

Chapter 55

Dimethylsulfide Chemistry: Annual, Seasonal, and Spatial Impacts on Sulfate

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Abstract We incorporated oceanic emissions and atmospheric chemistry of dimethylsulfide (DMS) into the hemispheric Community Multiscale Air Quality model and performed annual model simulations without and with DMS chemistry. The model without DMS chemistry predicts higher concentrations of sulfate (SO_4^{2-}) over land compared to the low concentrations over seawater. Including DMS chemistry substantially increases (SO_4^{2-}) concentrations over seawater and many coastal areas. It enhances the annual mean surface (SO_4^{2-}) by $>0.8 \mu\text{g}/\text{m}^3$ in some areas of the Pacific Ocean, Atlantic Ocean, Arabian Sea, and Caribbean Sea. The largest enhancement occurs in summer in which DMS chemistry increases surface SO_4^{2-} by 70% over seawater. The model without DMS chemistry underestimates the summer-time observed SO_4^{2-} in the U.S. while the model with DMS chemistry improves model performance in the U.S. coastal areas.

55.1 Introduction

Anthropogenic sources emit sulfur dioxide (SO_2) into the atmosphere which is oxidized by gas- and aqueous-phase chemical reactions to form sulfate (SO_4^{2-}). Dimethylsulfide (DMS), emitted from oceans, can undergo atmospheric reactions to

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produce SO_2 . Here, we study the annual, seasonal, and spatial impacts of DMS chemistry on SO_4^{2-} using the coupled hemispheric Community Multiscale Air Quality (CMAQ) model (Mathur et al. 2012).

55.2 Method

The model uses a horizontal resolution of 108 km and 44 vertical layers. Emissions and meteorological fields previously described by Sarwar et al. (2015) are also used here. Annual anthropogenic SO_2 emissions of ~ 54 Tg are used in the model (<http://edgar.jrc.ec.europa.eu/index.php>). Two model simulations are performed for 2006. One simulation uses the Carbon Bond chemical mechanism (CB05) without any DMS chemistry while the other simulation uses the CB05 with DMS. Differences in the results are attributed to DMS chemistry. In CMAQ without DMS chemistry, SO_4^{2-} can be formed via oxidation of SO_2 by one gas-phase reaction and five aqueous-phase reactions. DMS chemistry contains seven additional reactions (Sander 2011) (two reactions with hydroxyl radical and five reactions with nitrate, chlorine radical, chlorine monoxide, iodine monoxide, and bromine monoxide) for oxidation of DMS to SO_2 . DMS emissions are calculated using the monthly oceanic climatological DMS concentrations and the total resistance to gas-transfer at the air/sea interface (Lana et al. 2011). We calculate an annual DMS emissions total of 16.1 Tg for the Northern Hemisphere compared to the global annual DMS emissions total of ~ 28 Tg reported by Kloster et al. (2006) and Lana et al. (2011).

55.3 Results and Discussion

Predicted annual-mean SO_2 and SO_4^{2-} over the seawater in the Northern Hemisphere without and with DMS chemistry are shown in Fig. 55.1. Predicted SO_2 and SO_4^{2-} concentrations generally decrease with altitude, with DMS chemistry effectively increasing SO_2 and SO_4^{2-} levels particularly near surface.

DMS chemistry enhances annual mean SO_4^{2-} over seawater by 48% compared to the simulation without DMS chemistry. It increases SO_4^{2-} by 42% in winter, 42% in spring, 70% in summer, and 43% in fall. The largest impact occurs in summer due to the combination of high DMS emission rates and high oxidant concentrations.

The spatial distribution of the predicted annual-mean surface SO_2 and SO_4^{2-} concentrations are shown in Fig. 55.2. The model without DMS chemistry predicts higher concentrations of SO_2 and SO_4^{2-} over land and small concentrations over seawater reflecting mainly the impact of anthropogenic SO_2 sources. DMS chemistry effectively enhances SO_2 and SO_4^{2-} concentrations over seawater and many

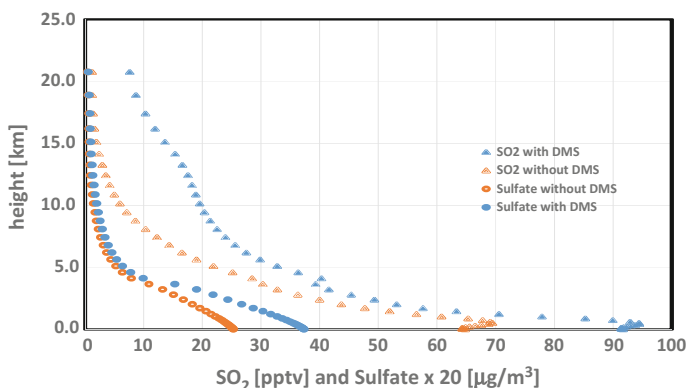


Fig. 55.1 Annual mean SO_2 and SO_4^{2-} over seawater without and with DMS chemistry

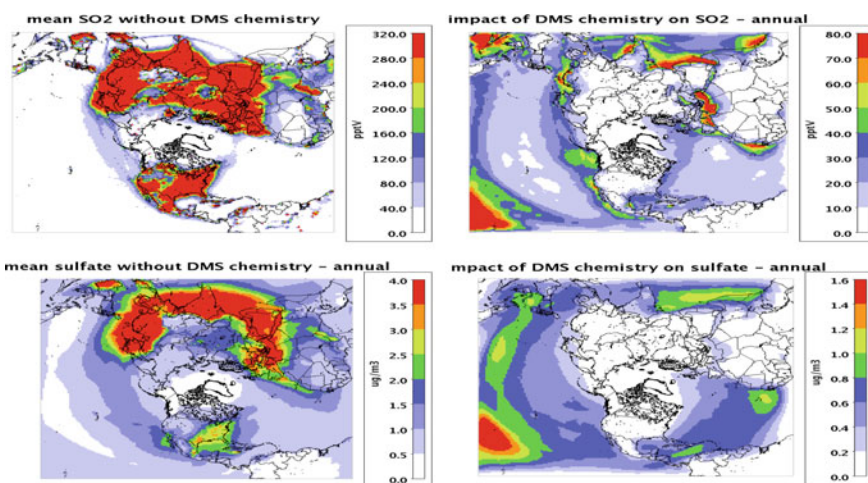


Fig. 55.2 (*Top row*) predicted annual mean SO_2 without DMS chemistry and enhancement due to DMS chemistry (*bottom row*) predicted annual mean SO_4^{2-} without DMS chemistry and enhancement due to DMS chemistry

coastal areas. Higher enhancements are predicted over seawater than over coastal areas. DMS chemistry enhances SO_2 concentrations by >40 pptv in many oceanic areas and SO_4^{2-} levels by $>0.8 \mu\text{g}/\text{m}^3$ in some areas of the Pacific Ocean, Atlantic Ocean, Arabian Sea, and Caribbean Sea.

Predicted SO_4^{2-} levels are compared to observed data from the Chemical Speciation Network (CSN) and the Interagency Monitoring of Protected Visual Environments (IMPROVE) sites in the U.S. (Fig. 55.3a). The model without DMS

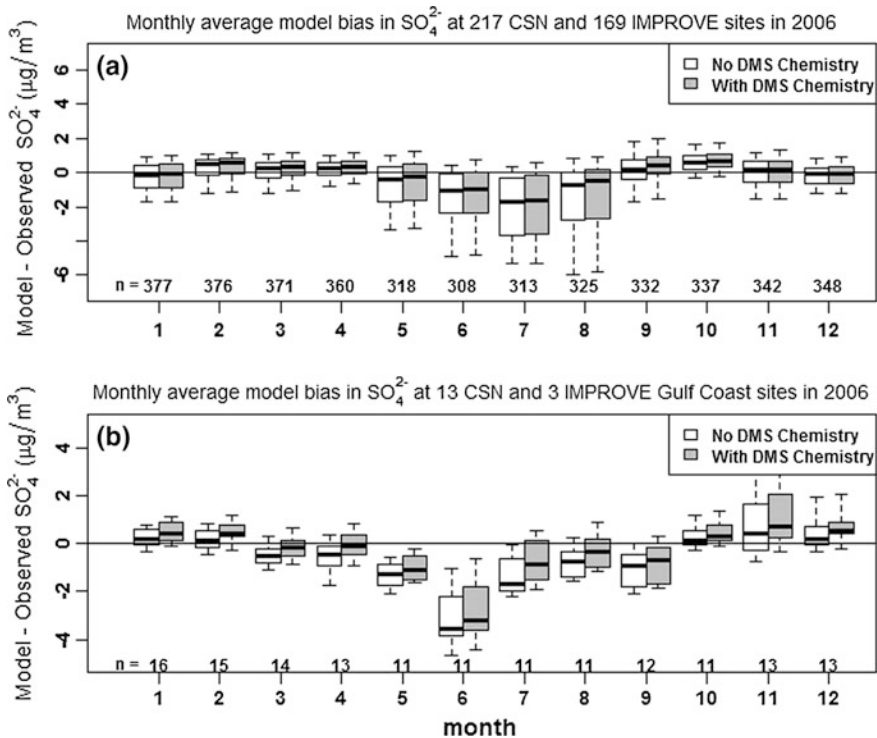


Fig. 55.3 A comparison of model predicted SO_4^{2-} with observed data from CSN and IMPROVE sites for **a** the entire U.S. and **b** sites only in the Gulf Coast areas of the U.S.

chemistry underestimates the summertime observed data. DMS chemistry only marginally improves the model performance when compared to observed data from all sites. However, it affects the model performance by larger margins when compared to the observed data from coastal sites (Fig. 55.3b). It improves the model performance from March to September but deteriorates the performance in other months.

55.4 Summary

We performed annual hemispheric CMAQ model simulations without and with DMS chemistry. The model without DMS chemistry predicts only small levels of SO_2 and SO_4^{2-} over seawater. However, DMS chemistry substantially enhances SO_2 and SO_4^{2-} over seawater and coastal areas. It enhances the annual mean surface SO_4^{2-} concentrations by 48% compared to that obtained without DMS

chemistry. It enhances summertime surface SO_4^{2-} by the largest margin among all seasons. The model without DMS chemistry tends to under-predict SO_4^{2-} compared to observed data in the US. DMS chemistry only marginally affects the model performance when compared to the observed data for the entire U.S. However, DMS chemistry affects model performance for SO_4^{2-} by larger margins in U.S. coastal areas.

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Questions and Answers on ITM Paper No. 6.40

1. **Questioner name:** Dick Derwent

Question: There is an oxidation product from the OH + DMS reaction which has a competitive fate between NO_2 and O_2 reactions. The NO_2 route produces NO which acts as an ozone sink in high NO_x environments. It would be interesting to see if a small increase in detail in the OH + DMS chemistry could produce this ozone sink along the coast of North America.

Answer: This reaction is not included in our current DMS chemistry. However, we can explore its impact in a future study.

2. **Questioner name:** Pavel Kishcha

Question: Could we expect any significant increase in sulfate aerosols in the future? Water temperature increases due to global warming which is followed by an increase in DMS emissions in one hand. On the other hand, anthropogenic SO_2 emissions could decrease. What factor is more effective?

Answer: Anthropogenic SO_2 emissions have decreased during the last 20 years and are likely to further decrease in the future. DMS emissions may increase in the future due to warmer water temperature. Thus, the relative importance of sulfate aerosols from DMS is likely to increase further in the future.

3. **Questioner name:** Pius Lee

Question: The enhancement plots you showed for sulfate and SO_2 production from considering DMS is much stronger in the Gulf Coast than in the Pacific Coast. It looks to me that there is a strong temperature dependency. Is it as great as halogen that is roughly dependent on water temperature (exponentially)?

Answer: Inorganic halogen (iodine) emissions depend on seawater iodide concentration, atmospheric O_3 , and wind speed. Seawater iodide concentration has a strong dependency on seawater temperature. DMS emissions depends on seawater DMS concentration and transfer velocity. Seawater DMS concentrations are obtained from a global database and the Nightingale et al. (2000) parameterization is used to calculate transfer velocity. While both the wind speed and temperature affect transfer velocity, wind speed has a stronger influence on transfer velocity and DMS emissions.

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