled concentrations between 0.09 and  $0.35 \mu\text{g m}^{-3}$ ). This overestimation could be due to a lack of sea salts salt deposition in the model which becomes significant for low concentrations far from seas. Such an underestimation of deposition was reported in Tsyro et al. (2011); Neumann et al. (2016) Tsyro et al. (2011) and Neumann et al. (2016).

### 3.2 Sulfate

Annual scores for  $\text{SO}_4^{2-}$  are given in Table 5. Comparisons are carried out over 56 stations. The simulated mean concentrations ( $1.66 \mu\text{g m}^{-3}$ ) and the measured mean concentrations ( $1.60 \mu\text{g m}^{-3}$ ) are very close. The spatiotemporal correlation is high (0.67). MFB is low (13%) but indicates a slight relative overestimation. MFE is below 50% (44%) and therefore the goal criteria of Boylan and Russell (2006) is respected for sulfate. The RMSE is equal to  $1.13 \mu\text{g m}^{-3}$ . Figure Fig. 3 shows the annual concentrations and MFB of  $\text{SO}_4^{2-}$  at each station. Most stations give satisfactory results, 41 stations have a MFB between  $\pm 30\%$  and 33 stations respect the goal criteria. The model gives no stations where  $\text{SO}_4^{2-}$  concentrations would be significantly underestimated (MFB < -30%) but results at some stations are significantly overestimated, especially in the North of Europe. This overestimation is similar to the overestimation of sea salts in Northern Europe. However, the contribution of sulfate from sea salts in the model (7.68 %) is not enough to explain the overestimation of sulfate in the Northern Europe. However, it may be due to an overestimation of north boundary conditions (as the stations in Northern Europe are close to the limit of the domain), a lack of deposition or errors on meteorological data that create the same overestimation than for sea salts.

Figure ?? Fig. S3 shows the seasonal evolution of the statistics for  $\text{SO}_4^{2-}$  by regions.

Like  $\text{Na}^+$ ,  $\text{SO}_4^{2-}$  concentrations seem to be underestimated for the stations in the Southern Europe (mostly stations in Spain) in summer and overestimated in winter and late autumn with a MFB between -30% and 40%. However, this behavior is probably not due to sulfate from sea salts (due to the low contribution of sea salt to sulfate, only a small part of sulfate would be originating from sea salts). In Western, Central and Eastern Europe the model succeeds in reproducing the seasonal evolution with a MFB generally between  $\pm 30\%$  and MFE below 50% except for Western Europe in late autumn where MFB exceeds 50% and for Central Europe in November where MFB reaches 40%.  $\text{SO}_4^{2-}$  concentrations seem to be slightly relatively overestimated with a MFB > 0 in Eastern Europe whereas MFB is between  $\pm 30\%$  for Central and Western Europe. In Northern Europe, like sea salts, concentrations of  $\text{SO}_4^{2-}$  are overestimated with a MFB higher than 30% and reaching 90%.

### 3.3 Ammonium and nitrate

Annual scores for  $\text{NO}_3^-$  and  $\text{NH}_4^+$  are given in Table 5. Comparisons of  $\text{NO}_3^-$  and  $\text{NH}_4^+$  are carried out over 37 and 33 stations respectively. The model gives higher mean values than measurements ( $1.99 \mu\text{g m}^{-3}$  against  $1.46 \mu\text{g m}^{-3}$  for  $\text{NO}_3^-$  and  $1.29 \mu\text{g m}^{-3}$  against  $0.89 \mu\text{g m}^{-3}$  for  $\text{NH}_4^+$ ). This kind of overestimation have been reported for numerous models (Bessagnet et al., 2014; Lecœur and Seigneur, 2013). RMSE are higher than mean measured concentrations ( $1.87 \mu\text{g m}^{-3}$  and  $0.97 \mu\text{g m}^{-3}$ ) due to the high bias. The performance criteria are respected but not the goal criteria for both  $\text{NO}_3^-$  (MFB = 15% and MFE = 57%) and  $\text{NH}_4^+$  (MFB = 36% and MFE = 55%). However, the spatiotemporal correlation is rather high (0.71 for  $\text{NO}_3^-$  and 0.71 for  $\text{NH}_4^+$ ). Figure 4 shows the annual concentrations and MFB of  $\text{NO}_3^-$  and  $\text{NH}_4^+$  at each station. Both,  $\text{NO}_3^-$  and  $\text{NH}_4^+$  are overestimated at some stations in Germany, one station near Barcelona and two stations in Eastern Europe indicating there may be too much ammonium nitrate at these stations.  $\text{NH}_4^+$

$\text{NH}_4^+$  is strongly overestimated in Northern Europe which may be linked to the overestimation of sulfate and the formation of ammonium sulfate over this region whereas  $\text{NO}_3^-$  is overestimated at some stations in Southern Europe.

Figures [S4 and S5](#) show the seasonal evolution of the statistics for  $\text{NO}_3^-$  and  $\text{NH}_4^+$  by regions.

For Southern Europe, both  $\text{NO}_3^-$  and  $\text{NH}_4^+$  concentrations are overestimated significantly in November-December 2013 with MFB exceeding 40% for  $\text{NO}_3^-$  and 60% for  $\text{NH}_4^+$ . Concentrations of  $\text{NH}_4^+$  are also overestimated from January to May with a MFB higher than 40% whereas  $\text{NO}_3^-$  is overestimated to a smaller extent.  $\text{NO}_3^-$  is also a bit underestimated from June to August. These results may indicate the formation of too high ammonium nitrate concentrations at the end of the year. For  $\text{NH}_4^+$ , errors on concentrations seem related to the errors on  $\text{SO}_4^{2-}$  concentrations indicating that  $\text{NH}_4^+$  may be better represented with a better representation of sulfates. [Part of the errors may be also due to errors on  \$\text{NO}\_3^-\$  and  \$\text{HNO}\_3\$  concentrations.](#) Monthly correlations are low for  $\text{NH}_4^+$  (lower than 0.4) and slightly higher for  $\text{NO}_3^-$  (between 0.4 and 0.6).

For Western Europe, results on  $\text{NO}_3^-$  are very similar to the results for  $\text{NH}_4^+$  with an overestimation of both  $\text{NO}_3^-$  and  $\text{NH}_4^+$  in November and December (MFB higher than 40% for  $\text{NO}_3^-$  and higher than 60% for  $\text{NH}_4^+$ ) and a slight overestimation for the peak in March (MFB around 30% for both  $\text{NO}_3^-$  and  $\text{NH}_4^+$ ). All together the MFB for  $\text{NH}_4^+$  is higher than the MFB for  $\text{NO}_3^-$  which may be due to the slight overestimation of  $\text{SO}_4^{2-}$  (and therefore the overestimation of ammonium sulfate). Monthly correlations are a bit higher for  $\text{NO}_3^-$  (higher than 0.8 for most of the year) than for  $\text{NH}_4^+$  (between 0.6 and 0.8 for most of the year).

Over Central Europe,  $\text{NO}_3^-$  and  $\text{NH}_4^+$  concentrations are strongly overestimated at the end of the year where high concentrations are simulated.  $\text{NH}_4^+$  is also slightly overestimated at the beginning of the year with a MFB higher than 30%. Monthly correlations are high (between 0.6 and 0.8) for  $\text{NO}_3^-$  whereas monthly correlations are lower for  $\text{NH}_4^+$  in summer (below 0.5).

The results over Eastern Europe are similar to the results of Central Europe, however  $\text{NO}_3^-$  concentrations are overestimated at the beginning of the year and underestimated in [Summer](#).

For Northern Europe,  $\text{NH}_4^+$  concentrations are overestimated throughout the year with a MFB around 40% in May to August and up to 120% at the end of the year. These results are very similar to the results for  $\text{SO}_4^{2-}$  and  $\text{NO}_3^-$  concentrations are underestimated in summer and are strongly overestimated for the rest of the year (especially in February with a MFB close to 100%).

Generally, statistics for  $\text{SO}_4^{2-}$  and  $\text{NO}_3^-$  seem better than the statistics for  $\text{NH}_4^+$ , this may be due to the cumulative errors on ammonium nitrate and ammonium sulfate. To investigate the highlighted results on ammonium and nitrate, scores were computed for total nitrate  $\text{TNO}_3$  (particulate  $\text{NO}_3^-$  + gaseous  $\text{HNO}_3$ ) and for total ammonium  $\text{TNH}_4$  (particulate  $\text{NH}_4^+$  + gaseous  $\text{NH}_3$ ). The [performances are performance is](#) close to the goal criteria with a slight overestimation of concentrations. The mean seasonal evolutions of  $\text{TNO}_3$  and  $\text{TNH}_4$  are plotted in [Figure 6- Fig. 6. Annual scores for  \$\text{TNO}\_3\$  and  \$\text{TNH}\_4\$  are given in Table 5.](#)

[TNO<sub>3</sub> and TNH<sub>4</sub>](#) share the same pattern with a slight underestimation of concentrations in summer and an overestimation of concentrations in autumn and winter.

This feature could be explained by:

- An overestimation of the gas-particle conversion of  $\text{HNO}_3$  and  $\text{NH}_3$ . Indeed, Peters and Bruckner-Schatt (1995) measured higher deposition velocity of  $\text{HNO}_3$  and  $\text{NH}_3$  over spruce stand and Seinfeld and Pandis (1998) reported higher deposition velocity for gases than for particles lower than  $2.5 \mu\text{m}$  over water surfaces. An overestimation of the partitioning can therefore lead to an overestimation of total concentrations because the deposition ~~velocity~~ velocities of these gases are generally higher than those of particles (Peters and Bruckner-Schatt, 1995).
- An underestimation of the deposition velocity.
- An overestimation of  $\text{HNO}_3$  production rate by the gas-phase mechanism MELCHIOR 2, leading to an overestimation of the partitioning of  $\text{NH}_3$  and  $\text{HNO}_3$  toward the particle phase and therefore leading to an overestimation of both  $\text{TNO}_3$  and  $\text{TNH}_4$ .
- An overestimation of  $\text{NH}_3$  emissions in winter and autumn and an underestimation of  $\text{NH}_3$  emissions in summer. An overestimation of  $\text{NH}_3$  would lead to an overestimation of the partitioning of  $\text{NH}_3$  and  $\text{HNO}_3$  toward the particle phase and therefore lead to an overestimation of both  $\text{TNO}_3$  and  $\text{TNH}_4$  because the deposition velocity of these gases are generally higher than those of particles (Peters and Bruckner-Schatt, 1995).

The last assumption seems to be supported by the shape of the seasonal profile of  $\text{NH}_3$  emissions used in CHIMERE illustrated in Figure Fig. 7 which gives high emissions in November-December whereas Skj  th et al. (2011) (who developed a dynamical method to estimate  $\text{NH}_3$  emissions based on the different types of agriculture) estimated very low emissions during this period. Using dynamical emissions may give a better representation of  $\text{NH}_3$  and  $\text{NO}_{3-3}$  concentrations. Moreover, in some countries from Northern Europe like Sweden,  $\text{NH}_3$  emissions are mainly due to livestock (87 % of ammonia emissions in Sweden) whereas the temporal profile for Sweden is similar to the one of other countries with two peaks of emissions (one in March-April and one in October-November) corresponding to the application of fertilizers in Spring and Autumn spring and autumn. It could explain why for Northern Europe,  $\text{NO}_{3-3}$  is significantly underestimated in summer and significantly overestimated at the beginning and the end of the year.

Coarse  $\text{NO}_3^-$  modeled concentrations and biases are shown in Fig. 5. Coarse  $\text{NO}_3^-$  measurements were estimated by difference between  $\text{PM}_{10}$  and  $\text{PM}_{2.5}$  concentrations. Low values should therefore be uncertain due to uncertainties of the two measurements.

Concentrations of coarse  $\text{NO}_3^-$  are underestimated over stations ES0008R, CY0002R and DE0044R. Concentrations of coarse  $\text{NO}_3^-$  are high over the Mediterranean Sea due to high concentrations of  $\text{HNO}_3$  (formed the oxidation by high concentrations of OH of high concentrations of  $\text{NO}_x$  originating from maritime traffic) combined to high concentrations of dust and sea salt. The high concentrations of coarse  $\text{NO}_3^-$  over the Mediterranean Sea are confirmed by measurements in Spain and in Cyprus. High concentrations of coarse  $\text{NO}_3^-$  are also simulated over the English Channel and the North Sea due to high concentrations of sea salt and  $\text{HNO}_3$ . However, the model seems to underestimate the high concentrations of coarse  $\text{NO}_3^-$  observed at station DE0044R. This underestimation is not linked to sea salt (which are overestimated at this station) nor to the presence of ammonium nitrate in coarse particle: observed concentrations of coarse ammonium are not enough ( $0.16 \mu\text{g}/\text{m}^3$  in April) to explain observed concentrations of coarse  $\text{NO}_3^-$  ( $1.44 \mu\text{g}/\text{m}^3$  in April). One possibility is that the coarse  $\text{NO}_3^-$

observed at this station originates directly from primary coarse PM emission (which is not taken into account in the model). Coarse Concentrations seems to be in the right order of magnitude for other stations but temporal correlations at each stations were poor (inferior to 0.6) possibly due to the uncertainty of the determination of measured concentrations by differences.

### 3.3.1 Organic aerosol

5 Organic Aerosol concentration measurements are not available in the database. However, measurements for organic carbon (OC) concentrations are available. OC is the mass of carbon inside the organic aerosols. For the comparison, OM/OC ratios (that depend on the composition of organic aerosols, especially the degree of oxidation of compounds) have to be assumed to estimate OC concentrations from modeled OM concentrations. Turpin and Lim (2001) measured the OM/OC ratios at different locations and found ratios between 1.2 and 2.5 and recommended to use a ratio of 2.1 for rural areas. Following Couvidat  
10 et al. (2012), modeled OC concentrations were calculated directly from the modeled concentrations of each organic surrogate compounds using their molecular structure to estimate the OM/OC ratio of the surrogate compounds. Several sensitivity tests were conducted by Couvidat et al. (2012) and has shown that the OM/OC ratio simulated by the H<sup>2</sup>O mechanism is generally quite low compared to the OM/OC ratio recommended by Turpin and Lim (2001). An overestimation of OC concentrations by the model could therefore be due to an underestimation of the OM/OC ratio.

15 Table 6 shows the annual statistics for organic carbon (OC) for each station. Time series of the concentrations for each station are shown in Figures 9 and 10 for stations in the southern half and northern half of Europe respectively. Figure 8 shows the maps of OC concentrations over Europe for January and July 2013 as well as the MFB at stations. These figures show for January and July an underestimation of OC concentrations over Central Europe.

Annual concentrations at some stations seem to be overestimated (ES1778R, IT0004R and DE0003R) with MFB between  
20 36% and 40%. However, the performance criteria is-are respected for these stations. It could also be possible that the overestimation of OC concentrations at these stations de-does not correspond to an underestimation of OC if the OM/OC ratio is underestimated. The performance goal is respected for stations CH0002R and SI0008R whereas the performance criteria are respected for stations CY0002R, DE0008R, PL0005R and SE0011R. Concentrations are underestimated at the other stations with MFB between -56% and -87%.

25 Although OC concentrations are slightly overestimated in ES1778 (near Barcelona, Spain) and IT0004 (in Ispra, Italy) the seasonality of OC concentrations is well captured by the model. Moreover, the overestimation of concentrations could be due to the proximity of high emissions sources and the low resolution of the model (ES1778 is only at 50 km from Barcelona whereas the resolution is only of 0.25° and IT0004 is close to Milan). Concentrations and the seasonal evolution are well reproduced in SI0008 (Iskbra, Slovenia). For the other stations in the south of Europe, summer concentrations are underestimated in-summer  
30 whereas the winter concentrations seem to be well reproduced. This may indicate a lack of secondary organic aerosol formation. These stations all have strong modeled concentrations of biogenic SOA in summer and strong modeled concentrations of anthropogenic organic aerosol in winter.

For the northern half of Europe, except for stations DE0003(~~for which concentrations are overestimated in Winter~~), the ~~station~~, CH0005R in Switzerland and PL0005R in Poland which have strong concentrations of modeled biogenic SOA, sum-



mer concentrations of organic aerosol are underestimated. Only a peak of organic aerosol (due to biogenic aerosols in the model) at the end of August for several stations (CZ0003R, DE0002R, DE0007R, DE0008R, DE0044R) is well-reproduced by the model. These stations correspond to areas with strong anthropogenic emissions. A lack of anthropogenic SOA could therefore explain this pattern. However, this underestimation could be also due to a lack of biogenic emissions over these areas.

5 During winter, OC is overestimated over a few stations: ES1778R, IT0004R, CH0005R and DE0003R. These 4 stations are under meteorological conditions difficult to simulate at such a low resolution (25 km). They are often close to cities: ES1778R is close to Barcelona (60 km), IT0004R (Ispra) is in the Po valley (an area with strong anthropogenic emissions) not far from Milan, CH0005 is at less than 20 km of Lucerne (with 205 000 inhabitants) and DE0003R is at 12 km from Freiburg (a city of 206 000 inhabitants). Moreover, these stations are in mountainous regions with high variations of altitude that are difficult to  
10 represent at such a resolution. Except for these 4 stations, concentrations of organic aerosol in winter simulated by the model tend to be underestimated although reasonable performance could be attained for numerous stations emphasizing the need to better represent anthropogenic emissions in winter.

### 3.3.2 PM concentrations

15 Annual scores for PM<sub>2.5</sub> and PM<sub>10</sub> are given in Table 5. Comparisons are carried out over 41 stations for PM<sub>2.5</sub> and 59 stations for PM<sub>10</sub>. The goal criteria is-are respected for both PM<sub>2.5</sub> and PM<sub>10</sub>. However, PM<sub>2.5</sub> concentrations are slightly overestimated (MFB = 22%). The MFB for PM<sub>10</sub> is lower (8%) indicating that coarse particles may be underestimated. This is confirmed by the fact that comparing the modeled coarse particle concentrations with estimated measured coarse concentrations (by subtracting PM<sub>2.5</sub> to PM<sub>10</sub>) for the stations with measurements of both PM<sub>2.5</sub> and PM<sub>10</sub>, the MFB for PM<sub>2.5</sub> (17%) is  
20 higher than the MFB for PM<sub>10</sub> (4%). The comparison gives a MFB of -25%, confirming that concentrations of coarse particles are underestimated. The underestimation of coarse particles was reported for numerous models in the intercomparison model projet-project AQMEII (Solazzo et al., 2012; Pirovano et al., 2012).

The simulated mean concentrations (10.54  $\mu\text{g m}^{-3}$  for PM<sub>2.5</sub> and 14.42  $\mu\text{g m}^{-3}$  for PM<sub>10</sub>) are close to the measured mean concentrations (9.06  $\mu\text{g m}^{-3}$  for PM<sub>2.5</sub> and 13.51  $\mu\text{g m}^{-3}$  for PM<sub>10</sub>) and the spatiotemporal correlations are high (0.68 for  
25 PM<sub>2.5</sub> and 0.60 for PM<sub>10</sub>).

Figure-Fig. 11 shows the annual concentrations and MFB of PM<sub>2.5</sub> and PM<sub>10</sub> at each station. The model strongly underestimates annual concentrations of PM<sub>10</sub> only for the ES0008R station, probably due to the underestimation of sea salt at this station. However, the model overestimates PM concentrations with a MFB above 30% at several locations (14 stations for PM<sub>2.5</sub> and 12 stations for PM<sub>10</sub> especially over the Alps). The overestimation over the Alps is probably due to difficulties in  
30 reproducing the complexity of mountainous meteorology for a model with such a coarse resolution.

Figures ?? and ?? S6 and S7 show the seasonal evolution of the statistics by regions for PM<sub>2.5</sub> and PM<sub>10</sub>, respectively.

PM<sub>2.5</sub> concentrations seem to be underestimated for the stations in the Southern Europe from June to August and overestimated the rest of the year (especially in March, November and December with MFB reaching 60%). A similar feature is obtained with PM<sub>10</sub> but with lower MFB in March, November and December, which is probably due to some compensation

effects and an underestimation of the coarse fraction of PM. Based on these results, this overestimation is probably mainly due to the overestimation of ammonium nitrate observed during these months while the underestimation from June to August is probably due to the underestimation of all PM components.

For Western Europe, PM<sub>2.5</sub> ~~are-is~~ overestimated from September to December with a MFB between 40% and 60% which may be due at least partly to the overestimation of ammonium nitrate. The overestimation could also be due to an overestimation of organic matter observed at some stations or to an overestimation of primary particles. Similar results are obtained for PM<sub>10</sub>.

In Central Europe, the model reproduces well the strong concentrations of PM<sub>2.5</sub> and PM<sub>10</sub> in ~~Winter and Spring~~ winter and spring (with a MFE around 40%). However, concentrations are slightly underestimated in summer (with a negative MFB reaching -30% for PM<sub>2.5</sub> and -40% for PM<sub>10</sub>) and are overestimated from October to December with a MFB between 40% and 80% for PM<sub>2.5</sub> (probably due to the strong overestimation of ammonium nitrate) and reaching 50% for PM<sub>10</sub>.

For Eastern and Northern Europe, similar features are obtained. PM<sub>2.5</sub> and PM<sub>10</sub> are overestimated in ~~Winter and Fall~~ winter and autumn (probably due ~~to~~ mostly to the overestimation of ammonium nitrate) and underestimated in ~~Summer~~ summer (probably due to the summer underestimation of ammonium nitrate and organic aerosols).

A Quantile-Quantile (QQ) scatter plot of modeling results against measurements for PM<sub>10</sub> and PM<sub>2.5</sub> is shown in ~~Figure Fig. 12~~. QQ plots can be used to assess the similarity of the distribution of two compared datasets. ~~Fig. 12 shows the quantile of modeled concentrations against the corresponding quantile of measured concentrations~~. For Southern Europe, concentrations higher than 40  $\mu\text{g m}^{-3}$  for PM<sub>10</sub> and higher than 20  $\mu\text{g m}^{-3}$  for PM<sub>2.5</sub> ~~are-is~~ significantly underestimated, especially for high concentrations of PM<sub>2.5</sub>. Western Europe and Central Europe have a similar distribution of concentrations with a strong overestimation of high concentrations of PM<sub>2.5</sub> (higher than 35  $\mu\text{g m}^{-3}$ ) and of PM<sub>10</sub> (higher than 55  $\mu\text{g m}^{-3}$ ). This overestimation is probably due to the high overestimation of ammonium nitrate during the late autumn for these regions. For Eastern Europe and Southern Europe, the distributions of modeled concentrations are similar to the distributions of observed concentrations.

### 3.3.3 Case of the Cyprus station

The Cyprus station (CY0002R) was analyzed due to the ~~specificities~~ specificity of this station close to the boundary conditions, influenced by high concentrations of PM due to mineral ~~dusts~~ dust and high anthropogenic emissions from the Mediterranean maritime traffic. ~~Moreover~~ Moreover, numerous measurements were carried out at this station: PM<sub>2.5</sub> and PM<sub>10</sub> and measurements of speciation (both in the fine fraction and in PM<sub>10</sub>) covering NO<sub>3</sub>, NH<sub>4</sub>, ~~SO<sub>4</sub>, Na, Cl<sup>+</sup>, SO<sub>4</sub><sup>2-</sup>, Na<sup>+</sup>, Cl<sup>-</sup>~~ and also Ca<sup>2+</sup> (originating mainly from dust). The temporal evolution of PM<sub>2.5</sub> and PM<sub>10</sub>, Ca<sup>2+</sup> (fine fraction and ~~totalPM<sub>10</sub> fraction~~), NO<sub>3</sub><sup>-</sup> (fine fraction and ~~totalPM<sub>10</sub> fraction~~) are shown in ~~Figure Fig. 13~~ and the temporal evolution of Na<sup>+</sup>, Cl<sup>-</sup>, Cl<sup>-</sup>, NH<sub>4</sub> and SO<sub>4</sub> are shown in ~~Figure Fig. 14~~. The temporal evolution of OC concentrations is shown in ~~Figure 10~~ Fig. 9.

The model gives at this station good performances for the simulation of PM<sub>2.5</sub> (correlation = 0.54, MFB=-10%, MFE=35%) and PM<sub>10</sub> (correlation=0.64, MFB=26%, MFE=39%). The temporal evolution of PM<sub>2.5</sub> and PM<sub>10</sub> are well reproduced by the model. The good results at this station are mainly due to the good representation of ~~dusts~~ dust transport in the simulation

(coming here from the boundary conditions taken from Mezart-MOZART v4.0). Simulated concentrations of  $\text{Ca}^{2+}$  (assuming a fraction of 6% in dusts) were compared to the measurements of  $\text{Ca}^{2+}$ . The model gives good results for  $\text{Ca}^{2+}$  concentrations in  $\text{PM}_{10}$  (correlation=0.65, MFB=6% and MFE=45%) but Ca. However,  $\text{Ca}^{2+}$  concentrations in fine particles are overestimated (correlation=0.53, MFB=63% and MFE=81%) but the concentrations ( $0.19 \mu\text{g m}^{-3}$  in measurements) are low compared to  $\text{Ca}^{2+}$  in  $\text{PM}_{10}$  ( $1.32 \mu\text{g m}^{-3}$  in measurements). Na and Cl<sup>+</sup> and Cl<sup>-</sup> are strongly underestimated (MFB=-85% and MFB=-40% for Cl<sup>-</sup>).

The model almost respects the goal criteria for  $\text{NO}_3^-$  in  $\text{PM}_{10}$  (MFB=24% and MFE=51%) but with a low correlation (0.38). The modeled annual mean of  $\text{NO}_3^-$  in  $\text{PM}_{10}$  ( $1.66 \mu\text{g m}^{-3}$ ) is close to the measured annual mean ( $1.53 \mu\text{g m}^{-3}$ ). However, the measured-modeled annual mean of  $\text{NO}_3^-$  in fine particles is strongly overestimated ( $0.71 \mu\text{g m}^{-3}$  against  $0.18 \mu\text{g m}^{-3}$ ). The model seems here to underestimate the coarse fraction of  $\text{NO}_3^-$  fraction of  $\text{NO}_3^-$ . Even if the model gives strong  $\text{NO}_3^-$  concentrations in the coarse fraction due to the coarse mode formation with dusts, a significant part of  $\text{NO}_3^-$  in the model seems to be due to ammonium nitrate formation in PM whereas most of  $\text{NH}_4^+$  seems to be due to ammonium sulfate formation (correlation of 0.85 between observed sulfate and ammonium). A similar feature is observed at station ES0008R with a good order of magnitude for  $\text{NO}_3^-$  in  $\text{PM}_{10}$  ( $1.23 \mu\text{g m}^{-3}$  in the model and  $1.19 \mu\text{g m}^{-3}$  in measurements) but with an overestimation of  $\text{NO}_3^-$  in the fine fraction ( $1.22 \mu\text{g m}^{-3}$  in the model and  $0.38 \mu\text{g m}^{-3}$  in measurements). These results may be partly due to a lack of  $\text{HNO}_3$  condensing onto dusts but the underestimation is probably mainly due to sea salts salt which are underestimated at these two stations.

$\text{NH}_4^+$  concentrations are overestimated (probably due to the with a MFB of 49%. This overestimation of ammonium nitrate and is likely due to the lack of  $\text{HNO}_3$  condensing onto dusts) with a MFB of 49% whereas  $\text{SO}_4$  dust and sea salt (with more  $\text{HNO}_3$  condensing onto dust and sea salt, less  $\text{HNO}_3$  will be available to form ammonium nitrate).  $\text{SO}_4^{2-}$  concentrations are underestimated (MFB=-0.29%) especially in July and November 2013 where the model is not able to reproduce the high concentrations of sulfate. Correlation are very low (0.23 for  $\text{NH}_4^+$  and 0.13 for  $\text{SO}_4^{2-}$ ).

### 3.3.4 Case of the Melpitz station (Germany)

Numerous simultaneous types of measurements were also carried out at the Melpitz station (DE0044R) in Germany. The temporal evolution of  $\text{PM}_{2.5}$  and  $\text{PM}_{10}$ ,  $\text{Ca}^{2+}$  (fine fraction and total  $\text{PM}_{10}$  fraction),  $\text{NO}_3^-$  (fine fraction and total  $\text{PM}_{10}$  fraction) are shown in Figure Fig. 15 and the temporal evolution of  $\text{Na}^+$ ,  $\text{Cl}^-$ ,  $\text{Cl-NH}_4$ ,  $\text{SO}_4$  and elemental carbon (EC) are shown in Figure Fig. 16. The temporal evolution of OC concentrations is shown in Figure 9 Fig. 10.

At this station,  $\text{PM}_{2.5}$  and  $\text{PM}_{10}$  share a similar pattern. For  $\text{PM}_{2.5}$ , annual concentrations are underestimated by the model ( $13.2 \mu\text{g m}^{-3}$  against  $17.8 \mu\text{g m}^{-3}$  in measurements) especially in summer with an underestimation ranging from 7 and  $11 \mu\text{g m}^{-3}$  from June to August and a monthly MFB between -65% and -95% and in a lesser extent in winter (except in February) with an underestimation of about  $7 \mu\text{g m}^{-3}$ . For  $\text{PM}_{10}$ , the underestimation is stronger ( $15.7 \mu\text{g m}^{-3}$  against  $22.1 \mu\text{g m}^{-3}$ ) especially between april and august April and August with an underestimation between 10 and  $15 \mu\text{g m}^{-3}$ .

Concentrations of  $\text{SO}_4^{2-}$  are well reproduced by the model with a high correlation (0.83) and low MFB and MFE (0.12%

and 0.35%). The model succeeds to capture the high concentrations of  $\text{SO}_4^{2-}$  in winter.  $\text{NO}_3^-$  concentrations and  $\text{NH}_4^+$  concentrations are also well reproduced by the model except at the end of the year where concentrations are strongly overestimated. The high concentrations of  $\text{NO}_3^-$  in February and March are well reproduced by the model (temporal correlation of 0.91 and 0.73, MFE=30% and 40%). The low concentrations of  $\text{Na}^+$  and  $\text{Cl}^-$  are a bit overestimated. The overestimation reaches  $0.34 \mu\text{g m}^{-3}$  for  $\text{Na}^+$  and  $0.41 \mu\text{g m}^{-3}$  for  $\text{Cl}^-$  in January.

Most of the underestimation of  $\text{PM}_{2.5}$  concentrations is probably due to the underestimation of organic aerosols at this station. Indeed, OC concentrations are underestimated by  $2.9 \mu\text{g m}^{-3}$  from June to August. Using the OM/OC ratio of 2.1 measured by Turpin and Lim (2001) for rural areas, the underestimation of organic aerosol could explain most of the differences between modeled and measured  $\text{PM}_{2.5}$ . However, in June, the underestimation of OC concentrations is only of  $3.3 \mu\text{g m}^{-3}$  which would correspond to an underestimation of OM of  $7 \mu\text{g m}^{-3}$  whereas  $\text{PM}_{2.5}$  concentrations are underestimated by  $11 \mu\text{g m}^{-3}$ . It appears difficult that in June, the underestimation alone of organic aerosols could explain all the underestimation of PM. The remaining underestimation in June cannot be explained by  $\text{SO}_4^{2-}$ ,  $\text{NO}_3^-$ ,  $\text{NH}_4^+$ ,  $\text{Na}^+$  or  $\text{Cl}^-$ . The sum of these concentrations is  $4.0 \mu\text{g m}^{-3}$  for the model and  $3.0 \mu\text{g m}^{-3}$  for measurements. The fine fraction of  $\text{Ca}^{2+}$  is a bit underestimated by the model ( $0.08 \mu\text{g m}^{-3}$  against  $0.11 \mu\text{g m}^{-3}$  in measurements), which could explain an underestimation of  $0.75 \mu\text{g m}^{-3}$  (assuming that there is 4% of  $\text{Ca}$  in dusts<sup>2+</sup> in dust) which is just enough to compensate the overestimation by the model of inorganic aerosols. The remaining underestimation in June could be ~~explain~~ explained by an underestimation of primary aerosols. However, EC concentrations are well reproduced by the model (annual correlation of 0.62, MFB=0.34% and MFE=47%) and are slightly overestimated by the model ( $0.42 \mu\text{g m}^{-3}$  against  $0.22 \mu\text{g m}^{-3}$  in measurements).

#### 20 4 Perspectives on model improvement

The following list provides a list of possible developments that may be addressed in the future:

- The formation of ammonium nitrate in the model for which the strongest errors were obtained need to be improved. As  $\text{NH}_3$  emissions is a key element, implementing a dynamic method to improve the spatial and temporal evolution of  $\text{NH}_3$  emissions from agriculture like the method described in Skjøth et al. (2011) depending on temperature and wind speed could be a major improvement.
- The formation of anthropogenic SOA has to be better represented in the model. For that, SVOC and IVOC emissions should be better represented. The inventory of Denier van der Gon et al. (2015) could be used to better estimate SVOC from residential biomass burning. More generally, to take into IVOC emissions, emission inventory by volatility classes should be developed based for example on the method developed by Zhao et al. (2016b). Moreover, mechanisms of formation of SOA from IVOC oxidation and the aging of SVOC have to be better understood. Bruns et al. (2016) showed that the formation of SOA from SOA precursors traditionally taken into account in models (like toluene, xylene, alkanes) only ~~amount~~ account for a small amount of SOA (between 3 and 27% of SOA formed) from biomass burning

and that most of the SOA is due to non-traditional SOA precursors (like phenol, naphthalene, benzaldehyde, etc...). These precursors should be added in the SOA mechanism. Aging has also a major impact on SOA formation (Donahue et al., 2012; Zhao et al., 2016a) and should be studied into greater details.

- 5 – The influence of the gas-phase mechanism on PM formation should be tested within CHIMERE. Indeed, Sarwar et al. (2013) found significant differences over the United States of America between CB05 (Sarwar et al., 2008) and RACM2 (Goliff et al., 2013) in OH concentrations (46% in OH concentrations) and PM components (10 % in sulfate, 6% in nitrate, 10% in ammonium, 42% in anthropogenic SOA and 5% in biogenic SOA). The strong differences in radical concentrations may strongly affect the aging of SVOC compounds and the seasonal evolution of PM components. It may also be important to compare the results of the MELCHIOR 2 mechanisms with more recent gas-phase mechanisms.
- 10 – The formation of inorganic aerosol could be integrated in the SOAP thermodynamic model. SOAP would then be able to simulate both inorganic and organic aerosols and take into account the influence between inorganic and organic aerosols which can affect the partitioning of compounds and the hygroscopicity of the aerosol (Jing et al., 2016). This could also be important to take into account the formation of some acid organics/ammonium ~~salts~~-salt which can be in competition with ammonium nitrate formation. Some organonitrogen compounds were also found by condensation of ammonia onto  
15 organic aerosols (Liu et al., 2015).
- Interactions of dust with inorganic aerosols could be better represented in the model. The interactions could for example be simulated by taking into account the mineralogy of dust within CHIMERE, by emitting dust particles with different composition depending on the location of emissions.
- Some recent experimental studies emphasize the need to account for dynamical aspects of the organic aerosols formation  
20 rather than assuming thermodynamic equilibrium with the gas phase because organic aerosols can be highly viscous (Virtanen et al., 2010; Cappa and Wilson, 2011; Pfrang et al., 2011; Shiraiwa et al., 2011; Vaden et al., 2011; Shiraiwa and Seinfeld, 2012; Abramson et al., 2013). To our knowledge, this phenomenon was never investigated inside a 3D air quality model. However, to take it into account, a dynamic method for SOA formation taking into account the diffusion inside a few layers was developed in the thermodynamic model SOAP. This method could be used to test the influence  
25 of the organic-phase viscosity on SOA formation inside a 3D air quality model.
- Aqueous-phase chemical mechanism can be extensively improved. Several studies highlight the importance of aqueous-phase chemistry for SOA formation from isoprene. An isoprene-derived epoxidol (IEPOX) has been shown to form methyltetrols and C<sub>5</sub>-alkene triols in the aqueous phase of particles and droplets by hydrolysis as well as organosulfates by reaction with sulfate or bisulfate ions and oligomers (Surratt et al., 2010). Froyd et al. (2010) found very high concentrations of SOA formed from IEPOX in Atlanta, USA (910 ng.m<sup>-3</sup>), due to a very acidic aerosol. The formation of  
30 SOA from IEPOX was investigated in a previous study (Couvidat et al., 2013). Using a Henry's law constant of IEPOX of  $2 \times 10^7$  M/atm and a mechanism based on available information, the model could simulate concentrations of SOA from IEPOX in the right order of magnitude and simulates concentrations of SOA from IEPOX in summer that could

could reach  $1 \mu\text{g m}^{-3}$  over some regions and could give strong peaks of SOA. Nguyen et al. (2014) found a Henry's law constant of  $3 \times 10^7 \text{ M/atm}$ . However, this modeling study did not take into account interactions with ~~inorganics~~ inorganic aerosol. Aqueous-phase processing of glyoxal (which is formed from the oxidation of toluene and isoprene) was also found to be possibly a significant source of SOA as it can form oxalic acid via reaction in clouds (Griffin et al., 2003) and could form oligomers or form SOA in particles via reaction with hydroxyl radical or from reactions ~~catalysed~~ catalyzed by ammonium (Knote et al., 2014) which could be important to take into account. Implementing a complete cloud chemical mechanism should be tested. A mechanism similar to Leriche et al. (2013) could be implemented to improve the representation of the cloud chemistry inside the model.

- The number of particles has also an effect on health, especially in urban areas (Jing et al., 2001). To properly estimate the effects on health of particles in urban areas, more complete parameterization of nucleation should be implemented (taking for example the impact of organic compounds (Lupascu et al., 2015)) and model results should be compared to available data on European Megacities, for example (Pikridas et al., 2015).
- The possibility to take into account the mixing state (as done by Zhu et al. (2015, 2016a, b) should be added to the model as it can impact the aerosol formation and composition and their optical and hygroscopic properties.

## 15 5 Conclusions

Concentrations were compared to available information on PM concentrations and composition thanks to the EBAS database. Whereas the model gives satisfactory results in regard of the criteria defined by Boylan and Russell (2006), results could be improved in terms of seasonality and PM composition. Strongest errors were found to be probably due to ammonium nitrate which is often overestimated especially in late autumn (probably due to an overestimation of  $\text{NH}_3$  emissions during this period). Only in summer, concentrations of ammonium nitrate could be underestimated. Strong errors were also found on OC concentrations in summer (especially over the northern half of Europe) indicating that strong concentrations of anthropogenic SOA could be missing from the models. ~~Sea salts~~ The underestimation could also be due to a lack of biogenic emissions over the northern half of Europe. Sea salt concentrations were properly simulated at most stations but were overestimated over regions with low concentrations and underestimated for regions with very strong concentrations (which could lead to an underestimation of  $\text{HNO}_3$  condensation onto coarse particles).

However, the model has good performances in general and respects the goal criteria for both  $\text{PM}_{2.5}$  and  $\text{PM}_{10}$ . For ~~salts~~ salt, the model almost respects the goal criteria of Boylan and Russell (2006) and ~~succeed~~ succeeds in reproducing the seasonal evolution of concentrations for Western and Central Europe. For sulfate, except for an overestimation of sulfate in Northern Europe, modeled concentrations are close to observations with a good seasonal evolution of concentrations. For organic aerosol, the model performs well for stations with strong modeled biogenic SOA concentrations.

Several improvements should be tested. Taking into account the ~~dynamic~~ dynamics of  $\text{NH}_3$  emissions could greatly improve the results of the model in simulating ammonium nitrate. Taking into account SOA formation from missing SVOC/IVOC

emissions probably has an important impact on SOA formation and could probably improve results on SOA concentrations. Moreover, the impact of inorganic-organic interactions and the effect of aqueous-phase chemistry on SOA formation should be investigated.

## 5 6 Code availability

~~The code is~~ [CHIMERE2017 \$\beta\$  is a version of chimere developed for research on aerosol modeling. It is](#) available on request by contacting the authors.

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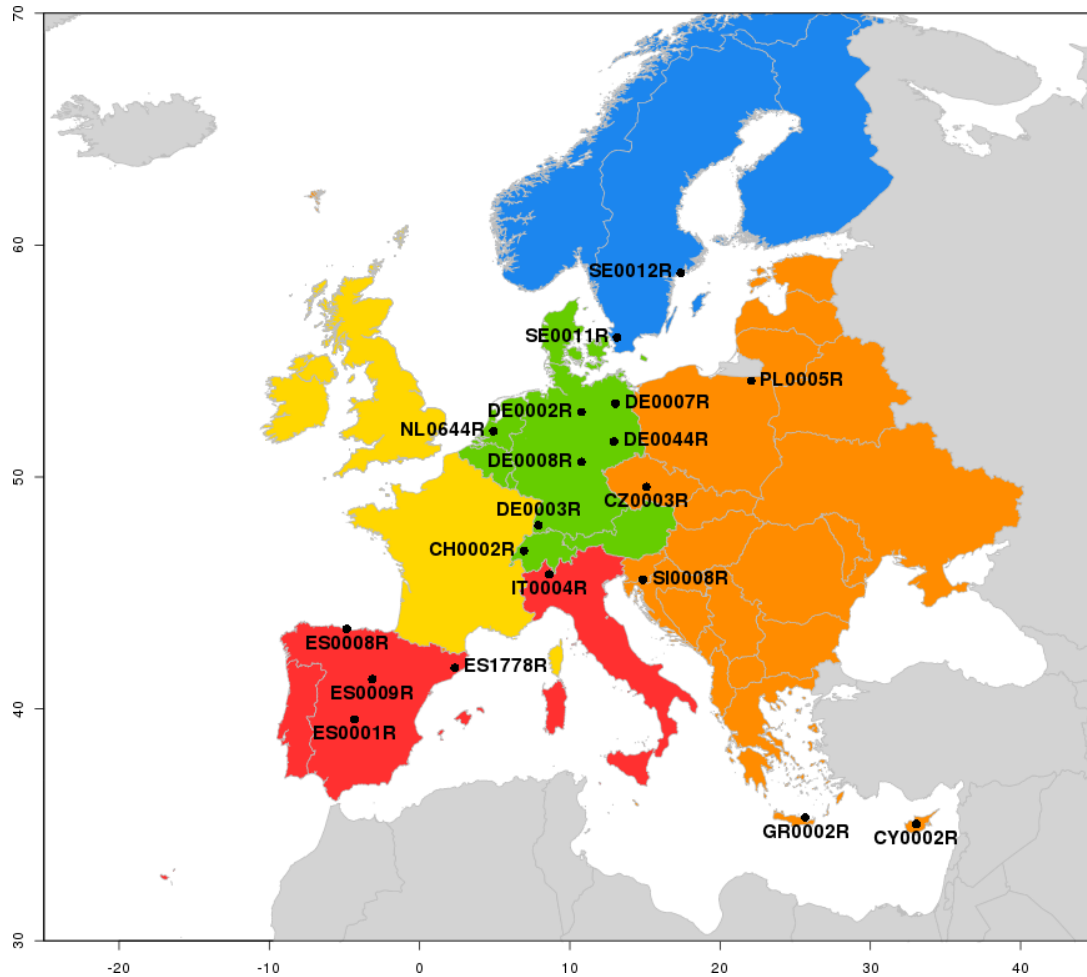
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**Figure 1.** Maps of regions defined in this study and of ~~mentioned-mentioned~~ stations. The chosen regions are: Southern Europe (Red), Western Europe (Yellow), Central Europe (Green), Eastern Europe (Orange), Northern Europe (Blue). Dots represent the specific stations that are referred in the text (mostly stations with measurements of OC).

**Table 1.** Reactions leading to SOA formation<sup>a</sup>. C<sub>5</sub>H<sub>8</sub> refers to isoprene, APINEN to  $\alpha$ -pinene, BPINEN to  $\beta$ -pinene, LIMONE to limonene, HUMULE to sesquiterpenes, TOL to toluene, XYL to xylene.

Reaction	Kinetic rate parameter (s <sup>-1</sup> or molecule <sup>-1</sup> .cm <sup>3</sup> .s <sup>-1</sup> )
<u>ISOP-C<sub>5</sub>H<sub>8</sub></u> + OH → ISOR + OH	$2.54 \times 10^{-11} \times \exp\left(\frac{408}{T}\right)$
<u>ISOP-C<sub>5</sub>H<sub>8</sub></u> + NO <sub>3</sub> → ISON + NO <sub>3</sub>	$3.03 \times 10^{-12} \times \exp\left(\frac{-448}{T}\right)$
ISOR + HO <sub>2</sub> → 0.282 BiPER + 0.030 BiDER + HO <sub>2</sub>	$2.05 \times 10^{-13} \times \exp\left(\frac{1300}{T}\right)$
ISOR + <u>C<sub>2</sub>O<sub>3</sub>-CH<sub>3</sub>COO</u> → 0.026 BiMT + 0.219 MACR + <u>C<sub>2</sub>O<sub>3</sub>-CH<sub>3</sub>COO</u>	$8.40 \times 10^{-14} \times \exp\left(\frac{221}{T}\right)$
ISOR + <u>MeOCH<sub>3</sub>O<sub>2</sub></u> → 0.026 BiMT + 0.219 MACR + <u>MeOCH<sub>3</sub>O<sub>2</sub></u>	$3.40 \times 10^{-14} \times \exp\left(\frac{221}{T}\right)$
ISOR + NO → 0.418 MACR + 0.046 ISON + NO	$2.43 \times 10^{-12} \times \exp\left(\frac{360}{T}\right)$
ISOR + NO <sub>3</sub> → 0.438 MACR + NO <sub>3</sub>	$1.20 \times 10^{-12}$
ISON + OH → OH	$1.30 \times 10^{-11}$
ISON + NO <sub>3</sub> → 0.074 BiNIT3 + NO <sub>3</sub>	$6.61 \times 10^{-13}$
MACR + NO → NO	$2.54 \times 10^{-12} \times \exp\left(\frac{360}{T}\right)$
MACR + HO <sub>2</sub> → HO <sub>2</sub>	$1.82 \times 10^{-13} \times \exp\left(\frac{1300}{T}\right)$
MACR + <u>MeOCH<sub>3</sub>O<sub>2</sub></u> → <u>MeOCH<sub>3</sub>O<sub>2</sub></u>	$3.40 \times 10^{-14} \times \exp\left(\frac{221}{T}\right)$
MACR + NO <sub>2</sub> → MPAN + NO <sub>2</sub>	$2.80 \times 10^{-12} \times \exp\left(\frac{181}{T}\right)$
MPAN → MACR	$1.60 \times 10^{16} \times \exp\left(\frac{-13486}{T}\right)$
MPAN + OH → 0.067 BiMGA + 0.047 BiNGA + OH	$3.20 \times 10^{-11}$
MPAN + NO <sub>3</sub> → 0.067 BiMGA + 0.047 BiNGA + NO <sub>3</sub>	$3.20 \times 10^{-11}$
BiPER + h $\nu$ → Degradation products	k = 50 × kinetic of photolysis of H <sub>2</sub> O <sub>2</sub>



Reaction	Kinetic rate parameter (s <sup>-1</sup> or molecule <sup>-1</sup> .cm <sup>3</sup> .s <sup>-1</sup> )
<del>API</del> - <del>APINEN</del> + OH → 0.30 BiA0D + 0.17 BiA1D + 0.10 BiA2D + OH <del>API</del> - <del>APINEN</del> + O <sub>3</sub> → 0.18 BiA0D + 0.16 BiA1D + 0.05 BiA2D + O <sub>3</sub> <del>API</del> - <del>APINEN</del> + NO <sub>3</sub> → 0.70 BiA0D + 0.10 BiNIT + NO <sub>3</sub>	$1.21 \times 10^{-11} \times \exp\left(\frac{440}{T}\right)$ $5.00 \times 10^{-16} \times \exp\left(\frac{-530}{T}\right)$ $1.19 \times 10^{-12} \times \exp\left(\frac{-490}{T}\right)$
<del>BPI</del> - <del>BPINEN</del> + OH → 0.07 BiA0D + 0.08 BiA1D + 0.06 BiA2D + OH <del>BPI</del> - <del>BPINEN</del> + O <sub>3</sub> → 0.09 BiA0D + 0.13 BiA1D + 0.04 BiA2D + O <sub>3</sub> <del>BPI</del> - <del>BPINEN</del> + NO <sub>3</sub> → 0.02 BiA0D + 0.63 BiNIT + NO <sub>3</sub>	$2.38 \times 10^{-11} \times \exp\left(\frac{357}{T}\right)$ $1.50 \times 10^{-17}$ $2.51 \times 10^{-12}$
<del>LIM</del> - <del>LIMONE</del> + OH → 0.35 BiA0D + 0.20 BiA1D + 0.0035 BiA2D + OH <del>LIM</del> - <del>LIMONE</del> + O <sub>3</sub> → 0.09 BiA0D + 0.10 BiA1D + O <sub>3</sub> <del>LIM</del> - <del>LIMONE</del> + NO <sub>3</sub> → 0.69 BiA0D + 0.27 BiNIT + NO <sub>3</sub>	$4.20 \times 10^{-11} \times \exp\left(\frac{401}{T}\right)$ $2.95 \times 10^{-15} \times \exp\left(\frac{783}{T}\right)$ $1.22 \times 10^{-11}$
<del>HUM</del> - <del>HUMULE</del> + OH → 0.74 BiBmP + 0.26 BiBIP + OH	$2.93 \times 10^{-10}$
TOL + OH → ... + 0.25 TOLP TOLP + HO <sub>2</sub> → 0.78 AnCIP + HO <sub>2</sub> TOLP + <del>C<sub>2</sub>O<sub>3</sub>-CH<sub>3</sub>COO</del> → 0.78 AnCIP + <del>C<sub>2</sub>O<sub>3</sub>-CH<sub>3</sub>COO</del> TOLP + <del>MeOCH<sub>3</sub>O<sub>2</sub></del> → 0.78 AnCIP + <del>MeOCH<sub>3</sub>O<sub>2</sub></del> TOLP + NO → 0.097 AnBIP + 0.748 AnBmP + NO TOLP + NO <sub>3</sub> → 0.097 AnBIP + 0.748 AnBmP + NO <sub>3</sub>	$1.80 \times 10^{-12} \times \exp\left(\frac{355}{T}\right)$ $3.75 \times 10^{-13} \times \exp\left(\frac{980}{T}\right)$ $7.40 \times 10^{-13} \times \exp\left(\frac{765}{T}\right)$ $3.56 \times 10^{-14} \times \exp\left(\frac{708}{T}\right)$ $2.70 \times 10^{-12} \times \exp\left(\frac{360}{T}\right)$ $1.2 \times 10^{-12}$
XYL + OH → ... + 0.274 XYLP XYLP + HO <sub>2</sub> → 0.71 AnCIP + HO <sub>2</sub> XYLP + <del>C<sub>2</sub>O<sub>3</sub>-CH<sub>3</sub>COO</del> → 0.71 AnCIP + <del>C<sub>2</sub>O<sub>3</sub>-CH<sub>3</sub>COO</del> XYLP + <del>MeOCH<sub>3</sub>O<sub>2</sub></del> → 0.71 AnCIP + <del>MeOCH<sub>3</sub>O<sub>2</sub></del> XYLP + NO → 0.063 AnBIP + 0.424 AnBmP + NO XYLP + NO <sub>3</sub> → 0.063 AnBIP + 0.424 AnBmP + NO <sub>3</sub>	$1.70 \times 10^{-11} \times \exp\left(\frac{116}{T}\right)$ $3.75 \times 10^{-13} \times \exp\left(\frac{980}{T}\right)$ $7.40 \times 10^{-13} \times \exp\left(\frac{765}{T}\right)$ $3.56 \times 10^{-14} \times \exp\left(\frac{708}{T}\right)$ $2.70 \times 10^{-12} \times \exp\left(\frac{360}{T}\right)$ $1.2 \times 10^{-12}$

<sup>a</sup> Oxidants may be present as both reactants and products so that a reaction added to ~~CB05-the mechanism~~ will not affect the original photochemical oxidant concentrations.

**Table 2.** Properties of the surrogate SOA species of  $H^2O$  (Couvidat et al., 2012).

Surrogate	Type <sup>a</sup>	H <sup>b,a</sup>	P <sup>0</sup> <sup>c,b</sup>	$\Delta H_{vap}$ <sup>d,c</sup>	Comments
BiMT	hydrophilic	<del>0.805</del> $3.3 \times 10^{10}$	$1.45 \times 10^{-6}$	38.4	-
BiPER	hydrophilic	<del>0.111</del> $8.1 \times 10^9$	$2.61 \times 10^{-6}$	38.4	-
BiDER	<del>hydrophilic</del> hydrophilic	<del>2.80</del> $8.91 \times 10^{10}$	$4.10 \times 10^{-7}$	38.4	-
BiMGA	hydrophilic	<del>1.13</del> $5.25 \times 10^{-2.8}$	$1.4 \times 10^{-5}$	43.2	$pK_a = 4.0$
BiNGA	hydrophobic	-	$1.4 \times 10^{-5}$	43.2	$K_{p,eff} = K_p(1 + K_{oligo})^{ed}$
BiNIT3	hydrophobic	-	$1.45 \times 10^{-6}$	38.4	-
BiA0D	hydrophilic	<del>4.82</del> $1.98 \times 10^{-5.6}$	$2.70 \times 10^{-4.6}$	50	See Eq. 8
BiA1D	hydrophilic	<del>2.73</del> $1.12 \times 10^{-3.8}$	$2.17 \times 10^{-7}$	50	$pK_a = 3.2$
BiA2D	hydrophilic	<del>6.52</del> $2.67 \times 10^{-3.8}$	$1.43 \times 10^{-7}$	50	$pK_{a1} = 3.4, pK_{a2} = 5.1$
BiNIT	hydrophobic	-	$2.5 \times 10^{-6}$	109	-
BiBIP	hydrophobic	-	$6.0 \times 10^{-10}$	175	-
BiBmP	hydrophobic	-	$3.0 \times 10^{-7}$	175	-
AnBIP	hydrophobic	-	$6.8 \times 10^{-8}$	50	-
AnBmP	hydrophobic	-	$8.4 \times 10^{-6}$	50	-
AnCIP	hydrophobic	-	-	non volatile	-

<sup>a</sup> ~~Type A: hydrophilic species, type B: hydrophobic species, type C: hydrophobic non-volatile species, which is not used to compute activity coefficients~~ Henry's law constant [ $(\mu g M / \mu g \text{ water}) L / (\mu g / m^3) atm$ ]

<sup>b</sup> Saturation vapor pressure [torr]

<sup>c</sup> Enthalpy of vaporization [ $kJ.mol^{-1}$ ]

<sup>d</sup>  $K_{oligo}$  (equal to 64.2) is used to take into account the formation of oligomers (Couvidat et al., 2012).  $K_{p,eff}$  is the effective partitioning constant and  $K_p$  is the partitioning constant calculated as in Pankow (1994).

**Table 3.** Properties of primary and aged SVOC.

Surrogate	MW <sup>a</sup>	$K_p$ <sup>b</sup>	$\Delta H_{vap}$ <sup>c</sup>
POAIP	280	1.1	106
POAmP	280	0.0116	91
POAhP	280	0.00031	79
SOAIP	392	110	106
SOAmP	392	1.16	91
SOAhP	392	0.031	79

<sup>a</sup> Molecular weight [ $g.mol^{-1}$ ]

<sup>b</sup> Partitioning constant [ $m^3.\mu g^{-1}$ ]

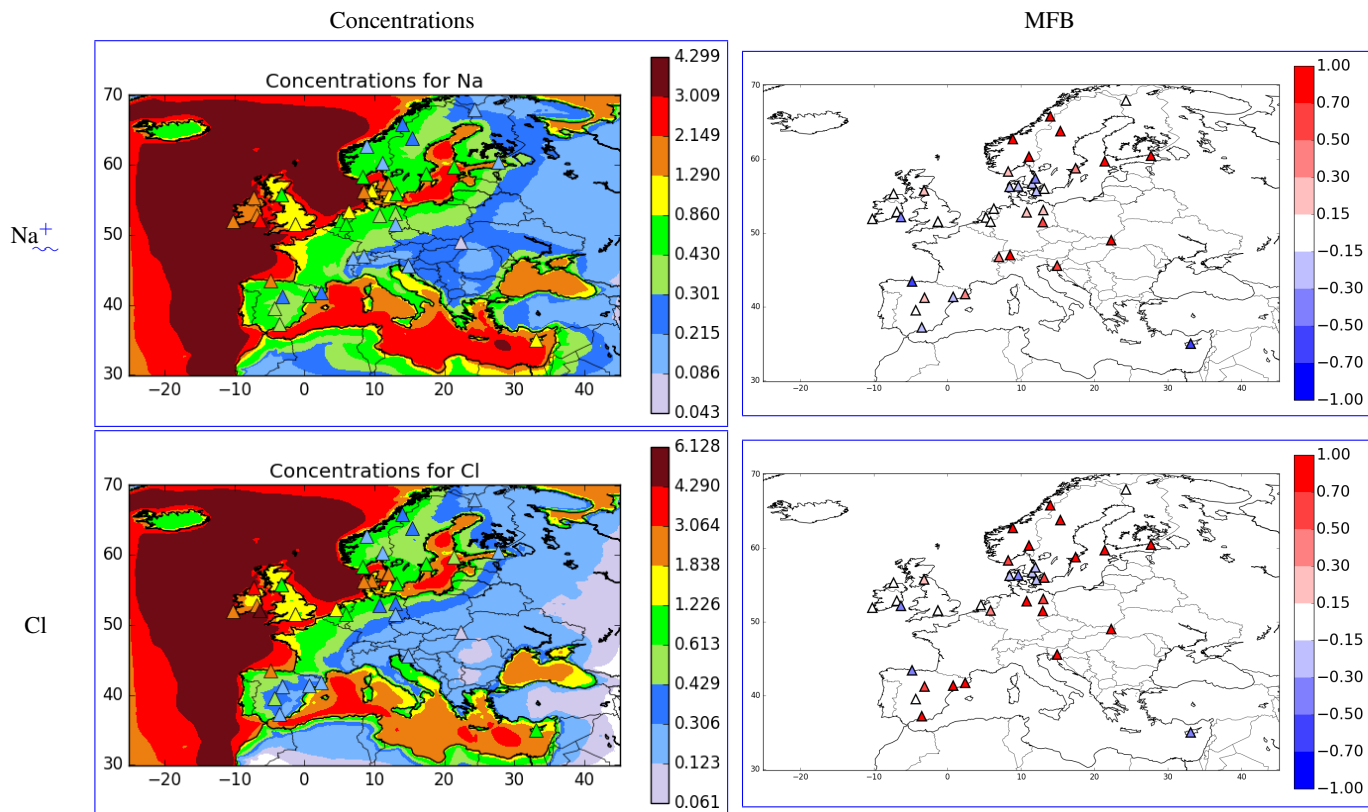
<sup>c</sup> Enthalpy of vaporization [ $kJ.mol^{-1}$ ]

**Table 4.** Effective Henry's law ~~constant constants~~ used for dry and wet deposition. High numerical values were used for HNO<sub>3</sub> and for gaseous H<sub>2</sub>SO<sub>4</sub> to take into account their hydrophilic properties.

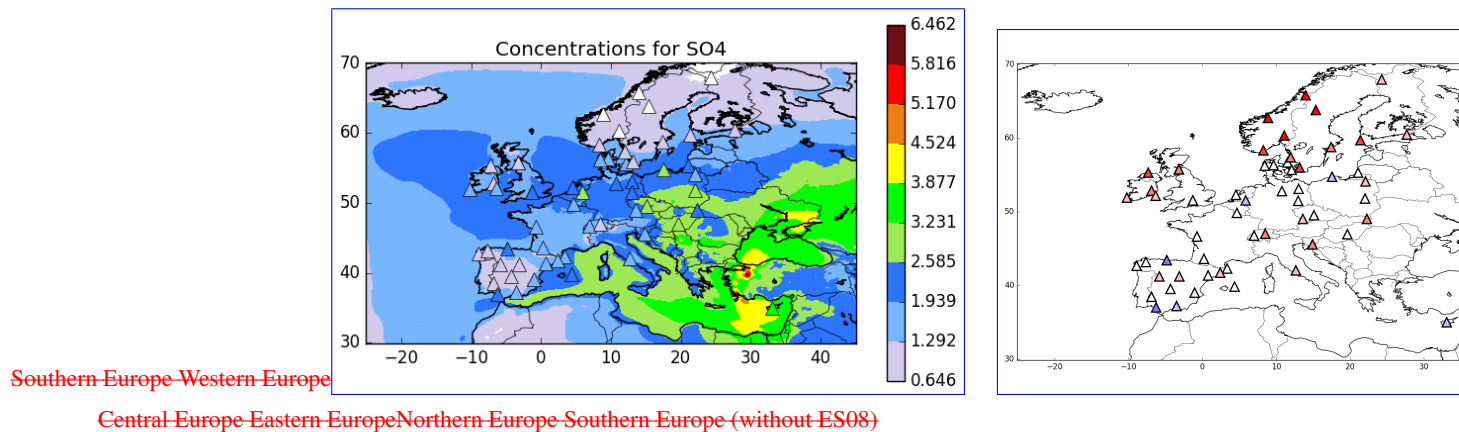
Compound	H (mol/L/atm)
O <sub>3</sub>	0.01
SO <sub>2</sub>	10 <sup>5</sup>
NO <sub>2</sub>	0.01
NO	2 × 10 <sup>-3</sup>
NH <sub>3</sub>	10 <sup>5</sup>
BiA0D	1.8e6
BiA1D	2.92e10
BiA2D	4.23e10
BiMT	3.3e10
BiPER	<del>8.098.1</del> e9
BiDER	8.91e10
BiMGA	2.15e10
AnBIP	0.01
AnBmP	0.01
BiBIP	1.17e8
BiBmP	3.05e5
AnCIP	0.01
BiNGA	2.71e9
BiNIT3	4.75e6
BiNIT	7.66e4
POAIP	0.01
POAmP	0.01
POAhP	0.01
SOAIP	3000
SOAmP	3000
SOAhP	3000

**Table 5.** Annual statistics for the comparison of daily concentrations. Means and RMSE are in  $\mu\text{g m}^{-3}$ . SE: Southern Europe. WE: Western Europe. CE: Central Europe. EE: Eastern Europe. NE: Northern Europe.

height	<del>O<sub>3</sub></del> -NO <sub>2</sub> -PM <sub>10</sub>	PM <sub>2.5</sub>	NO <sub>3</sub> <sup>-</sup>	NH <sub>4</sub> <sup>+</sup>	SO <sub>4</sub> <sup>2-</sup>	Na <sup>+</sup>	Cl <sup>-</sup>	TNO <sub>3</sub>	TNH <sub>4</sub>
Number of stations	<del>117</del> <u>54</u>	<del>81</del> <u>39</u>	<del>59</del> <u>41</u> -37	33	<del>56</del> <u>55</u>	38	35	42	42
<del>Model mean</del> <u>Number of stations in SE</u>	<del>71</del> <u>78</u> -16	<del>6</del> <u>8</u> -13	<u>15</u>	<u>7</u>	<u>15</u>	<u>6</u>	<u>6</u>	<u>13</u>	<u>13</u>
<u>Number of stations in WE</u>	<u>9</u>	<u>5</u>	<u>5</u>	<u>5</u>	<u>9</u>	<u>6</u>	<u>6</u>	<u>4</u>	<u>4</u>
<u>Number of stations in CE</u>	<u>19</u>	<u>12</u>	<u>5</u>	<u>9</u>	<u>11</u>	<u>12</u>	<u>9</u>	<u>8</u>	<u>8</u>
<u>Number of stations in EE</u>	<u>6</u>	<u>5</u>	<u>4</u>	<u>4</u>	<u>8</u>	<u>2</u>	<u>2</u>	<u>5</u>	<u>5</u>
<u>Number of stations in NE</u>	<u>4</u>	<u>4</u>	<u>8</u>	<u>8</u>	<u>12</u>	<u>12</u>	<u>12</u>	<u>12</u>	<u>12</u>
<u>Number of measurements</u>	<u>18210</u>	<u>11640</u>	<u>10583</u>	<u>7800</u>	<u>16564</u>	<u>10554</u>	<u>7207</u>	<u>13249</u>	<u>13249</u>
<u>Model mean</u>	14.42	10.54	1.99	1.29	1.66	0.67	1.28	2.55	2.16
Measurement mean	<del>63</del> <u>90</u> - <del>6</del> <u>57</u> -13.51	9.06	1.46	0.89	1.6	0.69	1.17	2.07	1.49
RMSE	<del>19</del> <u>62</u> - <del>6</del> <u>4</u> -9.34	6.95	1.87	0.97	1.13	0.76	1.49	2.0	2.0
Correlation	<del>0</del> <u>62</u> -0.6	<del>0</del> <u>6</u> -0.68	0.71	0.71	0.67	0.66	0.67	0.69	0.56
MFB	<del>0</del> <u>02</u> - <del>0</del> <u>03</u> -0.08	0.22	0.15	0.36	0.13	0.06	0.09	0.10	0.20
MFE	<del>0</del> <u>16</u> - <del>0</del> <u>51</u> -0.44	0.48	0.57	0.55	0.44	0.52	0.49	0.50	0.55



**Figure 2.** Modeled concentrations (in  $\mu\text{g m}^{-3}$ ) and MFB for  $\text{Na}^+$  and  $\text{Cl}^-$  in 2013. Triangles correspond to measured concentrations in the left and to the MFB value in the right.



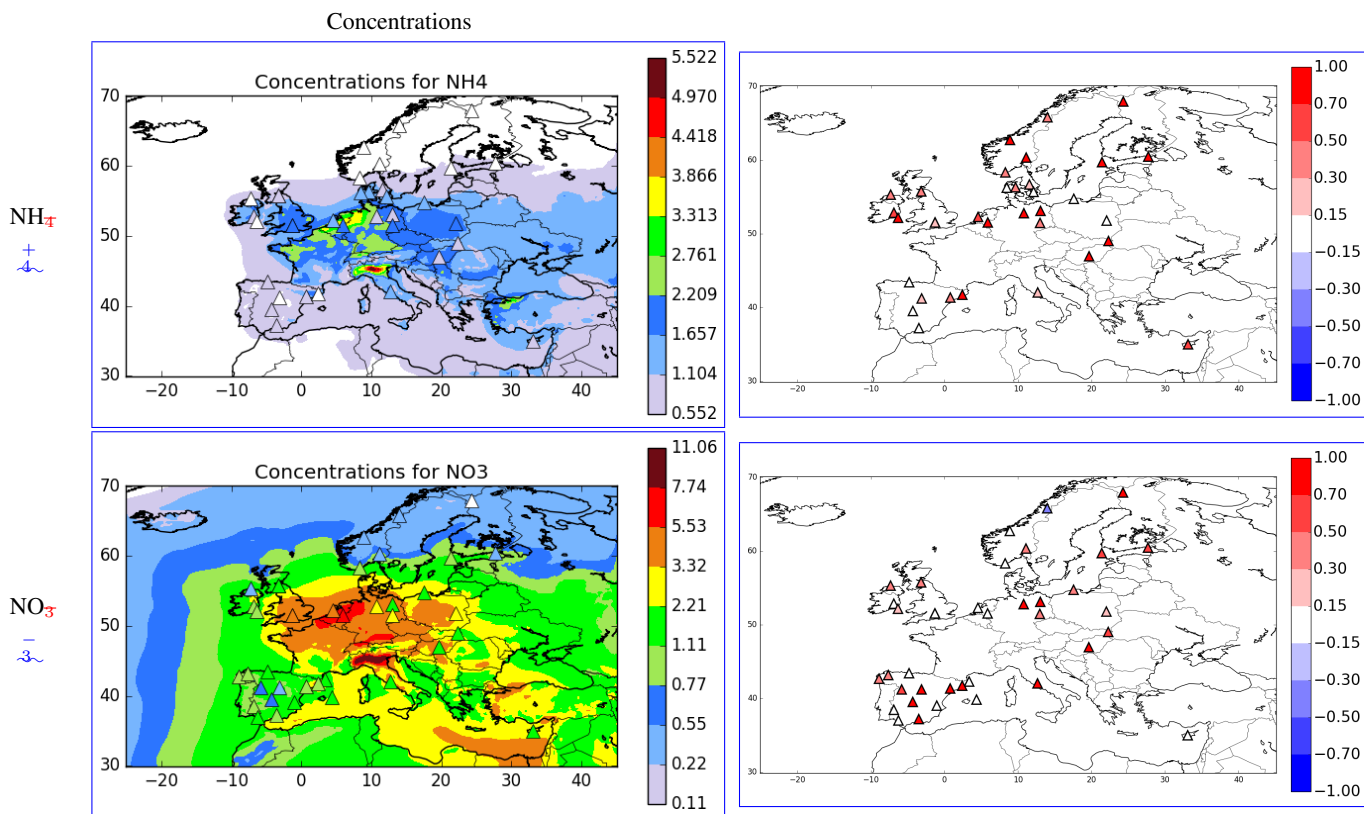
**Figure 3.** Seasonal evolution of statistics by regions for Na: Monthly mean measured Modeled concentrations (black in  $\mu\text{g m}^{-3}$ ), monthly mean modeled concentrations (red), monthly RMSE (blue), monthly spatiotemporal correlations (green), monthly MFB (cyan) and monthly MFE (magenta). Solid curves refer MFB for  $\text{SO}_4^{2-}$  in 2013. Triangles correspond to measured concentrations in the left axis while dotted curves refer and to the MFB value in the right axis.

Modeled concentrations (in  $\mu\text{g m}^{-3}$ ) and MFB for  $\text{SO}_4$  in 2013. Triangles correspond to measured concentrations in the left and to the MFB value in the right.

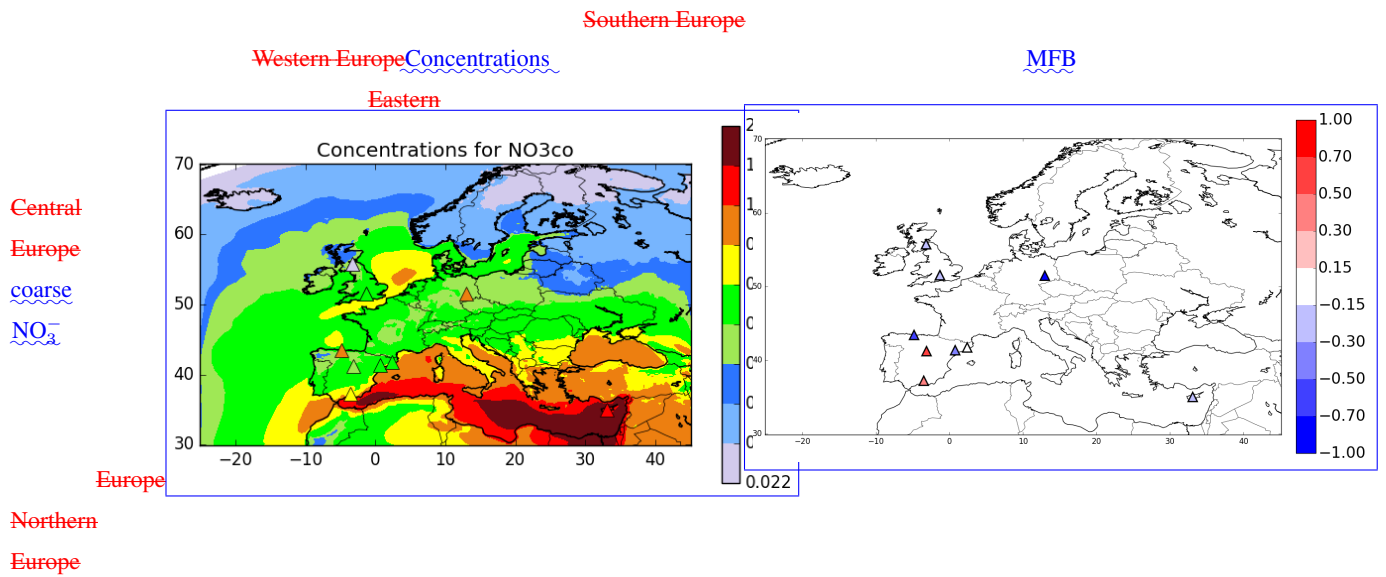
Southern Europe  
 Western Europe Central Europe Eastern Europe Northern Europe

Seasonal evolution of statistics by regions for  $\text{SO}_4$ : Monthly mean-measured concentrations (black), monthly mean-modeled concentrations (red), monthly RMSE (blue), monthly spatiotemporal correlations (green), monthly MFB (cyan) and monthly MFE (magenta). Solid curves refer to the left axis while dotted curves refer to the right axis.

MFB



**Figure 4.** Modeled concentrations (in  $\mu\text{g m}^{-3}$ ) and MFB for  $\text{NH}_4^+$  and  $\text{NO}_3^-$  in 2013. Triangles correspond to measured concentrations in the left and to the MFB value in the right.

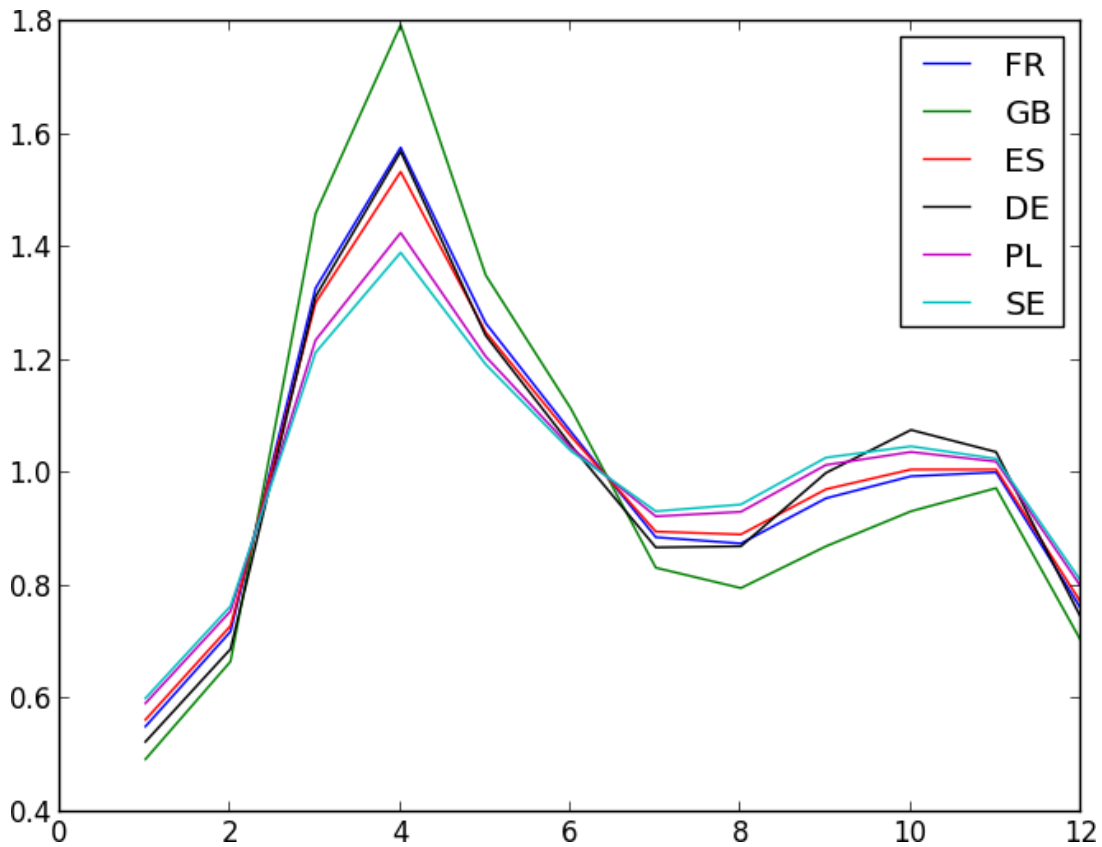


**Figure 5.** Seasonal evolution of statistics by regions for  $\text{NO}_3$ : Monthly mean measured Modeled concentrations (black in  $\mu\text{g m}^{-3}$ ), monthly mean modeled concentrations (red), monthly RMSE (blue), monthly spatiotemporal correlations (green), monthly MFB (cyan) and monthly MFE (magenta). Solid curves refer MFB for coarse  $\text{NO}_3^-$  in 2013. Triangles correspond to measured concentrations in the left axis while dotted curves refer and to the MFB value in the right axis.

Southern Europe Western Europe Central Europe Eastern Europe Northern Europe Seasonal evolution of statistics by regions for  $\text{NH}_4$ : Monthly mean m

**Figure 6.** Seasonal evolution of statistics for the all Europe for  $\text{TNO}_3$  and  $\text{TNH}_4$ : Monthly mean measured concentrations (black), monthly mean modeled concentrations (red), monthly RMSE (blue), monthly spatiotemporal correlations (green), monthly MFB (cyan) and monthly MFE (magenta).

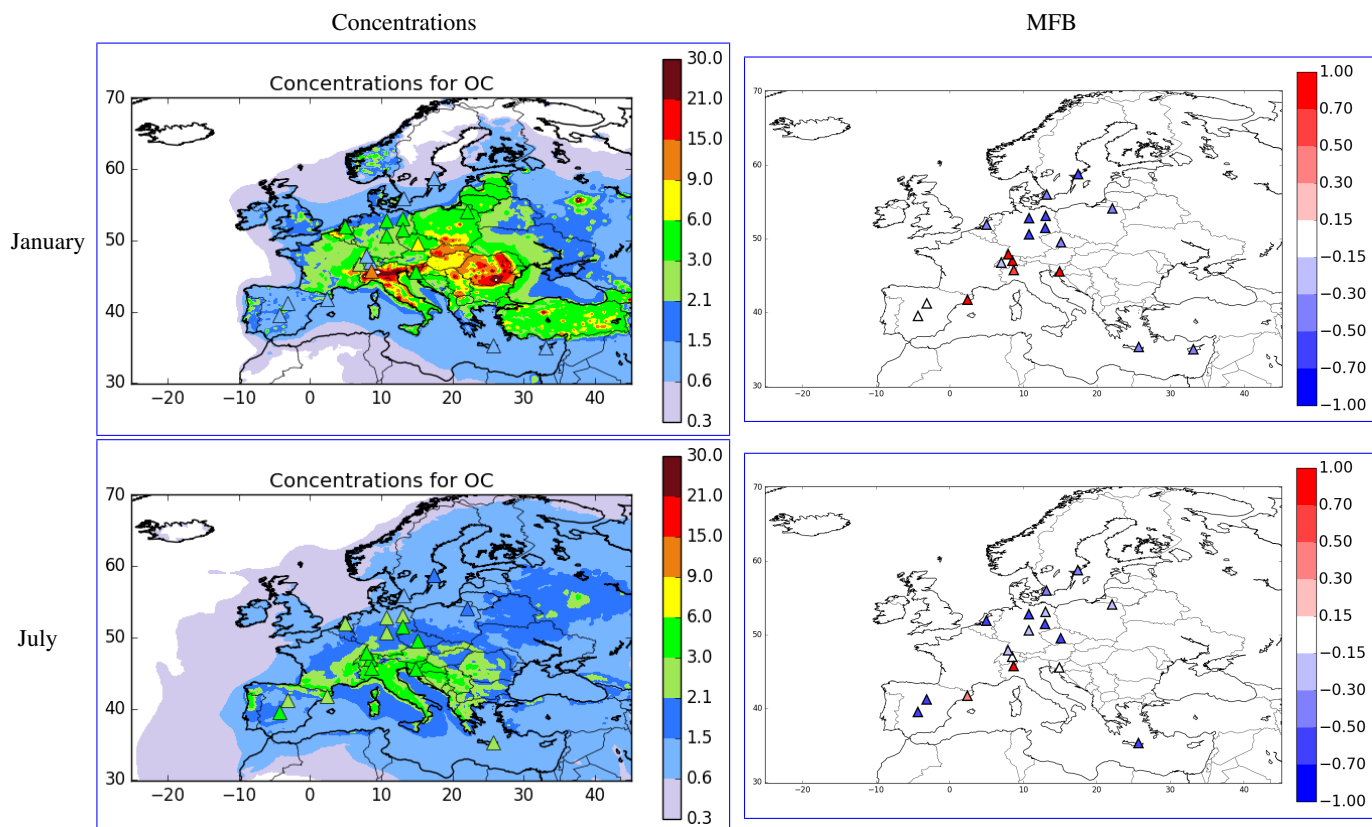




**Figure 7.** Seasonal [factors used in CHIMERE to compute the](#) evolution of NH<sub>3</sub> emissions ~~used in CHIMERE~~ for several countries. [The factors originate from GENEMIS \(Ebel et al., 1997\).](#)

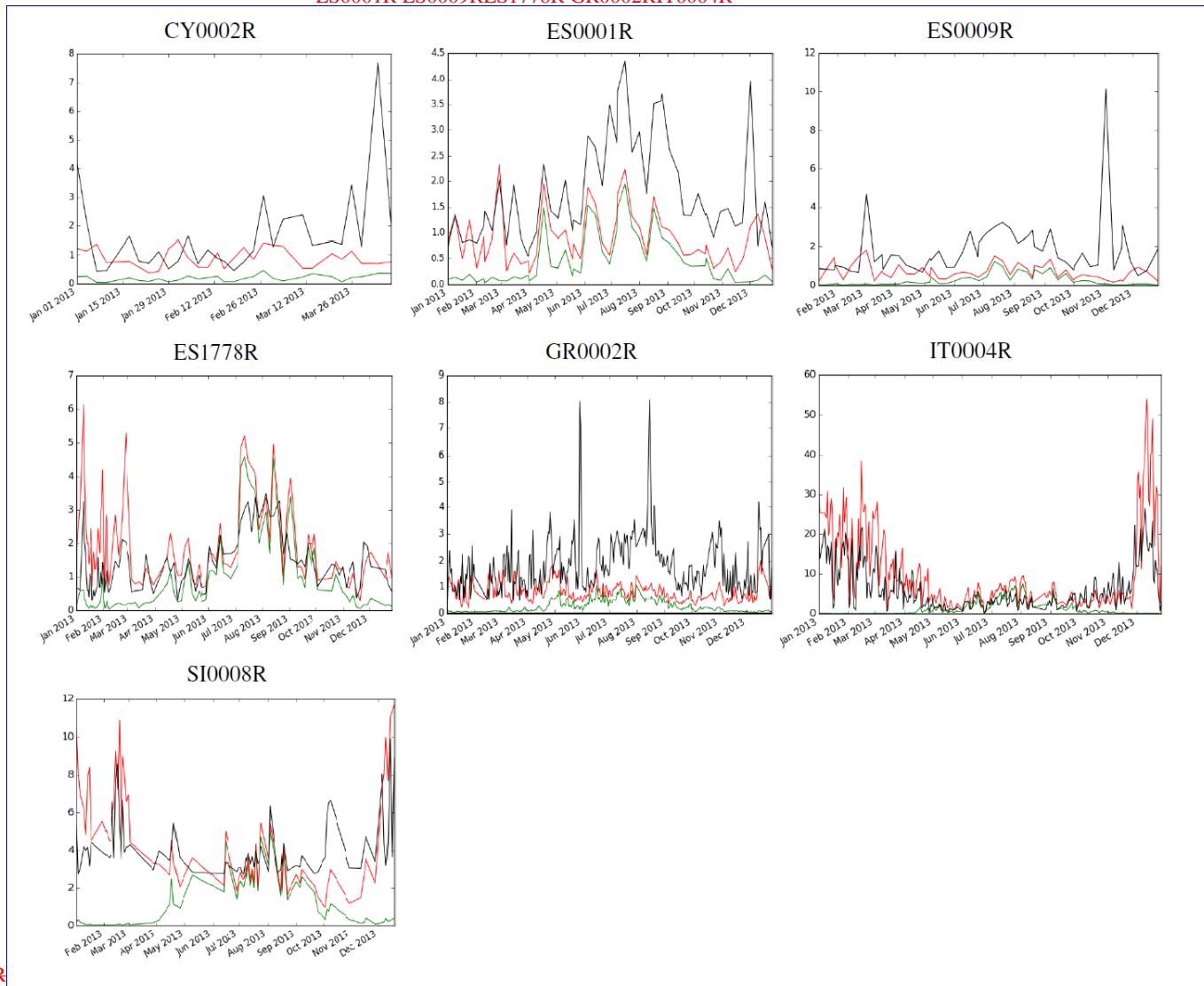
**Table 6.** Comparison of modeled concentrations to measured concentrations of OC. Means and RMSE are in  $\mu\text{g m}^{-3}$ .

Station	Modeled mean	Measured mean	RMSE	correlation	MFB	MFE
CH0002R	2.48	3.29	1.70	0.67	-0.13	0.37
CY0002R	0.91	1.65	1.65	0.07	-0.35	0.65
CZ0003R	1.97	3.64	2.28	0.72	-0.63	0.67
DE0002R	1.20	2.40	1.79	0.40	-0.68	0.75
DE0003R	1.83	1.27	1.28	0.35	0.40	0.63
DE0007R	1.28	2.26	2.03	0.29	-0.56	0.73
DE0008R	1.49	1.73	1.18	0.49	-0.03	0.54
DE0044R	1.67	3.65	2.45	0.82	-0.74	0.76
ES0001R	0.90	1.79	1.18	0.64	-0.65	0.70
ES0009R	0.69	1.79	1.87	0.07	-0.77	0.87
ES1778R	1.97	1.60	1.07	0.68	0.36	0.48
IT0004R	10.4	6.36	7.43	0.84	0.40	0.55
NL0644R	1.21	2.57	1.53	0.84	-0.87	0.87
PL0005R	1.87	3.04	2.18	0.71	-0.42	0.49
SI0008R	4.70	4.19	2.45	0.53	-0.01	0.40
GR0002R	0.82	1.78	1.42	0.19	-0.65	0.72
SE0011R	0.84	1.14	0.71	0.41	-0.32	0.50
SE0012R	0.73	1.53	1.16	0.74	-0.70	0.72



**Figure 8.** Modeled concentrations (in  $\mu\text{g m}^{-3}$ ) and MFB for Organic Carbon in January and July 2013. Triangles correspond to measured concentrations in the left and to the MFB value in the right.

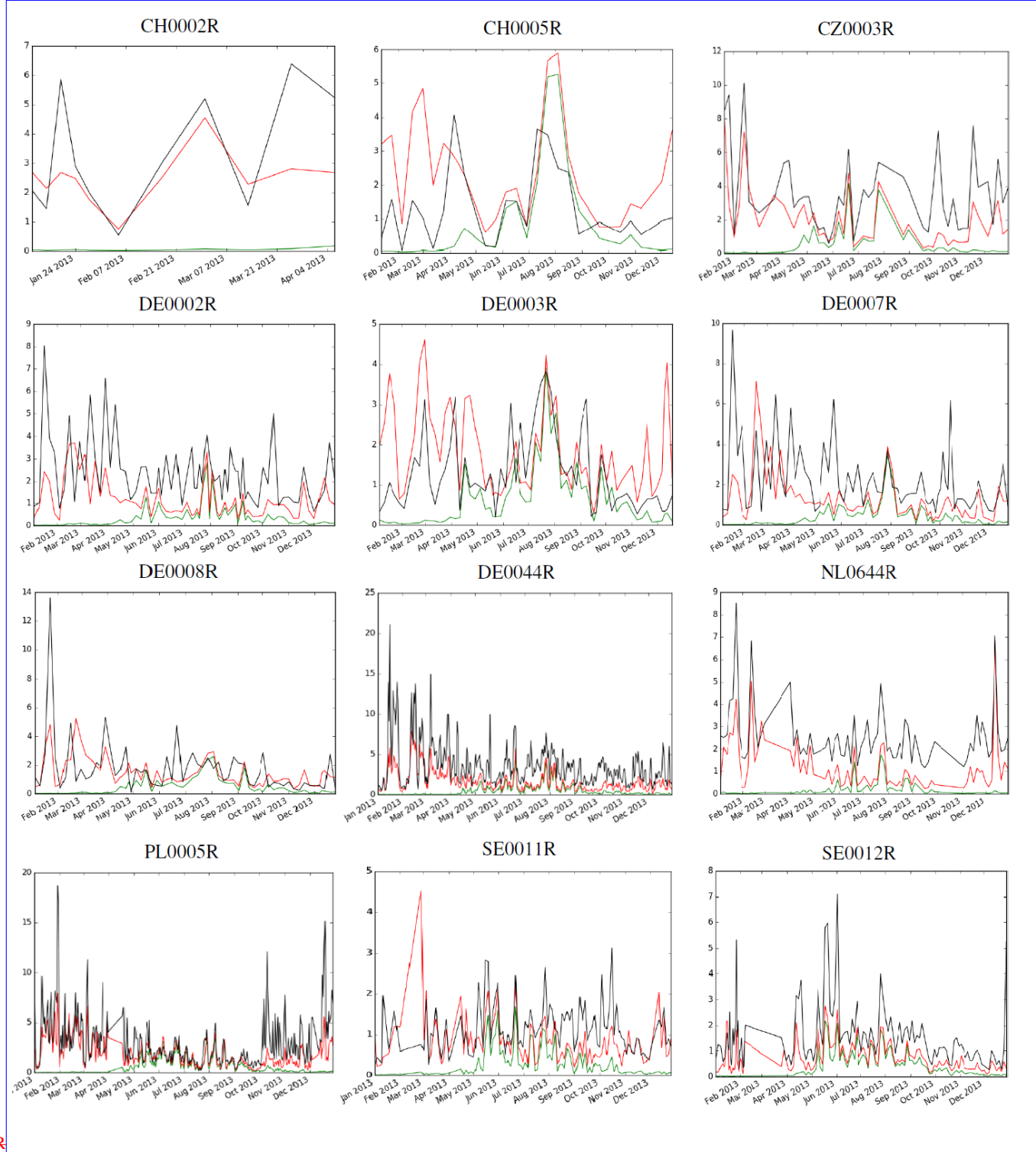
ES0001R-ES0009RES1778R-GR0002RIT0004R



SI0008R

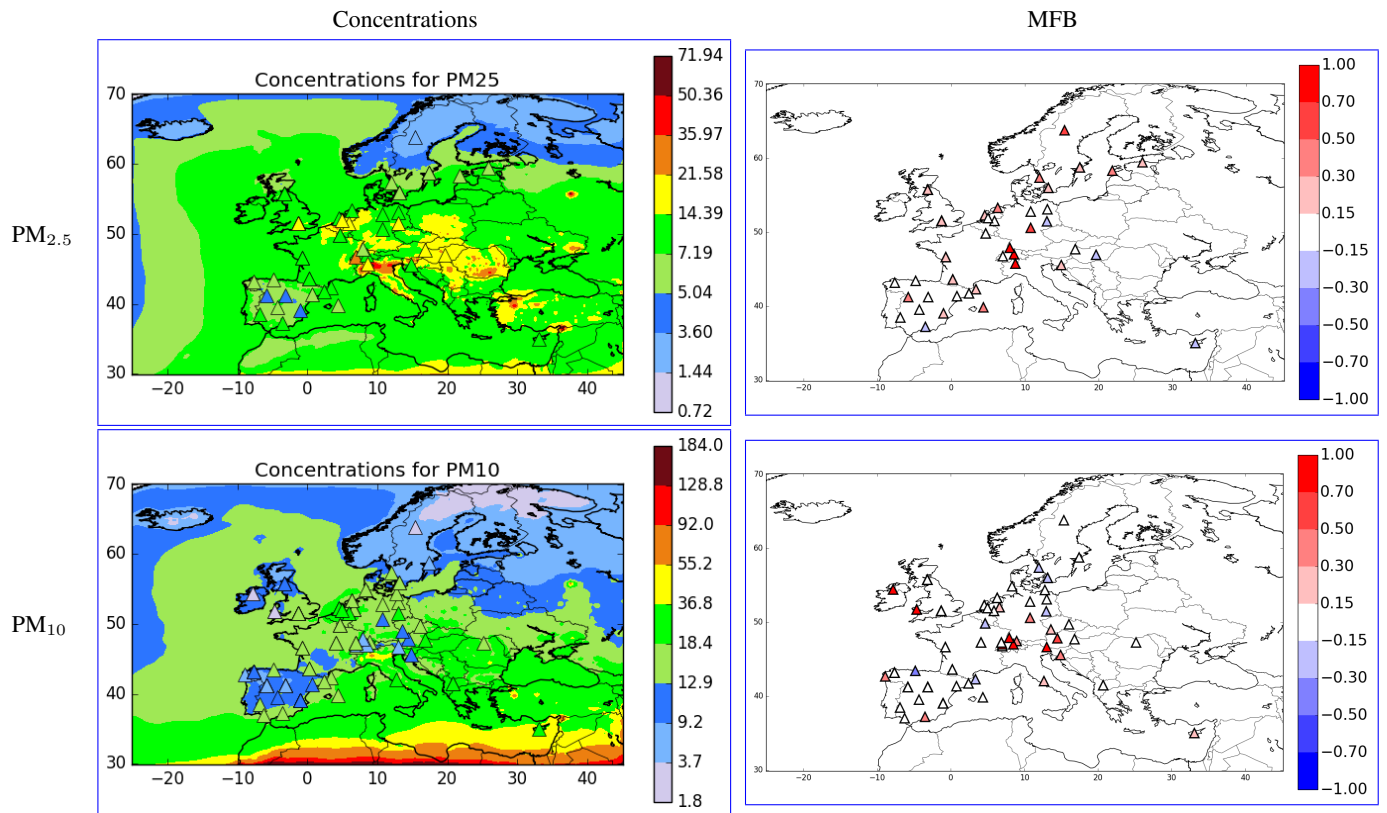
**Figure 9.** Temporal evolution of modeled (red line) and measured (black line) OC concentrations (in in  $\mu\text{g m}^{-3}$ ) for stations in the South of Europe. The green line corresponds to Organic Carbon from biogenic compounds.

CH0002R CH0005R CZ0003R DE0002R DE0003R DE0007R DE0008R DE0044R NL0644R PL0005R SE0011R

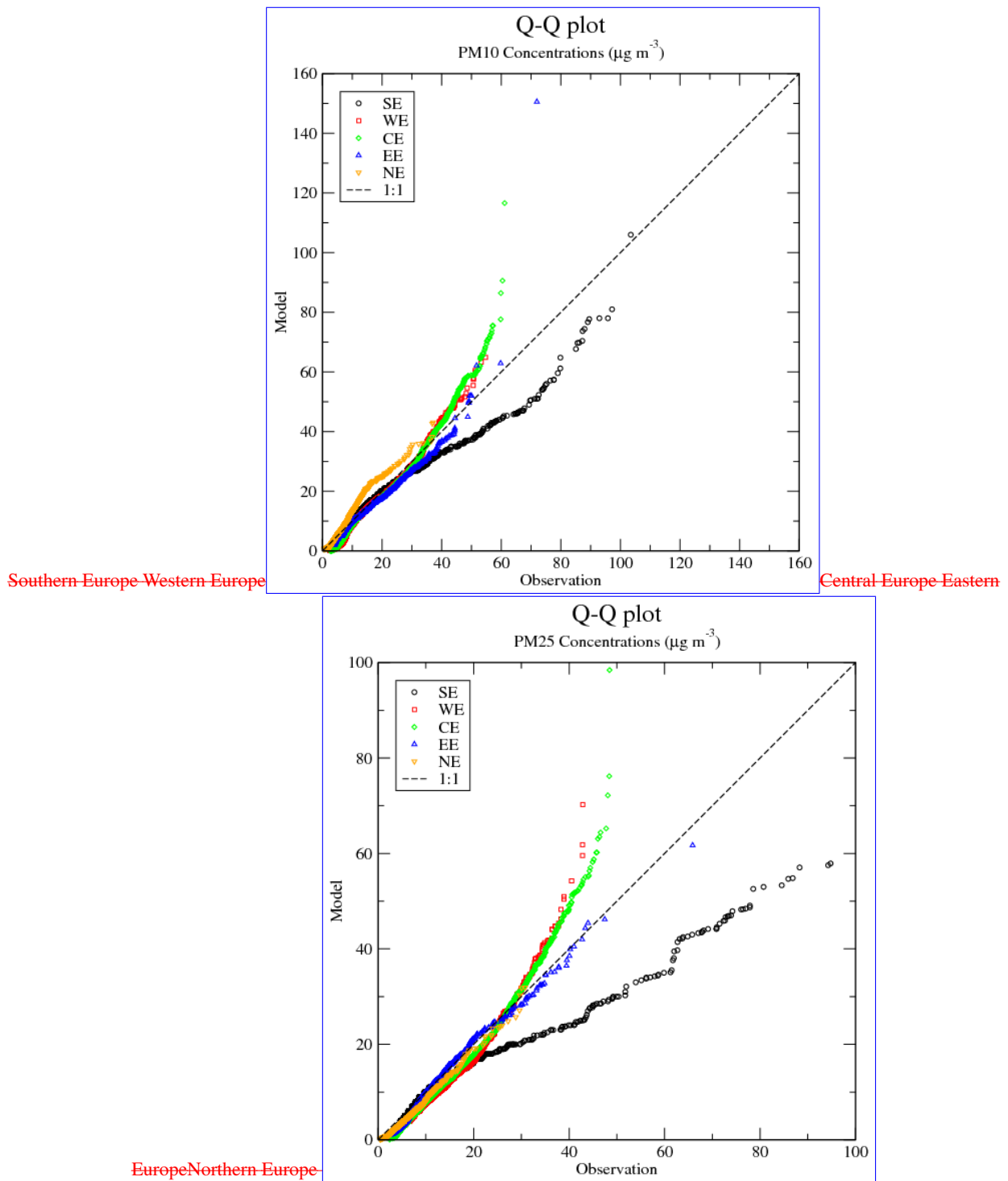


SE0012R

**Figure 10.** Temporal evolution of modeled (red line) and measured (black line) Organic Carbon concentrations (in  $\mu\text{g m}^{-3}$ ) for stations in the South of Europe. The green line corresponds to OC from biogenic compounds.



**Figure 11.** Modeled concentrations (in  $\mu\text{g m}^{-3}$ ) and MFB for PM<sub>2.5</sub> and PM<sub>10</sub> in 2013. Triangles correspond to measured concentrations in the left and to the MFB value in the right.



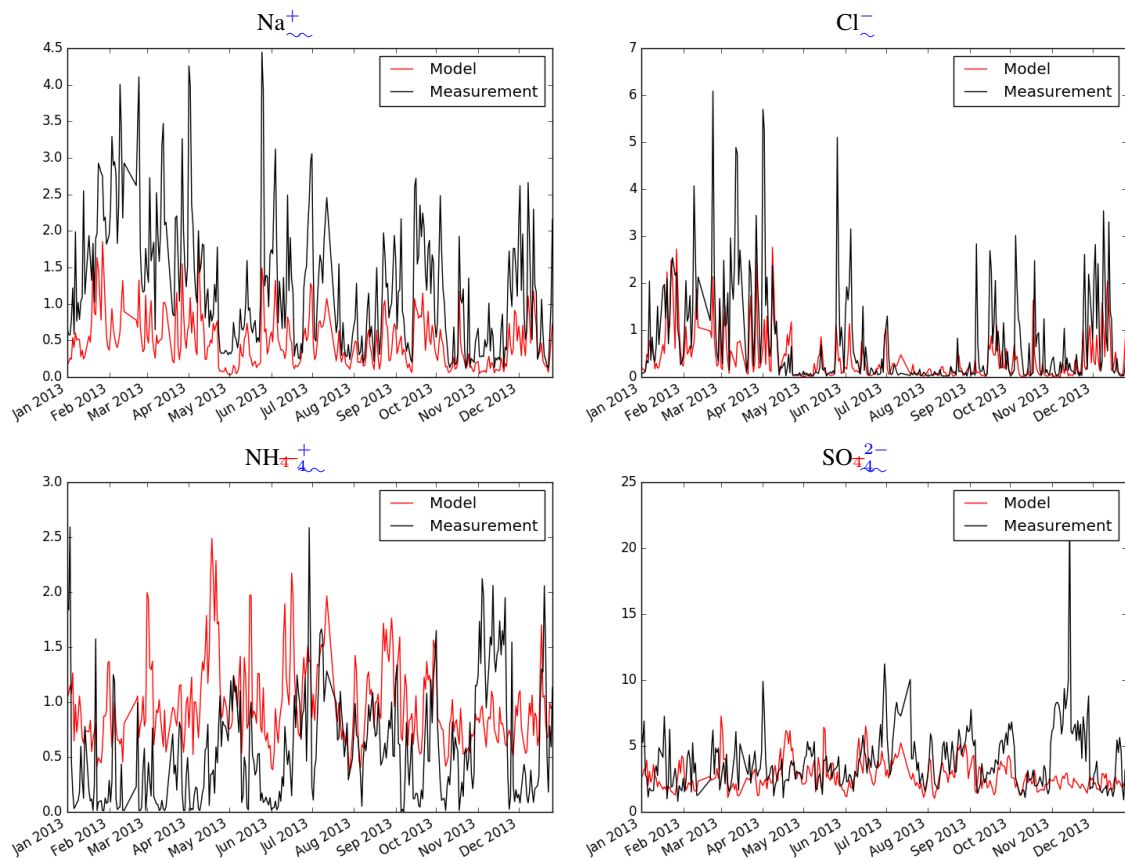
**Figure 12.** Seasonal evolution QQ scatter plot of statistics by regions for  $PM_{2.5}$ : Monthly mean measured concentrations (black left) ; monthly mean modeled concentrations (red), monthly RMSE (blue), monthly spatiotemporal correlations (green), monthly MFB (cyan) and monthly MFE of  $PM_{2.5}$  (magenta right) . Solid curves refer to modeling results against measurements for the left axis while dotted curves refer to the right axis several regions. SE: Southern Europe. WE: Western Europe. CE: Central Europe. EE: Eastern Europe. NE: Northern Europe.

QQ scatter plot of  $PM_{10}$  and of  $PM_{2.5}$  (bottom right panel) modeling results against measurements for the several regions. SE: Southern

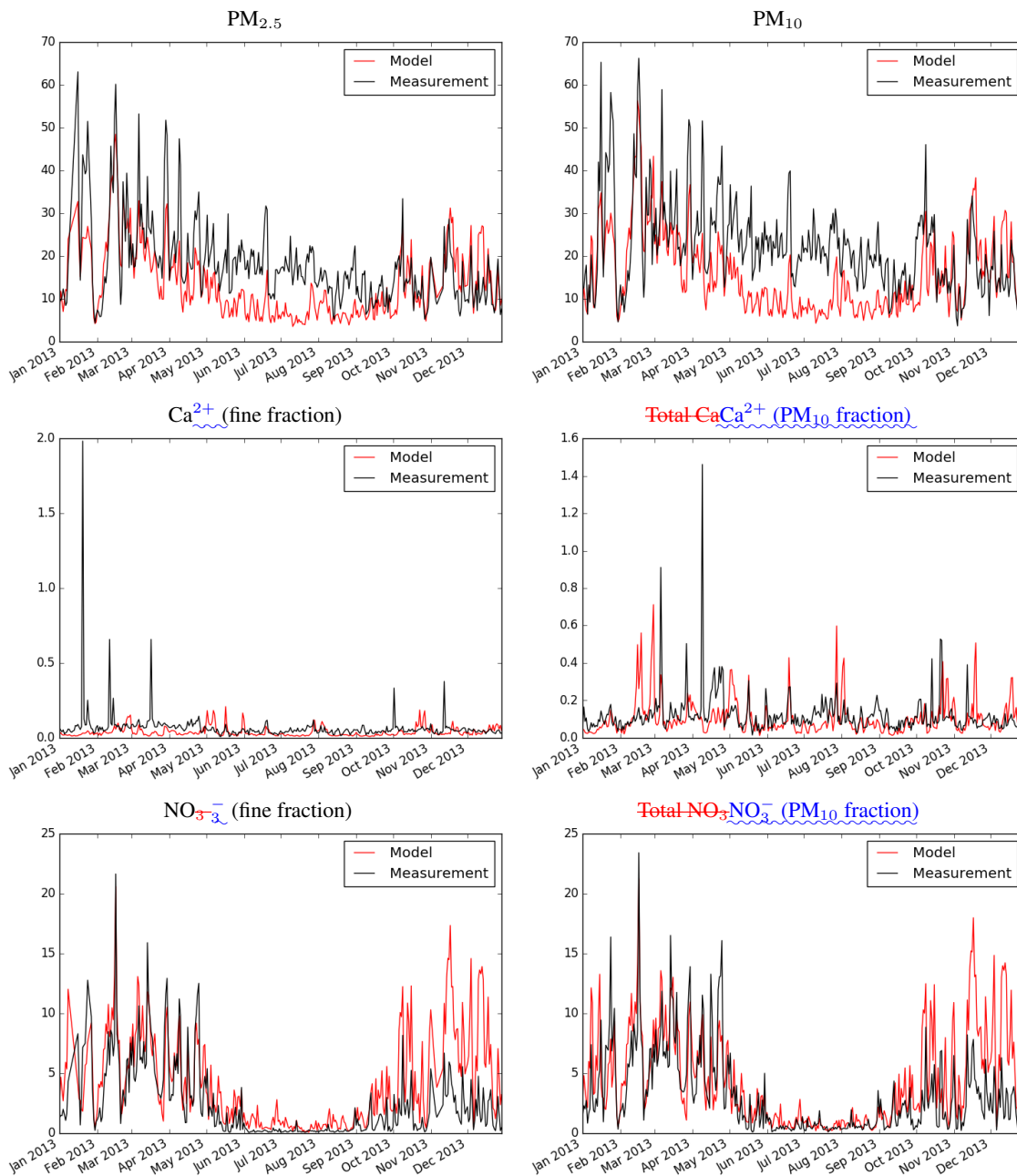
Southern Europe Western Europe Central Europe Eastern Europe Northern Europe Seasonal evolution of statistics by regions for PM<sub>10</sub>: Monthly mean r

**Figure 13.** Modeled (red) and measured (black) concentrations of PM<sub>2.5</sub>, PM<sub>10</sub>, Ca<sup>2+</sup> (fine fraction and totalPM<sub>10</sub> fraction) and NO<sub>3</sub><sup>-</sup> (fine fraction and totalPM<sub>10</sub> fraction) in  $\mu\text{g m}^{-3}$  for the Cyprus station CY0002R.

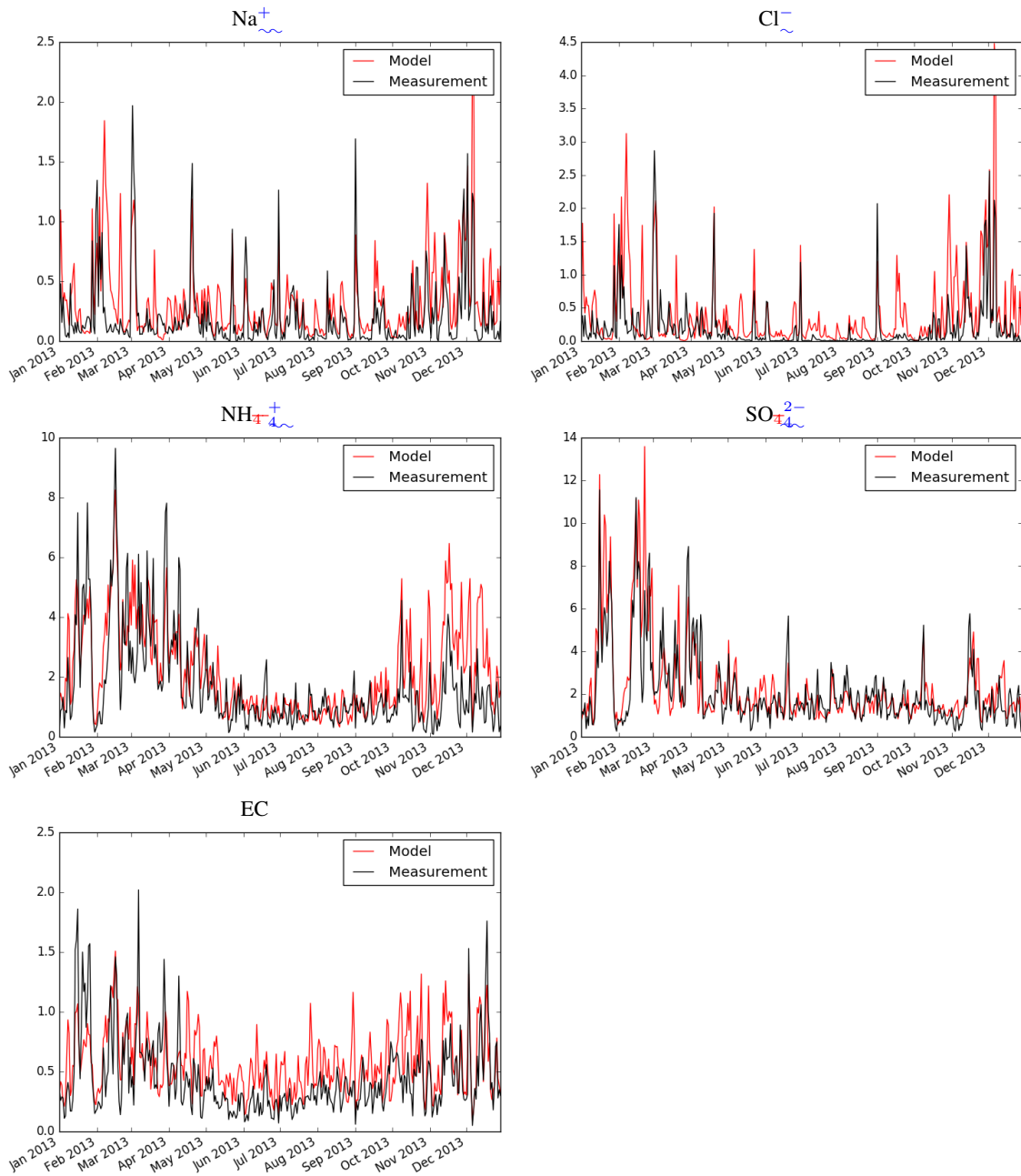




**Figure 14.** Modeled (red) and measured (black) concentrations of  $\text{Na}^+$ ,  $\text{Cl}^-$ ,  $\text{NH}_4^+$ ,  $\text{SO}_4^{2-}$  in  $\mu\text{g m}^{-3}$  for the Cyprus station CY002R.



**Figure 15.** Modeled (red) and measured (black) concentrations of  $PM_{2.5}$ ,  $PM_{10}$ ,  $Ca^{2+}$  (fine fraction and total) and  $NO_3^-$  (fine fraction and total) in  $\mu g m^{-3}$  for the station DE0044R (Germany)



**Figure 16.** Modeled (red) and measured (black) concentrations of  $\text{Na}^+$ ,  $\text{Cl}^-$ ,  $\text{NH}_4^+$ ,  $\text{SO}_4^{2-}$ , EC in  $\mu\text{g m}^{-3}$  for the station DE0044R (Germany).