

Reviewer 1

We thank Reviewer 1 for valuable comments.

1. Kinetic database (in section 3.1.1):
  - a.) The comprehensive kinetic database is given in the supplementary section. It is interesting to note that the authors use the detailed isoprene chemistry from the latest version of the Master Chemical Mechanism (<http://mcm.leeds.ac.uk/MCM>). However, they seem to have not used or even referenced the comprehensive semi-explicit DMS chemistry also available in MCMv3.2. It would have also been a useful test of the MCM if its DMS chemistry were evaluated in the model against the chamber data.
  - b.) It is also strange that although the authors do briefly acknowledge the 2006 Chemical Review on dimethyl sulfide and dimethyl sulfoxide chemistry by Barnes et al., (106, 940-975), they do not reference it further and seem to not make that much use of the detail information available in this comprehensive review.

**Response:**

- a) There is no mechanism present in the MCM v3.2 to produce MSA and DMSO<sub>2</sub> *via* DMSO oxidation. Thus we have constructed the explicit kinetic model for DMS oxidation mechanisms. For the gas phase reactions, the mechanisms proposed by Yin et al. (1990), which is relatively complete, were employed.
  - b) The review paper by Barnes et al. (2006) is very important to our study since this paper provides many of the updated rate constants and a variety of references, which are documented in the supplementary material of our manuscript. We have cited the paper by Barnes et al. (2006) in several places of the revised manuscript. For example, in the introduction section,  
“In this study, a new DMS kinetic model was developed by including not only the most recently reported reactions and their rate constants (Barnes et al., 2006; Sander et al., 2006), but also the heterogeneous reactions of DMS gaseous products in aerosol phase.”  
“Although halogen compounds are known to react fast with DMS (Barnes et al., 2006), in the coastal watersheds with human activities, OH radical reactions with DMS and its products will be dominant, so in this study, reactions between halogen compounds and DMS are not included.”
2. Description of heterogeneous chemistry (section 3.1.2):
    - a) More detail is required on the partitioning methodology applied. How did you exactly calculate/estimate  $K_p$  (Pankow, Kamens etc.)?.

- b) What are the values of  $k_{ad}$  and  $k_{des}$  you calculate? The chemical nomenclature in this section is also very confusing; Kinetic equations need to be written in a mathematical form. In what context are you using “@”?

**Response:**

- a) The detail descriptions for heterogeneous chemistry of DMSO, DMSO<sub>2</sub>, and MSIA have been added into the revised manuscript in the section of "Formation of MSA and H<sub>2</sub>SO<sub>4</sub> through heterogeneous reactions of gaseous DMS oxidation products".

“ $K_p$  is treated using a traditional absorptive partitioning theory (Pankow et al., 1994) as follows,

$${}^iK_p = 7.501RT / (10^9 MW^i \gamma^i p_L) \quad (3)$$

where  $MW$  is the average molecular weight of the aerosol medium (e.g., 45 g mol<sup>-1</sup> at relative humidity = 30%),  $p_L$  is the vapor pressure of compound  $i$ , and  $\gamma^i$  is the activity coefficient of  $i$  at a given medium. The  $\gamma^i$  values for the compounds (e.g., DMSO, DMSO<sub>2</sub> and MSIA) of interest in this study are unknown. For DMSO, the  ${}^iK_p$  value is estimated from the relationship between  $K_p$  and its known Henry's law constant ( $H$ ).

$$\frac{K_p}{H} = \frac{7.501 \times RTV}{10^9 MW} \quad (4)$$

where  $V$  is molar volume of the medium. The calculated  ${}^iK_p$  value of DMSO is  $1.3 \times 10^{-5}$  μg m<sup>-3</sup> and the estimated  $\gamma^i$  is 0.023 at T= 298 K. Then the  $\gamma^i$  for DMSO was applied to the estimation of  ${}^iK_p$  values of DMSO<sub>2</sub> and MSIA using eq 3 although the  $\gamma^i$  value of DMSO might be somewhat different from those of DMSO<sub>2</sub> and MSIA.

The detailed description of the determination of  ${}^i k_{abs}$  and  ${}^i k_{des}$  are shown in the supplementary materials. In brief, based on the analysis of the characterization times ( $\tau$ ), the equilibrium process ( $\tau \sim 10^1$ ) governed by the absorption and the desorption processes of the compound between the gas and the particle is much faster than the reaction in the gas phase ( $\tau \sim 10^5$  s). Hence, the determination of the absolute values of  ${}^i k_{abs}$  and  ${}^i k_{des}$  becomes less important as long as the  $\tau$  values of both absorption and desorption are much shorter (within computer process time) than  $\tau$  of gas-phase reaction. In this study, the  $\tau$  value of the absorption process is set to  $< \sim 10^{-4}$  s and applied to the estimation of both  ${}^i k_{abs}$  and  ${}^i k_{des}$ . The  $\tau$  of the desorption process of all three compounds are in the order of  $\sim 10^{-8}$  s.”

- b) The description of the determination of  ${}^i k_{abs}$ ,  ${}^i k_{des}$  and  ${}^i k_r$  has been added in the supplementary material in details.

“In order to find the rate determining step including partitioning processes and chemical reactions in gas phase, the characterization time of each step was analyzed. The characterization time ( $\tau$ ) to establish equilibrium ( $\tau_{eq}$ ) and  $\tau$  of the gas phase reaction ( $\tau_{gas}$ ) of a compound with OH radicals are calculated using the equations below,

$$\tau_{eq} = D_l (4HRT / \alpha u_{av})^2 \quad \text{eq. S1}$$

where  $T$  is temperature,  $H$  is Henry's constant,  $\alpha$  is accommodation coefficient, and  $u_{av}$  is mean thermal speed.

$$\tau_{gas} = 1 / (k[\text{OH}]) \quad \text{eq. S2}$$

where  $k$  is the reaction rate constant in the gas phase and  $[\text{OH}]$  is the concentration of OH radicals.

For example,  $\tau_{eq}$  of DMSO at the gas-liquid interface is in the order of  $\sim 10^1$  s and much shorter than  $\tau_{gas}$  of the gas phase reaction of DMSO, which is in the order of  $\sim 10^5$  s. Based on the short  $\tau_{eq}$ , the equilibrium process governed by both the absorption of a compound onto a particle and its desorption from the particle should also be much faster than the reaction in the gas phase.

Hence the determination of the absolute values of  ${}^i k_{abs}$  (absorption rate constant of a compound onto the particle) and  ${}^i k_{des}$  (desorption rate constant of a compound from the particle) becomes less important as long as, within computer process time, the characteristic times of both absorption and desorption are much shorter than that of gas-phase reaction. In addition, the  ${}^i k_{abs}$  and  ${}^i k_{des}$  values are constrained by  ${}^i k_{abs} / {}^i k_{des} = {}^i K_p$ . In this study, the characteristic time for the absorption process is set to  $< \sim 10^{-4}$  s and applied to the estimation of both the adsorption and the desorption rate constants of the compound of interest. The characteristic times of desorption of the three compounds of interest are in the order of  $\sim 10^{-8}$  s.  ${}^i k_r$  is empirically determined using experimental data (the formation of MSA and sulfuric acid).

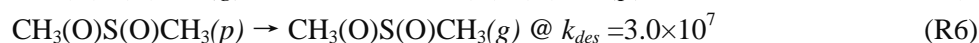
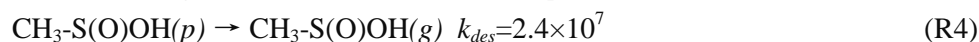
In order to confirm the nature (surface reaction vs. bulk phase reaction) of the reaction of DMSO, DMSO<sub>2</sub>, and MSIA, the diffuso-reactive parameter,  $q$  is characterized using the following equation:

$$q = a \sqrt{\frac{k_r}{D_l}} \quad \text{eq. S3}$$

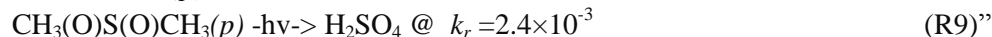
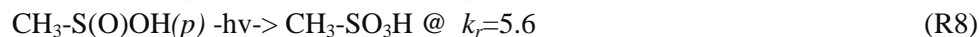
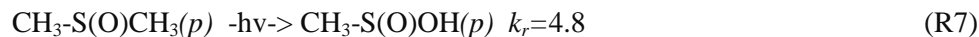
where  $a$  is the particle radius (here assuming 50 nm),  $k_r$  is the aqueous phase reaction rate constant and  $D_l$  is diffusion coefficient. In general,

high  $q$  value indicates that the reaction occurs on the surface. For all three compounds,  $q$  is smaller than 0.003 suggesting that their reactions are slow compared to diffusion so that reactions take place throughout the entire volume of the aerosol. The characterization of  $q$  value also implies that the gas-particle partitioning can be approached by the absorptive mode.”

According to the reviewer’s suggestion, we have rewritten the kinetic equations in the revised manuscript.



The reactions of heterogeneous oxidation of DMSO, MSIA and DMSO<sub>2</sub> in aerosol bulk phase are described as follows.



3. DMS photooxidation with coexisting isoprene (section 3.3.2): a). This title doesn’t really make sense to me, I would re-word it: DMS photooxidation in the presence of isoprene. b) It is unclear to me what the motivation is of using isoprene as the co-reactant VOC, apart from the fact someone else has seen isoprene can effect DMS oxidation indoors. Would be good to discuss why isoprene in context in the introduction.

**Response:**

- a) We have changed the title of section 3.3.2 to “DMS photooxidation in the presence of isoprene” as requested by the reviewer.
- b) The reason of using isoprene as a co-reactant VOC has been given in the end of the introduction section.

“Isoprene has been chosen as a representative of the biogenic VOC here mainly because it has a large emission (440~660 TgC yr<sup>-1</sup>) (Guenther et al., 2006) and it is also known to be an important VOC from the ocean (Palmer et al. 2005). In addition to the high flux of isoprene, the secondary organic aerosol (SOA) yields from isoprene are sensitive to the aerosol acidity from sulfuric acid (Czochke et al. 2003; Edney et al. 2005) as well as from the DMS photooxidation products (Chen et al., 2012). It

is therefore interesting to study the impact of isoprene on the formation of DMS photooxidation products.

Field studies show that the mean isoprene concentration in the remote oceans and coastal watersheds can be as high as 300 ppt, varying with time of day, season and location (Shaw et al., 2010), and the coastal concentration of DMS is usually 50~200 ppt (Ramanathan et al., 2001). In our study the mixing ratio of isoprene to DMS was controlled between 2 and 8 to mimic the ambient air in coastal watersheds. The NO<sub>x</sub> concentration we use is in the range of 15~200 ppb, representing areas of different levels of anthropogenic air pollution. Although halogen compounds are known to react fast with DMS (Barnes et al., 2006), in the coastal watersheds with human activities, OH radical reactions with DMS and its products will be dominant. In this study, we mainly focus on the OH radical reaction with DMS.”

4. In section 3.3.2 the authors mainly focus on the fact that model under predicts MSA under high isoprene conditions, there is little discussion on the fact that the model molar yields of H<sub>2</sub>SO<sub>4</sub> are consistently under predicted by a factor of 2 for all concentrations of isoprene. A plausible explanation for this under prediction could be that during the photooxidation process, a significant amount of ozone is produced, which can react with isoprene and its unsaturated products, such as MVK and methacrolein. The ozonolysis reaction forms excited Criegee Intermediates (CI) which can be stabilized (SCI) and react in a bimolecular manner with species such as H<sub>2</sub>O and SO<sub>2</sub>. These reactions are described in the MCMv3.2 isoprene chemistry, with the reaction with H<sub>2</sub>O being dominant. However, Welz et al., (Science 335, 204 (2012)) have recently been able for the first time to measure the (upper limit) rate constants for the reaction of the CH<sub>2</sub>OO SCI with a number of important atmospheric species, concluding that reaction with NO<sub>2</sub> and SO<sub>2</sub> is fast (very fast in the latter case) leading to the formation of SO<sub>3</sub> (i.e. H<sub>2</sub>SO<sub>4</sub>). It would be interesting to see the effect of the new rate data from Welz et al., (assuming the CH<sub>2</sub>OO + SO<sub>2</sub> rate constant can be generalized to other SCIs) has in the isoprene/DMS model.

**Response:**

We include the update of the reaction rate constants in section 3.1.3

“Welz et al. (2012) have recently measured the upper limit of the rate constants for the reaction of the stabilized Criegee radical (.CH<sub>2</sub>OO.) with a number of important atmospheric species. They concluding that the reaction of .CH<sub>2</sub>OO. with NO<sub>2</sub> ( $7.0 \times 10^{-12} \text{ cm}^3 \text{ molecules}^{-1} \text{ s}^{-1}$ ) and SO<sub>2</sub> ( $3.9 \times 10^{-11} \text{ cm}^3 \text{ molecules}^{-1} \text{ s}^{-1}$ ) is much faster than the previous estimation.

These new reaction rate constants were applied to the reaction of Criegee radicals with  $\text{SO}_2$  in the MCM v3.2.”

We have updated the rate constants between Criegee radicals and  $\text{SO}_2$  applied to the MCM v3.2 mechanism. However, the model prediction with new reactions doesn't show significant changes in  $\text{H}_2\text{SO}_4$  concentrations simulated for exp iso-DMS-1, iso-DMS-2 and iso-DMS-3.

Even when the concentration of isoprene and DMS are reduced to the ambient level (~0.5 ppb), no significant change in the prediction of  $\text{H}_2\text{SO}_4$  appears due to the addition of SCI reactions.

5. P14671, line 16: The authors refer to the “updated mechanism” updated from what? Please give reference to previous work

**Response:**

We have made it clear in the introduction.

“Tables S1~S3 of the supplementary material summarize the reaction mechanisms and their rate constants of the DMS oxidation used in this study. Tables S1~S3 have been constructed mainly based on the study by Yin et al. (1990b). In this study, some of the reaction rate constants have been updated using recently reported values. The new reaction mechanisms (e.g., the DMS reaction with DMS origin radical species) have also been included in this study.”

6. P14672, line 25: MCM need proper referencing throughout the manuscript (see website: <http://mcm.leeds.ac.uk/MCM/citation>. <http://mcm.leeds.ac.uk/MCM/citation> website and most recent protocol (Saunders et al., Atmos. Chem. Phys., 3, 161-180, 2003).

**Response:**

We have cited the paper as requested by the reviewer.

7. P14673, Experimental procedures: what was the reasoning for the RH levels. a) How was water injected into the chamber and RH maintained throughout the experiment? b) How is chamber dilution accounted for?

**Response:**

- a) The amount of water vapor, which is related to humidity, is important in the photooxidation of both DMS and isoprene because it influences the production of OH radicals. The experimental procedure to control chamber humidity has been added to experimental section of the revised manuscript. Now this reads,

“The chamber humidity was controlled by introducing humidified air streams into the chamber until the relative humidity (RH) in the chamber

reached the desired value. The RH was measured at the beginning of experiment and corrected for temperature change ( $< 5\text{K}$ ) over the course of the experiment.”

The humidity change is small during the course of chamber experiments. For example, the humidity change is less than 5% for low humidity (25%~30%).

b) The way chamber dilution is accounted for is described in the experimental section. It now reads.

“ $\text{CCl}_4$  was injected into the chamber for chamber dilution.”

The factor which counts the chamber dilution using  $\text{CCl}_4$  data was included in the reaction mechanisms. Thus, the model simulation includes the chamber dilution of chemical species in the gas phase.

8. Do you take into account chamber wall reactions (apart from wall losses)? It is well known that irradiated Teflon chambers suffer from:

(1) The introduction of free radicals from heterogeneous wall reactions

(2) (Light dependent) adsorption/desorption of  $\text{NO}_y$  species (including HONO) to/from the chamber walls

(3) The off-gassing of various reactive species from the chamber walls, which can contribute significantly to the radical budget of the system and subsequent ozone formation See Rickard et al., (Atmospheric Environment 44 (2010) 5423-5433 2010) and references therein.

**Response:**

We have included the wall chemistry for  $\text{HNO}_3$ ,  $\text{N}_2\text{O}_5$ , and  $\text{NO}_x$ . We believe that a variety of radicals (e.g.,  $\text{RO}_2$ ,  $\text{RO}$ ,  $\text{OH}$ ) can react on the surface of the chamber wall but under the current knowledge we are limited to describing those radical reactions. In general, radicals are very reactive and have a very short life time. Thus, for radicals, the gas phase reaction is much important than the reactions on the chamber wall.

The responses to these questions has been included in section 3.2.1 (chamber characterization)

“Details of the auxiliary mechanism that includes the wall chemistry of  $\text{NO}_y$  species were described by Jeffries et al. (2000).”

Here is the summary of the  $\text{NO}_y$  reactions in the auxiliary mechanism.

N2O5	---->	2.0*WHNO3	k=4.2E-5
N2O5 + WHNO3	---->	2.0*NO + NO2	k=5E-20
HNO3	---->	WHNO3	k=8.2E-5
HNO3 + WH2O	---->	WHNO3	k=2.5E-21
WHNO3	-hv->	NO2	k=8.0E-4
*j[NO2_to_O3P]			
NO + NO2 + WHNO3	---->	2.0*HONO + 1.0*NO2	k=5.0E-30;
NO + WHNO3	---->	1.5*HONO + 0.5*NO2	k=6.09E-17
NO2 + WHNO3	---->	1.5*HONO + 0.5*NO2	k=3.38E-18
NO2	-hv->	HONO	k=1E-3
*j[NO2_to_O3P];			

9. P14673, line 6: “evaluate”, not “validate”.

**Response:**

Done.

10. P14675, line 16: “existing explicit model for DMS” what model? Reference?

**Response:**

We have added a reference in the original sentence. This reads now:

“For the prediction of DMS oxidation products in aerosol, most explicit models expressing DMS photooxidation (e.g., Yin et al. 1990a) in the gas phase lack the description of heterogeneous chemistry of DMS oxidation products.”

11. P14675, line 21: “semi-volatile” gaseous DMS products

**Response:**

Done.

12. P14677, line 11: What does “PAR-NIR and UV-PAR, Apogee” mean?

**Response:**

PAR-NIR: photosynthetically active radiation-near infrared. UV-PAR: ultraviolet- photosynthetically active radiation. They are the names from the manual. We have changed the name to “PS-300, Apogee”.

13. P14679, line 1: Again, reference “existing” models.

**Response:** done.

14. P14680, line 24: a) the H<sub>2</sub>SO<sub>4</sub> model and measurement profiles are difficult to see. b) Whilst NO is well simulated, NO<sub>2</sub> is certainly not in the latter stages of all experiments, c) glyoxal also not that well simulated (why?)

**Response:**



- a) Figure 4 has been changed to make it easy to read.
- b) The  $\text{NO}_x$  meter monitors oxygenated nitrogen other than NO.  $\text{NO}_2$  is estimated by subtracting NO from  $\text{NO}_x$ . In general, the measured  $\text{NO}_2$  actually contains other oxygenated nitrogen species such as organic nitrates and PAN types compounds. Thus, simulated  $\text{NO}_2$  is often lower than the measured  $\text{NO}_2$  ( $\text{NO}_x - \text{NO}$ ).
- c) Glyoxal is produced by multi-generation reactions. The model can predict better for the 1<sup>st</sup> generation compound (e.g., MACR and MVK) than for multi-generation products such as glyoxal.

15. P14681, line 18: How important are  $\text{O}(^3\text{P})$  reactions with organics in the “real” atmosphere?

**Response:**

The importance of  $\text{O}(^3\text{P})$  reaction has tested for two different levels of DMS concentrations: high concentration used in chamber experiments of this study and the low concentrations relevant to the ambient air. For the high concentration experiments the presence of the  $\text{O}(^3\text{P})$  reaction with DMS significantly affect the simulation result of DMS decay (compared to the absence of  $\text{O}(^3\text{P})$  reaction) while for the low concentration simulations, the  $\text{O}(^3\text{P})$  reaction with DMS was insignificant for the DMS decay. Hence, the  $\text{O}(^3\text{P})$  reaction with DMS is important only for the high concentration experiments.

16. P14683, line 3: MSA production appears to increase “in the presence of isoprene”.

**Response:**

Done.

17. P14683, line 12: This sentence does not make any sense!

**Response:**

We have rewrote the sentence to make it clear in the conclusion section

“In the presence of isoprene, the inorganic constituents in DMS aerosol are internally mixed with isoprene SOA and differently influence heterogeneous reactions due to changes in the chemical and physical properties of DMS aerosol. Furthermore, the coexisting SOA can also affect reactions of DMS oxidation products. Meanwhile, the DMS acidic products such as MSA and sulfuric acid are able to catalyze aerosol phase reactions of isoprene oxidation products increasing SOA production (Jang et. al., 2002). To improve the DMS oxidation model, the synergetic interaction between DMS oxidation products and isoprene SOA should be discovered in the future.”

18. Table 1: Give speciated initial NO<sub>x</sub> (i.e. NO and NO<sub>2</sub>) concentrations in the table.

**Response:**

Please find the updated tables in the manuscript.

19. Table 3: a) A graphical representation of the differences between model and measured molar yields of MSA and H<sub>2</sub>SO<sub>4</sub> would be useful to the reader. b) In footer legend, “Table 3” should read “Table S3”.

**Response:**

a) Since the main goal for this table is not focused on comparing the simulated and measured yields of MSA and H<sub>2</sub>SO<sub>4</sub>, we feel that it is not necessary to include a separate figure for the yields.

b) Done.

20. Fig 1: DMSO-1 Profile A: DMSO line should read “DMSO2(E)”

**Response:**

Done.

21. Supplementary Material: a) For consistency, put the DMS chemistry tables before DMSO. In the table footers, explain how you estimated the rate constants. b) The correct mathematical way of giving an Arrhenius expression in the tables should be, e.g:  $1.13E-11*EXP(-254/TEMP)$  -- thereby a computer model or spreadsheet can directly interpret the rate expression. Note all other rate constants given are for 298K and 1atm (otherwise give the full temperature and pressure dependent rate expressions).

**Response:**

a) Since the section of the experimental results start from the description of DMSO photooxidation reaction, it is better to keep the DMSO mechanism first for consistency.

b) Proper changes have been made to the footnotes of the Tables S1~3 in the supplementary material per reviewer’s request.

The following sentence has been added to the footnote for Table S1-S3.

“All the rate constants other than those expressed using an Arrhenius equation are based on 298 K and 1 atm.”