

## Responses to referee#1

We thank Referee #1 for his/her useful comments. Each response to the referee's comments is organized as follows: (1) comments from the Referee in bold, (2) author's response and author's changes in manuscript in normal font. Some responses are given to several comments at the same time when these comments are related to each other. The changes in the revised manuscript, except the small edit corrections, are highlighted in green color in the revised manuscript.

Following the suggestion of the referee #2, the measurements of total sulfates are now compared to the sum of the sulfate field and 7,68% of the sea salt field of the model. This is based on the composition of sea water (Seinfeld and Pandis, 1998) in order to easily take into account the part proportion of sulfates in the sea salt aerosols.

## General comments

**1.) The introduction includes a general overview of secondary inorganic aerosol. However, it fails to put this work in the context of other efforts to include SIA formation in global models. To demonstrate the novelty of the work described here, the following questions should be addressed in the introduction: a) What treatments of SIA are currently included in other global models? b) How is the approach described here, or the nature of the MOCAGE model, expected to provide insight into global SIA that until now was not available?**

The work presented here corresponds to a representation that is fairly similar to that used in other global or regional models. The special interest of this work is linked to the specificity of the model MOCAGE which is to be able to simulate several domains at different scales via grid-nesting. The aim is here to develop a representation able to simulate SIA well at different scales from global to regional. The introduction has been modified accordingly in the revised version.

**2.) In general, the paper is well organized and clear. However, there are several 'uncommon' phrasings and grammatical errors in the text, and therefore the manuscript may benefit from general (non-technical) editing. At this point the quality of the writing of the paper makes it unacceptable for publication. Authors are strongly encouraged to work with an English speaker to edit the paper.**

Following this comment, the revised version of the paper has been corrected by an English speaker.

## Specific comments

**P3596 L7-10. It is not clear how chlorine chemistry is related to this work. If it is just to provide an example of gas-aerosol interactions, could an example more directly related to the species involved in this work be found? Or, is this an example of multiphase dynamics/chemistry that has been added to MOCAGE? If so, it should be clearly stated, and then shown how this work relates to those efforts.**

We agree that this sentence was misleading. This is just an example of gas-aerosol interactions

which is not included in the model MOCAGE. In the revised manuscript, the chlorine chemistry example has been removed and a short paragraph has been added on the hydrolysis of  $\text{N}_2\text{O}_5$  into  $\text{HNO}_3$  since it is taken into account in the MOCAGE model. This is a reaction happening on the sulfate aerosol surface.

**P3601 L8-11. Although the need for computational efficiency is understandable, Capaldo et al. also find that aerosol nitrate concentrations are poorly represented by the equilibrium method compared to the dynamic and hybrid methods in their box model simulations (results being off by as much as a factor of four for coarse-mode PM). Nitric acid concentrations in this work have a greater FGE and lower correlation compared to HTAP observations for RACMSIA than for RACM (Table 7). Could the assumption of equilibrium be a factor in this?**

**P3612 L13-20. See comment on the assumption of equilibrium (P3601 L8-11).**

We agree with the referee on the statement that nitrates are poorly represented by the equilibrium method, especially for the coarse mode nitrate, according to Capaldo et al.,(2000). In the paper, the authors claim the nitrate underestimation is due, at least partially, to the lack of reaction with sodium chloride which here is taken into account. In the future, it would be necessary to work on this assumption and to have a more realistic treatment of the gas/aerosol equilibrium processes. This aspect has been added in the conclusion.

When looking at the behavior of the different stations measuring nitric acid between both simulations, we can not determine a specific pattern for every station. Some stations show a better agreement with the RACM experiment while others show a better agreement with the RACMSIA experiment. One could expect the best agreement being on stations far from coastlines because of the interactions with sea salt being far from the equilibrium hypothesis. It is not a systematic result. Moreover, nitric acid is a compound which is difficult to model because there are many reactions involving nitric acid. Nevertheless, we agree with the referee that the assumption of thermodynamic equilibrium can be an additional factor explaining the nitric acid performance. This is now stated in the revised version of the manuscript.

**P3602 L13-17. This paragraph should be revised. There seems to be some confusion (possibly between  $(\text{NH}_4)_2\text{SO}_4$  and  $\text{NH}_4\text{NO}_3$ ?) in the first and last sentences.**

The referee is right, there is a mistake in this paragraph.  $(\text{NH}_4)_2\text{SO}_4$  is formed from  $\text{NH}_3$  and  $\text{H}_2\text{SO}_4$  and not from  $\text{HNO}_3$  and  $\text{H}_2\text{SO}_4$ . This has been changed in the revised manuscript.

**P3604 L 23-26. What effects will the assumptions made in section 2.3.2 regarding the size distribution of SIA have on modeled AOD? Will SIA in certain size bins have more impact on modeled AOD than those in other bins.**

In order to answer to this question, we made some tests on modeled AOD. Firstly, we computed the modeled AOD for a gridbox containing one aerosol type (for the example we used sulfate aerosols). A sensitivity analysis was carried out whereby the same aerosol mass concentration was distributed into each size bin in turn to observe the effect of the different aerosol sizes on AOD. These calculations show stronger AODs for the size bins located between 0.1 and 2.5 microns. In order to have further confirmation, we also computed the resulting AOD for a constant mass concentration but using different distribution modes from the literature. To do this, we used the

measured modes of Zhuang et al., (1999), which is the one used in the SIA module. We also tested modes from Hering et al., (1982) and John et al., (1990). Again the computation was made for sulfate aerosols. The Table “Tableau 2” presents the results of this computation. It shows that despite the huge differences in AOD between the different size bin, when using different realistic distribution modes, the differences in AOD are not significant.

*Tableau 1: Computed AOD following different distribution modes using the AOD computation framework of MOCAGE. The results are presented for sulfate aerosols.*

	AOD Computed	Diff with Zhuang In pct
Zhuang et al.,(1999)	0,312	0,00%
Hering et al., (1982)	0,313	0,13%
John et al., (1990)	0,310	-0,89%

**P3605 L10-13. Do the same stations that measure sulfate also measure the other species? If not, are there significant differences in the spatial distribution of station for the other species? (It might be more useful to have color-coded species measurements and include all the measurement stations in Fig. 1, as opposed to including altitude and only the sulfate stations.)**

**P3605 L26 – P3606 L1. Same comment as for P3605 L10-13.**

All the stations are measuring sulfates, but not necessarily nitrates or ammonium. Following the referee's suggestion, Fig. 1 and 2 have been changed in order to show the measured SIA composition parameters instead of the altitude of the measuring stations.

**P3610 L2-4. The remaining negative bias in the model is attributed to secondary organic aerosol (SOA) not be included in the model. Can the spatial distribution of the remaining bias be used to suggest whether or not this is the primary contribution? (Aside from the specific case mentioned in L10-13.)**

The referee is right to raise this question. When looking at global distribution of SOA from Tsigaridis and Kanakidou (2003) and Heald et al. (2008), it becomes clear that the main spots of SOA concentrations are located over Asia, western Europe, eastern US and central Africa. Our results show a significant negative bias in AOD over Asia, eastern US and central Africa that can be linked to missing SOA. Both RACM and RACMSIA simulations exhibit large negative biases on the western coast of South and North America. When comparing to AEROCOM results, these biases can also be linked to dust emissions missing in MOCAGE over these regions. The manuscript has been revised accordingly.

**P3611 L17-19. Why was it important to choose a rural location for this comparison?**

The gridbox size of the model is quite large, approximately 220 km × 220 km at the equator, and can only be compared to stations measuring background concentrations. EMEP stations are all supposed to be measuring background concentrations but depending on their location they can be sometimes affected by urban effects. The Irish station is rural but was chosen because it is not under any direct urban influence and samples the transport of chemical species from America leading to significant concentrations of SIA. The manuscript has been changed to make this clearer.

**P3617 L16. How can the improvement in MNMB and FGE be interpreted in light of the decrease in correlation for PM2.5?**

We thank the referee for this comment which allowed us to detect an error in the manuscript. Indeed the correlations are inverted in Table 12 (Table 14 in the revised version). The RACMSIA simulation has a correlation of 0.58 and the RACM experiment of 0.47. The numbers were right in the text (“The correlation also rises from 0.47 to 0.58”). Table 14 in the original manuscript) has been corrected in the revised manuscript.

### **Technical Corrections**

**P3596 L2-4. This statement could use a reference.**

The reference Seinfeld and Pandis, 1998 has been added to the text.

**P3596 L7-8. This statement could use a reference.**

The reference corresponding to this statement is Saiz-Lopez and von Glasow, 2012, it has been moved to an earlier position in the text.

**P3596 L21-22. The wording of this sentence makes it sound like the SIA module has been described previously.**

We agree that the sentence was not very clear. It has been changed.

**P3611 L22. Is there any reason to expect Table 6 and Fig. 7 to be inconsistent? Are they not based on the same simulation data.**

Indeed, Table 6 (Table 7 in the revised version) and Fig. 7 represent the same simulation compared to the same observations. The sentence highlighted here might be confusing. We wanted to show through two different ways the good results of the model against these measurements. We have removed this sentence.

## Responses to referee#2

We thank Referee #2 for his/her useful comments. Each response to the referee's comments is organized as follows: (1) comments from Referee in bold, (2) author's response and author's changes to the manuscript in normal font. The changes in the revised manuscript, except the small edit corrections, are highlighted in green color in the revised manuscript. Note that following referee#1's comment, the revised manuscript has been edited by an English speaker to improve its phrasing and grammar.

### Major comments:

**1) My main concerns are about the representation of distribution between bins of particulate concentrations (given by Isorropia) between bins and the absence of coagulation in the code.**

**- I was quite surprised that the first bin of aerosol ranged from 2 to 10 nm whereas nucleation is not represented and there is no mention of nucleation in the text. How can coagulation be neglected when there is a bin constituted by nanoparticles? Those particles are expected to coagulate very quickly with bigger particles.**

**- I think there is confusion between the fine mode and the accumulation mode. The two expressions are used in the text. According to Seinfeld and Pandis, the accumulation mode covers particles between 0.1 and 2.5 $\mu$ m. The fine mode cover particle with a diameter lower than 2.5 $\mu$ m and is constituted by the accumulation mode and the nuclei mode (for particle lower than 0.1 $\mu$ m). I guess that the author used fine mode instead of nuclei mode or the sentences like "we implicitly assumed that the coagulation has already been acting to transform fine model aerosols into accumulation mode aerosols" does not have any sense. But again, in that case, why are there bins between 2 and 100 nm?**

**- I find the fact to not represent coagulation (with almost no explanation) quite difficult to digest. As coagulation impact strongly the size of aerosol and therefore the deposition rate of aerosols, it is expected to impact strongly aerosol formation. More justification and references should at least be added in the text.**

As a first approach for introducing SIA into MOCAGE, the choice made here was to assume that each type of aerosols is distributed into its bins all along its lifetime following the defined modes (and associated parameters) based on observations published in the literature. By doing this, we assume that the defined modes already include all the aerosol microphysical processes implicitly. This is why nucleation and coagulation are not explicitly in the model. This is a simple approach which has the advantage of requiring low computation time. The next steps will be to improve this formation part by working on the microphysical processes (nucleation, coagulation, etc) and will use the smallest bin. This is made clear in the revised version.

Concerning the specific remark on the confusion between the fine mode and the nuclei mode, the referee is right and we thank them for this remark. This is the nuclei mode that is not used in our study. The text has been corrected.

**- When sea salts are taken into account in ISORROPIA, the model replaces all the Cl by NO<sub>3</sub> (if concentrations of HNO<sub>3</sub> are sufficient) because HNO<sub>3</sub> is less volatile and a stronger acid than HCl. However, Cl in sea salt is mainly present in coarse particle for which the assumption of equilibrium can be too strong because the kinetic of condensation/evaporation of HCl on coarse particles can be very slow and that it can be best to not take into account sea salt into an**

**inorganic equilibrium model. Have the authors look into that matter? It would have been best to add comparisons of modeled concentrations of Na and Cl to measurements to know if there is too much evaporation of HCl or not.**

When using ISORROPIA, sea salts are taken into account for the calculation of the equilibrium. The nitric acid is allowed to be transferred in the aerosol phase but the chlorine is not transferred in the gas phase because the chlorine chemistry is not present yet in the model. Future work will include a better representation of the exchange between the aerosol and the gas phase, by using a method taking into account the kinetic of transfer between the two phases at least for big particles. Another planned work is to implement chlorine chemistry in order to use HCl evaporated from sea salt. This is now stated in the conclusion section as one of the next developments.

**2) The manuscript lacks of description of the parameterization used in MOCAGE which could be critical for the understanding of the results of the model. This lacks of details make the paper difficult to read, especially if the reader doesn't know very well MOCAGE. Often, the manuscript cites other papers but does not describe the processes. It would be great to modify the manuscript so that the reader can have a good overview of all the processes impacting aerosol formation without having to look inside other papers as this manuscript could be one of the reference papers for the aerosols in MOCAGE. Maybe, the authors should present every of the main phenomena affecting aerosol formations with one part for each phenomena whether than presenting the old MOCAGE (and only referring to past studies) and separately the modifications.**

Following the referee's suggestion, we have added description of the parameterizations used in MOCAGE and in particular for aerosol-related processes. Please note that the nucleation and coagulation are not described because they are not explicitly represented in the model.

**- There is almost no mention in the paper of aqueous-phase chemistry except for some references of past studies which is one of the pathways of oxidation of SO<sub>2</sub> into H<sub>2</sub>SO<sub>4</sub>. How aqueous-phase is taken into account? The authors mention (lines 3-10, page 3620) that pH and liquid water content can be sources of uncertainties. Therefore, the manuscript should be modified to clearly present aqueous-phase chemistry, how it is taken into account, how the cloud pH is computed, etc.**

Note: Referee#3 asked a similar question. The liquid phase oxidation is taken into account following Pham et al. (1995) and Boucher et al. (2002). It takes into account the oxidation of SO<sub>2</sub> by H<sub>2</sub>O<sub>2</sub> and O<sub>3</sub> after dissolving the necessary gases into the liquid water content. Liquid water content is a variable of the model extracted from analysed meteorological forcing fields. The pH is supposed to always be equal to 5 (Charlson and Rodhe, 1982). Details about aqueous phase chemistry and SO<sub>2</sub> oxidation are given in Section 2.2.1 in the revised manuscript.

**- For deposition, the authors cite, in section 2.3.1, a paper of Sic et al al. (2005) where they check the parameterization and propose improvement. But, the main conclusions are not cited.**

The manuscript has been modified to include the main conclusions of Sic et al. (2015) as suggested by the referee.

**Deposition is only described in section 2.4 without giving any formula to summarize how this process is represented. Deposition should be presented clearly inside one paragraph. What about deposition of gaseous precursors? How is deposition of SO<sub>2</sub>, NO<sub>2</sub>, NH<sub>3</sub> and HNO<sub>3</sub> taken into account? The authors mention sedimentation incorporating hygroscopicity. What does it stand for? Does the author compute a humid diameter (taking into account the amount of water inside the aerosol) that is used for sedimentation?**

In order to be more explicit on the deposition processes affecting the aerosols, section 2.4 has been splitted into 2.4.1 concerning the advection scheme, 2.4.2 concerning the gaseous compounds and 2.4.3 concerning aerosols. Section 2.4.3 describes more precisely the processes affecting the aerosols. Concerning aerosols sedimentation, the referee is right. The hygroscopicity is taken into account by computing a humid diameter. Concerning dry deposition of SO<sub>2</sub>, NO<sub>2</sub>, NH<sub>3</sub> and HNO<sub>3</sub> are treated like the other gaseous compounds, following Wesely (1989).

**- Heterogeneous reactions and gas-phase reactions: a reaction for the hydrolysis of N<sub>2</sub>O<sub>5</sub> is mentioned. Are there any other heterogeneous reactions taken into account? What are the reaction of formation of H<sub>2</sub>SO<sub>4</sub> and HNO<sub>3</sub> and their reaction rate constant (models often have different values)? A table to summarize the formation of semi-volatile inorganic compounds could be added.**

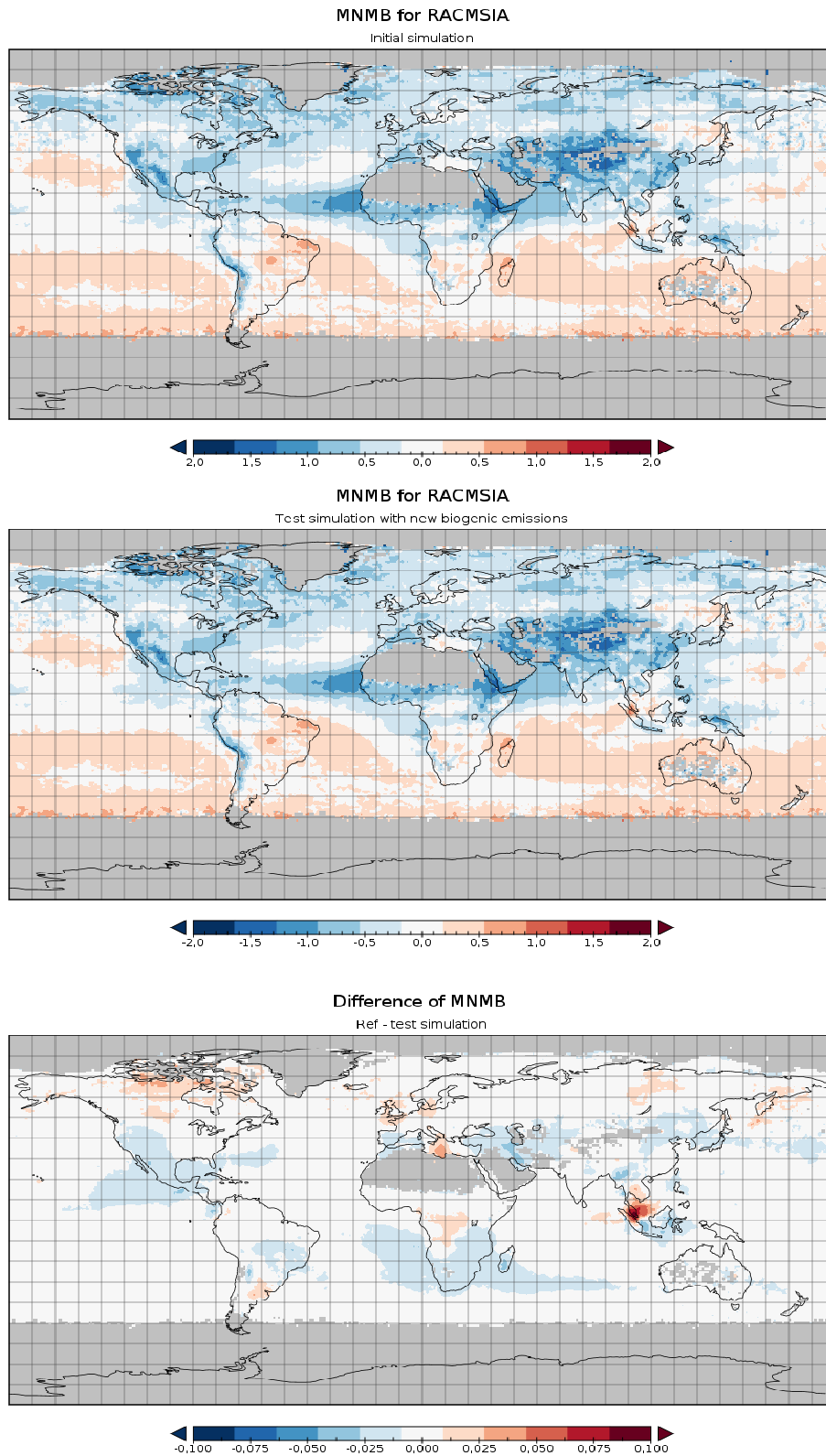
The other heterogeneous reactions taken into account are the reactions of aqueous phase oxidation of SO<sub>2</sub> by O<sub>3</sub> and H<sub>2</sub>O<sub>2</sub>. Concerning H<sub>2</sub>SO<sub>4</sub>, please refer to one of the preceding answer. Concerning HNO<sub>3</sub>, there are two ways for its formation. The first one, through gas phase reactions, corresponds to the RACM chemical scheme (Stockwell et al., 1997). The second way of forming HNO<sub>3</sub>, through heterogeneous hydrolysis of N<sub>2</sub>O<sub>5</sub>. As suggested by the referee, a Table summarizing the formation of semi-volatile inorganic compounds and their associated reaction rate constant has been added to the revised version of the manuscript.

**- Nucleation: is it taken into account? There is no mention about it in the text.**

This issue has already been discussed in a previous response about coagulation.

**- On emissions (page 3604): the authors mix emissions for 2000 at the global scale with emissions for 2009 over Europe and biogenic emissions for 1990 and compare to measurements for 2005. Isn't there too much inconsistency in the years of used data? Due to reductions of emissions, the emissions are quite different between 2000, 2005 and 2009. It is important to be quite precise on emissions as the authors compare to a lot of measurements to evaluate the model but these results could be biased due to the inconsistency of emissions. Furthermore, biogenic emissions are very dependent on meteorology. Can biogenic emissions estimated for 1990 really be used for a complete different year?**

Note: Referee#3 asked a similar question about biogenic emissions. Therefore, the part of the response dealing with biogenic emissions is the same.



*Illustration 1: Maps of Modified Normalised Mean Bias (MNMB) of aerosol optical depth against MODIS observations. The upper panel shows the RACMSIA experiment from the paper, the middle panel the test simulation realized with updated biogenic emissions and the lower panel shows the difference between the two first maps.*

We agree that the emissions used here are not fully satisfying. This work started in 2013 with this



old set of emissions, the new one not being available at this time. We realise now that we should have checked the availability of updated ones. Since it is not possible to entirely rerun all the experiments because of their computational cost and the time required, we have tried to address this issue in different ways. Firstly, we compared the MEGAN-MACC biogenic emissions for 2005 to those used in this study. This showed that differences are not very large. For example, when summing all emitted species it comes 972 Tg for MEGAN-MACC and 988 Tg for this study. The emissions for some species are close, like for isoprene for which the difference is about 5% (602 Tg for MEGAN-MACC and 566 Tg for this study). Other species shows more different emissions. Alkenes for example are emitted at 48,4Tg in MEGAN-MACC and 5,99Tg in this study. Secondly we run a two months global simulation using MEGAN-MACC 2005 emissions for the biogenic part, starting on 1<sup>st</sup> of June 2005, from the simulation used in the paper. We looked at the month of July after a one month spin-up. Illustration 1 shows the MNMB of simulated AOD against MODIS observations of AOD. It shows small differences with a maximum local difference over Malaysia.

*Table 1: Secondary inorganic aerosol compound statistics of RACMSIA simulation against HTAP observations. This table is the same as Table 5 in the paper but only on the period June/July.*

	MNMB	FGE	Correlation
Sulfate total	-0,34	0,75	0,41
Sulfate corrected	-0,17	0,64	0,67
Nitrate	-0,31	1,13	0,32
Ammonium	0,28	0,77	0,62

*Table 2: Secondary inorganic aerosol compound statistics of the test simulation using updated biogenic emissions against HTAP observations.*

	MNMB	FGE	Correlation
Sulfate total	-0,39	0,78	0,4
Sulfate corrected	-0,18	0,7	0,66
Nitrate	-0,1	1,18	0,29
Ammonium	0,26	0,8	0,6

Tables 1 and 2 present the statistics of the initial RACMSIA simulation and the test simulation using updated biogenic emissions. These tables show the good coherence for sulfates and ammoniums between the two simulations using different biogenic emissions. For nitrates there is a larger difference between the two simulations which is still small. This indicates that the use of updated biogenic emissions does not change significantly the results presented in the paper. Moreover, a study on the Mediterranean basin based on the RACMSIA version of the model is ongoing and uses recent emission inventories. It is not published yet but it shows, on the Mediterranean region, similar statistical results as those discussed in this paper for Europe. This also indicates that the use

of an old set of biogenic emissions does not affect the general conclusions of the paper.

Concerning 2009 emissions with 2005 measurements, the text was not clear enough. There are two separated sets of simulations. Each set of simulation is composed of one simulation noted RACM (without SIA) and one simulation noted RACMSIA (with formation of SIA). The first set of simulation is devoted to the global scale and corresponds to the simulation of the year 2005. For this set of simulation we use biogenic emissions representative of the year 1990 and anthropogenic representative of the year 2000. These simulations are compared to 2005 observations.

The second set of simulation focuses on the regional scale over Europe, while simulating the year 2010. We use for these simulations the same biogenic emissions but a regional emission inventory over Europe representative for the year 2009. These simulations are compared to 2010 observations. The paragraph concerning emissions in the text has been modified to make it clearer.

### **Technical comments:**

**Page 3600: Isorropia has two configurations (metastable and deliquescent) that can give different results (especially at low humidity). The configuration has to be added into the text. The authors compare modeled sulfate with the measurement of total sulfate and with corrected sulfate (without the contribution of sea salt) as the model simulates only the anthropogenic part of sulfate. Without changing the model, the authors could improve the comparison to measurements by assuming that there is a mass fraction of sulfate in the modeled concentrations of sea salt (7.68% according to Seinfeld and Pandis). If possible, it would be nice to compare the results of the models to other models by comparing to reported statistics in other studies.**

ISORROPIA is used here within the deliquescent configuration. This information has been added in the text. We have performed the comparison asked by the referee using the sulfate fraction in the sea salts. Table 3 (below) presents the statistics obtained for Tables 5, 8, 9 and 10 in the original manuscript (Tables 6, 10, 11 and 12 in the new version). Taking into account the sulfate mass fraction from sea salt improves the bias (MNMB) against the total sulfate observations. The comparison to daily HTAP data (Table 6) shows nevertheless a decrease of the correlation coefficient and an increase of the error (FGE). The comparison with weekly HTAP data shows similar results (Table 10). Finally, when comparing the model results to daily EMEP data (Table 12), there is an improvement on both the bias and the error, the correlation being very similar. We thank the referee for this very constructive remark. We put these new results in the revised manuscript.

Table 3: Comparison of the statistics of sulfate total against MOCAGE simulation. "Initial" corresponds to the comparison with model nss and "including sss" corresponds to the use of sea salt to correct the sulfate concentrations in the model.

Table 5	MNMB	FGE	Corr
Initial	-0,32	0,79	0,52
Including sss	0,05	0,94	0,33

Table 8	MNMB	FGE	Corr
Initial	-0,1	0,68	0,66
Including sss	-0,05	0,67	0,64

Table 10	MNMB	FGE	Corr
Initial	-0,36	0,75	0,58
Including sss	-0,16	0,67	0,57

## Responses to referee#3

We thank Referee #3 for his/her useful comments. Each response to the referee's comments is organized as follows: (1) comments from Referee in bold, (2) author's response and author's changes to the manuscript in normal font. The changes in the revised manuscript, except the small edit corrections, are highlighted in green color. Note that following referee #1's comment, the revised manuscript has been edited by an English speaker to improve its phrasing and grammar.

Following the suggestion of referee #2, the measurements of total sulfates are now compared to the sum of the sulfate field and 7,68% of the sea salt field of the model. This is based on the composition of sea water (Seinfeld and Pandis, 1998) in order to easily take into account the proportion of sulfates in the sea salt aerosols.

## Specific comments

**p.3597 l.19 give also resolution in km : have you tried the sensitivity to different resolutions? If not, what do you think the impact would be?**

Approximate resolutions in km have been put in the text in addition to the latitude/longitude resolutions. We assume the question is about the sensitivity of the secondary inorganic aerosols formation versus the horizontal resolution. We have not tested the sensitivity to different resolutions at the global scale. In this paper two resolutions are used,  $2^\circ \times 2^\circ$  and  $0.5^\circ \times 0.5^\circ$ , showing similar behavior. Moreover, this version of MOCAGE is currently used for operational forecasts with a regional domain at  $0.1^\circ \times 0.1^\circ$  and an other study (not published yet) is in progress at a resolution of  $0.2^\circ \times 0.2^\circ$ . All these configurations show stable statistical performances against observations when using the secondary inorganic aerosols scheme.

**p.3600 l.10-15 It's not clear to me how internal mixing is assumed when the species are treated separately, or are they all lumped into the different bins together? Please explain.**

We agree that this part is not clear. When the partition between the gas phase and the aerosol phase is done, each aerosol type is treated using the six sectional size bins. To do this, for each different aerosol species given by ISORROPIA, we distribute the mass over these same size bins. Internal mixing is therefore assumed implicitly during this distribution. The manuscript has been modified to make this point clearer.

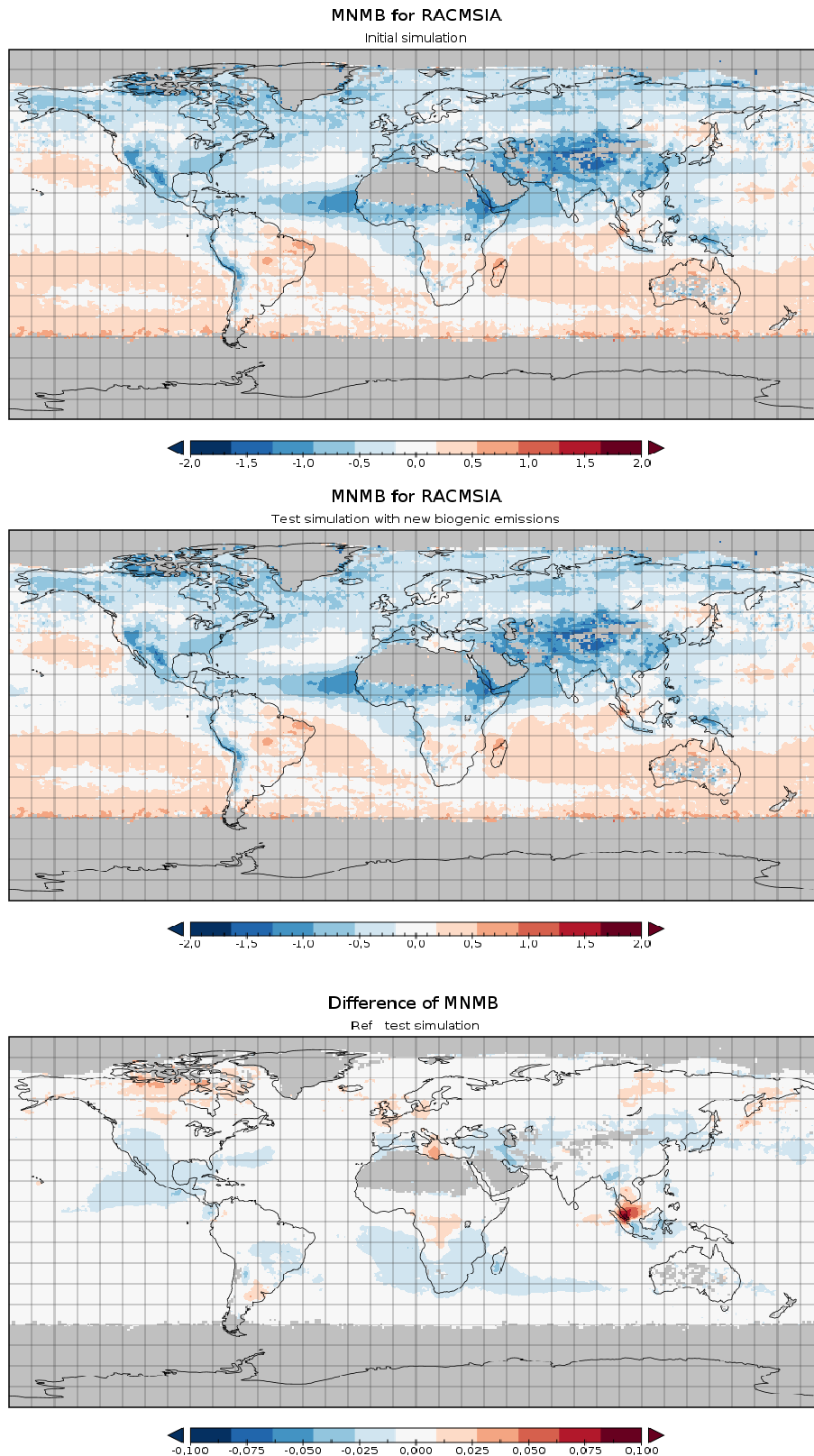
**p.3602 l.19 what are the mass conservation properties of the scheme? Has this been looked into?**

The advection scheme used in the model MOCAGE is a semi-lagrangian scheme. Semi-lagrangian advection schemes are known to not be conservative. Nevertheless, at the global scale a correction to ensure the mass conservation has been added. It can only be done at the global scale because of the lateral flux of the different regional domains. Moreover, at the scales considered here, the errors linked to the mass conservation properties of the semi-lagrangian scheme are of an order of

magnitude lower than the uncertainties of all the other processes.

**p.3606 I.4 This biogenic emissions seem too old: how can it be assessed that they are still representative?**

Note: Referee#2 asked a similar question, the part of the response dealing with biogenic emissions is the same.



*Illustration 1: Maps of Modified Normalised Mean Bias (MNMB) of aerosol optical depth against MODIS observations. The upper panel shows the RACMSIA experiment from the paper, the middle panel the test simulation realized with updated biogenic emissions and the lower panel shows the difference between the two first maps.*

We agree that the emissions used here are not fully satisfying. This work started in 2013 with this

old set of emissions, the new one not being available at this time. We believe now that we should have checked the availability of updated ones. Since it is not possible to entirely rerun all the experiments because of their computational cost and the time required, we have tried to address this issue in different ways. Firstly, we compared the MEGAN-MACC biogenic emissions for 2005 to those used in this study. This showed that differences are not very large. For example, when summing all emitted species it comes 972 Tg for MEGAN-MACC and 988 Tg for this study. The emissions for some species are close, like for isoprene for which the difference is about 5% (602 Tg for MEGAN-MACC and 566 Tg for this study). Other species show more different emissions. Alkenes for example are emitted at 48,4Tg in MEGAN-MACC and 5,99Tg in this study. Secondly we run a two month global simulation using MEGAN-MACC 2005 emissions for the biogenic part, starting on 1<sup>st</sup> of June 2005, from the simulation used in the paper. We looked at the month of July after a one month long spin-up. Illustration 1 shows the MNMB of simulated AOD against MODIS observations of AOD. It shows small differences with a maximum local difference over Malaysia.

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*Table 2: Secondary inorganic aerosol compound statistics of the test simulation using updated biogenic emissions against HTAP observations.*

	MNMB	FGE	Correlation
Sulfate total	-0,39	0,78	0,4
Sulfate corrected	-0,18	0,7	0,66
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Moreover, a study on the Mediterranean basin based on the RACMSIA version of the model is ongoing and uses recent emission inventories. It is not published yet but over the Mediterranean region it shows similar statistical results as those discussed in this paper for Europe. This also indicates that the use of an old set of biogenic emissions does not affect the general conclusions of the paper.

**p.3607 I.3 In what sense misleading? Please elaborate.**

The formulation is not clearly explained. Seigneur et al. (2000), explain the reasons for the use of MNMB and FGE. They state that past model performance evaluations have generally used observations to normalize the error and the bias. This approach can be misleading when the denominator is small compared to the numerator (Seigneur et al., 2000).

**p.3609 I.6 The differences in figure 5 are really huge.**

For ammonia, in the RACM experiment there is no chemistry. As explained in the original manuscript, ammonia is emitted, transported and deposited. In the RACMSIA experiment ammonia can be transferred in the aerosol phase leading to very large differences for NH<sub>3</sub> and consequently on HNO<sub>3</sub> between RACM and RACMSIA simulations. This point is more clearly stated in the revised manuscript.

**p.3610 I.4 The bias in AOD over central Asia is also likely due to lack of adequate dust emissions as well as the lack of secondary organic aerosols. What is the positive bias over the ocean in Figure 6 due to, given the lack of DMS emissions (as I understood it)? Please elaborate.**

We agree that the AOD bias over central Asia is likely not only due to the lack of SOA but also to an underestimation of the dust emissions in this region. MOCAGE includes desert dust emissions over Eastern Asia but the large uncertainties of the wind fields over this region due to complex orography produce large uncertainties on desert dust emissions.

Over ocean, there are no DMS emissions in the model indeed and therefore we expect AOD underestimation instead of overestimation. The positive bias over the ocean is likely due to the sea salt aerosols. The function used to calculate the sea salt emissions follows an exponential for big particles. These big particles remain in the atmosphere for a very short time and are very close to the surface but are often emitted in the model. The model overestimation can be linked to an uncertainty on the exponential emission function that possibly gives a too large number of big particles. Also the AOD measurements may not capture the transient presence of big particles in the very low levels. More explanations on the model AOD biases are given in the revised manuscript.

**p.3611 I.7 what do you mean by "sulfate emissions combined with sea salt"?**

Sea salt corresponds to a mixture of different ions, including sulfates. Referee #2 pointed out that a part of sea salt emissions is composed of sulfates (7,68% according to Seinfeld and Pandis). We agree the formulation is not very clear, it has been changed in the text.



**p.3611 I.16 I was expecting to see also the RACM simulation for comparison in table 5, table 6 and figure 7. Can this be added? It would also be good to see how other stations behave (at least one more). Is the "Sulphate" in table 6 total or corrected?**

The RACM simulation does not have any secondary inorganic aerosols i.e. sulfates, nitrates and ammoniums. It is then not possible to compare it the model SIA composition in RACM to the observations. An other station (CA0008R), located East of Lake Superior in Canada has been added to the text. Table 6 (Table 7 in the revised version) shows a comparison with corrected sulphate. This information has been added in the table caption and in the text.

**p.3612 I.9 briefly explain how the SO<sub>2</sub> oxidation is included (i.e. parametrization, explicit chemistry, etc)**

Note: Referee#2 asked a similar question. The SO<sub>2</sub> oxidation is included in the model by explicit chemistry. Gaseous oxidation by OH is a reaction from the RACM chemical scheme. The liquid phase oxidation is taken into account following Pham et al. (1995) and Boucher et al. (2002). It includes the oxidation of SO<sub>2</sub> by H<sub>2</sub>O<sub>2</sub> and O<sub>3</sub> after dissolving the necessary gases into the liquid water content which is a variable of the model. A reference to the description of the SO<sub>2</sub> oxidation scheme (section 2.2.1) has been added in the text.

**p.3613 I.4 I find it surprising that over the United States there are no daily data!**

We checked again on the EBAS website (<http://ebas.nilu.no/>) and the data available on this platform for the United States are only weekly data and we have not found these data elsewhere.

**p.3614 I.7 Compensation of what? Please explain.**

Over Asia, the comparison to the aerosol composition shows an overestimation of secondary inorganic aerosols. The comparison of the AOD, in Fig. 6, where the stations in Japan and in the Islands south of China (see Fig. 1) are located, shows a good agreement. These good results for these AOD comparisons might therefore be due to an overestimation of secondary inorganic aerosols compensated by an underestimation linked to the lack of secondary organic aerosols. This part of text has been modified to make it clearer.

All other technical/small corrections have been taken into account in the revised manuscript.

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# **Simulating Secondary Inorganic Aerosols using the chemistry transport model MOCAGE version R2.15.0**

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## Abstract

In this study we develop a Secondary Inorganic Aerosol (SIA) module for the chemistry transport model MOCAGE developed at CNRM. **The aim is to have a module suitable for running at different model resolutions and for operational applications with reasonable computing times.** Based on the thermodynamic equilibrium module ISORROPIA II, the new version of the model is **presented and** evaluated both at the global and regional scales.

The results show high concentrations of secondary inorganic aerosols in the most polluted regions: Europe, Asia and the eastern part of North America. Asia shows higher sulfate concentrations than other regions thanks to emission reductions in Europe and North America.

Using two simulations, one with and the other without secondary inorganic aerosol formation, the global model outputs are compared to previous studies, to MODIS AOD retrievals, and also to in situ measurements from the HTAP database. The model shows a better agreement with MODIS AOD retrievals in all geographical regions after introducing the new SIA scheme. It also provides a good statistical agreement with in situ measurements of secondary inorganic aerosol composition: sulfate, nitrate and ammonium. In addition, the simulation with SIA generally gives a better agreement with observations for secondary inorganic aerosol precursors (nitric acid, sulfur dioxide, ammonia) in particular with a reduction of the Modified Normalised Mean Bias (MNMB).

At the regional scale, over Europe, the model simulation with SIA is compared to the in situ measurements from the EMEP database and shows a good agreement with secondary inorganic aerosol composition. The results at the regional scale are consistent with those obtained from the global simulations. The AIRBASE database was used to compare the model to regulated air quality pollutants: particulate matter, ozone and nitrogen dioxide concentrations. Introduction of the SIA in MOCAGE provides a reduction in the  $PM_{2.5}$  MNMB of 0.44 on a yearly basis and up to 0.52 for the three spring months (March, April, May) when SIA are at their maximum.

## 1 Introduction

Aerosols are a suspension of airborne solid or liquid particles, with a typical size between a few nanometres and  $10\ \mu\text{m}$ , that reside in the atmosphere from at least several hours (Stocker et al., 2013) and up to several days. Atmospheric aerosols play a key role in various fields. Their radiative properties allow them to absorb and scatter radiation and play a significant role in the global climate system especially in a climate change context. The estimation of radiative forcing due to aerosols is negative, but with a strong uncertainty. Most aerosols seem to have a cooling effect except for black carbon (Stocker et al., 2013). This radiative aspect also affects the horizontal dimension while being a possible source of visibility reduction (Bäumer et al., 2008).

Aerosols are also important pollutants affecting air quality. Aerosols in air quality applications are characterised in terms of Particulate Matter (PM).  $\text{PM}_x$  is the amount of particulate matter with diameters less than  $x$  microns.  $\text{PM}_{10}$  and  $\text{PM}_{2.5}$  are measured quantities and used for the legal concentrations in air quality regulations. The World Health Organization's guidelines for particulate matter are a  $20\ \mu\text{g m}^{-3}$  annual mean for  $\text{PM}_{10}$  and a  $10\ \mu\text{g m}^{-3}$  annual mean for  $\text{PM}_{2.5}$  (WHO, 2006).

One can distinguish between primary aerosols, which are directly emitted from sources, desert dust for example, and secondary aerosols, which are formed in the atmosphere from chemical and physical processes involving gaseous precursors. Secondary aerosols can be split into two types: Secondary Organic Aerosols (SOA) and Secondary Inorganic Aerosols (SIA). Gaseous precursors for SOA are Volatile Organic Compounds (VOCs), like isoprene for example, and correspond to a mixture of many different organic gases mainly composed of carbon, hydrogen and oxygen. Secondary inorganic aerosols' main precursors are the gaseous species: ammonia, nitric acid and sulfuric acid. The proportion of SIA in the Particulate Matter is generally significant. For example, in Europe, SIA represents between 30 and 50% by mass of the  $\text{PM}_{2.5}$  (Querol et al., 2004). Ammonia comes from emissions, while nitric acid and sulfuric acid mostly result from the oxidation of nitrogen oxides and sulfur dioxide, respectively. SIA are therefore controlled by the emissions of ammonia, nitrogen oxides and sulfur dioxide, and also

by the ambient conditions, temperature and humidity. While typical sources of nitrogen oxides more varied (fossil fuel combustion, soils, biomass burning and lightning), sulfur compounds are mostly from anthropogenic sources and volcanoes (Seinfeld and Pandis, 1998). Ammonia emissions mostly come from domestic animals' excreta, synthetic fertilizers, biomass burning and crops (Olivier et al., 1998).

Gas phase aerosol interactions result in modifications of the gas phase equilibrium. Hydrolysis of  $\text{N}_2\text{O}_5$  into  $\text{HNO}_3$  on aerosols particles is an example. The nitric acid produced is more soluble and can then be deposited through wet deposition processes more easily than  $\text{N}_2\text{O}_5$ . Nitric acid can also condense in nitrate aerosols. This can potentially result in a decrease of  $\text{NO}_x$ , which can cause a decrease in  $\text{O}_3$  concentrations up to 25% during spring (Dentener and Crutzen, 1993).

Modelling the aerosols is important at the local scale but also at the regional and global scales. At the local or regional scales, modelling the aerosols is a way to provide air quality forecasts for  $\text{PM}_{10}$  and  $\text{PM}_{2.5}$ . At the global scale, aerosols modelling is important for properly taking into account the long range transport of pollutants. It can also be used to study the evolution of the large scale background concentrations in current evolving climate conditions.

The representation of SIA in models simulating the composition of the atmosphere is, to our knowledge, always based on the assumption of an equilibrium between the gas and the aerosol phases both in global (Hauglustaine et al., 2014; Paulot et al., 2015) or regional models (Bessagnet et al., 2004; Vogel et al., 2009).

MOCAGE is the Chemical Transport Model (CTM) developed and used at CNRM/Météo-France. It is a global model that includes the capability for simulating smaller domains with finer resolutions. MOCAGE is used for simulating stratospheric and tropospheric chemical concentrations (ozone for example) and also for air quality forecasts including ozone, nitrogen oxides and aerosols. Recently, new developments have been made to account for the formation of secondary inorganic aerosols in MOCAGE. This SIA module is based on the gas-aerosol equilibrium assumption like in other models. It aims to be valid at different scales and resolutions since MOCAGE can simulate simultaneously the global and the regional scales thanks to grid-nesting. These new developments are aimed at being used for research purposes but also for

eventually being incorporated into operational systems. Therefore, choices were made to have, at first, a simple and computationally efficient module. The aim of this paper is to present and evaluate the MOCAGE SIA module both at the global and regional (European) scales.

Section 2 presents the MOCAGE model including the newly developed secondary inorganic aerosol module. Then in Sect. 3 we define the experimental setup of the simulations and the observations used for the model evaluation. Results are discussed in Sect. 4 for global simulations and Sect. 5 for regional simulations. Finally Sect. 6 concludes this study.

## 2 Model description

MOCAGE (*Modele de Chimie Atmospherique à Grande Echelle*) is an off-line global Chemistry Transport Model (CTM) used for research at Météo-France and serving in a wide range of scientific studies on tropospheric and stratospheric chemistry at various spatial and temporal scales. It was used for example for studying the impact of climate on chemistry (Teysse re et al., 2007; Lacressonni re et al., 2012; Lamarque et al., 2013) or tropospheric–stratospheric exchanges using data assimilation (El Amraoui et al., 2010; Barr e et al., 2013). MOCAGE is also used for daily operational air quality forecasts in the framework of the French platform Prev’ Air ((Rouil et al., 2009), <http://www2.prevaire.org/>) and in the European MACC-III (Monitoring Atmospheric Composition and Climate) project by being one of the seven models contributing to the [regional ensemble forecasting system over Europe](http://macc-raq-op.meteo.fr/index.php) ((Mar ecal et al., 2015), <http://macc-raq-op.meteo.fr/index.php>).

### 2.1 Model geometry and inputs

MOCAGE can be used both as a global model and as a regional model. Thanks to its two-way grid-nesting capacity, it can use several overlapping grids. The typical resolution at the global scale is  $2^\circ$  longitude  $\times$   $2^\circ$  latitude (approximately  $220\text{ km} \times 220\text{ km}$  at the equator and  $220\text{ km} \times 160\text{ km}$  at mid-latitudes),  $0.5^\circ$  longitude  $\times$   $0.5^\circ$  latitude at a regional scale (approx-

imately  $55 \text{ km} \times 40 \text{ km}$  at mid-latitudes), and  $0.1^\circ$  longitude  $\times$   $0.1^\circ$  latitude at the local scale (approximately  $11 \text{ km} \times 8 \text{ km}$  at mid-latitudes).

MOCAGE has 47 levels from the surface up to 5 hPa. It uses  $\sigma$ -pressure vertical coordinates giving a non-uniform resolution of about 40 m in the lower troposphere increasing to 800 m in the upper troposphere. There are seven levels in the planetary boundary layer, twenty in the free troposphere and twenty in the stratosphere.

MOCAGE, being an off-line CTM, gets its meteorological fields from two possible independent meteorological models. Wind, temperature, humidity and pressure come from the IFS model (Integrated Forecast System) operated at ECMWF (European Centre for Medium-Range Weather Forecasts, <http://www.ecmwf.int/>) or from the ARPEGE model (*Action de Recherche Petite Echelle Grande Echelle*) operated at Météo-France (Courtier et al., 1991). The meteorological fields driving MOCAGE are available every 3 or 6 h, and are linearly interpolated on one hour intervals, one hour being the dynamical time step of the model.

The chemical time-step used in the solver varies with altitude from 15 min in the stratosphere to a few seconds in the planetary boundary layer. Emissions are injected every 15 min, into the five lowest levels using an hyperbolic decay. Chemical fields are then updated every 15 min.

## 2.2 Gaseous species

### 2.2.1 Current chemistry scheme

MOCAGE uses two chemical schemes in order to represent both the tropospheric and the stratospheric air composition. The Regional Atmospheric Chemistry Mechanism (RACM) (Stockwell et al., 1997) is used in the troposphere while the REPROBUS scheme is used for the stratosphere (REactive Processes Ruling the Ozone BUDget in the Stratosphere) (Lefèvre et al., 1994).

Compared with the initial RACM scheme, the sulfur cycle has been completed. Following Boucher et al. (2002) and Pham et al. (1995), MOCAGE takes into account the aqueous oxidation reaction of sulfur dioxide into sulfuric acid (Ménégoz et al., 2009; Lacressonnière, 2012). The fraction of gas dissolved in the liquid water content, the latter being a variable extracted from the input forcing fields, is calculated with Henry's law. The Henry's law constants for

$H_2O_2$ ,  $O_3$  and  $SO_2$  are respectively  $7.45 \times 10^4 \exp(7400(\frac{1}{T} - \frac{1}{298}))$ ,  $1.13 \times 10^{-2} \exp(2300(\frac{1}{T} - \frac{1}{298}))$  and  $1.23 \times \exp(2900(\frac{1}{T} - \frac{1}{298}))$ .  $SO_2$  can then be oxidized by  $H_2O_2$  and  $O_3$ . For  $H_2O_2$ , the reaction rate is given by:

$$\frac{dS}{dt} = \frac{k_1 [H^+] [H_2O_2] [HSO_3^-]}{1 + P [H^+]}, \quad (1)$$

where  $k_1 = 7.5 \times 10^7 e^{-4430(\frac{1}{T} - \frac{1}{298})}$ ,  $T$  is the ambient temperature and  $P$  the pressure. For  $O_3$ , the reaction rate is given by:

$$\frac{dS}{dt} = (k_2 [SO_{2aq}] + k_3 [HSO^-] + k_4 [SO_3^{2-}]) [O_3], \quad (2)$$

where  $k_2 = 2.4 \times 10^4$ ,  $k_3 = 3.7 \times 10^5 .e^{-5530(\frac{1}{T} - \frac{1}{298})}$  and  $k_4 = 1.5 \times 10^9 .e^{-5280(\frac{1}{T} - \frac{1}{298})}$ . The pH of the droplets, used to calculate the concentration of  $H^+$  is supposed to always be equal to 5. This value is consistent with pH measurements from Charlson et al. (1982). This information is summarized in the Table 1, which gives the heterogeneous formation processes of the secondary inorganic aerosol precursors.

MOCAGE represents 111 gaseous compounds, 377 thermal gas reactions and 55 photolysis. Reaction rates are calculated during the simulation, every 15 min. The photolysis reactions rates are interpolated every 15 min from a lookup table and modulated by accounting at each given point and time for the ozone column, solar zenith angle, cloud cover and surface albedo.

## 2.2.2 New developments for gaseous species

Ammonia ( $NH_3$ ) has been added to the model species in order to account for the formation of the ammonium aerosols. No extra gaseous reaction involving ammonia has been added since they are slow enough to be neglected (Adams et al., 1999).

Dentener and Crutzen (1993) showed that the hydrolysis reaction of  $N_2O_5$  on aerosols surface plays an important role in the atmosphere by lowering  $NO_x$  and  $O_3$  concentrations. It has



been added following Dentener and Crutzen (1993). The reaction rate is based on the available aerosol surface area,  $A$ , needed for the reaction to take place. The reaction rate is given by:

$$k_{N_2O_5} = \left( \frac{r}{G_g} + \frac{4}{v\gamma} \right)^{-1} A, \quad (3)$$

where  $D_g$  ( $\text{cm}^2\text{s}^{-1}$ ) is the gas phase diffusion coefficient,  $r$  the aerosol radius,  $v$  the mean molecular speed ( $\text{cm s}^{-1}$ ), and  $\gamma$  the reaction probability being 0.1. Table 1 also includes this reaction.

## 2.3 Aerosols

### 2.3.1 Current aerosol module

The model in its current state is able to represent primary aerosols (Martet et al., 2009; Sič et al., 2015). The latest version of the primary aerosol scheme in MOCAGE has been evaluated by Sič et al. (2015). Sič et al. (2015) checked the aerosol physical parameterizations and proposed improvements. Based on simulations including only primary aerosols, they checked the consistency and validated the dry and wet deposition, the sedimentation and the emission processes. Concerning emissions, emission changes produced a strong impact by lowering known biases of sea salt and African dust. The wet deposition scheme changes also have a strong impact but they are more complex to analyse. Regarding sedimentation, changes produced a less important effect. Results obtained from Sič et al. (2015) confirm that the use of parameterizations can induce large uncertainties.

MOCAGE uses the sectional approach with six size bins per type of aerosol, especially chosen to fit the different characteristics of each aerosol. Primary aerosols in MOCAGE are composed of four species: desert dust, sea salt, primary organic carbon and black carbon. Black carbon and organic carbon emissions rely on emission inventories while sea salt and desert dust are dynamically emitted.

### 2.3.2 Emission parameterizations for aerosols

Desert dust and sea salt emissions are managed dynamically through parameterizations. Sea salt emissions are computed using Gong (2003) with a rate (particles  $\text{m}^{-2}\text{s}^{-1}\text{m}^{-1}$ ) given by:

$$\frac{dF}{dr} = 1.373u_{10}^{3.41}r^{-A} (1 + 0.057r^{3.45}) \times 10^{1.607e^{-b^2}}, \quad (4)$$

where  $r$  is the particle radius at 80% relative humidity,  $u_{10}$  is the wind speed at 10m above the surface ( $\text{ms}^{-1}$ ) and the parameters  $A = 4.7(1 + 30r)^{-0.017r^{-1.44}}$  and  $B = (0.433 - \log(r))/0.433$ . This expression is modulated by the sea surface temperature in order to correct Gong (2003) formulation which overestimates sea salt emissions over cold water and underestimates them over warm water. The modified sea salt source function includes a sea surface temperature dependence (Jaeglé et al., 2011):

$$\frac{dF}{dr} = (0.3 + 0.1T_s - 0.0076T_s^2 + 0.00021T_s^3) 1.373u_{10}^{3.41}r^{-A} (1 + 0.057r^{3.45}) \times 10^{1.607e^{-b^2}}, \quad (5)$$

where  $T_s$  is the sea surface temperature. The emission spectrum is integrated over each bin range.

Desert dust emissions are dynamically managed using Marticorena and Bergametti (1995):

$$F = \alpha G, \quad (6)$$

where  $F$  is the vertical flux of desert dust aerosols,  $G$  is the horizontal flux of desert dust aerosols and  $\alpha$  is a parameter depending on the soil specificity. The horizontal flux,  $G$ , is defined by:

$$G = EC \frac{\rho_a}{g} u^*{}^3 \int_{D_p} (1 + R) (1 - R^2) dS_{rel}(D_p) dD_p, \quad (7)$$

where  $E$  is the erodible fraction of the soil,  $C$  is a constant ( $C = 2.61$ ),  $\rho_a$  is the density of the air,  $g$  the gravitational constant,  $D_p$  the particle size and  $u^*$  the friction velocity.  $R$  is defined by:

$$R = \frac{u_t^*}{u^*} \quad (8)$$

where  $u_t^*$  is the threshold friction velocity allowing particle emissions. The total emission is divided into the bins using 3 modes of mean number diameters  $r_1 = 0.64 \mu\text{m}$ ,  $r_2 = 3.45 \mu\text{m}$  and  $r_3 = 8.67 \mu\text{m}$  of standard deviation  $\sigma_1 = 1.7$ ,  $\sigma_2 = 1.6$  and  $\sigma_3 = 1.5$ . Desert dust emission is available over Sahara and Eastern Asian desert.

Emissions of desert dusts and sea salts are calculated using the meteorological forcing at the resolution of each domain. Primary organic carbon and black carbon emissions are managed through emission inventories.

### 2.3.3 New developments of the aerosol module

In Sič et al. (2015), they only take into account primary aerosols that do not interact with each other. Therefore external mixing was assumed and each type of aerosols used specific size bins. To introduce SIA into MOCAGE, we assume aerosol internal mixing in order to represent interactions between aerosols. To implement internal mixing, we use a new set of bin sizes that are the same for all types of aerosols, ranging from 2 nm to 50  $\mu\text{m}$  with size bin limits of: 2, 10, 100 nm, 1, 2.5, 10 and 50  $\mu\text{m}$ . These new bin limits have been tested on a one year global simulation only with primary aerosols and compared to a similar simulation that used the aerosol specific size bins following Sič et al. (2015). The use of these new size bins gives similar results to when using the aerosol dependent ones with a resulting difference of less than 5% on the estimation of  $\text{PM}_{10}$  and  $\text{PM}_{2.5}$  burden on the annual mean at the global scale.

From this basis, it was possible to introduce secondary inorganic aerosols in MOCAGE. SIA results from a partition between the gaseous phase and the aerosol phase. This partition depends on compound concentrations both in the gaseous and the aerosol phases and the ambient conditions: temperature and humidity. This partition can be solved using a thermodynamic equilibrium model. We choose for this purpose to use the latest version of the thermodynamic equi-

librium model called ISORROPIA II (Nenes et al., 1998; Fountoukis and Nenes, 2007), which is used here in the deliquescent configuration. ISORROPIA is commonly used in state-of-the-art CTMs for instance in CHIMERE (Bessagnet et al., 2004) and LOTOS-EUROS (Schaap et al., 2008). Sulfate, nitrate and ammonium aerosol concentrations are simulated by ISORROPIA, each of these species being represented in MOCAGE with six concentrations for each of the six size bins. ISORROPIA gives the thermodynamic equilibrium between 12 liquid aerosol species (see Table 2), 9 solid aerosol species (see Table 3) and 3 gaseous compounds (see Table 4). Wexler and Seinfeld (1990) showed that the time constant to achieve the equilibrium ranges from a few seconds for high aerosol mass concentrations and small aerosol sizes to more than a day for low mass concentrations and large particle radii. Nevertheless, we assume in MOCAGE that the equilibrium is reached in the 15 min chemical update frequency for the following reasons. The aim of the model is to be used mainly for air quality, especially the forecast of  $PM_{10}$  and  $PM_{2.5}$ . According to Capaldo et al. (2000), the forecast of total  $PM_{10}$  and  $PM_{2.5}$  using an equilibrium method is in good agreement with more complex methods including a dynamic method. According to the authors, nitrate aerosols, especially in the coarse mode are poorly represented in their simulations. They claim the nitrate underestimation is due, at least partially, to the lack of reaction with sodium chloride, which is taken into account here. Moreover, for the operational use of MOCAGE, it is important to have the lowest computational cost possible. The equilibrium approach is about 400 times faster than a dynamic method and about 12 times faster than a hybrid approach (Capaldo et al., 2000).

ISORROPIA outputs include the total concentrations of different solid, liquid or gaseous compounds (see Tables 2–4). The aerosol outputs from ISORROPIA then have to be distributed over the MOCAGE model size bins. The secondary inorganic aerosols are distributed in the bins as follows. We assume that the compounds related to sea salts, i.e., sodium and chlorine, are distributed with the same size distribution as the sea salt aerosol variables in the model. Sea salts are emitted with a specific size distribution. Their time evolution in the model modifies this distribution because of the different physical phenomena affecting sea salts such as sedimentation (incorporating hygroscopicity) or wet and dry deposition. Thus, at a given point and at a given time, sea salts have a specific size distribution taking into account their evolution since

the emission. ISORROPIA outputs including sodium or chlorine are distributed proportionally according to this specific distribution.

The other compounds are distributed following the measured accumulation mode for SIA from Zhuang et al. (1999) (see Table 5). The **nuclei** mode is not used because of the lack of the coagulation processes in the model allowing mass transfer from the condensation mode to the accumulation mode. Thus by distributing only into the accumulation mode, we implicitly assume that the coagulation has already been acting to transform fine mode aerosols into accumulation mode aerosols. The coarse mode is also not used because the formation of coarse particles through reaction with sea salts is treated separately (cf. explanations in the previous paragraph). The remaining coarse particles, are assumed negligible. Indeed, Zhuang et al. (1999) found that sulfate coarse mode is mainly due to reaction of sulfur dioxide on sea salts or soil particles and nitrate coarse mode is mainly due to reaction of gas phase  $\text{HNO}_3$  with sea salts particles. The nitrate and sulfate fraction that reacts with sea salts is treated separately using the sea salt size distribution. Zhuang et al. (1999) also found that ammonia gas prefers to react in the fine mode. It forms coarse mode ammonium only if ammonia gas is present in excess to form ammonium chloride in sea salt.

For example, we can consider two forms of nitrate  $\text{NaNO}_3$  and  $(\text{NH}_4)_2\text{SO}_4$ .  $\text{NaNO}_3$  results from an interaction between nitric acid ( $\text{HNO}_3$ ) and sea salts ( $\text{NaCl}$ ), this is why some nitrate is split into size bins with the same proportions as the sea salts.  $(\text{NH}_4)_2\text{SO}_4$  results from **ammonia** ( $\text{NH}_3$ ) and sulfuric acid ( $\text{H}_2\text{SO}_4$ ), then we will use measured modes from Zhuang et al. (1999) to distribute nitrate into the corresponding size bins.

In summary, the choice made here was to assume that each type of aerosol is distributed into its bins all along its lifetime following the defined modes (and associated parameters) based on observations published in the literature. By doing this, we assume that the defined modes already include all the aerosol microphysical processes implicitly. This is why nucleation and coagulation are not explicitly in the model. This simple approach, which has the advantage of requiring low computation time, can be regarded as the first stage in the development of SIA in MOCAGE.

## 2.4 Transport and physical parameterizations

### 2.4.1 Transport

MOCAGE uses a semi-lagrangian advection scheme (Williamson and Rasch, 1989) to transport chemical species at the resolved scale. For the convective transport, the numerical model uses the parameterization of Bechtold et al. (2001). The species are diffused by the turbulent mixing in the planetary boundary layer as described by the scheme of Louis (1979).

### 2.4.2 Physical parameterizations for gaseous compounds

Dry deposition of gaseous compounds is taken into account following Wesely (1989). Dry deposition is calculated as follows:

$$F_{dg} = -v_d C \quad (9)$$

where  $F_{dg}$  represents the vertical dry deposition flux,  $v_d$  the deposition velocity of the considered compound and  $C$  its concentration.  $v_d$  is calculated using the concept of surface resistances in series as follow:

$$v_d = \frac{1}{R_a + R_b + R_c} \quad (10)$$

where  $R_a$  represents the aerodynamic resistance,  $R_b$  the quasi-laminar layer resistance and  $R_c$  the canopy resistance (Wesely, 1989). Wet deposition of gaseous species for the convective part is based on Mari et al. (2000) while the stratiform part from Liu et al. (2001) based on Giorgi and Chameides (1986). Wet deposition is divided into two parts. The rainout is the process occurring when gases are dissolved into the droplets during their formation. It is also called in-cloud scavenging. When the droplets fall, they can collect some material. This process is called washout or below-cloud scavenging.

### 2.4.3 Physical parameterizations for aerosols

Dry deposition of aerosols and gravitational settling are implemented as described in Seinfeld and Pandis (1998). The dry deposition velocity is defined as:

$$V_{dd} = \frac{1}{R_a + R_b} + V_p, \quad (11)$$

where  $R_a$  is the aerodynamical resistance ( $\text{sm}^{-1}$ ),  $R_b$  is the quasi-laminar layer resistance ( $\text{sm}^{-1}$ ) and  $V_p$  is the settling velocity ( $\text{ms}^{-1}$ ).

The settling velocity is based on Stokes' law and is a function of the particle diameter, particle density and air viscosity:

$$V_p = \frac{D_p^2 \rho_p g C_c}{18 \mu_a}, \quad (12)$$

where  $D_p$  is the ambient aerosol diameter (m), taking into account hygroscopicity by computing a humid diameter.  $\rho_p$  is the aerosol particle density ( $\text{kgm}^{-3}$ ),  $g$  is the gravitational constant ( $\text{ms}^{-2}$ ),  $\mu_a$  is the dynamical viscosity of air (Pas) and  $C_c$  is the slip correction factor which accounts for noncontinuum effects when the particle diameter and the air mean free path are of the same order of magnitude (Seinfeld and Pandis, 1998).

Aerosol wet deposition takes into account in-cloud scavenging (Giorgi and Chameides, 1986), below-cloud scavenging (Slinn, 1977) and below-cloud scavenging due to snowfall (Slinn, 1982). The fraction of aerosols removed at each time step by precipitation is calculated as:

$$F = f_{prec} (1 - e^{-\Lambda \Delta t}), \quad (13)$$

where  $F$  is the fraction of removed aerosols,  $f_{prec}$  is the fraction of precipitating cloud cover,  $\Lambda$  is the scavenging coefficient ( $\text{s}^{-1}$ ) which describes a rate of loss of particles due to scavenging and  $\Delta t$  is the model time step for scavenging (s). The scavenging coefficient,  $\Lambda$ , consists of the

in-cloud scavenging coefficient,  $\Lambda_{ro}$ , and the below-cloud scavenging coefficient due to rainfall,  $\Lambda_{wo}$ . To represent properly the precipitating cloud an estimation of the fraction of precipitation forming clouds is made for stratiform and convective clouds. For stratiform clouds, the fraction of precipitating clouds is given by:

$$f_{strat} = \frac{Q}{L_{st}R_{st} + Q}, \quad (14)$$

where  $Q$  is the gridbox mean rate of precipitation formation including both liquid and solid precipitation ( $\text{kgm}^{-3}\text{s}^{-1}$ ).  $L_{st}$  is the typical in-cloud liquid water content in precipitation forming stratiform clouds (Brost et al., 1991).  $R_{st}$  is the in-cloud rate constant for conversion of cloud water to precipitation for stratiform clouds. For convective clouds, the fraction of precipitating cloud cover within a gridbox for any given time step of the model ( $\Delta t$ ) is:

$$f_{conv} = \frac{F_0 Q \frac{\Delta t}{t_c}}{Q \frac{\Delta t}{t_c} + F_0 R_{cv} L_{cv}}, \quad (15)$$

where  $F_0$  is the maximum cumulus cloud cover assumed in the radiation calculations backed by observations,  $t_c$  is the typical duration of precipitation from a cumulonimbus cloud ( $t_c = 30\text{min}$ , Liu et al. (2001)). The in-cloud scavenging coefficient is different for stratiform and convective precipitation (Giorgi and Chameides, 1986). For stratiform precipitation, it is defined by:

$$\Lambda_{rost} = R_{st} + \frac{Q}{L_{st}}. \quad (16)$$

For convective precipitation it is:

$$\Lambda_{rocv} = R_{cv}. \quad (17)$$

Concerning below-cloud scavenging, the scavenging coefficient is defined as shown in Seinfeld and Pandis (1998):

$$\Lambda_{wo} = \frac{3}{2} \frac{E_r P}{D_d}, \quad (18)$$



where  $E_r$  is the collection efficiency of a raindrop to collect a particle during its fall. It is calculated following Slinn (1977).  $P$  is the precipitation rate ( $\text{kgm}^{-2}\text{s}^{-1}$ ) and  $D_d$  is the raindrop diameter (m). For more details on sedimentation and wet deposition of aerosols, see Sič et al. (2015).

### 3 Experimental setup and observations

#### 3.1 Simulations

Two series of simulations are conducted in order to evaluate the developments to the model secondary inorganic aerosol scheme on the global and the regional scales. Two simulations were run at the global scale, at a resolution of  $2^\circ \text{lon} \times 2^\circ \text{lat}$ , for the year 2005. We chose the year 2005 because a large set of observations are available all over the world for this year. One of the simulations takes into account the newly integrated secondary inorganic aerosols (hereafter referred to as RACMSIA). The other one corresponds to the original version of MOCAGE without SIA (hereafter referred to as RACM). Simulations are run with a spin-up of 3 months and are driven by the meteorological fields from ARPEGE analyses.

The second series of simulations corresponds to a more recent period and focuses on the European domain to do an evaluation at the regional scale. Two simulations, with and without secondary inorganic aerosols, are conducted for the year 2010 and are compared to the EMEP measurement dataset. Both simulations have the global domain at  $2^\circ \text{lon} \times 2^\circ \text{lat}$ , and a nested European domain at  $0.5^\circ \text{lon} \times 0.5^\circ \text{lat}$  resolution. The latter domain covers the western part of the European continent between  $16^\circ \text{W}$  to  $36^\circ \text{E}$  and  $32$  to  $72^\circ \text{N}$ . The two domains communicate with each other by a two-way grid nesting scheme.

##### 3.1.1 Gaseous and aerosol emissions

At the global scale, the IPCC/AR5 emissions are used, representative for the year 2000, for the anthropogenic species and biomass burning emissions (Lamarque et al., 2010). Biogenic emissions, representative for 1990, are based on GEIA. Nitrous oxides from lightning are taken into account following Price et al. (1997). [The IPCC/AR5 emissions for organic carbon and](#)

black carbon aerosols are used (Lamarque et al., 2010). This first set of emissions is used to simulate the year 2005 using a global domain.

At the regional scale, over the European continent, the MACC project emissions, representative for the year 2009, are used for anthropogenic gaseous compounds (Kuenen et al., 2014) and completed by GEIA emissions for biogenic sources. The MACC project emissions are also used for the aerosols (Kuenen et al., 2014). This second set of emissions is used for simulating the year 2010 over the Europe. At the global scale we use the same emissions as for the global simulation.

### 3.2 Observations for global simulation evaluation

MODIS daily mean AODs were used to evaluate the model simulations. For this purpose, we use the daily MODIS data level 3 (L3, collection 5.1) for the year 2005 and perform an additional quality control and screening as presented in Sič et al. (2015). This processing is done to minimize the number of observations that are cloud contaminated and those with statistically low confidence which often artificially increase AOD (Zhang et al., 2005; Koren et al., 2007; Remer et al., 2008). Moreover, Ruiz-Arias et al. (2013) showed there is a rapid increase of the relative underestimation of AODs when the MODIS' L3 AODs are below 0.1. We then perform an additional screening by rejecting all AOD values below 0.05. Below this value, the underestimation of AOD leads to a mean relative error higher than 50% (Ruiz-Arias et al., 2013).

AODs in MOCAGE are calculated at 550 nm using Mie theory with refractive indices taken from Global Aerosol Data Set (Köpke et al., 1997) and extinction efficiencies derived with Wiscombe's Mie scattering code for homogeneous spherical particles (Wiscombe, 1980).

For the model evaluation, we also use the HTAP observation database. It includes data from several measurement networks: EMEP, IMPROVE, NAtChem, EANET, CREATE, EUSAAR, NILU and the WMO-PCSAG global assessment precipitation dataset (<http://www.htap.org/>). We use observations of gaseous concentrations (nitric acid, nitric oxides, sulfur dioxide, ammonia), and the particulate matter composition (sulfate, nitrate, ammonium). The release used here is dated from 1 April 2014. Daily observations and weekly observations are used separately in order to consider comparisons at the same temporal scale. Daily observations cover both Euro-

pean countries and Canada. Weekly observations cover essentially the north of America and the eastern part of Asia. This is illustrated by Fig. 1 represents the location of the stations measuring SIA composition. It shows a good coverage of sulfate and nitrate measurements in the Northern Hemisphere. There are fewer ammonium aerosol measuring stations, with some zones that are not covered like the western part of the United States or some parts of Europe. Note also that the lack of ground observations in the Southern Hemisphere does not allow us to make the model evaluation in this part of the world, except for the comparison against MODIS AOD retrievals.

### 3.3 Observations for the model evaluation over Europe

The evaluation at the regional scale is split into two parts. The first part is based on the EMEP observation database and is aimed to check the good simulation of secondary inorganic aerosols. We use daily observations of concentrations. The second part is based on the AIRBASE observation database. It is aimed to check the performance of the model against air quality monitoring station observations on a hourly base.

#### 3.3.1 EMEP database

The European Monitoring and Evaluation Programme (EMEP) is a scientifically based and policy driven programme under the Convention on Long-range Transboundary Air Pollution (CLRTAP) for international co-operation to solve transboundary air pollution problems (<http://www.emep.int>). Observations were downloaded through the EBAS repository (<http://ebas.nilu.no>). Daily observations are used to evaluate secondary inorganic aerosol composition (sulfate, nitrate, ammonium) over Europe. Figure 2 represents the location of the stations measuring SIA composition on a daily basis. One can note similar remarks as for the measurements shown in Fig. 1 with a good coverage of sulfates and nitrates measurements and to a lower extent for ammonium measurements. Nevertheless, some areas, in France for example, are not very well covered. The EMEP monitoring sites are located such that significant local influences are minimised (Tørseth et al., 2012). Therefore measurements are assumed to be directly comparable to model outputs which here are at  $0.5^\circ \times 0.5^\circ$ .

### 3.3.2 AIRBASE database

To make a complementary evaluation, and because SIA directly affects major regulated air pollutants, we also make comparisons with air quality indicators monitored over Europe. For this we use AIRBASE, which is a dense measurement network used for air quality issues. It is managed by the European Topic Centre on Air Pollution and Climate Change Mitigation on behalf of the European Environment Agency. For this study, we use the latest version (version 8) of the AIRBASE database (<http://acm.eionet.europa.eu/databases/airbase>). AIRBASE data are used in this study to evaluate the performance of the model for  $PM_{10}$ ,  $PM_{2.5}$ , ozone and nitrogen dioxide. For 2010, a total of 38 countries, including the 27 European Union countries have provided air quality data.

AIRBASE measuring stations are located on various sites: urban, periurban, rural, etc. In order to be able to compare the model simulations at the  $0.5^\circ$  longitude  $\times$   $0.5^\circ$  latitude resolution, we select the stations which are representative of the model resolution. Following Joly and Peuch (2012), each station is characterised with a class between 1 and 10 according to its statistical characteristics, 1 corresponding to a fully rural behaviour and 10 to a highly polluted station. The selection of stations is done following Lacressonnière et al. (2012) who conducted an evaluation of MOCAGE at the regional scale over several years. Only the stations corresponding to 1 to 5 classes are kept for ozone. For nitrogen dioxide, only the station corresponding to 1 and 2 classes are kept since nitrogen dioxide is a short lived species. For  $PM_{10}$  we select the stations with classes ranging from 1 to 5. Joly and Peuch (2012) do not provide a classification for  $PM_{2.5}$ . We choose to use the same stations for  $PM_{2.5}$  as for  $PM_{10}$ .

### 3.4 Metrics used for evaluation

Several statistical indicators can be used for model evaluation against in situ data. Seigneur et al. (2000) state that past model performance evaluations have generally used observations to normalize the error and the bias. This approach can be misleading when the denominator is small compared to the numerator. Following Seigneur et al. (2000), we chose to use the

fractional bias and the fractional gross error instead of the bias and the root-mean-square error (rmse).

The fractional bias, also called modified normalized mean bias (MNMB) or mean fractional bias (MFB), used to quantify, for  $N$  observations, the mean between modeled ( $f$ ) and observed ( $o$ ) quantities is defined as follow:

$$\text{MNMB} = \frac{2}{N} \sum_{i=1}^N \frac{f_i - o_i}{f_i + o_i} \quad (19)$$

The fractional bias ranges between  $-2$  and  $2$  varying symmetrically with respect to under and overestimation.

The fractional gross error (FGE), also called mean fractional error (MFE) aims at quantifying the model error. It varies between  $0$  and  $2$  and is defined by:

$$\text{FGE} = \frac{2}{N} \sum_{i=1}^N \left| \frac{f_i - o_i}{f_i + o_i} \right| \quad (20)$$

The correlation coefficient  $r$  indicates the extent to which patterns in the model match those in the observations and is defined by:

$$r = \frac{\frac{1}{N} \sum_{i=1}^N (f_i - \bar{f})(o_i - \bar{o})}{\sigma_f \sigma_o} \quad (21)$$

Where  $\sigma_f$  and  $\sigma_o$  are standard deviation respectively from the modelled and the observed time series and  $\bar{f}$  and  $\bar{o}$  their mean values.

Boylan and Russell (2006) give criteria to characterize a model performance against observations based on MNMB and FGE. It gives two types of performance. The “performance goal” is the level of accuracy that is considered to be close to the best a model can be expected to achieve. The “performance criteria” is the level of accuracy that is considered to be acceptable for modelling applications. For example, for particulate matter, for stations having a mean concentration superior to  $2.25 \mu\text{g m}^{-3}$  the “performance goal” is reached when the MNMB and the

FGE are equal or less than  $\pm 0.3$  and 0.5 respectively. These recommendations depend on the mean concentration of an observation point (see Table 1 in Boylan and Russell, 2006). In particular, less polluted stations might have large errors for MNMB and FGE but still be satisfactory.

## 4 Results and evaluation of the global simulations

This section presents results at the global scale. Firstly, we show and discuss the global concentrations before comparing results with measurements.

### 4.1 Global concentrations

Figure 3 represents the annual emission of the SIA precursors: sulfur dioxide, nitrous oxides and ammonia. The zones with highest emissions are mostly in the Northern Hemisphere located in the eastern part of Asia, North America and Europe. Ammonia emissions are larger in Europe and Eastern Asia than in North America. Ammonia and nitrous oxides also have high emissions in South America and Africa albeit to a lesser extent.

Figure 4 shows annual mean surface concentrations of the secondary inorganic compounds: sulfate, nitrate, ammonium and the sum of all these components. These fields are consistent with the emissions. High concentration zones correspond to zones of high emissions of precursors, being Europe, Eastern Asia and North America. However North American concentrations are slightly lower than the other areas of high concentrations. This might be due to the emissions of ammonia which are lower, being then less able to form aerosol with sulfate and nitrate. These mean annual secondary inorganic aerosol concentrations from MOCAGE are globally consistent in terms of geographical distribution and concentration values with Hauglustaine et al. (2014) model fields representative for 2000.

Figure 5 represents the comparison of  $\text{HNO}_3$  and  $\text{NH}_3$  annual mean concentrations between the RACM and the RACMSIA experiments. In the RACM experiment, ammonia does not chemically react. Dry and wet deposition are the only removal processes in this configuration. Ammonia is thus accumulating over time in the model's atmosphere. **This is why there are very**

large differences between RACM and RACMSIA for  $\text{NH}_3$  leading to important changes also for  $\text{HNO}_3$ . In the RACMSIA experiment, ammonia can take part in aerosol production under favorable conditions (thermodynamic and availability of other inorganic compounds). The ammonia field in RACMSIA is more consistent than RACM with the modelling results from Xu and Penner (2012).

For  $\text{HNO}_3$ , there is 200 pptv less  $\text{HNO}_3$  in the RACMSIA experiment than in the RACM experiment. In the RACM experiment, geographic patterns agree with Xu and Penner (2012), but concentrations are overestimated. In the RACMSIA experiment, part of the nitric acid is transformed into aerosol and nitric acid concentrations are therefore lower and more consistent with Xu and Penner (2012).

## 4.2 Comparison to MODIS AOD

Figure 6 presents the 2005 annual modified normalized mean bias against MODIS AOD observations. In Fig. 6, one can see that the Northern Hemisphere has a negative MNMB globally between  $-1$  and  $-0.5$  in the RACM experiment. In the RACMSIA experiment it is closer to 0 (between  $-0.5$  and  $0.5$ ). This shows an improvement of the model AOD at the global scale when including SIA. This is confirmed by the global mean MNMB which is  $-0.41$  for the RACM experiment and  $-0.21$  for the RACMSIA experiment. Sič et al. (2015) made a similar comparison for primary aerosols only: AOD against MOCAGE simulations. They conclude their study by stating that one reason of MOCAGE negative bias in AOD might be due to the lack of secondary aerosols in their model version. Here we show that adding secondary inorganic aerosols improves MOCAGE results. The global modified normalised mean bias generally remains negative. A negative bias is expected over Asia, western Europe, eastern US and central Africa since the secondary organic aerosols are still missing in the model and are expected to be important in these areas (Tsigaridis and Kanakidou, 2003; Heald, C. L., et al., 2008). The AOD bias over central Asia is likely not only due to the lack of SOA but also to an underestimation of the dust emissions in this region. MOCAGE includes desert dust emissions over Eastern Asia but the large uncertainties of the wind fields over this region due to complex orography produce large uncertainties on desert dust emissions. Over ocean, there are no DMS emissions in the

model and thus we expect AOD underestimation instead of overestimation. The positive bias over the ocean is likely due to the sea salt aerosols. The function used to calculate the sea salt emissions follows an exponential curve for big particles. These big particles remain in the atmosphere for a very short time and very close to the surface but are often emitted in the model. The model AOD overestimation can be linked to an uncertainty on the exponential emission function that possibly gives too many big particles. Also the AOD measurements may not capture the transient presence of big particles in the very low levels.

When comparing Fig. 6 with Fig. 4 one can notice that areas where AODs are increased correspond to areas where secondary inorganic aerosol concentrations are the most important, i.e. in Europe, Asia and Eastern part of North America. Near the coasts, where the influence from land is stronger, the bias is negative in the RACM experiment and is closer to zero by taking into account secondary inorganic aerosols (RACMSIA). In the Guinea Gulf, the improvement is noteworthy but the MNMB is still negative. This could be due to insufficient biomass-burning aerosol emissions, especially through secondary organic aerosol formation, or due to too low desert dust aerosol emissions. **The large negative biases in both simulations on the western coast of South and North America can be linked to dust emissions missing over these regions in MOCAGE, when comparing to the AEROCOM intercomparison project results (<http://aerocom.met.no/>).**

### 4.3 Atmospheric chemical composition against HTAP observations

In this section, we use the daily observations as one time series to calculate the statistics. This allows us to give the same weight to every observation instead of every measuring station because measuring stations do not always provide the full set of observations for the whole year.

Modelled fields are interpolated to the observation location. We take the concentration at the surface, knowing that the altitude difference between the model and the actual station altitude can lead to significant differences. This is why stations with an altitude difference higher than 1000 m with the model orography have been suppressed for the statistics. After this screening, there are 98 stations left on daily observations (104 before screening). For weekly observations, there are 214 stations left (225 before screening).



### 4.3.1 Daily observations

Table 6 presents the statistical results against daily observations for the main components of the secondary inorganic aerosols: sulfate, nitrate and ammonium. As presented in Fig. 1 this type of observations is mainly located in Europe and Canada. Sulfate measurements are divided into two parts, sulfate total and sulfate corrected. The sulfate corrected corresponds to non sea salt sulfate (nss). The use of non sea salt sulfate is better for our comparison because we do not **take into account the emission of sulfates being a part of sea salt aerosols**. But to have the largest number of stations, we use both measures. **In order to improve the comparison, we suppose that 7.68% of the mass of sea salt aerosols is composed of sulfates. This value corresponds to the proportion of sulfate in the sea water (Seinfeld and Pandis, 1998).** For all the comparisons, the sulfate total measurements are then compared to the sulfate field of the model to which we added a fraction of the sea salt aerosol field.

Sulfate totals are well simulated, with a MNMB of 0.05. With a correlation of 0.33, and a FGE of 0.94, **the model performs fairly**. Observations corrected for sea salt sulfate compare better with the model with a correlation of 0.70. The model slightly underestimates sulfate with a MNMB of  $-0.12$ . Ammonium is slightly overestimated with a MNMB of 0.19, and with a good correlation of 0.69. Nitrate is also well modeled with a low MNMB of 0.13, a fairly good correlation (0.53) but with a relatively high FGE (0.94).

The model is able to well simulate the time-series at a given point. As an example, Fig. 7 shows the time-series of **corrected** sulfate, nitrate and ammonium daily observations against MOCAGE values at an Irish measuring station. **We choose this rural station because it is not under direct urban activity and it samples chemical export from North America. Therefore it measures background concentrations that can be compared to the model coarse resolution and these concentrations are not very low and have variations because of the North American export.** The model performs well on the three components by capturing the daily variations and their values. Statistics over this station are given in Table 7. MOCAGE is able to represent well the SIA components with low MNMB and FGE and good correlations. **Results for another station in Canada are presented in Table 8 while the time-series of sulfate, nitrate and ammo-**

mium daily observations against MOCAGE values are presented in Fig. 8. Observations of total sulfate are presented here, using the correction to account for the sea-salt origin sulfate. The RACMSIA simulation for this station has lower performances than for the Irish station. This can be explained for different reasons. Firstly one can note that the Fig. 8 shows the model is able to reproduce the different pollution episodes. The concentrations of secondary inorganic aerosols are nevertheless underestimated, except during winter time. The mean flux in winter and in summer comes from the Western part of Canada and from the Central United-States of America, respectively. As presented in Fig. 3 emissions are at a maximum in the Eastern part of the United States. In summer there is more pollution importation at the measuring station considered here. This importation can be underestimated due to the resolution of the model which is about 200km in this region implicating a mixing of the emissions in the model gridbox on one hand and a diffusion of the pollution plume.

We also checked the behaviour of the model against the diagnostic proposed by Boylan and Russell (2006), i.e., “performance goal” and “performance criteria”. As expected, sulfate corrected, all of the 21 stations are well modelled according to both criteria. Sulfate totals are not as well represented by the model, out of 94 stations, 5 do not comply with the “performance criteria” and 14 do not respect the “performance goal”. For nitrate, only 2 stations do not respect both diagnostics over a set of 61 stations. There are 51 stations measuring ammonium concentrations and only 6 stations do not fit the “performance goal” while all do for the “performance criteria”. The Boylan and Russell (2006) perspective confirms the good performance of the model for secondary inorganic aerosols compounds.

Table 9 presents the statistics for gaseous precursors of SIA both for RACM and RACMSIA experiments. Sulfur dioxide is not really affected by the SIA because there are no direct reactions newly integrated in the model. Oxidation of sulfur dioxide into sulfate was already taken into account in the RACM simulation (see section 2.2.1). But the scores for ammonia are significantly improved. The correlation rises from 0.18 to 0.33, the fractional gross error drops from 1.84 to 1.27 and the modified mean mean bias from 1.84 to 0.79. The nitrogen dioxide statistics are slightly better with the fractional gross error which decreases from 0.83 to 0.77 with SIA formation. Nitric acid seems better simulated with SIA formation looking at the MNMB, but

the fractional gross error and the correlation are worse in the RACMSIA simulation including secondary inorganic aerosols. Depending on atmospheric conditions, SIA formation can be either a sink or a source of nitric acid. Also nitric acid undergoes many other processes that drive its concentration. Therefore simulating nitric acid variations with time and space is challenging and is not only related to the ability of the model to produce realistic SIA. This is why it is difficult to interpret nitric acid performances.

In summary on HTAP daily data, concerning Europe and Canada, the model is able to well simulate secondary inorganic aerosols. We note that the model tends to overestimate ammonium and ammonia. There is also an overestimation of sulfur dioxide while sulfates are slightly underestimated. Nevertheless these comparisons show the ability of the model to reproduce secondary inorganic aerosols at a global scale. It also shows than on a specific location the model is able to reproduce very well the SIA concentrations and their temporal evolution.

#### 4.3.2 Weekly observations

Table 10 presents the statistical results against weekly observations for the main components of secondary inorganic aerosols. As presented in Fig. 1, weekly observations are mainly located in North America and Asia, so this type of observation is complementary to the daily ones. For sulfate, one can see that **sulfate totals are well simulated with a MNMB of  $-0.05$  and a correlation coefficient of  $0.64$** . The results for the sulfate corrected observations should not be interpreted as a general behaviour because there is only one measuring station in this case. As for daily observations, ammonium is overestimated with a MNMB of  $0.34$  and a FGE of  $0.84$ . Similarly for daily observations, the nitrate MNMB is low with a similar FGE of  $1.00$ . As for the daily observations, the bias is low but the error is fairly high.

For gaseous compounds, statistics are not presented here because there are only between 16 and 28 stations depending on the parameter and there are no nitrogen dioxide measurements. Nevertheless the behaviour for this limited number of stations is similar to that of the daily observations.

Figure 1 presents the location of the HTAP stations used in this study. By looking at the weekly station localisation, one can see that there are two main groups of stations, one in North

America and one in Asia. By splitting the dataset between Asian and American stations, there are 29 stations for the Asian area and 156 for the American one. The results are presented in Table 11.

Sulfates, based on total sulfate data, have a similar MNMB in both zones. The correlations too are similar for both continents (65 in North America and 64 in Asia). Nitrates are better simulated in North America. Indeed, MNMBs are 0.30 and 0.05 in Asia and North America, respectively. Moreover, the correlation is also better (0.41) than in Asia (0.13). MNMB of ammonium is also worse in Asia (0.35) than in North America (0.27). Nevertheless, the correlation of ammonium is better in Asia (0.41) compared to North America (0.19).

When comparing Figs. 1 and 6 one can observe that North American stations are located on areas where the model underestimates the AOD when simulating SIA while the Asian stations are located on areas where the AODs are well simulated by the model when taking into account SIA. When looking at stations in North America, comparisons to in situ measurements shows a good agreement for SIA fields. The negative bias on Fig. 6 over this area might then be due to the lack of secondary organic aerosols in the model. The Asian stations comparisons however shows an overestimation of SIA. The good results on AOD comparison might there be due to an overestimation of SIA in this area compensated by an underestimation linked to the lack of SOA.

## 5 Results and evaluation of the regional simulation

The first set of simulations showed that the model was able to simulate correctly SIA on the global scale. The next step is to check the behaviour of the model over a regional domain, Europe, with a better resolution and different emission inventories.

This section presents results on the second set of simulations over the year 2010 including two nested domains: the global one (at  $2^\circ$  lon  $\times$   $2^\circ$  lat) and a regional one (at  $0.5^\circ$  lon  $\times$   $0.5^\circ$  lat). As we already looked at model results at a global scale (see Sect. 4), the focus in this section is put on the regional European domain. Firstly, we analyse the results before comparing them

with measurements from the EMEP database for secondary inorganic aerosol components. Then we make a comparison to AIRBASE measurements from an air quality point of view.

## 5.1 European concentration fields

Figure 9 presents SIA precursor emissions ( $\text{SO}_2$ ,  $\text{NO}_x$  and  $\text{NH}_3$ ) for the year 2010 on the regional domain.  $\text{SO}_2$  emissions are at a maximum in an area covering the Benelux, England and Central Europe.  $\text{NO}_x$  emissions are significant almost everywhere in Western Europe but with a maximum emission in Benelux and England.  $\text{NH}_3$  is emitted everywhere except in Scandinavia with maxima in Brittany (France), Benelux and the Po Valley (Italy).

Figure 10 presents the annual mean surface concentration for the year 2010 over the regional domain. SIA are present almost everywhere especially over the continent, with very high concentrations in the Po valley, Benelux and Central Europe.

Sulfate aerosols are mainly present in Central Europe. This is due to the high emission zone of  $\text{SO}_2$  in this region. These results are consistent with Schaap et al. (2004) who simulated the year 1995. Schaap et al. (2004) also found high sulfate concentrations over Benelux and England. There are no high sulfate concentrations over these locations in our simulation. These differences are due to the emission reduction program. Indeed Western Europe has strongly decreased its  $\text{SO}_2$  emissions since 1995.

Nitrate aerosols are mainly present in Benelux and the Po Valley. Benelux has high nitrate concentrations due to high  $\text{NO}_x$  emissions in this area, while the Po Valley has not such high  $\text{NO}_x$  emissions, but a climate and a topography which favours pollution events.

Ammonium aerosols are less important in terms of mass concentration and are more smoothly distributed over the domain. Ammonium is present where either sulfate or nitrate are present, because the main SIA components are ammonium sulfates and ammonium nitrates.

Figure 11 presents the comparison of  $\text{HNO}_3$  and  $\text{NH}_3$  annual mean concentrations between the RACM and the RACMSIA experiments. Similarly to the global simulation,  $\text{HNO}_3$  and  $\text{NH}_3$  concentrations are lowered in the RACMSIA experiment compared to the RACM experiment. Compared to Schaap et al. (2004)  $\text{NH}_3$  concentrations are too high in the RACM experiment while having closer values in the RACMSIA experiment. Patterns are also similar except for

the Po Valley where both MOCAGE simulations show very high concentrations of ammonia. Concerning  $\text{HNO}_3$ , patterns are the same for both experiments.

## 5.2 Atmospheric chemical composition over a regional domain against EMEP observations

For this part, the observations are used in the same way as for the global scale. However here we only use daily observations because there are very few weekly observations (between 3 and 5 stations depending on the parameter observed).

Table 12 presents the statistical results for the main components of the secondary inorganic aerosols: sulfate, nitrate and ammonium. Sulfate, both total and corrected, are underestimated with an MNMB of  $-0.16$  and  $-0.35$  respectively and a FGE of  $0.67$  and  $0.73$ . Correlation is slightly better ( $0.68$ ) for corrected sulfate than for total sulfate ( $0.57$ ). Ammonium is only slightly overestimated, with an MNMB of  $0.18$ , and is well modelled with a correlation of  $0.71$ .

Table 13 presents the statistics for the gaseous precursors of SIA. The model has a similar behaviour as on the global scale against daily HTAP observations. In both simulations, the species with the best performances is  $\text{NO}_2$  while the one with the worse scores is  $\text{NH}_3$ . The use of SIA mainly affects  $\text{NH}_3$  with a very significant improvement of all statistical indicators. The differences between the model results and the observations can partly be explained by uncertainties in the emission inventories used. In (Kuenen et al., 2014), they report uncertainties in ammonia emission of about 50%. For  $\text{NO}_x$ , uncertainties are lower but still about 30%.  $\text{SO}_2$  only has about 10% uncertainty. These uncertainties in emission might explain differences for species ammonia, ammonium and for nitrogen dioxide. For sulfur compounds, there is an underestimation of sulfate aerosols and a strong overestimation of  $\text{SO}_2$ , which can not be explained only by the emission uncertainties. The oxidation process transforming  $\text{SO}_2$  into sulfuric acid depends on several variables (gaseous concentrations, liquid water content, temperature, etc). It is therefore more difficult to represent it correctly since all these variables have also some associated uncertainties.

### 5.3 Air quality indicators

In order to complete the validation, we check the change on air quality pollutants due to the introduction of secondary inorganic aerosols. These indicators are surface concentrations of  $O_3$  and  $NO_x$  ( $NO$  and  $NO_2$ ) for gaseous species and  $PM_{10}$  and  $PM_{2.5}$  for aerosols.

We also examine the impact of the seasonal basis, which is based on the statistics from three seasons: spring (March, April and May), summer (June, July, August) and fall (September, October and November). Winter is not analyzed here because winter months (December, January and February) are not simulated as a continuous series.

#### 5.3.1 Particulate matter forecast: $PM_{2.5}$ and $PM_{10}$

Table 14 presents statistics for  $PM_{2.5}$  over Europe for the year 2010 based on AIRBASE hourly observations. One can see that  $PM_{2.5}$  is better represented in the RACMSIA version. Indeed, MNMB increases from  $-0.58$  in RACM to  $-0.14$  in RACMSIA and the FGE decreases from  $0.77$  in RACM to  $0.56$  in RACMSIA. MOCAGE still underestimates  $PM_{2.5}$ , but the error is smaller with the new version of the model with SIA. The correlation also rises from  $0.47$  to  $0.58$ . Secondary organic aerosols are still missing in the model and likely explain the  $PM_{2.5}$  negative bias. Table 14 also presents the statistics for  $PM_{10}$  over Europe for the year 2010 based on AIRBASE hourly observations. The conclusions for  $PM_{10}$  are similar to those of  $PM_{2.5}$  but with slightly poorer statistics.

Table 15 presents the variation of  $PM_{2.5}$  MNMB according to the season. The  $\Delta$  represents the improvement of the RACMSIA experiment compared to the RACM experiment. Since the MNMB are all negative, a positive value of  $\Delta$  means that adding secondary inorganic aerosols has a positive effect on the simulation.

Over the whole year, the MNMB is improved by  $0.44$ . By looking at the behaviour on the different seasons, one can see that in spring (MAM) the improvement of  $PM_{2.5}$  forecasts is larger than for the other seasons ( $0.52$ ). When taking a look to the  $PM_{10}$  seasonal variability, the conclusion is the same. This behaviour is due to the fact that spring, especially March and April, is the most favourable period for secondary inorganic aerosols formation in Europe. In Summer,

the MNMB is improved by 0.35 in the RACMSIA simulation, which is very significant. But the normalised bias in RACMSIA experiment is higher than for the other seasons. This is due to the fact that summer is a season favourable to secondary organic aerosol, still lacking in our model, especially with a biogenic origin. Indeed, biogenic volatile organic compounds such as isoprene for example, have higher emissions in summer which leads to higher biogenic secondary organic aerosols in summer.

### 5.3.2 Feedback on the gaseous chemistry

Figure 12 represents the annual mean concentrations of surface ozone for the RACM and the RACMSIA experiments. One can see a significant decrease in surface ozone, especially over oceans, between 5 and 10 ppbv. On land, concentrations are nearly the same. By being absorbed into the aerosol phase, nitric acid is not available for forming  $\text{NO}_x$  again and then the ozone equilibrium is displaced. The effect is less important over the land because of the proximity of  $\text{NO}_x$  sources which drive its concentrations.

Table 14 presents the statistics for ozone against hourly observations from the AIRBASE database. The statistics are very similar between the two experiments, only the MNMB is slightly better for the RACMSIA experiment. It is linked with the ozone maps showing a decrease over the ocean while the field is similar over land. Although the ozone maps show a decrease over the ocean the field is similar over land where the AIRBASE stations are located.

Table 14 presents the statistics for nitrogen dioxide against hourly observations from the AIRBASE database. All statistical indicators are close in both experiments (RACM and RACMSIA) indicating that the  $\text{NO}_2$  equilibrium in MOCAGE is not affected by the introduction of SIA in the model. The comparison between Tables 13 and 14 shows that the MOCAGE simulations have similar performances against EMEP and AIRBASE. For these statistics we use 44 EMEP stations and 610 AIRBASE stations. This shows that the MOCAGE model with or without SIA provides robust  $\text{NO}_2$  fields at the surface even when compared to a large number of data.



## 6 Conclusions

In this study we developed a secondary inorganic aerosol module into the CTM MOCAGE. These developments were made with the objectives of having a simple and computationally efficient module able to give good results while being able to be used in an operational framework and of being valid at different scales. We showed that the model is able to represent secondary inorganic aerosols on both the global scale and the European regional scale. The different constituents of the secondary inorganic aerosols being sulfate, nitrate and ammonium simulated by the model fit well against the different observational datasets used: HTAP and EMEP. These databases and the AIRBASE database were also used to assess gaseous species concentrations. Comparisons show a neutral impact of SIA on  $\text{SO}_2$  and  $\text{NO}_2$ , a mixed impact on  $\text{HNO}_3$  (with a much better MNMB but slightly worse FGE and correlation) and a large improvement of  $\text{NH}_3$ . Simulations with SIA do not show a significant improvement on statistical scores for ozone. Nevertheless, there is an impact on ozone fields at the surface over the sea that is significant but very little change over land as reflected by the scores. The comparison with satellite AODs shows that the global aerosol budget is significantly better when SIA are used in the model. Finally, the model is able to perform generally very well at reproducing daily variations of SIA as illustrated by the comparison between MOCAGE and observations at a station in Ireland.

By comparing the MOCAGE model results to the AIRBASE dataset over Europe in terms of particulate matter concentration, we also showed that the model performs better with the introduction of secondary inorganic aerosols. Especially in spring (March, April, May), the MNMB of the  $\text{PM}_{2.5}$  is improved by 0.52 rising from  $-0.55$  to  $-0.03$ . Over the full year of simulation, there is still a negative bias in  $\text{PM}_{2.5}$  and  $\text{PM}_{10}$  concentrations, which can be due to the lack of secondary organic aerosols in the model. The implementation of secondary organic aerosols in MOCAGE is the next major development foreseen to fully complete the aerosol scheme.

Model simulations with SIA show that  $\text{SO}_2$  is significantly overestimated and the sulfates are underestimated. For instance at the regional scale, the  $\text{SO}_2$  MNMB is 1.15 and the sulfates'

MNMB is  $-0.36$ . This indicates that the model is not able to fully convert  $\text{SO}_2$  into sulfate. This can be related to several sources of uncertainty within the conversion process such as temperature, liquid water content and its pH and gaseous concentrations of precursors that are partly linked to their emissions (Kuenen et al., 2014). Some work will be done in the future to identify the main sources of uncertainties in order to improve the representation of the  $\text{SO}_2$  oxidation process into sulfuric acid. Concerning ammonia and ammonium, they have both positive bias that can at least be partly explained by the large uncertainties in ammonia emissions of about 50% (Kuenen et al., 2014).

In the implementation, we made choices for representing phenomena favouring computational efficiency over a very detailed representation while keeping a good accuracy. **There are weaknesses in this SIA module which could be improved. Firstly, all the microphysical processes have been treated implicitly in a very simple way. A next step would be to include them using physical parameterizations. In particular, nucleation, condensation and coagulation which are very important for the time evolution of the aerosol sizes. Another aspect to work on is the thermodynamic equilibrium hypothesis which leads to uncertainties. To improve this, it is necessary to account for the kinetics of the transfer between the gas phase and the aerosol phase, especially for big particles (Wexler and Seinfeld, 1990; Capaldo et al., 2000). A third improvement would be to take into account the formation of secondary organic aerosols in order to have the complete range of atmospheric particles and be able to represent properly the different interactions and impact of aerosols.** One of the final goals is to integrate this module for operational forecasts into the Prev'Air and the COPERNICUS programs. The model MOCAGE will also be used to make research studies including long run simulations for instance for the CCMi program (Chemistry–Climate Model initiative) and the analysis of the aerosol budget in the Mediterranean area.

## Code availability

This paper is based on source code that is presently incorporated inside the MOCAGE model. The MOCAGE source code is the property of Météo-France and CERFACS, and it is based

on libraries that belong to some other holders. The MOCAGE model is not open source and routines from MOCAGE cannot be freely distributed. Therefore, we cannot provide the code openly to the GMD website.

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**Table 1.** Summary of the heterogeneous formation processes of secondary inorganic aerosols precursors that have been in the model.  $k_1 = 7.5 \times 10^7 e^{-4430(\frac{1}{T} - \frac{1}{298})}$ ,  $T$  is the ambient temperature,  $P$  the pressure,  $k_2 = 2.4 \times 10^4$ ,  $k_3 = 3.7 \times 10^5 e^{-5530(\frac{1}{T} - \frac{1}{298})}$  and  $k_4 = 1.5 \times 10^9 e^{-5280(\frac{1}{T} - \frac{1}{298})}$ .  $D_g$  ( $\text{cm}^2\text{s}^{-1}$ ) is the gas phase diffusion coefficient,  $r$  the aerosol radius,  $v$  the mean molecular speed ( $\text{cm s}^{-1}$ ), and  $\gamma$  the reaction probability being 0.1.

Compound	Formation reaction	Reaction rate
$\text{H}_2\text{SO}_4$	Aqueous phase oxydation	$\text{H}_2\text{O}_2 : \frac{dS}{dt} = \frac{k_1 [\text{H}^+] [\text{H}_2\text{O}_2] [\text{HSO}_3^-]}{1 + P [\text{H}^+]}$ $\text{O}_3 : \frac{dS}{dt} = (k_2 [\text{SO}_{2aq}] + k_3 [\text{HSO}^-] + k_4 [\text{SO}_3^{2-}]) [\text{O}_3]$
$\text{HNO}_3$	$\text{N}_2\text{O}_5$ hydrolysis	$\left( \frac{r}{G_g} + \frac{4}{v\gamma} \right)^{-1} A$
$\text{NH}_3$	Only emitted	–

**Table 2.** List of the liquid aerosol species given by ISORROPIA model.

Liquid aerosol species
H <sup>+</sup>
NA <sup>+</sup>
NH <sub>4</sub> <sup>+</sup>
Cl <sup>-</sup>
SO <sub>4</sub> <sup>2-</sup>
HSO <sub>4</sub> <sup>-</sup>
NO <sub>3</sub>
H <sub>2</sub> O
NH <sub>3</sub>
HCl
HNO <sub>3</sub>
OH <sup>-</sup>

**Table 3.** List of the solid aerosol species given by ISORROPIA model.

Solid aerosol species
$\text{NaNO}_3$
$\text{NH}_4\text{NO}_3$
$\text{NaCl}$
$\text{Na}_2\text{SO}_4$
$\text{NaHSO}_4$
$(\text{NH}_4)_2\text{SO}_4$
$\text{NAHSO}_4$
$\text{NH}_4\text{HSO}_4$
$(\text{NH}_4)_4\text{H}(\text{SO}_4)_2$

**Table 4.** List of the gaseous compounds given by ISORROPIA model.

Gaseous compounds
HCl
HNO <sub>3</sub>
NH <sub>3</sub>

**Table 5.** Mass mean aerodynamic diameter of the distribution modes from Zhuang et al. (1999).

mode in $\mu\text{m}$	Sulfates	Ammoniums	Nitrates
Condensation mode	$0.2 \pm 0.15$	$0.21 \pm 0.10$	$0.14 \pm 0.22$
Droplet mode	$0.58 \pm 0.11$	$0.56 \pm 0.10$	$0.46 \pm 0.33$
Coarse mode	$4.2 \pm 2$	$5.7 \pm 2$	$3.95 \pm 0.69$

**Table 6.** Secondary inorganic aerosol compound statistics of RACMSIA simulation daily HTAP observations.

Compound	number of stations	number of observations	MNMB	FGE	Correlation
Sulfate total	94	30 754	0.05	0.94	0.33
Sulfate corrected	21	7098	-0.12	0.73	0.70
Nitrate	61	19 410	-0.13	0.94	0.53
Ammonium	51	15 765	0.19	0.74	0.69

**Table 7.** Statistics of daily observation at the same Irish as in Fig. 7 against RACMSIA simulation. The parameter sulfate corresponds to corrected sulfate.

Compound	MNMB	FGE	Correlation
Sulfate	-0.19	0.53	0.65
Nitrate	0.17	0.54	0.77
Ammonium	0.02	0.46	0.71



**Table 8.** Statistics of daily observation at the canadian station (CA0008R) located east of Lake Superios against RACMSIA simulation. The parameter sulfate corresponds to total sulfate and the modelled field takes into account a part of sulfate in sea salt.

Compound	MNMB	FGE	Correlation
Sulfate	-0.41	0.85	0.50
Nitrate	-0.60	1.24	0.16
Ammonium	-0.29	0.86	0.56

**Table 9.** Gaseous compounds statistics of simulation results against daily HTAP observations. Comparison between a simulation with SIA (RACMSIA) and without SIA formation (RACM).

Compound	number of stations	number of observations	MNMB		FGE		Correlation	
			RACM	RACMSIA	RACM	RACMSIA	RACM	RACMSIA
Sulfur dioxide	69	23325	1.21	1.21	1.37	1.37	0.53	0.53
Nitrogen dioxide	41	14122	0.61	0.53	0.83	0.77	0.55	0.57
Nitric acid	30	10033	0.45	-0.13	0.88	0.99	0.46	0.33
Ammonia	20	6381	1.84	0.79	1.84	1.27	0.18	0.33

**Table 10.** Secondary inorganic aerosol compounds statistics of RACMSIA simulation against weekly HTAP observations.

Compound	number of stations	number of observations	MNMB	FGE	Correlation
Sulfate total	192	19 203	-0.05	0.67	0.64
Sulfate corrected	1	52	-0.12	0.63	0.51
Nitrate	190	19 066	0.06	1.00	0.41
Ammonium	43	1595	0.34	0.84	0.43

**Table 11.** Secondary inorganic aerosol compounds statistics of RACMSIA simulation against weekly HTAP observations, separation between North America (N. A.) and Asia.

Compound	Stations		MNMB		FGE		Correlation	
	N. A.	Asia	N. A.	Asia	N. A.	Asia	N. A.	Asia
Sulfate total	161	28	-0.03	-0.05	0.67	0.68	0.65	0.64
Nitrate	161	28	0.05	0.30	0.99	1.16	0.41	0.13
Ammonium	14	28	0.27	0.35	0.60	0.96	0.19	0.41

**Table 12.** Secondary inorganic aerosols statistics of RACMSIA simulation against daily EMEP observations.

Compound	number of stations	number of observations	MNMB	FGE	Correlation
Sulfate total	66	19 861	-0.16	0.67	0.57
Sulfate corrected	34	9705	-0.33	0.73	0.68
Nitrate	49	13 360	-0.08	0.87	0.53
Ammonium	40	10 406	0.18	0.69	0.71

**Table 13.** Gaseous compounds statistics of simulation results against daily EMEP observations. Comparison between a simulation with SIA (RACMSIA) and without SIA formation (RACM).

Compound	number of stations	number of observations	MNMB		FGE		Correlation	
			RACM	RACMSIA	RACM	RACMSIA	RACM	RACMSIA
Sulfur dioxide	47	14 861	0.97	0.98	1.15	1.15	0.60	0.60
Nitrogen dioxide	44	14 809	0.18	0.10	0.74	0.69	0.57	0.59
Nitric acid	12	3290	0.55	-0.15	0.99	1.08	0.36	0.26
Ammonia	40	5324	1.61	0.46	1.62	1.18	-0.01	0.24

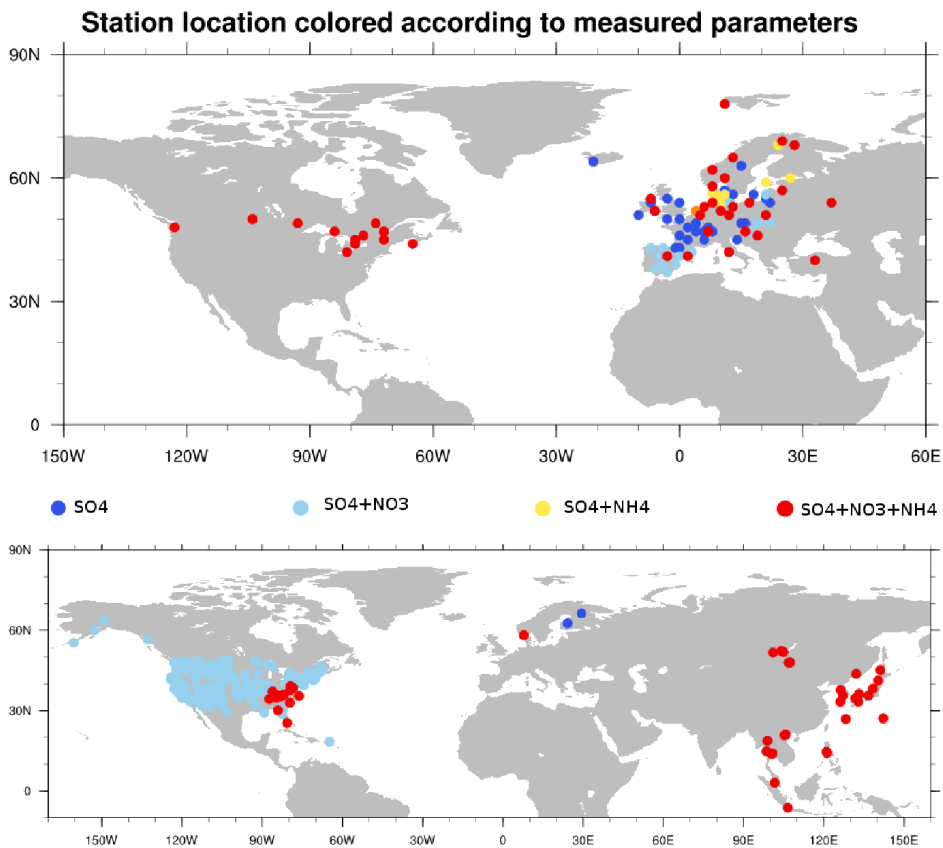
**Table 14.** Air quality regulated pollutants statistics of simulations against hourly AIRBASE observations. Comparison between a simulation with SIA (RACMSIA) and without SIA formation (RACM).

Compound	number of Stations	MNMB		FGE		Correlation	
		RACM	RACMSIA	RACM	RACMSIA	RACM	RACMSIA
PM <sub>2.5</sub>	1082	-0.58	-0.14	0.77	0.56	0.47	0.58
PM <sub>10</sub>	1082	-0.89	-0.45	0.97	0.66	0.39	0.50
O <sub>3</sub>	1168	0.31	0.27	0.42	0.41	0.63	0.60
NO <sub>2</sub>	610	-0.10	-0.13	0.66	0.65	0.54	0.53

**Table 15.** Comparison of MNMB statistics between MOCAGE simulations (RACM and RACMSIA) and AIRBASE data over Europe for  $\text{PM}_{2.5}$  according to different seasons.

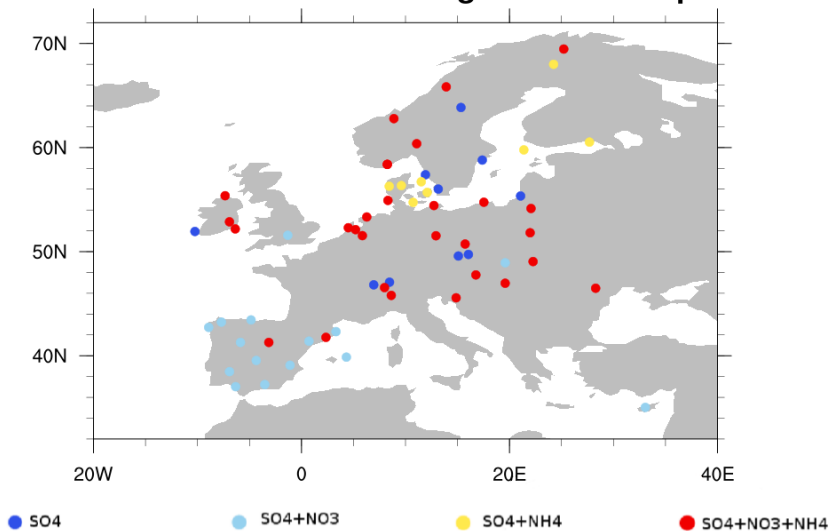
$\text{PM}_{2.5}$ MNMB	RACM	RACMSIA	$\Delta$
Year	-0.58	-0.14	+0.44
MAM	-0.55	-0.03	+0.52
JJA	-0.62	-0.27	+0.35
SON	-0.44	-0.07	+0.37



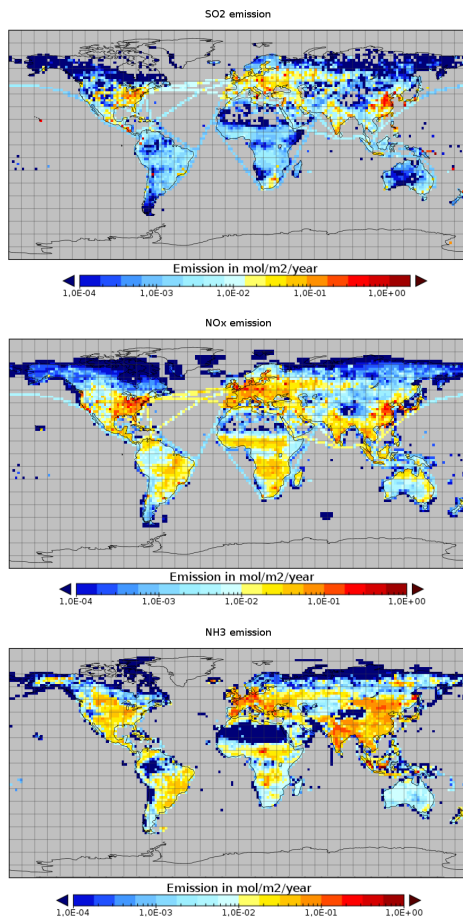


**Figure 1.** Maps with the location of the stations measuring in 2005 used to evaluate the model. Colors represent the measured parameters at the station. The upper panel represents daily observation stations while the bottom panel represents weekly observation stations.

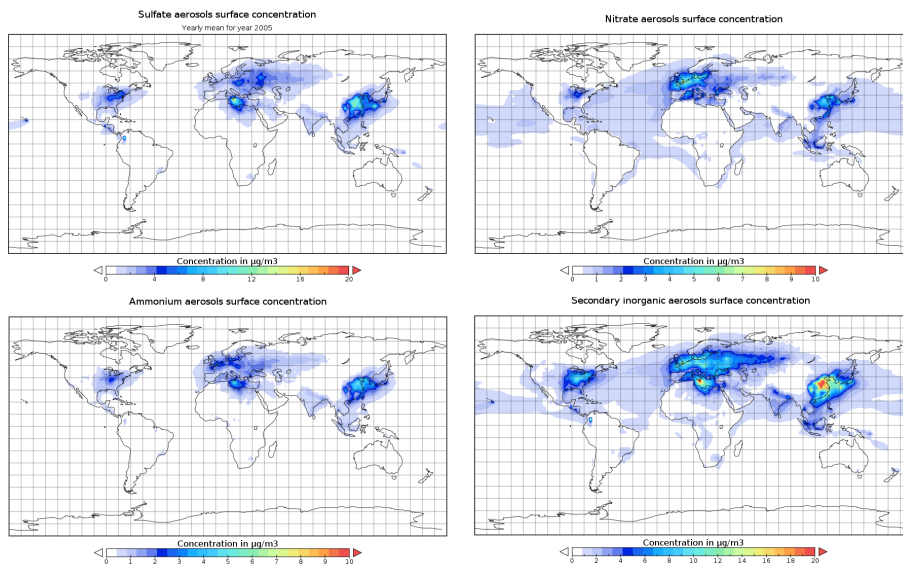
## Station location colored according to measured parameters



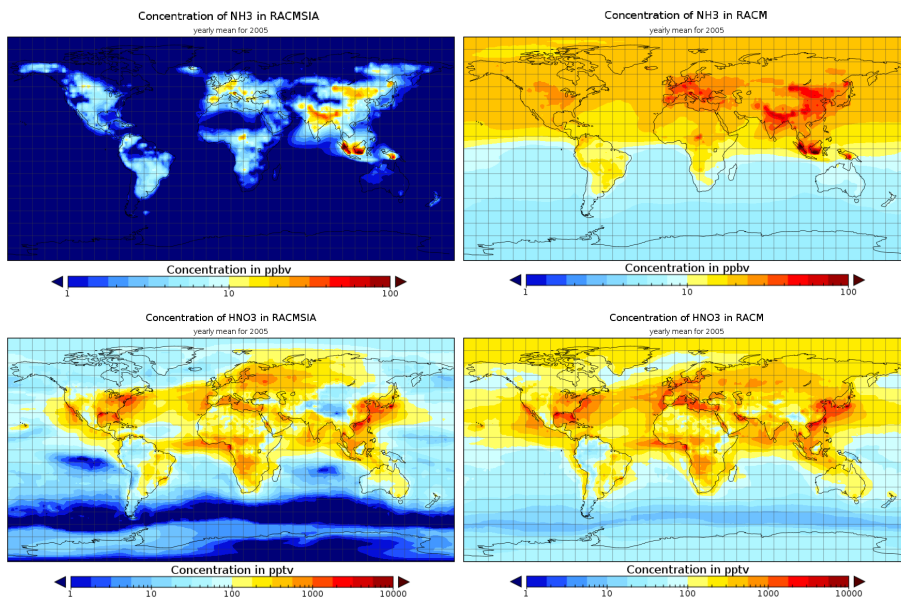
**Figure 2.** Map with the location of the stations measuring SIA composition on a daily basis, from the EMEP database used to evaluate the regional model results. Colors represent the measured parameters at the station. The domain plotted corresponds to the limit of the regional domain of the simulation. Colors represent the altitude of the stations.



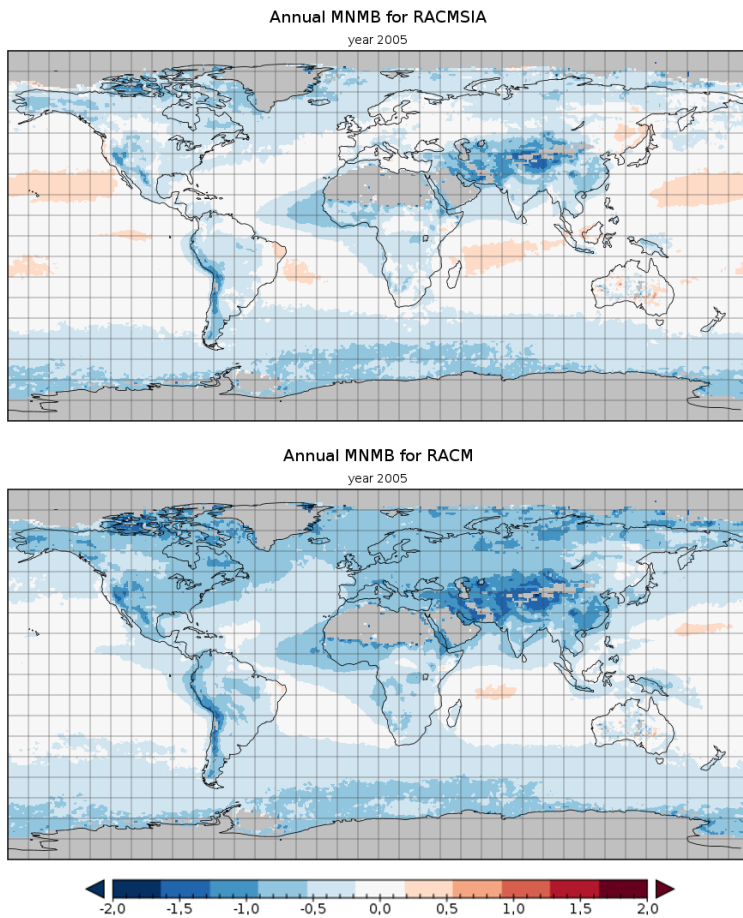
**Figure 3.** Maps of 2005 annual emissions of sulfur dioxide ( $\text{SO}_2$ ) (top panel), nitrous oxides ( $\text{NO}_x$ ) (middle panel) and ammonia ( $\text{NH}_3$ ) (bottom panel), in  $\text{mol m}^{-2} \text{year}^{-1}$  for the MOCAGE simulations (RACM and RACMSIA).



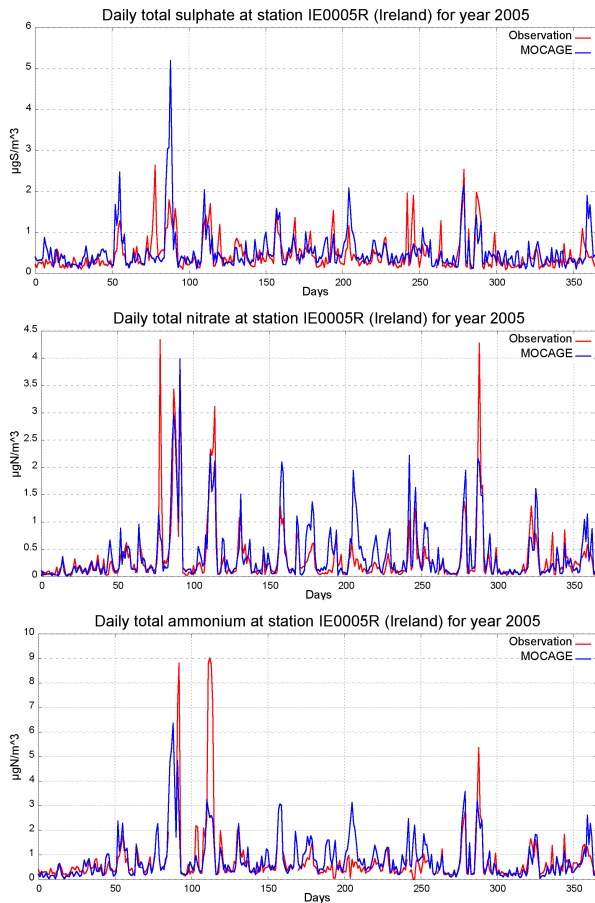
**Figure 4.** Maps of global annual mean concentrations at the surface, in  $\mu\text{g m}^{-3}$  of secondary inorganic aerosols components from the RACMSIA simulation. Top left panel is sulfate, top right panel nitrate, bottom left panel ammonium and bottom right panel is the sum of the three components.



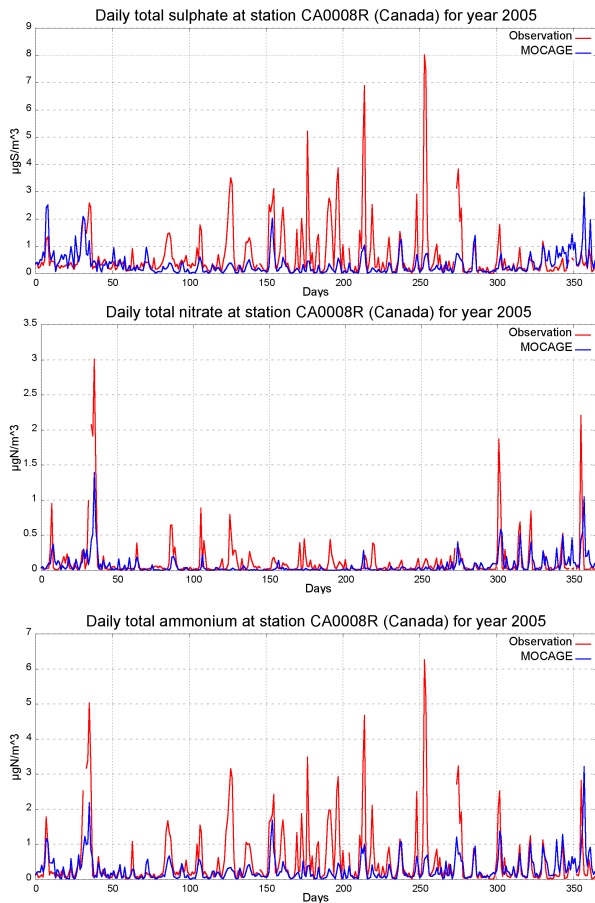
**Figure 5.** Maps of global annual mean concentrations of  $\text{NH}_3$  in ppbv (top panels) and  $\text{HNO}_3$  in pptv (bottom panels) for both simulations RACMSIA (left side) and RACM (right side).



**Figure 6.** Maps of annual modified normalised mean bias (MNMB) of aerosol optical depth against MODIS observations. The upper panel shows the RACM experiment while the lower panel the RACM-SIA experiment with secondary inorganic aerosols.

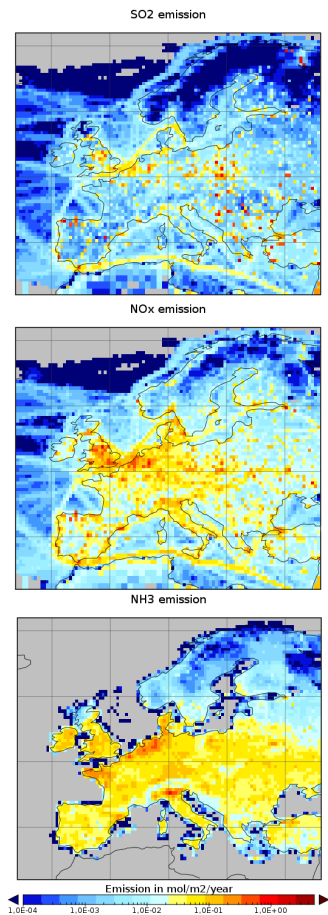


**Figure 7.** Time-series of daily values (in  $\mu\text{g m}^{-3}$ ) of sulfate (top panel), nitrate (middle panel) and ammonium (bottom panel) at an Irish station ( $52.87^\circ\text{ N}$ ;  $6.92^\circ\text{ W}$ ) against RACMSIA simulation for the year 2005.

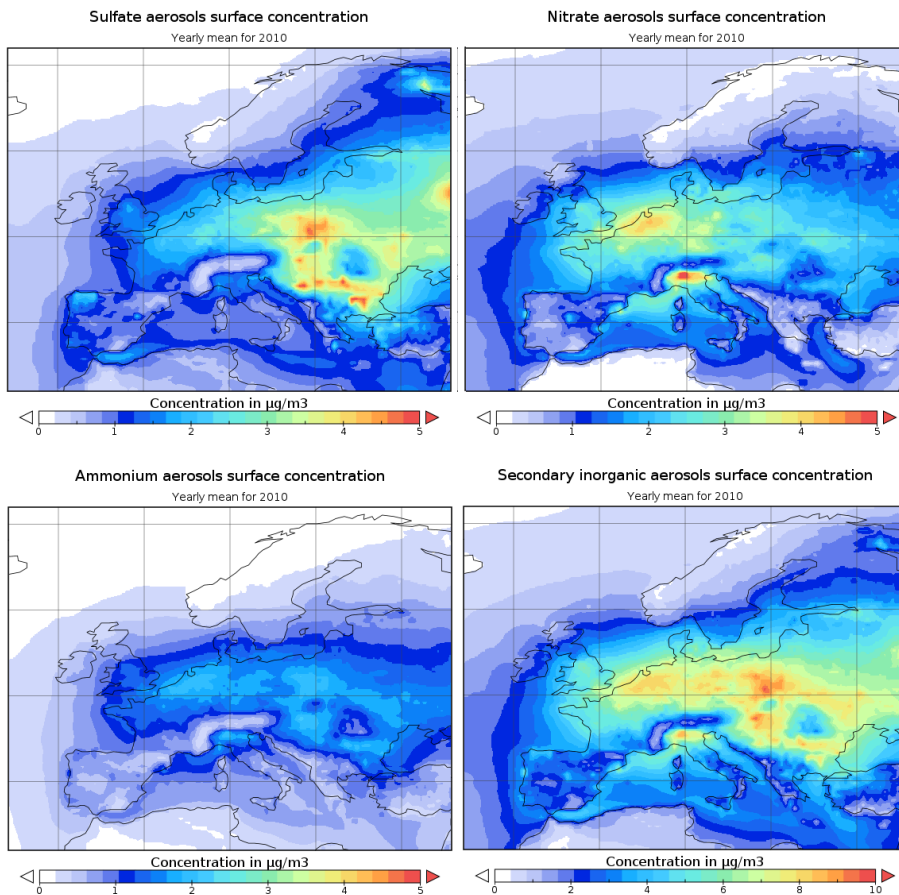


**Figure 8.** Time-series of daily values (in  $\mu\text{g m}^{-3}$ ) of sulfate (top panel), nitrate (middle panel) and ammonium (bottom panel) at a Canadian station ( $47.03^\circ\text{ N}$ ;  $-84.38^\circ\text{ W}$ ) against RACMSIA simulation for the year 2005.

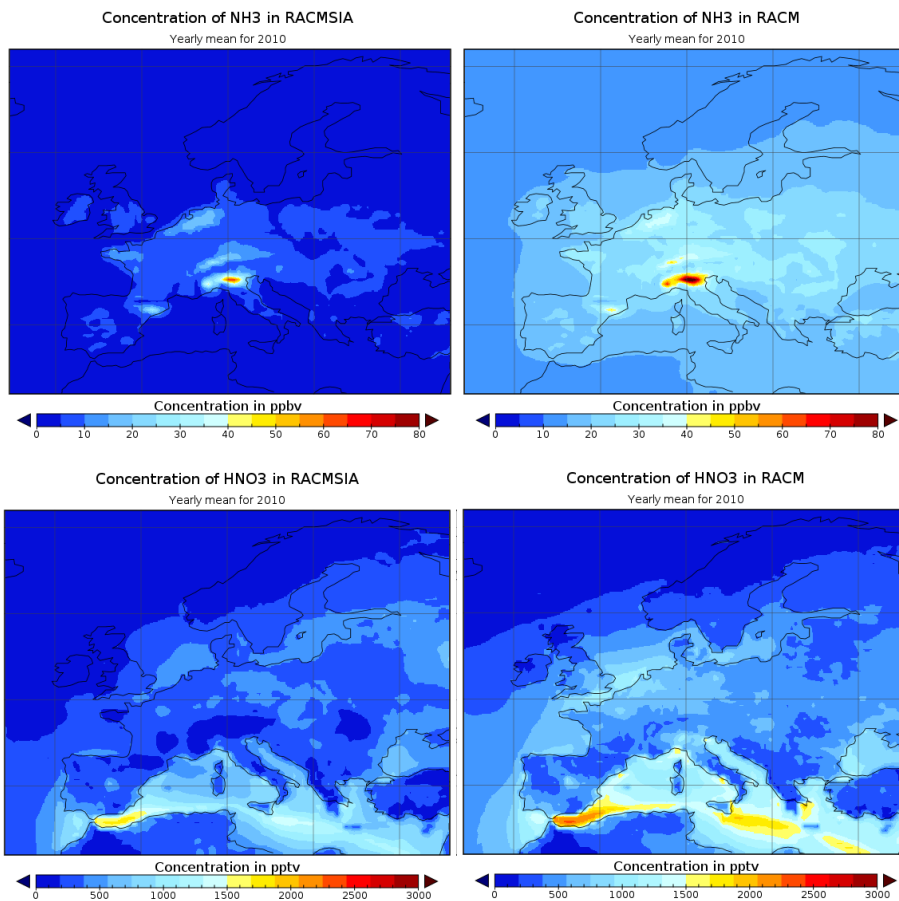




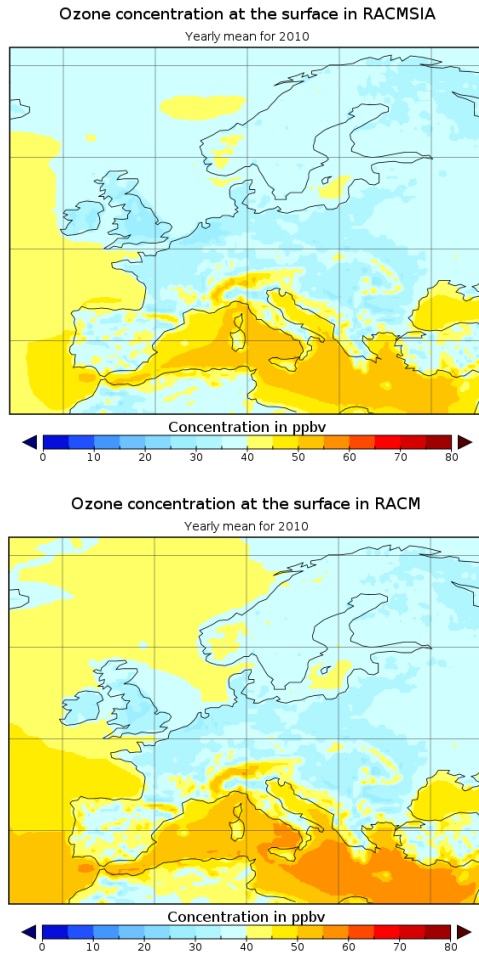
**Figure 9.** Maps of annual emissions for sulfur dioxide (top panel), nitrous oxides (middle panel) and ammonia (bottom panel) in  $\text{mol m}^{-2} \text{year}^{-1}$  for the MOCAGE simulations (RACM and RACMSIA).



**Figure 10.** Maps of regional annual mean concentrations, in  $\mu\text{g m}^{-3}$  of secondary inorganic aerosols components over a regional domain for the year 2010 for the RACMSIA simulation. Top left panel represents sulfate concentration, top right nitrate, bottom left ammonium and bottom right represents the sum of these three SIA components.



**Figure 11.** Maps of regional annual mean concentrations of  $\text{NH}_3$  in ppbv (top panels) and  $\text{HNO}_3$  in pptv (bottom panels) for both simulations RACMSIA (left side) and RACM (right side).



**Figure 12.** Maps of regional annual mean ozone concentrations for the year 2010 in ppbv. Top panel represents RACMSIA simulation and bottom panel the RACM simulation.