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# Impact of dimethylsulfide chemistry on air quality over the Northern Hemisphere

Junri Zhao<sup>a</sup>, Golam Sarwar<sup>b,\*</sup>, Brett Gantt<sup>c</sup>, Kristen Foley<sup>b</sup>, Barron H. Henderson<sup>c</sup>, Havala O. T. Pye<sup>b</sup>, Kathleen M. Fahey<sup>b</sup>, Daiwen Kang<sup>b</sup>, Rohit Mathur<sup>b</sup>, Yan Zhang<sup>a</sup>, Qinyi Li<sup>d</sup>, Alfonso Saiz-Lopez<sup>d</sup>

<sup>a</sup> Shanghai Key Laboratory of Atmospheric Particle Pollution and Prevention (LAP3), Department of Environmental Science and Engineering, Fudan University, Shanghai, 200438, China

<sup>b</sup> Center for Environmental Measurement and Modeling, Office of Research and Development, U.S. Environmental Protection Agency, Research Triangle Park, NC, 27711, USA

<sup>c</sup> Office of Air Quality Planning and Standards, U.S. Environmental Protection Agency, Research Triangle Park, NC, 27711, USA

<sup>d</sup> Department of Atmospheric Chemistry and Climate, Institute of Physical Chemistry Rocasolano, CSIC, Madrid, 28006, Spain

#### HIGHLIGHTS

• Dimethylsulfide enhances sulfate over seawater and coastal areas.

• The impact of dimethylsulfide on sulfate is the largest in the summer.

• Hydroxyl and nitrate radical-initiated pathways oxidize 75% and halogen-initiated pathways oxidize 25% of dimethylsulfide.

• Dimethylsulfide leads to more acidic particles.

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#### ABSTRACT

We implement oceanic dimethylsulfide (DMS) emissions and its atmospheric chemical reactions into the Community Multiscale Air Quality (CMAQv53) model and perform annual simulations without and with DMS chemistry to quantify its impact on tropospheric composition and air quality over the Northern Hemisphere. DMS chemistry enhances both sulfur dioxide (SO<sub>2</sub>) and sulfate (SO<sub>4</sub><sup>2-</sup>) over seawater and coastal areas. It enhances annual mean surface SO<sub>2</sub> concentration by +46 pptv and SO<sub>4</sub><sup>2-</sup> by +0.33  $\mu$ g/m<sup>3</sup> and decreases aerosol nitrate concentration by -0.07  $\mu$ g/m<sup>3</sup> over seawater compared to the simulation without DMS chemistry. The changes decrease with altitude and are limited to the lower atmosphere. Impacts of DMS chemistry on SO<sub>4</sub><sup>2-</sup> are largest in the summer and lowest in the fall due to the seasonality of DMS emissions, atmospheric photochemistry and resultant oxidant levels. Hydroxyl and nitrate radical-initiated pathways oxidize 75% of the DMS while halogeninitiated pathways oxidize 25%. DMS chemistry leads to more acidic particles over seawater by decreasing aerosol pH. Increased SO<sub>4</sub><sup>2-</sup> from DMS enhances atmospheric extinction while lower aerosol nitrate reduces the extinction so that the net effect of DMS chemistry on visibility tends to remain unchanged over most of the seawater.

#### 1. Introduction

In the 30+ years since Charlson et al. (1987) hypothesized that biogenically-produced dimethyl sulfide (DMS) from marine phytoplankton participates in a negative climate feedback loop affecting cloud condensation nuclei and cloudiness, the study of DMS from the world's oceans has been a vigorous area of research. Though the CLAW hypothesis (named after the authors of Charlson et al., 1987) has been criticized as too simplistic (Quinn and Bates, 2011), the resulting knowledge gained about the sources, oceanic concentrations, and

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<sup>\*</sup> Corresponding author. US EPA, 109 T.W. Alexander Drive, Research Triangle Park, NC 27711, USA. *E-mail address:* sarwar.golam@epa.gov (G. Sarwar).

emissions of oceanic DMS has enabled chemical transport and earth systems models to realistically simulate its impacts on air quality and climate. DMS in the ocean is produced from the breakdown of dimethylsulfoniopropionate (DMSP) generated from microalgal metabolic processes and exudation/mortality (Stefels et al., 2007). The concentration of DMS in seawater has been sampled extensively, leading to the construction of the Global Surface Seawater DMS Database (http://saga.pmel.noaa.gov/dms) and interpolated estimates of the global concentration distribution (Kettle et al., 1999; Kettle and Andreae, 2000). An updated climatology of oceanic DMS concentrations using over 47,000 measurements was reported by Lana et al. (2011).

Chemical transport and earth systems models typically utilize oceanic DMS climatology along with parameterizations of the sea-to-air transfer velocity based on surface wind speed to simulate DMS emissions from the ocean (Rasch et al., 2000; Chin et al., 2000; Park et al., 2004). Regional air quality models such as Community Multiscale Air Quality (CMAQ, https://www.epa.gov/cmaq) have historically not included oceanic DMS emissions because of their 1) typical application to high pollution areas, 2) relatively high anthropogenic emissions of sulfur dioxide (SO<sub>2</sub>) resulting in sulfate (SO<sub>4</sub><sup>2-</sup>) concentrations that overwhelm the DMS contribution, and 3) small fraction of oceanic area in a typical model domain. Smith and Mueller (2010) implemented several natural sulfur emission sources including oceanic DMS into the CMAQ model for a domain covering the continental U.S., southern Canada, and northern Mexico and surrounding oceans based on the year 2002. For that domain and simulation year, natural gaseous sulfur emissions made up only 16% of the total gaseous sulfur emissions but increased SO<sub>4</sub><sup>2-</sup> concentrations over seawater and land by as much as 2 and  $0.1-0.2 \,\mu\text{g/m}^3$ , respectively (Mueller et al., 2011). Mueller and Mallard (2011) found that natural SO<sub>4</sub><sup>2-</sup> concentrations predicted by CMAQ with DMS and other natural sulfur sources were slightly overpredicted in the western U.S. and well predicted in the eastern U.S. when compared with natural condition values used in the Regional Haze Rule. Mueller and Mallard (2011) also reported that the background and natural  $SO_4^{2-}$  as a percentage of total  $SO_4^{2-}$  was >60% over much of the Pacific Ocean within the domain and between 20% and 60% over broad regions of the western U.S.

In recent years, changes to both air quality and the Regional Haze Rule have led to a renewed interest in the U.S. in quantifying the contribution of DMS to natural  $SO_4^{2-}$  concentrations. In terms of air quality, the substantial reduction in SO<sub>2</sub> emissions from power plants in the U.S. (https://www3.epa.gov/airmarkets/progress/datatren ds/ index.html) and resulting decrease in  $SO_4^{2-}$  concentrations (Chan et al., 2018) has led to increases in the fraction of sulfur from natural sources across the U.S. Furthermore, differentiating natural and anthropogenic sources of haze is an important component of the recommended metric for tracking visibility progress in the Regional Haze Rule (Gantt et al., 2018; EPA, 2018). In the recommended metric, the 20% most impaired days used to track visibility have the highest anthropogenic extinction relative to natural extinction. Because air quality models used to support the Regional Haze Rule need to accurately differentiate the natural and anthropogenic sources of haze, previously overlooked natural sources such as DMS have gained renewed attention. In this work, oceanic DMS emissions and its atmospheric chemistry are implemented in the CMAQ model and simulated for the year 2016.

#### 2. Methodology

#### 2.1. Model description

The CMAQ model (USEPA, 2019) (https://www.epa.gov/cmaq) is a widely used air quality modeling system (Appel et al., 2017; Foley et al., 2015; Gantt et al., 2017; Kang et al., 2013; Sarwar et al., 2014) containing interactions of multiple complex emission inventories and atmospheric processes. Applications of the CMAQ model have ranged from state-of-the-science air quality research to regulatory efforts such

as reviews of the U.S. Ozone and Particulate Matter National Ambient Air Quality Standards. To assess the impact of DMS chemistry on air quality across the Northern Hemisphere, we performed simulations for the year 2016 using the offline hemispheric version (Mathur et al., 2017) of CMAQ v5.3. The simulation domain covers the entire Northern Hemisphere (0-90°N, 180°W-180°E) and some small regions of the Southern Hemisphere near the equator. Details of the model and domain can be founded in Mathur et al. (2017). The CMAQ model was configured to use AERO7 as the aerosol module (including organic aerosols (Murphy et al., 2017; Pye et al., 2017; Xu et al., 2018)) and CB6r3 (Luecken et al., 2019) as the gas-phase mechanism along with detailed halogen chemistry (Sarwar et al., 2019). The meteorological fields for the model were generated using the Weather Research and Forecasting (WRFv3.8) model (Skamarock and Klemp, 2008) and processed using the Meteorology-Chemistry Interface Processor (MCIP4.3) (Otte and Pleim, 2009). We use model-ready emissions for hemispheric CMAQ developed by Vukovich et al. (2018). SO2 emissions from volcanic eruptions (Beirle et al., 2014) are not included in this study.

#### 2.2. DMS emissions

The sea-air flux of DMS is estimated using the gas transfer velocity and DMS concentrations in seawater as described in the Supplementary Information (Lana et al., 2011). Using the monthly mean climatological DMS concentrations in seawater of Lana et al. (2011) and the Liss and Merlivat (1986) parameterization, we estimate annual DMS emissions of 10.6 Tg(S) over the Northern Hemisphere. Our estimate compares favorably with the estimate of 10.8 Tg(S) reported by Lana et al. (2011) and with the estimates of 7.4-11.4 Tg(S) reported by Boucher et al. (2003). Annual estimates of global DMS emissions range between 15 and 34 Tg(S) (Kloster et al., 2006; Thomas et al., 2010; Hezel et al., 2011; Lana et al., 2011; Chen et al., 2018). DMS emission estimates for the Northern Hemisphere are generally lower than that of the Southern Hemisphere due to the smaller ocean surface area and lower abundance of plankton species with high DMSP production rates (Kloster et al., 2006). Several groups of marine phytoplankton can produce DMSP (Stefels et al., 2007); however, specific groups including coccolithophorids can abundantly generate it (Kloster et al., 2006). Annual anthropogenic SO<sub>2</sub> emissions in the model are  $\sim$ 40 Tg(S). Thus, sulfur in DMS emissions was equal to 26% of the total anthropogenic sulfur emission in our model. The highest DMS emissions in the Northern Hemisphere occur in the winter and summer and the lowest in the spring and fall (Fig. 1). This is due to the higher wind speed driving the emissions in winter and higher seawater DMS concentrations driving the emissions in the summer. Relatively lower wind speed (compared to winter) and seawater DMS concentrations (compared to summer) in the spring and fall lead to reduced DMS emissions in those seasons.

#### 2.3. DMS chemistry

Seven gas-phase chemical reactions related to DMS are incorporated in CMAQv5.3 (Table 1). These reactions involve oxidation of DMS by hydroxyl radical (OH), nitrate radical (NO<sub>3</sub>), chlorine radical (Cl), chlorine monoxide (ClO), iodine monoxide (IO), and bromine monoxide (BrO) to produce SO<sub>2</sub> and methanesulfonic acid (MSA). The primary sink of DMS occurs by reactions with OH during the daytime (via two channels: H-abstraction and addition pathways) and NO<sub>3</sub> radicals at night (Wilson and Hirst, 1996). NO3 is more abundant in polluted areas due to oxides of nitrogen (NO<sub>x</sub>) emissions from anthropogenic activities, while in clean marine conditions OH is the dominant oxidant of DMS. The H-abstraction primarily leads to SO<sub>2</sub>, while the addition of OH forms SO<sub>2</sub> and MSA. We add R1-R3 following Chin et al. (1996) with updated reaction rate constants from Sander et al. (2011). Hoffmann et al. (2016) reported that DMS oxidation by halogen oxides is ignored in current model parameterizations of atmospheric chemistry. DMS oxidation by halogens oxides is known to occur in the atmosphere and is treated as a



Fig. 1. (a) Seasonal variation of DMS emissions (b) seasonal variation of DMS concentration in seawater ( $DMS_{sw}$ ) (c) seasonal variation of 10-m wind speed (WSPD<sub>10</sub>) (d) seasonal variation of seawater temperature ( $TEMP_{sw}$ ) over the Northern Hemisphere. Bars represent ±1-standard deviation. Winter is December–February, spring is March–May, summer is June–August, and fall is September–November.

Table 1					
List of chemical reaction	s for DMS	oxidation	in	CMA	Ç

No.	Reaction	Rate Expression ( $cm^3$ molecule <sup>-1</sup> sec <sup>-1</sup> )	References
1	DMS + OH = SO <sub>2</sub> + MEO2 + FORM (abstraction channel)	$\begin{array}{l} k = 1.12 \times 10^{-11} \\ e^{-250/T} \\ T = temperature in \\ Kelvin \end{array}$	Sander et al. (2011)
2	$\label{eq:DMS} \begin{split} DMS + OH &= 0.75 \times SO_2 + \\ 0.25 \times MSA + MEO2 \\ (addition \ channel) \end{split}$	$\begin{array}{l} k_{o} = 1.99 \times 10^{-39} \\ e^{-5270/T} \\ k_{\infty} = 1.26 \times 10^{-10} \\ e^{+340/T} \\ k = \{k_{o}[M] / \\ (1+k_{o}[M]/k_{\infty})\} \ F^z \\ Z = \{(1/N) + log_{10}[k_{o} \\ [M]/k_{\infty}]^2\}^{-1} \\ F = 1.0 \ and \ N = 1.0 \end{array}$	Sander et al. (2011)
		[M] = total pressure, molecules/cm <sup>3</sup>	
3	$\begin{array}{l} \text{DMS} + \text{NO}_3 = \text{SO}_2 + \\ \text{HNO}_3 + \text{MEO2} + \text{FORM} \end{array}$	$\substack{k=1.93\times 10^{-13}\\e^{+520/T}}$	Sander et al. (2011)
4	$\begin{split} DMS + BrO &= 0.75 \times SO_2 \\ + 0.25 \times MSA + MEO2 + \\ Br \end{split}$	$\substack{k = 1.5 \times 10^{-14} \\ e^{+1000/T}}$	Atkinson et al. (2006)
5	$\begin{array}{l} \text{DMS} + \text{IO} = 0.75 \times \text{SO}_2 + \\ 0.25 \times \text{MSA} + \text{MEO2} + \text{I} \end{array}$	$\substack{k=3.3\times 10^{-13}\\ e^{-925/T}}$	Atkinson et al. (2006)
6	$\begin{split} DMS+Cl &= 0.86\times SO_2 + \\ 0.14\times MSA + MEO2 + \\ 0.45\times FORM + 0.45\times \\ HCl + 0.55\times ClO \end{split}$	$\begin{array}{l} k = 3.4 \times 10^{-13} \\ e^{+2081/T} \end{array}$	Atkinson et al. (2006); Sommariva and von Glasow (2012)
7	$\begin{array}{l} \text{DMS} + \text{ClO} = 0.75 \times \text{SO}_2 \\ + 0.25 \times \text{MSA} + \text{MEO2} + \\ \text{Cl} \end{array}$	$\substack{k=1.7\times 10^{-15}\\ e^{+340/T}}$	Atkinson et al. (2006)

Note: DMS = dimethyl sulfide, OH = hydroxyl radical,  $SO_2$  = sulfur dioxide, MSA = methanesulfonic acid,  $NO_3$  = nitrate radical, BrO = bromine monoxide, IO = iodine monoxide, Cl = chlorine radical, ClO = chlorine monoxide, MEO2 = methyl peroxy radical, FORM = formaldehyde, Br = bromine radical, I = iodine radical, HNO<sub>3</sub> = nitric acid, HCl = hydrochloric acid.

potential sink of DMS (Barnes et al., 1989; Sayin and McKee, 2004). We added R4-R7 using rate constants suggested by Atkinson et al. (2006) and simulate BrO, ClO, IO and Cl concentrations using the detailed halogen chemistry recently incorporated into CMAQ (Sarwar et al., 2012, 2014, 2015, 2019). The reaction between Cl and DMS could play an important role in coastal areas where Cl mixing ratios can reach high

levels due to surf zone sea spray emissions and dechlorination of sea spray by anthropogenic pollutants. CMAQ contains one gas-phase reaction involving OH and five aqueous-phase chemical reactions involving hydrogen peroxide (H2O2), ozone (O3), metal catalysis (iron/manganese), methylhydroperoxide (MHP), and peroxyacetic acid (PACD) for oxidation of SO<sub>2</sub> into SO<sub>4</sub><sup>2-</sup> (Sarwar et al., 2011). Once SO<sub>2</sub> is produced by the oxidation of DMS, subsequent reactions in CMAQ then transform  $SO_2$  into  $SO_4^{2-}$ . In our current implementation, MSA produced from DMS can undergo dry and wet deposition but cannot form aerosols. Veres et al. (2020) recently analyzed data from airborne observations and reported a new DMS oxidation product (identified as hydroperoxy methyl thioformate). They developed a new DMS oxidation scheme by including the formation of hydroperoxy methyl thioformate, implemented it into a global model (CAM-Chem - the Community Atmosphere Model with Chemistry), and reported that the new scheme slows the formation of  $SO_2$  as well as  $SO_4^{2-}$  at the surface between  $60^\circ N$  and  $60^\circ S$ and increases the formation of those products in other parts of the Earth compared to the traditional DMS oxidation scheme. This new scheme is not included in our study.

#### 2.4. Simulation details

We performed two different annual simulations to investigate the importance of the DMS chemistry and its impact on air quality. One simulation used the CB6r3 chemical mechanism along with the halogen chemistry but without any DMS chemistry while the other simulation used the CB6r3 mechanism along with the halogen and the DMS chemistry. Differences in model results between the simulations can be attributed solely to the DMS chemistry. We employed the Integrated Reaction Rate (IRR) option in the model which enabled estimates of the relative contribution of each reaction to the total DMS oxidation rate.

#### 3. Results and discussion

#### 3.1. Impacts on annual mean $SO_2$ and $SO_4^{2-}$ over seawater

Annual mean DMS concentrations over seawater with DMS chemistry are shown in Fig. 2a. DMS concentrations peak around 110 ppt at the surface and rapidly decrease with altitude reaching values < 5 ppt at an altitude of 2 km. This result is consistent with Khan et al. (2016) and



Fig. 2. (a) Annual mean DMS concentration with DMS chemistry and SO<sub>2</sub> concentrations over seawater without and with DMS chemistry with altitude and (b) annual mean  $SO_4^{2-}$  concentrations over seawater without and with DMS chemistry with altitude.

Chen et al. (2018) who reported that DMS mainly exists in the lower atmosphere (2–5 km). The vertical distributions of annual mean SO<sub>2</sub> and SO<sub>4</sub><sup>2–</sup> concentrations without and with DMS chemistry over seawater are presented in Fig. 2a and (b), respectively. The enhancements of SO<sub>2</sub> and SO<sub>4</sub><sup>2–</sup> concentrations by the DMS chemistry are highest at the surface and decrease with altitude. The impacts on SO<sub>2</sub> and SO<sub>4</sub><sup>2–</sup> are limited to the lower troposphere. DMS chemistry increases surface SO<sub>2</sub> concentration by ~90% and surface SO<sub>4</sub><sup>2–</sup> concentration by ~30% over seawater. All simulations include SO<sub>2</sub> emissions from shipping activities and oil rigs over seawater; however, most of these emissions are released above the surface layer due to plume rise. Because the model surface layer over seawater contains very little SO<sub>2</sub> emissions, peak SO<sub>2</sub> concentrations occur above sea level (Fig. 2a). In contrast, sea-salt emissions (which are speciated into different aerosol components including SO<sub>4</sub><sup>2–</sup>) occur at the surface and result in peak SO<sub>4</sub><sup>2–</sup> concentrations at sea level (Fig. 2b).

Analysis of the IRR results suggests that 63.5% of DMS is oxidized by OH (33.0% via abstraction channel and 30.5% via addition channel) which are within the ranges (52%–85%) reported by previous studies (Berglen et al., 2004; Boucher et al., 2003; Chen et al., 2018; Khan et al., 2016; Kloster et al., 2006). The oxidation of DMS by NO<sub>3</sub> accounts for 11.8%. Previous studies reported that NO<sub>3</sub> can account for 15%–29% of DMS oxidation (Berglen et al., 2004; Boucher et al., 2006). The contribution of NO<sub>3</sub> to the total DMS oxidation is slightly lower than those studies due to lower abundance of DMS over the Northern Hemisphere. BrO, Cl, IO and ClO oxidation pathways contributed 16.0%, 8.2%, 0.4% and 0.1% to the total DMS oxidation, respectively. The BrO oxidation of DMS is similar to the ranges (12–16%) reported by Breider et al. (2010) and Chen et al. (2018). Consistent with these findings, our results also suggest that OH and NO<sub>3</sub> are responsible for the majority (~75%) of the DMS oxidation

but that halogen-initiated pathways are also important processes accounting for  $\sim$ 25% of DMS oxidation. In our simulations, NO<sub>3</sub> is the only night-time oxidant for DMS oxidation; therefore, the magnitude of daytime DMS oxidation is far greater than that of the nighttime.

#### 3.2. Spatial distribution of the DMS impacts on $SO_2$ and $SO_4^{2-}$

The annual DMS emission and annual mean surface DMS concentrations are presented in Fig. 3a and Fig. 3b, respectively. The surface DMS concentration ranges up to  $\sim$ 400 pptv with a mean value of  $\sim$ 110 pptv over seawater. The higher predicted values of DMS concentrations occur over lower latitude oceanic areas compared to those over higher latitude oceanic areas, which generally agree with the estimated latitudinal DMS emissions distribution. Concentrations over the Indian Ocean can reach high levels (75-350 pptv) due to the large oceanic production of DMS along with strong sea surface winds. The high annual DMS concentrations over the Indian Ocean are largely driven by the very high summertime concentrations resulting from strong seasonal winds and associated large DMS emissions. The emissions of DMS depend on the sea surface wind speed, sea surface temperature, and oceanic productivity (Keller et al., 1989; Lana et al., 2011). However, the spatial distribution of DMS concentration does not exactly follow the emission distribution pattern due to the spatial variation in DMS oxidation rates. For instance, even though DMS emissions are not high in regions of the Norwegian Sea, high DMS concentrations are noted due to the low OH abundance at high latitudes (Lelieveld et al., 2016). Predicted DMS concentrations are lower over land than over seawater. DMS concentrations ranging up to  $\sim$ 70 pptv are predicted over some coastal areas of Northern Hemisphere while concentrations up to  $\sim 20$  pptv are predicted over coastal areas of North America.



Annual mean surface SO<sub>2</sub> and SO<sub>4</sub><sup>2-</sup> concentrations without DMS

Fig. 3. Spatial distribution of (a) annual DMS emission and (b) annual mean surface DMS concentration over Northern Hemisphere.

chemistry over the Northern Hemisphere are presented in Fig. 4(a) and (c), respectively. High  $SO_2$  and  $SO_4^{2-}$  concentrations are predicted over land due to anthropogenic sources, most pronounced over industrial areas of Europe, North America, India and China. Relatively higher levels of SO<sub>2</sub> and SO<sub>4</sub><sup>2-</sup> are predicted over seawater in areas of commercial shipping lanes. Very low  $SO_2$  and  $SO_4^{2-}$  concentrations are predicted over remote oceanic areas without the DMS chemistry. Annual mean surface  $SO_2$  and  $SO_4^{2-}$  enhancements by the DMS chemistry are presented in Fig. 4(b) and (d), respectively. DMS chemistry increases atmospheric SO<sub>2</sub> concentrations by 20–140 pptv and SO<sub>4</sub><sup>2–</sup> concentrations by 0.1–0.8  $\mu$ g/m<sup>3</sup> over most areas of seawater. For SO<sub>2</sub>, such enhancements are higher over low latitude areas and some coastal areas due to higher DMS concentrations and higher oxidant levels. The annual mean contribution of DMS to  $SO_2$  concentration over seawater is ~46 pptv, which is lower than 130 pptv over Northern Hemisphere reported by Gondwe et al. (2003) due to differences between models, DMS emission flux estimates, and reaction rate constants in the two studies. The pattern of  $SO_4^{2-}$  concentration enhancement by DMS is similar to that of the SO<sub>2</sub> enhancement. However, the high values are not limited to the areas with large DMS emission flux as  $SO_4^{2-}$  can be transported to a larger geographical footprint due to the longer atmospheric residence time of particles. DMS chemistry also decreases aerosol nitrate concentrations by 0.1–0.3  $\mu$ g/m<sup>3</sup> (not shown) over a large area of seawater as the increased  $SO_4^{2-}$  further limits ammonia availability. On average, such decreases ( $-0.07 \ \mu g/m^3$ ) of nitrate over seawater are lower than the enhancement (+0.33  $\mu$ g/m<sup>3</sup>) of SO<sub>4</sub><sup>2-</sup>.

To assess the relative importance of  $SO_4^{2-}$  enhancement by the DMS chemistry, we calculate the ratios of  $SO_4^{2-}$  enhancements by the DMS chemistry to total  $SO_4^{2-}$  concentrations (Fig. 5). Higher values (>0.32) occur over large areas of the tropical Pacific and Atlantic Oceans and along the Pacific Coast of the U.S.  $SO_4^{2-}$  enhancements from DMS over these areas are high while the total  $SO_4^{2-}$  concentrations are low, yielding the higher ratios. Ratios over the remaining oceanic areas tend to remain below 0.32. Total  $SO_4^{2-}$  concentrations are higher over these regions while  $SO_4^{2-}$  enhancements by the DMS chemistry are generally



**Fig. 5.** Spatial distribution of the ratio of  $SO_4^{2-}$  enhancement by the DMS chemistry to total  $SO_4^{2-}$  concentration (annual mean).

low, resulting in lower ratios. Our calculated ratios over the western U.S. are lower than the values reported by Mueller and Mallard (2011) due to the fact that their values include background sources like anthropogenic emissions outside the U.S., Canada, and Mexico and natural sulfur emissions other than DMS. Ratios of <0.08 are calculated for coastal waters near China and India; these values are consistent with Li et al. (2020) which reported that DMS chemistry contributes <10% of the total  $SO_4^{2-}$  over Chinese seawaters.

### 3.3. Seasonal variation of the SO<sub>2</sub> and $SO_4^{2-}$ enhancements by DMS chemistry

Seasonal mean atmospheric DMS concentrations over seawater are shown in Fig. 6a. The highest DMS concentrations occur in winter, followed closely by the summertime concentrations. The seasonal variation of DMS concentrations generally follows the seasonality of DMS emissions. DMS concentrations in spring and fall are lower than those in



**Fig. 4.** Spatial distribution of (a) annual mean surface  $SO_2$  (b) annual mean surface  $SO_2$  enhancement by the DMS chemistry (c) annual mean surface  $SO_4^{2-}$  (d) annual mean surface  $SO_4^{2-}$  enhancement by the DMS chemistry over Northern Hemisphere. The black box is the area over which enhancements are shown in Fig. 8.



**Fig. 6.** (a) Seasonal variation of DMS concentration (b) seasonal variation of the SO<sub>2</sub> enhancement by DMS chemistry and (c) seasonal variation of the SO<sub>4</sub><sup>2–</sup> enhancement by DMS chemistry over seawater. Bars represent  $\pm 1$ -standard deviation. Winter is December–February, spring is March–May, summer is June–August, and fall is September–November.

winter and summer primarily due to lower DMS emissions (section 2.2 and Fig. 1). Seasonal  $SO_2$  and  $SO_4^{2-}$  enhancements over seawater by DMS chemistry are shown in Fig. 6(b) and (c), respectively. The largest SO<sub>2</sub> enhancement occurs in the winter and summer months while the minimum enhancement occurs in spring and fall, closely following that of DMS concentrations. The average SO<sub>2</sub> production rate from DMS is the highest in summer due to higher levels of oxidants and relatively higher DMS concentration. However, the conversion rate of  $SO_2$  into  $SO_4^{2-}$  is also high in summer. Therefore, SO<sub>2</sub> concentrations in summer are not the highest among the seasons. The average SO<sub>2</sub> production rate from DMS in winter is lower than that in summer but greater than in the spring and fall. The higher production rates by the BrO and Cl initiated pathways in winter somewhat compensate for the slower production rates by the OH and NO<sub>3</sub> pathways. The conversion rate of SO<sub>2</sub> into  $SO_4^{2-}$ in winter is also slower. Consequently, SO2 concentrations in winter are the highest among the seasons. The SO<sub>2</sub> production rate is the third highest in spring and the lowest in fall due to lower DMS concentrations and lower oxidant levels.

The seasonality of  $SO_4^{2-}$  enhancement from DMS is distinct, with the largest enhancement occurring in summer followed by winter and spring and the lowest enhancement in the fall. Because the conversion of  $SO_2$  into  $SO_4^{2-}$  occurs mainly via the gas-phase reaction with OH and aqueous-phase reactions with  $H_2O_2$  and  $O_3$ , the higher summertime concentrations of OH and  $H_2O_2$  facilitates the conversion of  $SO_2$  into  $SO_4^{2-}$ . The combination of higher oxidant concentrations and relatively higher  $SO_2$  enhancement leads to the highest enhancement of  $SO_4^{2-}$  in summer.

There are important spatial differences in the seasonal impacts. To show such differences, we present the spatial distributions of the impact of DMS chemistry on  $SO_4^{2-}$  in different seasons in Figure S1. Higher impacts in winter occur over the low-latitude areas especially over some areas of the Pacific and the Indian Oceans (Figure S1a). DMS concentrations are higher over these areas (Fig. 3b). Relatively higher oxidants levels in these areas, due to abundant solar radiation and higher temperature, helps the conversion of DMS into SO<sub>2</sub> and subsequently SO<sub>2</sub> into  $SO_4^{2-}$ . For summer, however, the higher impacts occur over some of the mid and upper latitude areas (Figure S1c). The combination of higher DMS concentration, generated from elevated DMS emissions, and abundant oxidants contributes to higher  $SO_2$  and  $SO_4^{2-}$  over these areas. In contrast to winter, the summer enhancement is substantially higher along the U.S. Pacific and Alaska Coasts. Enhancements in spring (Figure S1b) and fall (Figure S1d) are smaller than those in winter and summer due to lower DMS emissions and oxidant levels.

#### 3.4. MSA concentration

Figure S2 shows the predicted annual mean gas-phase MSA concentrations. Higher concentrations are predicted at locations with higher DMS concentrations (Fig. 3b). Concentrations of 16–40 pptv are predicted over lower latitude oceanic areas and part of the Indian Ocean. In contrast, concentrations are generally <12 pptv over most coastal and surrounding areas. Concentrations of 4–16 pptv are predicted over the mid-latitude oceanic areas. The current understanding of atmospheric DMS oxidation pathways is not complete. MSA can be taken up in aerosols/clouds (Karl et al., 2007; Mungall et al., 2018) and the multiphase chemistry of DMS is needed for accurately calculating atmospheric MSA production (Chen et al., 2018). Future studies are needed to improve the DMS chemistry and the MSA predictions.

#### 3.5. Interactions of DMS chemistry and aerosol pH

Acidity is an important property of aerosols that can affect human health and deposition. We estimate fine-mode aerosol acidity (pH<sub>F</sub>) without and with DMS chemistry following the procedures described in Pye et al. (2020). Predicted annual average pH<sub>F</sub> levels (without DMS) range between 0.0 and 5.0 over land and are largely driven by variability in ammonia and nonvolatile cation emissions from sources such as dust (Fig. 7a). Dust outflow and sea-spray rich regions have pH<sub>F</sub> values approaching 6.0 without the presence of DMS. Locations over seawater influenced by anthropogenic activity, such as urban outflow or ships, experience pH<sub>F</sub> values approaching 1.0. Predicted levels are similar to those in the work of Pye et al. (2020) which contains a detailed discussion on the drivers of acidity.

DMS chemistry leads to more acidic particles over seawater (Fig. 7b) due to the enhancement of SO2 which eventually leads to additional  $SO_4^{2-}$ , hydrogen ion (H<sup>+</sup>), and lower aerosol pH<sub>F</sub>. Aerosol pH<sub>F</sub> is reduced by 0.5-1.5 over most seawater areas. However, in locations influenced by dust or anthropogenic emissions, pH<sub>F</sub> is less influenced by the addition of DMS chemistry as pH<sub>F</sub> is mainly dictated by nonvolatile cations in dust (assuming an internal mixture) or the more abundant anthropogenic species. In addition, over low latitude areas of the Pacific Ocean pH<sub>F</sub> is more sensitive to DMS and reduced by 1.5-2.5. Acidity changes of pH<sub>F</sub> values of 0.5 or less cannot be rigorously evaluated using current observations since differences in pH approximations of different models are of similar magnitude Pye et al. (2020).  $pH_F$  changes >0.5 could be evaluated, however, only three observations are available for marine environments in the Northern Hemisphere and all coincide with small changes in modeled  $pH_F$  due to DMS chemistry (Barbados  $pH_F = 2.8$ , Hawaii-volcanic influenced  $pH_F = 1.1$ , Hawaii-marine influenced  $pH_F =$ 4.6; Pye et al., 2020).



Fig. 7. Spatial distribution of (a) annual mean aerosol pH<sub>F</sub> without the DMS chemistry and (b) impact of the DMS chemistry on annual mean aerosol pH<sub>F</sub> over the Northern Hemisphere.



**Fig. 8.** Spatial distribution of (a) annual mean surface  $SO_2$  enhancement by the DMS chemistry over the U.S. and (b) annual mean surface  $SO_4^{2-}$  enhancement by the DMS chemistry over the U.S.

## 3.6. Impacts of DMS chemistry on $SO_2$ and $SO_4^{2-}$ enhancements over the U.S.

Annual mean SO<sub>2</sub> and SO<sub>4</sub><sup>2-</sup> enhancements by DMS chemistry over the U.S. are presented in Fig. 8(a) and (b), respectively. Relatively moderate impacts on annual average SO<sub>2</sub> and SO<sub>4</sub><sup>2-</sup> concentrations are predicted, with the largest enhancements of 10-30 pptv for SO<sub>2</sub> and 0.1–0.3  $\mu g/m^3$  for  $SO_4^{2-}$  occurring along the U.S. coastlines. Enhancements are less than 10 pptv for SO<sub>2</sub> and 0.1  $\mu$ g/m<sup>3</sup> for SO<sub>4</sub><sup>2-</sup> in the interior portions of the U.S. On average, DMS chemistry enhances annual mean SO<sub>2</sub> by 6 pptv and SO<sub>4</sub><sup>2–</sup> by 0.08  $\mu$ g/m<sup>3</sup> across the U.S. It enhances annual mean SO<sub>2</sub> by 10 pptv on average over the Pacific coast states, 11 pptv over the Gulf coast states, and 8 pptv over the Atlantic coastal states. It enhances annual mean  $SO_4^{2-}$  by 0.15 µg/m<sup>3</sup> averaged over the Pacific coast states, 0.13  $\mu$ g/m<sup>3</sup> over the Gulf coast states, and  $0.09 \,\mu\text{g/m}^3$  over the Atlantic coastal states. Our results are in qualitative agreement with the findings reported by Mueller et al. (2011) and Park et al. (2004) who reported that natural emissions enhance  $SO_4^{2-}$  by  $0.1-0.2 \,\mu\text{g/m}^3$  over south Texas and Florida, and  $0.03-0.11 \,\mu\text{g/m}^3$  over western and eastern U.S.

Predicted  $SO_4^{2-}$  concentrations are compared to observed data from the Clean Air Status and Trends Network (CASTNET), Chemical Speciation Network (CSN), and IMPROVE sites (Figure S3a) to examine the impacts on model performance. For all sites in the U.S., predicted  $SO_4^{2-}$ concentrations without DMS chemistry are higher than observed values for most months except in June–August (Figure S3b). DMS chemistry degrades model performance for most months. However, these changes are relatively small due to the limited impact of DMS chemistry in the interior of the U.S. For the subset of coastal sites, however, DMS chemistry has a larger and more nuanced impact on model performance. As seen in Figure S4, DMS chemistry has a relatively large impact on  $SO_4^{2-}$  in Alaska and the Pacific coasts during warmer months (May–September) while the impact is much smaller in the remaining months. It has mixed impact on the model performance at sites along the Alaska coast (Figure S4a), deteriorates the model performance for most months at sites along the Pacific coast (Figure S4b), but improves the comparison with observed data for most months at the Gulf of Mexico sites (Figure S4c).

#### 3.7. Impacts of DMS chemistry on atmospheric visibility

DMS contributes to visibility impairment as a natural source of SO<sub>4</sub><sup>2-</sup>. To quantify the impact of DMS on visibility, we calculate extinction following Pitchford et al. (2007) which uses an empirical equation to estimate light extinction from species-specific coefficients and site-specific hygroscopic growth factors. The species-specific coefficients are used, with the exception of nitrogen dioxide extinction and Rayleigh scattering which are not included. We use WRF estimated relative humidity (RH) for growth factor calculations to produce continuous spatial maps of the mean ammonium sulfate extinction for August because DMS chemistry has the largest impact on  $SO_4^{2-}$  in summer (Fig. 6cand Figure S1). Figure S5a shows the percent changes in ammonium sulfate extinction due to the DMS chemistry. Large increases are evident over the oceans with factor of two increases over much of the Pacific Ocean. Although increases in ammonium sulfate extinction are smaller (less than 30%) over the mainland of the continents, coastal zones and peninsulas have relatively large ammonium sulfate extinction impacts from DMS chemistry. Figure S5b shows that these increases in ammonium sulfate extinction are partially offset by decreased ammonium nitrate extinction. Figure S5c shows a moderate net increase in the total extinction due to DMS chemistry that is largest near the Pacific Northwest coast.

The Interagency Monitoring of Protected Visual Environments (IMPROVE) (http://vista.cira.colostate.edu/Improve) operates numerous monitors in the U.S. which measure extinction. We calculate extinction for annual as well as the 20% most impaired days used in the Regional Haze visibility tracking metric (EPA, 2018) and compared them to the observed data from monitors located near the Alaska coast, the Pacific Ocean coast, and the Gulf of Mexico coast. For calculating extinction at these monitors, we use climatological growth factors from the IMPROVE website. The regional performance is calculated using the site-specific monthly-mean predictions and observed data. The annual mean of regional biases is used to characterize the impact on magnitude while the correlation of the regional predictions with regional observations is used to illustrate the impact of DMS on observed variability.

All three coastal regions have seasonal signals for sulfate extinction bias in the model without DMS. Large negative regional biases are evident in the summer and fall months (June-November), which is also when the DMS impact peaks (Figure S6). As a result, DMS sulfate anticorrelates with regional bias in the Gulf (r = -0.39), the Pacific (r =-0.46) Alaskan (r = -0.63) coasts. The effect of adding DMS sulfate on regional bias, therefore, is largely dependent on the preexisting regional bias. The regional bias for sulfate extinction is initially negative in the Alaskan  $(-1.73 \text{ Mm}^{-1})$  and Gulf  $(-3.18 \text{ Mm}^{-1})$  coasts, so adding DMS improves the regional biases (to +1.4 Mm<sup>-1</sup> and -1.31 Mm<sup>-1</sup> respectively). The Pacific coast, however, is systematically high-biased in the model without DMS  $(+1.78 \text{ Mm}^{-1})$ , so adding DMS worsens the high bias (to  $+4.14 \text{ Mm}^{-1}$ ). The correlation of regional predicted sulfate extinction improves in the Alaskan (0.60-0.82) and Pacific (0.64-0.74) coasts, while the Gulf coast improvement is small (-0.15 to -0.12). The nitrate biases and updates largely mirror sulfate, due to nitrate displacement, though at a smaller magnitude (Table S1 and Figure S6).

The regional biases on the 20% most impaired days have an amplified seasonal signal compared to all days and tend to have larger negative biases. As a result, the addition of sulfate from DMS clearly improves regional bias in the Alaskan (-6.50 to -1.50 Mm<sup>-1</sup>) and Gulf (-8.18 to -6.34 Mm<sup>-1</sup>) coasts, while the Pacific coast is only moderately degraded (-0.40 to 2.01 Mm<sup>-1</sup>). In all cases, however, the nitrate extinction bias is degraded resulting in negative nitrate extinction biases in all regions. The nitrate is always a smaller extinction component of total extinction with smaller total change. Thus, DMS chemistry has important implications for regional haze calculations. The improvement in correlation on the Alaskan and Pacific coasts is encouraging, while the minor improvements in the warmer Gulf may suggest a contrast in conditions with a different relative role of DMS.

#### 3.8. Summary and future work

In this study, we have implemented oceanic emissions and gas-phase atmospheric chemistry of DMS in the CMAQ modeling system to better represent the impact of natural sources on airborne SO<sub>4</sub><sup>2-</sup> budget. As controls on anthropogenic sources of SO<sub>2</sub> emissions continue to reduce emissions, accurate representation of the contribution of natural sources to ambient  $SO_4^{2-}$  becomes more important both for better characterizing background particulate matter pollution as well as for accurately tracking improvements in visibility impairments. We assessed the impacts of the DMS emissions and chemistry treatment in the model on simulated tropospheric composition over the Northern Hemisphere through comparisons with measurements of ambient concentrations, pH and visibility. DMS chemistry increases annual mean SO2 concentration by 20–140 pptv and  $SO_4^{2-}$  concentration by 0.1–0.8  $\mu g/m^3$  over most areas of seawater. The impacts on  $SO_2$  and  $SO_4^{2-}$  concentrations vary by season. The largest SO<sub>2</sub> enhancement occurs in the winter while the largest SO<sub>4</sub><sup>2-</sup>enhancement occurs in the summer. DMS impacts over land

are relatively small with an annual mean SO<sub>2</sub> concentration enhancement of 6 pptv and SO<sub>4</sub><sup>2–</sup>concentration enhancement of 0.08  $\mu g/m^3$  across the U.S. DMS chemistry increases fine particle acidity, with  $pH_F$  reductions of 0.5–1.5 over most seawater areas. However, the impact on extinction tends to be unchanged over most of the seawater.

Improvements in model performance relative to these observations are mixed and result from uncertainties in current estimates of DMS emissions which in turn are dependent on highly variable parameters as well as evolving understanding of atmospheric chemical pathways dictating the fate of airborne DMS and its oxidation products. The model uses monthly mean climatological seawater DMS concentrations. In reality, there may be day-to-day variation in these concentrations that are not captured in the model. Nevertheless, the inclusion of DMS emissions and subsequent oxidation pathways is important for describing the atmospheric sulfur budget, fine particulate matter natural background levels, and for tracking improvements in reducing anthropogenically induced visibility impairment. Our current model calculations utilized a relatively coarse horizontal grid resolution which may have also influenced the performance metric relative to observations. Future modeling studies using finer horizontal grid resolutions may be needed to better quantify spatial and temporal variations in DMS emissions and further assess the impact of DMS chemistry over the U.S. Since the time we undertook this study several recent studies have further explored chemical pathways involved with chemistry of DMS in the atmosphere. For example, Chen et al. (2017) reported that hydrobromic acid can oxidize dissolved  $SO_2$  and potentially be an important source of  $SO_4^{2-}$ over seawater. Veres et al. (2020) suggested a new DMS oxidation scheme that can produce hydroperoxy methyl thioformate. These recent studies suggest a need for additional work on the representation of DMS oxidation pathways including formation of MSA from multi-phase DMS oxidation (Chen et al., 2018); oxidation of SO<sub>2</sub> by hydrobromic acid in marine environments (e.g., Chen et al., 2017); and the possible role of newly discovered intermediates of DMS oxidation (such as hydroperoxymethyl thioformate; Veres et al., 2020) as reservoirs of marine sulfur and their influence on large scale  $SO_4^{2-}$  distributions. These avenues for further research and dataset development could potentially improve the characterization of DMS emissions and representation of its atmospheric chemical pathways, both of which would improve the quantification of DMS impacts on air quality.

#### CRediT authorship contribution statement

Junri Zhao: Visualization, Writing - original draft, Software. Golam Sarwar: Investigation, Methodology, Visualization, Formal analysis, Writing - review & editing, Project administration. Brett Gantt: Writing - review & editing, Software. Kristen Foley: Visualization, Formal analysis, Writing - review & editing. Barron H. Henderson: Visualization, Writing - review & editing, Formal analysis. Havala O.T. Pye: Writing - review & editing, Formal analysis. Kathleen M. Fahey: Writing - review & editing, Resources. Daiwen Kang: Writing - review & editing, Resources. Rohit Mathur: Conceptualization, Formal analysis, Writing - review & editing, Resources. Yan Zhang: Writing - review & editing, Resources. Qinyi Li: Writing - review & editing, Resources. Alfonso Saiz-Lopez: Writing - review & editing, Resources.

#### Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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#### Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.atmosenv.2020.117961.

#### Disclaimer

The views expressed in this paper are those of the authors and do not necessarily represent the views or policies of the U.S. EPA.

#### References

- Appel, K.W., Napelenok, S.L., Foley, K.M., Pye, H.O.T., Hogrefe, C., Luecken, D.J., Bash, J.O., Roselle, S.J., Pleim, J.E., Foroutan, H., Hutzell, W.T., Pouliot, G.A., Sarwar, G., Fahey, K.M., Gantt, B., Gilliam, R.C., Heath, N.K., Kang, D., Mathur, R., Schwede, D.B., Spero, T.L., Wong, D.C., Young, J.O., 2017. Description and evaluation of the Community Multiscale Air Quality (CMAQ) modeling system version 5.1. Geosci. Model Dev. 10, 1703–1732.
- Atkinson, R., Cox, R.A., Crowley, J.N., Hampson, R.F., Hynes, R.G., Jenkin, M.E., Kerr, J. A., Rossi, M.J., Troe, J., October 2006. Summary of evaluated kinetic and photochemical data for atmospheric chemistry. Technical report, IUPAC subcommittee on gas kinetic data evaluation for atmospheric chemistry. http://www.iupac-kinetic.ch. cam.ac.uk/.
- Barnes, I., Becker, K.H., Martin, D., Carlier, P., Mouvier, G., Jourdain, J.L., Laverdet, G., Le Bras, G., 1989. Impact of halogen oxides on dimethyl sulfide oxidation in the marine atmosphere. In: Biogenic Sulfur in the Environment, vol. 393. American Chemical Society, pp. 464–475.
- Berglen, T.F., Berntsen, T.K., Isaksen, I.S.A., Sundet, J.K., 2004. A global model of the coupled sulfur/oxidant chemistry in the troposphere: the sulfur cycle. J. Geophys. Res.: Atmos. 109.
- Boucher, O., Moulin, C., Belviso, S., Aumont, O., Bopp, L., Cosme, E., von Kuhlmann, R., Lawrence, M.G., Pham, M., Reddy, M.S., Sciare, J., Venkataraman, C., 2003. DMS atmospheric concentrations and sulphate aerosol indirect radiative forcing: a sensitivity study to the DMS source representation and oxidation. Atmos. Chem. Phys. 3, 49–65.
- Breider, T.J., Chipperfield, M.P., Richards, N.A.D., Carslaw, K.S., Mann, G.W., Spracklen, D.V., 2010. Impact of BrO on dimethylsulfide in the remote marine boundary layer. Geophys. Res. Lett. 37.
- Chan, E.A.W., Gantt, B., McDow, S., 2018. The reduction of summer sulfate and switch from summertime to wintertime PM2.5 concentration maxima in the United States. Atmos. Environ. 175, 25–32.
- Charlson, R.J., Lovelock, J.E., Andreae, M.O., Warren, S.G., 1987. Oceanic phytoplankton, atmospheric sulphur, cloud albedo and climate. Nature 326, 655–661.
- Chen, Q., Schmidt, J.A., Shah, V., Jaeglé, L., Sherwen, T., Alexander, B., 2017. Sulfate production by reactive bromine: implications for the global sulfur and reactive bromine budgets. Geophys. Res. Lett. 44, 7069–7078.
- Chen, Q., Sherwen, T., Evans, M., Alexander, B., 2018. DMS oxidation and sulfur aerosol formation in the marine troposphere: a focus on reactive halogen and multiphase chemistry. Atmos. Chem. Phys. 18, 13617–13637.
- Chin, M., Jacob, D.J., Gardner, G.M., Foreman-Fowler, M.S., Spiro, P.A., Savoie, D.L., 1996. A global three-dimensional model of tropospheric sulfate. J. Geophys. Res.: Atmos. 101, 18667–18690.
- Chin, M., Rood, R.B., Lin, S.-J., Müller, J.-F., Thompson, A.M., 2000. Atmospheric sulfur cycle simulated in the global model GOCART: model description and global properties. J. Geophys. Res.: Atmos. 105, 24671–24687.
- EPA, 2018. In: Technical Guidance on Tracking Visibility Progress for the Second Implementation Period of the Regional Haze Program (No. EPA-454/R-18-010). U.S. Environmental Protection Agency, RTP, NC. URL: https://www.epa.gov/sites/pro duction/files/201812/documents/technical\_guidance\_tracking\_visibility\_progress. pdf.
- Foley, K.M., Hogrefe, C., Pouliot, G., Possiel, N., Roselle, S.J., Simon, H., Timin, B., 2015. Dynamic evaluation of CMAQ part I: separating the effects of changing emissions and changing meteorology on ozone levels between 2002 and 2005 in the eastern US. Atmos. Environ. 103, 247–255.
- Gantt, B., Beaver, M., Timin, B., Lorang, P., 2018. Recommended metric for tracking visibility progress in the Regional Haze Rule. J. Air Waste Manag. Assoc. 68, 438–445.
- Gantt, B., Sarwar, G., Xing, J., Simon, H., Schwede, D., Hutzell, W.T., Mathur, R., Saiz-Lopez, A., 2017. The impact of iodide-mediated ozone deposition and halogen chemistry on surface ozone concentrations across the continental United States. Environ. Sci. Technol. 51, 1458–1466.
- Gondwe, M., Krol, M., Gieskes, W., Klaassen, W., de Baar, H., 2003. The contribution of ocean-leaving DMS to the global atmospheric burdens of DMS, MSA, SO2, and NSS SO4=. Global Biogeochem. Cycles 17.
- Hezel, P.J., Alexander, B., Bitz, C.M., Steig, E.J., Holmes, C.D., Yang, X., Sciare, J., 2011. Modeled methanesulfonic acid (MSA) deposition in Antarctica and its relationship to sea ice. J. Geophys. Res.: Atmos. 116.
- Hoffmann, E.H., Tilgner, A., Schrödner, R., Bräuer, P., Wolke, R., Herrmann, H., 2016. An advanced modeling study on the impacts and atmospheric implications of

multiphase dimethyl sulfide chemistry. Proc. Natl. Acad. Sci. Unit. States Am. 113, 11776.

- Karl, M., Gross, A., Leck, C., Pirjola, L., 2007. Intercomparison of dimethylsulfide oxidation mechanisms for the marine boundary layer: gaseous and particulate sulfur constituents. J. Geophys. Res.: Atmos. 112.
- Kang, D., Hogrefe, C., Foley, K.L., Napelenok, S.L., Mathur, R., Trivikrama Rao, S., 2013. Application of the Kolmogorov–Zurbenko filter and the decoupled direct 3D method for the dynamic evaluation of a regional air quality model. Atmos. Environ. 80, 58–69.
- Keller, M.D., Bellows, W.K., Guillard, R.R.L., 1989. Dimethyl Sulfide Production in Marine Phytoplankton, Biogenic Sulfur in the Environment. American Chemical Society, pp. 167–182.
- Kettle, A.J., Andreae, M.O., 2000. Flux of dimethylsulfide from the oceans: a comparison of updated data sets and flux models. J. Geophys. Res.: Atmos. 105, 26793–26808.
- Kettle, A.J., Andreae, M.O., Amouroux, D., Andreae, T.W., Bates, T.S., Berresheim, H., Bingemer, H., Boniforti, R., Curran, M.A.J., DiTullio, G.R., Helas, G., Jones, G.B., Keller, M.D., Kiene, R.P., Leck, C., Levasseur, M., Malin, G., Maspero, M., Matrai, P., McTaggart, A.R., Mihalopoulos, N., Nguyen, B.C., Novo, A., Putaud, J.P., Rapsomanikis, S., Roberts, G., Schebeske, G., Sharma, S., Simó, R., Staubes, R., Turner, S., Uher, G., 1999. A global database of sea surface dimethylsulfide (DMS) measurements and a procedure to predict sea surface DMS as a function of latitude, longitude, and month. Global Biogeochem. Cycles 13, 399–444.
- Khan, M.A.H., Gillespie, S.M.P., Razis, B., Xiao, P., Davies-Coleman, M.T., Percival, C.J., Derwent, R.G., Dyke, J.M., Ghosh, M.V., Lee, E.P.F., Shallcross, D.E., 2016. A modelling study of the atmospheric chemistry of DMS using the global model, STOCHEM-CRI. Atmos. Environ. 127, 69–79.
- Kloster, S., Feichter, J., Maier-Reimer, E., Six, K.D., Stier, P., Wetzel, P., 2006. DMS cycle in the marine ocean-atmosphere system – a global model study. Biogeosciences 3, 29–51.
- Lana, A., Bell, T.G., Simó, R., Vallina, S.M., Ballabrera-Poy, J., Kettle, A.J., Dachs, J., Bopp, L., Saltzman, E.S., Stefels, J., Johnson, J.E., Liss, P.S., 2011. An updated climatology of surface dimethlysulfide concentrations and emission fluxes in the global ocean. Global Biogeochem. Cycles 25.
- Lelieveld, J., Gromov, S., Pozzer, A., Taraborrelli, D., 2016. Global tropospheric hydroxyl distribution, budget and reactivity. Atmos. Chem. Phys. 16, 12477–12493.
- Li, S., Zhang, Y., Zhao, J., Sarwar, G., Zhou, S., Chen, Y., Yang, G., Saiz-Lopez, A., 2020. Regional and urban-scale environmental influences of oceanic DMS emissions over coastal China seas. Atmosphere 11.
- Liss, P.S., Merlivat, L., 1986. Air-sea gas exchange rates: introduction and synthesis. In: Buat-Ménard, P. (Ed.), The Role of Air-Sea Exchange in Geochemical Cycling. Springer Netherlands, Dordrecht, pp. 113–127. Luecken, D.J., Yarwood, G., Hutzell, W.T., 2019. Multipollutant modeling of ozone,
- Luecken, D.J., Yarwood, G., Hutzell, W.T., 2019. Multipollutant modeling of ozone, reactive nitrogen and HAPs across the continental US with CMAQ-CB6. Atmos. Environ. 201, 62–72.
- Mathur, R., Xing, J., Gilliam, R., Sarwar, G., Hogrefe, C., Pleim, J., Pouliot, G., Roselle, S., Spero, T.L., Wong, D.C., Young, J., 2017. Extending the Community Multiscale Air Quality (CMAQ) modeling system to hemispheric scales: overview of process considerations and initial applications. Atmos. Chem. Phys. 17, 12449–12474.
- Wueller, S.F., Mallard, J.W., 2011. Contributions infinite and the missions to ozone and PM2.5 as simulated by the community Multiscale Air quality (CMAQ) model. Environ. Sci. Technol. 45, 4817–4823.
- Mueller, S.F., Mao, Q., Mallard, J.W., 2011. Modeling natural emissions in the Community Multiscale Air Quality (CMAQ) model – Part 2: modifications for simulating natural emissions. Atmos. Chem. Phys. 11, 293–320.
- Mungall, E.L., Wong, J.P.S., Abbatt, J.P.D., 2018. Heterogeneous oxidation of particulate methanesulfonic acid by the hydroxyl radical: kinetics and atmospheric implications. ACS Earth Space Chem. 2, 48–55.
- Murphy, B.N., Woody, M.C., Jimenez, J.L., Carlton, A.M.G., Hayes, P.L., Liu, S., Ng, N.L., Russell, L.M., Setyan, A., Xu, L., Young, J., Zaveri, R.A., Zhang, Q., Pye, H.O.T., 2017. Semivolatile POA and parameterized total combustion SOA in CMAQv5.2: impacts on source strength and partitioning. Atmos. Chem. Phys. 17, 11107–11133.
- Otte, T.L., Pleim, J.E., 2010. The Meteorology-Chemistry Interface Processor (MCIP) for the CMAQ modeling system: updates through MCIPv3.4.1. Geosci. Model Dev. (GMD) 3, 243–256.
- Park, R.J., Jacob, D.J., Field, B.D., Yantosca, R.M., Chin, M., 2004. Natural and transboundary pollution influences on sulfate-nitrate-ammonium aerosols in the United States: implications for policy. J. Geophys. Res.: Atmos. 109.
- Pitchford, M., Malm, W., Schichtel, B., Kumar, N., Lowenthal, D., Hand, J., 2007. Revised algorithm for estimating light extinction from IMPROVE particle speciation data. J. Air Waste Manag. Assoc. 57, 1326–1336.
- Pye, H.O.T., Murphy, B.N., Xu, L., Ng, N.L., Carlton, A.G., Guo, H., Weber, R., Vasilakos, P., Appel, K.W., Budisulistiorini, S.H., Surratt, J.D., Nenes, A., Hu, W., Jimenez, J.L., Isaacman-VanWertz, G., Misztal, P.K., Goldstein, A.H., 2017. On the implications of aerosol liquid water and phase separation for organic aerosol mass. Atmos. Chem. Phys. 17, 343–369.
- Pye, H.O.T., Nenes, A., Alexander, B., Ault, A.P., Barth, M.C., Clegg, S.L., Collett Jr., J.L., Fahey, K.M., Hennigan, C.J., Herrmann, H., Kanakidou, M., Kelly, J.T., Ku, I.T., McNeill, V.F., Riemer, N., Schaefer, T., Shi, G., Tilgner, A., Walker, J.T., Wang, T., Weber, R., Xing, J., Zaveri, R.A., Zuend, A., 2020. The acidity of atmospheric particles and clouds. Atmos. Chem. Phys. 20, 4809–4888.
- Quinn, P.K., Bates, T.S., 2011. The case against climate regulation via oceanic phytoplankton sulphur emissions. Nature 480, 51–56.
- Rasch, P.J., Barth, M.C., Kiehl, J.T., Schwartz, S.E., Benkovitz, C.M., 2000. A description of the global sulfur cycle and its controlling processes in the national center for atmospheric research community climate model, version 3. J. Geophys. Res.: Atmos. 105, 1367–1385.

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Sander, S., Friedl, R., Abbatt, J., Barker, J., Burkholder, J., Golden, D., Kolb, C., Kurylo, M., Moortgat, G., Wine, P.J.J.p., 2011. Chemical Kinetics and Photochemical Data for Use in Atmospheric Studies, Evaluation Number 14. 10.

- Sarwar, G., Fahey, K., Napelenok, S., Roselle, S., Mathur, R., 2011. Examining the Impact of CMAQ Model Updates on Aerosol Sulfate predictions. The 10th Annual CMAS Models-3 User's Conference, October. Chapel Hill, NC.
- Sarwar, G., Gantt, B., Foley, K., Fahey, K., Spero, T.L., Kang, D., Mathur, R., Foroutan, H., Xing, J., Sherwen, T., Saiz-Lopez, A., 2019. Influence of bromine and iodine chemistry on annual, seasonal, diurnal, and background ozone: CMAQ simulations over the Northern Hemisphere. Atmos. Environ. 213, 395–404.
- Sarwar, G., Gantt, B., Schwede, D., Foley, K., Mathur, R., Saiz-Lopez, A., 2015. Impact of enhanced ozone deposition and halogen chemistry on tropospheric ozone over the northern Hemisphere. Environ. Sci. Technol. 49, 9203–9211.
- Sarwar, G., Simon, H., Bhave, P., Yarwood, G., 2012. Examining the impact of heterogeneous nitryl chloride production on air quality across the United States. Atmos. Chem. Phys. 12, 6455–6473.
- Sarwar, G., Simon, H., Xing, J., Mathur, R., 2014. Importance of tropospheric CINO2 chemistry across the northern Hemisphere. Geophys. Res. Lett. 41, 4050–4058.
- Sayin, H., McKee, M.L., 2004. Computational study of the reactions between XO (X = Cl, Br, I) and dimethyl sulfide. J. Phys. Chem. 108, 7613–7620.
- Skamarock, W.C., Klemp, J.B., 2008. A time-split nonhydrostatic atmospheric model for weather research and forecasting applications. J. Comput. Phys. 227, 3465–3485.
- Smith, S.N., Mueller, S.F., 2010. Modeling natural emissions in the Community Multiscale Air Quality (CMAQ) Model–I: building an emissions data base. Atmos. Chem. Phys. 10, 4931–4952.
- Sommariva, R., von Glasow, R., 2012. Multiphase halogen chemistry in the tropical Atlantic Ocean. Environ. Sci. Technol. 46, 10429–10437.
- Stefels, J., Steinke, M., Turner, S., Malin, G., Belviso, S., 2007. Environmental constraints on the production and removal of the climatically active gas dimethylsulphide (DMS) and implications for ecosystem modelling. Biogeochemistry 83, 245–275.

- Thomas, M.A., Suntharalingam, P., Pozzoli, L., Rast, S., Devasthale, A., Kloster, S., Feichter, J., Lenton, T.M., 2010. Quantification of DMS aerosol-cloud-climate interactions using the ECHAM5-HAMMOZ model in a current climate scenario. Atmos. Chem. Phys. 10, 7425–7438.
- U.S. Environmental Protection Agency (EPA), August 2019. In: Office of Research and Development (ORD): CMAQ (Version 5.3). Zenodo, Washington, DC, USA. https:// doi.org/10.5281/zenodo.3379043.
- Veres, P.R., Neuman, J.A., Bertram, T.H., Assaf, E., Wolfe, G.M., Williamson, C.J., Weinzierl, B., Tilmes, S., Thompson, C.R., Thames, A.B., Schroder, J.C., Saiz-Lopez, A., Rollins, A.W., Roberts, J.M., Price, D., Peischl, J., Nault, B.A., Møller, K.H., Miller, D.O., Meinardi, S., Li, Q., Lamarque, J.-F., Kupc, A., Kjaergaard, H.G., Kinnison, D., Jimenez, J.L., Jernigan, C.M., Hornbrook, R.S., Hills, A., Dollner, M., Day, D.A., Cuevas, C.A., Campuzano-Jost, P., Burkholder, J., Bui, T.P., Brune, W.H., Brown, S.S., Brock, C.A., Bourgeois, I., Blake, D.R., Apel, E.C., Ryerson, T.B., 2020. Global airborne sampling reveals a previously unobserved dimethyl sulfide oxidation mechanism in the marine atmosphere. Proc. Natl. Acad. Sci. Unit. States Am. 117, 4505.
- Vukovich, J., Eyth, A., Henderson, B., Allen, C., Beidler, J., 2018. In: 2918. Development of 2016 Hemispheric Emissions for CMAQ," the 17<sup>th</sup> Annual CMAS Models-3 User's Conference, October, Chapel Hill, NC, October 22-24 last accessed on 4/16/2020. https://www.cmascenter.org/conference/2018/agenda.cfm.
- Wilson, C., Hirst, D.M., 1996. Kinetics of gas phase oxidation of reduced sulfur compounds. Prog. React. Kinet. 21, 69–132.
- Xu, L., Pye, H.O.T., He, J., Chen, Y., Murphy, B.N., Ng, N.L., 2018. Experimental and model estimates of the contributions from biogenic monoterpenes and sesquiterpenes to secondary organic aerosol in the southeastern United States. Atmos. Chem. Phys. 18, 12613–12637.