

# Impact of sulfur dioxide oxidation by Stabilized Criegee Intermediate on sulfate



Golam Sarwar<sup>a,\*</sup>, Heather Simon<sup>b</sup>, Kathleen Fahey<sup>a</sup>, Rohit Mathur<sup>a</sup>, Wendy S. Goliff<sup>c</sup>, William R. Stockwell<sup>d</sup>

<sup>a</sup> Atmospheric Modeling and Analysis Division, National Exposure Research Laboratory, U.S. Environmental Protection Agency, 109 T.W. Alexander Drive, RTP, NC 27711, USA

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

<sup>c</sup> College of Engineering Center for Environmental Research and Technology, University of California at Riverside, Riverside, CA 92507, USA

<sup>d</sup> Department of Chemistry, Howard University, Washington, DC 20059, USA

## HIGHLIGHTS

- Examine the impact of SO<sub>2</sub> oxidation by SCI on sulfate.
- SO<sub>2</sub> oxidation by SCI can substantially enhance summertime sulfate.
- Impact of SO<sub>2</sub> oxidation by SCI on wintertime sulfate is small.
- Use of MEGAN emissions produces more sulfate than BEIS emissions.
- Reaction of SCI and H<sub>2</sub>O strongly influences the production of sulfate by SCI.

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## ABSTRACT

We revise the Carbon Bond chemical mechanism to explicitly represent three Stabilized Criegee Intermediates (SCIs) and their subsequent reactions with sulfur dioxide, water monomer, and water dimer, and incorporate the reactions into the Community Multiscale Air Quality model. The reaction of sulfur dioxide with SCI produces sulfuric acid which partitions into sulfate. We examine the impact of sulfur dioxide oxidation by SCI on sulfate using two different measured rate constants for the reaction of sulfur dioxide and SCI. When we use the higher rate constant and emissions estimates from the Biogenic Emissions Inventory System, it enhances monthly mean sulfate in summer by ~20% in biogenically active areas. Enhancements are driven primarily by SCI produced from the reactions of biogenically derived alkenes and ozone. The use of the lower rate constant only marginally enhances sulfate since it is 65 times lower than the higher rate constant. We performed several sensitivity analyses to investigate the impacts of uncertain biogenic emissions and SCI loss rates. When we use the higher rate constant and emissions estimates from the Model of Emissions of Gases and Aerosols from Nature, it enhances monthly mean sulfate by ~75%. A simulation using the lowest reported rate constant for the reaction of SCI and water indicated the maximum enhancement of sulfate from this chemistry was up to 4 µg/m<sup>3</sup> over a 24-h period in some locations in the Southeastern U.S. Predictions without the SCI reaction are lower than observed sulfate while predictions with the SCI reaction improve the agreements with observations.

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## 1. Introduction

Aerosols cause adverse health impacts (Pope et al., 2002), degrade atmospheric visibility (Malm et al., 1994), and alter Earth's

energy balance (Murphy et al., 2009). Sulfate (SO<sub>4</sub><sup>2-</sup>) is an important component of atmospheric aerosols, comprising up to 60% of atmospheric aerosols in the U.S. (Hand et al., 2012). SO<sub>4</sub><sup>2-</sup> primarily forms from gas- and aqueous-phase oxidation of sulfur dioxide (SO<sub>2</sub>) by various atmospheric oxidants (Seinfeld and Pandis, 2006). Gas-phase oxidation by hydroxyl radical (HO) and aqueous-phase oxidation by hydrogen peroxide are thought to produce the majority of atmospheric SO<sub>4</sub><sup>2-</sup> (Sofen et al., 2011).

\* Corresponding author. Tel.: +1 919 541 2669; fax: +1 919 541 1379.

E-mail address: [sarwar.golam@epa.gov](mailto:sarwar.golam@epa.gov) (G. Sarwar).

Calvert and Stockwell (1983) first proposed that the reactions of Stabilized Criegee Intermediate (SCI) with  $\text{SO}_2$  are important for production of organic acids and sulfate and incorporated the reactions into the Regional Acid Deposition Mechanism (Stockwell, 1986). These studies found that SCI intermediates could be important oxidants for  $\text{SO}_2$  at high VOC to  $\text{NO}_x$  ratios ( $\text{VOC} = \text{Volatile Organic Compounds}$  and  $\text{NO}_x = \text{Oxides of Nitrogen}$ ) and at low relative humidity. Recent laboratory and field experiments (Welz et al., 2012; Mauldin et al., 2012; Carlsson et al., 2012; Taatjes et al., 2013) more strongly show that Criegee Intermediates can oxidize  $\text{SO}_2$  to  $\text{SO}_4^{2-}$ . Welz et al. (2012) studied the reaction of  $\text{SO}_2$  and formaldehyde oxide ( $\text{CH}_2\text{OO}$ ) using direct measurement technique and measured a rate constant of  $3.9 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  for the reaction. This value is greater than any other previously reported rate constant. They suggested that  $\text{SO}_2$  oxidation by Criegee Intermediates can enhance  $\text{SO}_4^{2-}$  by as much as  $\text{SO}_2$  oxidation by the HO pathway. Mauldin et al. (2012) reported a lower rate constant of  $6.0 \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  for the oxidation of  $\text{SO}_2$  by Criegee Intermediate though they used different Criegee Intermediates than the study of Welz et al. (2012). They suggested that oxidation of  $\text{SO}_2$  by HO alone could not explain the observed  $\text{SO}_4^{2-}$  in a boreal forest in Finland. However, the oxidation of  $\text{SO}_2$  by HO and SCI was sufficient to explain the  $\text{SO}_4^{2-}$  observed in their measurements in boreal forests. Carlsson et al. (2012) performed experiments in a static variable pressure reaction chamber to study particle formation during ozonolysis of  $\beta$ -pinene and 2-butene. They measured rate constant similar to the value reported by Welz et al. (2012) and suggested that it provides a reliable estimate for substituted and larger SCI. Taatjes et al. (2013) directly measured rate constants for the oxidation of  $\text{SO}_2$  by two conformers of acetaldehyde oxide (*syn*- $\text{CH}_3\text{CHOO}$  and *ant*- $\text{CH}_3\text{CHOO}$ ). They also reported high rate constant (similar to the findings of Welz et al., 2012) and suggested that *ant*- $\text{CH}_3\text{CHOO}$  is more reactive than *syn*- $\text{CH}_3\text{CHOO}$ .

The impact of  $\text{SO}_2$  oxidation by SCI depends on the relative abundance of SCI (Vereecken et al., 2012). The main loss mechanism of SCI from the atmosphere is its reaction with  $\text{H}_2\text{O}$ . While several recent studies directly measured the rate constant for the  $\text{SCI} + \text{SO}_2$  reaction, only Welz et al. (2012) and Taatjes et al. (2013) reported the direct measurement of the rate constant for the  $\text{SCI} + \text{H}_2\text{O}$  reaction. However, they reported an upper limit, not the actual rate constant. Previous studies determined the rate constant of the  $\text{SCI} + \text{H}_2\text{O}$  reaction either by indirect measurements or estimations. Indirect measurements quantified the relative rate to that of the  $\text{SCI} + \text{SO}_2$  reaction and used it to derive the rate constant for the  $\text{SCI} + \text{H}_2\text{O}$  reaction. Since the rate constant of the  $\text{SCI} + \text{SO}_2$  reaction varied among different studies, the reported rate constant for the  $\text{SCI} + \text{H}_2\text{O}$  reaction also varied (Hatakeyama and Akimoto, 1994).

Anglada et al. (2011) and Vereecken et al. (2012) noted that the type of conformer as well as the type of substitution in the SCI affects the rate constant for the reaction of SCI and  $\text{H}_2\text{O}$ . Anglada et al. (2011) used computational chemistry to study reactions of fifteen different SCIs with  $\text{H}_2\text{O}$  and found that rate constants vary by ten orders of magnitude for reactions of substituent carbonyl oxides and  $\text{H}_2\text{O}$ . They reported higher rate constants for the reactions for *anti*-conformers with  $\text{H}_2\text{O}$  than the reactions of *syn*-conformers with  $\text{H}_2\text{O}$ . When both H molecules in formaldehyde oxide were substituted by  $\text{CH}_3$ , the rate constant was calculated to be  $\sim 4 \times 10^{-17} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ ; however, substituting one H molecule by  $\text{CH}_3$  and one H molecule by  $\text{CH}=\text{CH}_2$  resulted in significant smaller rate constants between  $\sim 3 \times 10^{-19}$ – $8 \times 10^{-18} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ .

Several studies suggest that the SCI loss cannot be fully accounted for with the  $\text{SCI} + \text{H}_2\text{O}$  reaction alone and that reactions

with water dimers are key to properly characterizing this loss. Ryzhkov and Aiyi (2004) suggested that reaction rates of SCI and water dimer [ $(\text{H}_2\text{O})_2$ ] are greater than those of SCI and  $\text{H}_2\text{O}$ . Ryzhkov and Aiyi (2006) reported that  $\text{SCI} + (\text{H}_2\text{O})_3$  and  $\text{SCI} + (\text{H}_2\text{O})_4$  reactions proceed at much slower rates than  $\text{SCI} + (\text{H}_2\text{O})_2$  reaction [ $(\text{H}_2\text{O})_3 = \text{water trimer}$  and  $(\text{H}_2\text{O})_4 = \text{water tetramer}$ ]. Based on computational chemistry, Vereecken et al. (2012) calculated rate constants of the reactions of  $\text{CH}_2\text{OO}$  and  $\text{CH}_3\text{C(H)OO}$  with  $(\text{H}_2\text{O})_2$  to be five orders of magnitude greater than the corresponding reactions with  $\text{H}_2\text{O}$ . Finally, Long et al. (2011) conducted a theoretical study and reported that experimental rate constant for  $\text{SCI} + \text{H}_2\text{O}$  is inconsistent with the theoretical estimates since SCI also reacts with  $(\text{H}_2\text{O})_2$ .

Several studies have incorporated this chemistry into various types of models in order to quantify its effects on atmospheric  $\text{SO}_4^{2-}$  concentrations. Boy et al. (2013) incorporated SCI into a zero-dimensional model and compared predictions to the measurements in VOC-rich environments from Finland and Germany. They employed reactions of SCI with other compounds [including  $\text{H}_2\text{O}$  but not  $(\text{H}_2\text{O})_2$ ] contained in the Master Chemical Mechanism (MCM). They used the Mauldin et al. (2012) reported rate constant for the  $\text{SCI} + \text{SO}_2$  reaction and suggested that the  $\text{SO}_2$  oxidation by SCI contributes up to 50% of the measured atmospheric sulfuric acid ( $\text{H}_2\text{SO}_4$ ). Pierce et al. (2013) incorporated the Criegee chemistry into GEOS-Chem, used the Welz et al. (2012) reported rate constant for the  $\text{SCI} + \text{SO}_2$  reaction, and a rate constant of  $1.6 \times 10^{-17} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  for the  $\text{SCI} + \text{H}_2\text{O}$  reaction following the MCM. They reported that it enhanced predicted global  $\text{H}_2\text{SO}_4$  production by 4% with as much as 100% increase in  $\text{H}_2\text{SO}_4$  concentrations in forested regions. Sarwar et al. (2013) used the Community Multiscale Air Quality (CMAQ) model to examine the impact of  $\text{SO}_2$  oxidation by SCI on regional  $\text{SO}_4^{2-}$  concentrations. They used the absolute rate constant for the  $\text{SCI} + \text{SO}_2$  reaction reported by Welz et al. (2012). In the absence of any direct measurement for the  $\text{SCI} + \text{H}_2\text{O}$  reaction, they followed the suggestion of Hatakeyama and Akimoto (1994) and derived a rate constant of  $2.0 \times 10^{-15} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  for the reaction using the relative rate constant ratio. Using this value for the  $\text{SCI} + \text{H}_2\text{O}$  reaction and the Welz et al. (2012) reported value for the  $\text{SCI} + \text{SO}_2$  reaction, they found that the SCI chemistry does not enhance  $\text{SO}_4^{2-}$  since most SCI is lost by the reaction with  $\text{H}_2\text{O}$ . However, based on a sensitivity simulation using a lower rate constant for the  $\text{SCI} + \text{H}_2\text{O}$  reaction, the study concluded that the  $\text{SCI} + \text{SO}_2$  pathway would enhance  $\text{SO}_4^{2-}$  under those conditions. Due to the uncertainty in the  $\text{SCI} + \text{H}_2\text{O}$  rate constant, they suggested further investigation. Li et al. (2013) also applied the CMAQ model to examine the role of SCI on sulfate formation over the eastern U.S. They implemented the MCM into the CMAQ model, utilized 36-km horizontal grid-resolution, and simulated air quality for 10 summer days in 2006. When they used the higher rate coefficient for the reaction of  $\text{SO}_2 + \text{SCI}$  as reported by Welz et al. (2012) and the lower rate constant for the reaction of  $\text{H}_2\text{O} + \text{SCI}$  used in the MCM, mean sulfate concentration increased by up to 18% compared to those obtained with the lower rate constant for the  $\text{SO}_2 + \text{SCI}$  reaction used in the MCM. However, when they used a higher rate constant for the reaction of  $\text{H}_2\text{O} + \text{SCI}$  (the same value used by Sarwar et al., 2013), mean sulfate concentration increased by less than 0.5% compared to those obtained with the lower rate constant used in the MCM. The range of reported rate constants for both the  $\text{SCI} + \text{SO}_2$  and the  $\text{SCI} + \text{H}_2\text{O}$  reactions and the resulting range in modeling findings suggest that more work is needed to accurately quantify the impact of this chemistry on the conversion of  $\text{SO}_2$  to  $\text{SO}_4^{2-}$ . Here, we take into account the best current information on both the  $\text{SCI} + \text{SO}_2$  and  $\text{SCI} + \text{H}_2\text{O}$  reaction rates to re-examine the impact of  $\text{SO}_2$  oxidation by SCI on  $\text{SO}_4^{2-}$  using the CMAQ model.

## 2. Methodology

### 2.1. Model framework

The impact of Criegee chemistry on  $\text{SO}_4^{2-}$  concentrations is characterized by performing two sets of model simulations, one of which includes Criegee oxidation chemistry and the other does not. Differences in the results between the two simulations are attributed to the  $\text{SO}_2$  oxidation by SCI. Sarwar et al. (2013) described the details of the CMAQ v5.0.1 model ([www.cmascenter.org](http://www.cmascenter.org)) (Binkowski and Roselle, 2003; Byun and Schere, 2006) which is also used in this study. The model uses the 2005 Carbon Bond chemical mechanism with updated toluene chemistry (CB05TU) (Whitten et al., 2010).

Model inputs are summarized briefly here. The *Weather Research and Forecasting* (version 3.3) model (Skamarock et al., 2008) is used to derive meteorological fields. The Sparse Matrix Operator Kernel Emissions (SMOKE) model (Houyoux et al., 2000) is used to prepare model-ready emissions using the 2005 National Emissions Inventory ([www.epa.gov/ttn/chief/net/2005\\_nei\\_point.pdf](http://www.epa.gov/ttn/chief/net/2005_nei_point.pdf)). The Biogenic Emissions Inventory System (BEIS) (version 3.14) is used for preparing biogenic emissions (Schwede et al., 2005).

Model simulations are performed for January, July, and August, 2006. January is used as a representative winter month while July

and August are used as representative summer months. The model performance statistics for  $\text{O}_3$  and  $\text{PM}_{2.5}$  are similar to those reported by previous investigators (Eder and Yu, 2006; Appel et al., 2007; Foley et al., 2010); thus the model is suitable for examining the impact of the  $\text{SO}_2$  oxidation by SCI on  $\text{SO}_4^{2-}$ .

### 2.2. Criegee chemistry

In previous analysis, Sarwar et al. (2013) used a single SCI to describe the impact of Criegee chemistry on  $\text{SO}_4^{2-}$ . As indicated earlier, the relative importance of this chemistry depends on the abundance of different SCI species since they have vastly different removal rates from the atmosphere. Here we extend the Criegee chemistry based on MCMv3.2 (Jenkin et al., 1997; Saunders et al., 2003; [www.mcm.leeds.ac.uk/MCM](http://www.mcm.leeds.ac.uk/MCM)) to use three different SCIs due to their different reaction rate constants with  $\text{H}_2\text{O}$  (Anglada et al., 2011). CB05TU contains 6 alkenes (ETH, OLE, IOLE, ISOP, ISPD, TERP) and their reactions with  $\text{O}_3$ ; SCI yields for these reactions are added to CB05TU. In addition, reactions for each of these SCIs with  $\text{SO}_2$  and  $\text{H}_2\text{O}$  are added to the chemistry. These reactions are summarized in Table 1.

We use  $\text{CH}_2\text{OO}$  (SCI1) to represent SCI formed from both the reaction ethene (ETH) +  $\text{O}_3$  and the reaction of terminal olefins (OLE) +  $\text{O}_3$ . The SCI yield for the ETH/ $\text{O}_3$  reaction described by Sarwar et al. (2013) is consistent with the value used in MCMv3.2

**Table 1**  
Criegee chemistry for CB05TU mechanism.

Reaction no.	Reaction	Rate constant ( $\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ )	Note
118	$\text{O}_3 + \text{OLE} = \dots + 0.319^* \text{SCI1}$	Yarwood et al. (2005)	Sarwar et al., 2013
122	$\text{O}_3 + \text{ETH} = \dots + 0.37^* \text{SCI1}$	Yarwood et al. (2005)	Sarwar et al., 2013
126	$\text{O}_3 + \text{IOLE} = \dots + 0.316^* \text{SCI2}$	Yarwood et al. (2005)	Sarwar et al., 2013
159	$\text{O}_3 + \text{ISOP} = \dots + 0.11^* \text{SCI1} + 0.11^* \text{SCI3}$	Yarwood et al. (2005)	Used isoprene chemistry in MCMv3.2
162	$\text{O}_3 + \text{ISPD} = \dots + 0.2022^* \text{SCI1} + 0.0806^* \text{SCI3}$	Yarwood et al. (2005)	Used weighted average of MACR/ MVK rxns in MCM
167	$\text{O}_3 + \text{TERP} = \dots + 0.0518^* \text{SCI1} + 0.1592^* \text{SCI3}$	Yarwood et al. (2005)	Derived following MCMv3.2
CR01	$\text{SCI1} + \text{SO}_2 = \text{SULF}$	$3.90 \times 10^{-11}$	Welz et al., 2012
CR02	$\text{SCI2} + \text{SO}_2 = \text{SULF}$	$3.90 \times 10^{-11}$	Welz et al., 2012
CR03	$\text{SCI3} + \text{SO}_2 = \text{SULF}$	$3.90 \times 10^{-11}$	Welz et al., 2012
CR04	$\text{SCI1} + \text{H}_2\text{O} =$	$2.40 \times 10^{-15}$	Sarwar et al., 2013
CR05	$\text{SCI2} + \text{H}_2\text{O} =$	$3.23 \times 10^{-18}$	Anglada et al., 2011
CR06	$\text{SCI3} + \text{H}_2\text{O} =$	$1.97 \times 10^{-18}$	Anglada et al., 2011
CR07	$\text{SCI1} + (\text{H}_2\text{O})_2 =$	$1.00 \times 10^{-10}$	Vereecken et al., 2012
CR08	$\text{SCI2} + (\text{H}_2\text{O})_2 =$	$5.17 \times 10^{-13}$	Vereecken et al., 2012
CR09	$\text{SCI3} + (\text{H}_2\text{O})_2 =$	$8.08 \times 10^{-16}$	Vereecken et al., 2012
CR10	$\text{SCI1} + \text{NO}_2 = \text{NO}_3$	$7.00 \times 10^{-12}$	Welz et al., 2012
CR11	$\text{SCI2} + \text{NO}_2 = \text{NO}_3$	$7.00 \times 10^{-12}$	Welz et al., 2012
CR12	$\text{SCI3} + \text{NO}_2 = \text{NO}_3$	$7.00 \times 10^{-12}$	Welz et al., 2012

Note:

$\text{O}_3$  = ozone, OLE = terminal alkenes, ETH = ethene, IOLE = internal alkenes, ISOP = isoprene, ISPD = isoprene reaction product, TERP = monoterpene, SCI1 =  $\text{H}_2\text{COO}$  (Anglada et al., 2011; Vereecken et al., 2012), SCI2 = *syn*- $\text{CH}_3\text{CHOO}$  (Anglada et al., 2011; Vereecken et al., 2012), SCI3 = *syn*- $\text{CH}_3$ -anti-(*cis*- $\text{CH}=\text{CH}_2$ )  $\text{CHOO}$  (Anglada et al., 2011; Vereecken et al., 2012),  $\text{SO}_2$  = sulfur dioxide, SULF = sulfuric acid,  $\text{NO}_2$  = nitrogen dioxide,  $\text{NO}_3$  = nitrate radical,  $\text{H}_2\text{O}$  = water monomer,  $(\text{H}_2\text{O})_2$  = water dimer, MCM = Master Chemical Mechanism.

OLE is a lumped species, represents terminal olefins, and is composed of two carbons. Sarwar et al. (2013) derived a yield of 0.319 for OLE. However, they used only one SCI in the mechanism. Since three SCIs are used here, we use  $\text{O}_3 + \text{OLE} = 0.319^* \text{SCI1}$ .

ETH represents ethene and is composed of two carbons. Sarwar et al. (2013) derived a yield of 0.37 for ETH which is consistent with the value used in MCM. However, they used only one SCI in the mechanism. Since three SCIs are used here, we use  $\text{O}_3 + \text{ETH} = 0.37^* \text{SCI1}$ .

IOLE is a lumped species, represents internal olefins, and is composed of four carbons. Sarwar et al. (2013) derived a yield of 0.316 for IOLE. However, they used only one SCI in the mechanism. Since three SCIs are used here, we use  $\text{O}_3 + \text{IOLE} = 0.316^* \text{SCI2}$ .

ISOP represents isoprene for which Sarwar et al. (2013) derived a yield of 0.354. Here, we calculate the yields following MCM:  $\text{O}_3 + \text{ISOP} = 0.11^* \text{SCI1} + 0.11^* \text{SCI3}$ .

ISPD is a lumped species, represents isoprene reaction products (methyl acrolein, methyl vinyl ketone, unsaturated aldehydes, etc.) and is composed of four carbons. Based on MCM, we derive following yields for methyl acrolein:  $\text{O}_3 + \text{METHYL ACROLEIN} = 0.3256^* \text{SCI1} + 0.0216^* \text{SCI3}$  and methyl vinyl ketone:  $\text{O}_3 + \text{MVK} = 0.12^* \text{SCI1} + 0.12^* \text{SCI3}$ . Sarwar et al. (2013) derived a yield of 0.472 for ISPD. Here we use weighted average yields of methyl acrolein, methyl vinyl ketone, and unsaturated aldehydes following Carter (1996):  $\text{O}_3 + \text{ISPD} = 0.1045^* \text{SCI1} + 0.0741^* \text{SCI3}$ . We use 10% for methyl acrolein, 60% for methyl vinyl ketone, 30% for unsaturated aldehydes. SCI yields for unsaturated aldehydes were taken equal to those of methyl acrolein.

TERP is a lumped species, represents monoterpenes, and is composed of ten carbons. Sarwar et al. (2013) derived a yield of 0.268 for TERP. Here, we use the following equation to calculate SCI yield for TERP (Carter, 2000).

SCI yield for TERP =  $0.4^* \text{APINENE} + 0.25^* \text{BPINENE} + 0.1^* \text{DLIMONENE} + 0.15^* \text{3-CARENE} + 0.1^* \text{SABINENE}$ . Following MCM, we use  $\text{APINENE} = 0.2^* \text{SCI3}$ ,  $\text{BPINENE} = 0.148^* \text{SCI1} + 0.102^* \text{SCI3}$ ,  $\text{DLIMONENE} = 0.135^* \text{SCI3}$ . SCI yields for 3-CARENE and SABINENE are not available in MCM. Ma et al. (2009) suggested that SCI yield for 3-CARENE should be lower than APINENE. For this work, we assume that it is equal to that of APINENE. For SABINENE, we assume that SCI yield is equal to that of BPINENE since their structures are similar.

and is also used in this study. The yield of SCI1 formed from the reaction of OLE and O<sub>3</sub> is also taken from Sarwar et al. (2013).

SCI2 is produced from the reaction of O<sub>3</sub> + internal olefin (IOLE), a four carbon lumped alkene chemical species. The reaction of IOLE and O<sub>3</sub> produces an ozonide that breaks down to generate a two carbon SCI (CH<sub>3</sub>CHOO). Anglada et al. (2011) suggested two different isomers for CH<sub>3</sub>CHOO: *syn*-CH<sub>3</sub>CHOO and *anti*-CH<sub>3</sub>CHOO. They reported a rate constant of  $3.23 \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  for the reaction of *anti*-CH<sub>3</sub>CHOO with H<sub>2</sub>O and a rate constant of  $3.23 \times 10^{-18} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  for the reaction of *syn*-CH<sub>3</sub>CHOO with H<sub>2</sub>O. Here, we use *syn*-CH<sub>3</sub>CHOO (SCI2) to represent the SCI from IOLE/O<sub>3</sub> reaction to minimize the loss of SCI by H<sub>2</sub>O and maximize SO<sub>4</sub><sup>2-</sup> production, and the yield described by Sarwar et al. (2013). As discussed later, the choice of the rate constant is irrelevant since its impact on SO<sub>4</sub><sup>2-</sup> production is small.

Following the detailed chemistry in MCMv3.2, we supplement the CB05TU to include SCI yield of isoprene (ISOP). The reaction of ISOP and O<sub>3</sub> produces several different SCIs including CH<sub>2</sub>OO (SCI1) and four-carbon SCIs. Several different isomers are possible for the four-carbon SCIs and rate constants of their reactions with H<sub>2</sub>O also vary. Anglada et al. (2011) described the rate constants for nine different monomers. Seven of the rate constants are on the order of  $\sim 10^{-18} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ , one rate constant is  $\sim 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  while the other rate constant is  $\sim 10^{-19} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ . We represent the four-carbon SCI by using *syn*-CH<sub>3</sub>-anti-(*cis*-CH=CH<sub>2</sub>) CHOO (SCI3) following Anglada et al. (2011).

CB05TU uses a lumped species (ISPD) to represent isoprene reaction products. We use SCI3 to represent SCI from the ISPD/O<sub>3</sub> reaction. We apply the procedure described by Carter (1996) for deriving the SCI yield from the ISPD/O<sub>3</sub> reaction. Carter (1996) used 10% of methacrolein (MACR), 60% of methyl vinyl ketone (MVK) and 30% of unsaturated C5-aldehydes to derive parameters for ISPD/O<sub>3</sub> reaction. We use the SCI yields in MCMv3.2 for reactions of MACR and MVK with O<sub>3</sub>. For the SCI yield of unsaturated C5-aldehyde/O<sub>3</sub> reaction, we use the value of MACR/O<sub>3</sub> reaction. Such assumptions have been used in developing other chemical mechanisms (Goliff et al., 2013).

We follow the detailed chemistry in MCMv3.2 to refine the SCI of TERP/O<sub>3</sub> reaction and their yields. Carter (2000) described the chemistry of TERP using weighted averaging of  $\alpha$ -pinene,  $\beta$ -pinene,  $\delta$ -limonene, 3-carene, and sabinene. We use the SCI yields in MCMv3.2 for reactions of O<sub>3</sub> with  $\alpha$ -pinene,  $\beta$ -pinene, and  $\delta$ -limonene. The detailed chemistry of 3-carene is not available in MCMv3.2. Ma et al. (2009) conducted chamber experiments involving 3-carene and O<sub>3</sub> and suggested that SCI yield of 3-carene should be lower than that of  $\alpha$ -pinene. We use the SCI yield of  $\alpha$ -pinene for 3-carene. The detailed chemistry of sabinene is not available. However, the structure of sabinene is similar to  $\beta$ -pinene so we use the SCI yield to be the same as that for  $\beta$ -pinene. SCI3 is used to represent SCI from the TERP/O<sub>3</sub> reaction.

For reactions of SO<sub>2</sub> with SCI1, SCI2, and SCI3, we employ a single rate constant reported by Welz et al. (2012). For SCI1 + H<sub>2</sub>O we apply the rate constant of  $2.40 \times 10^{-15} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  (Table 1) suggested by Sarwar et al. (2013) which is two times lower than the upper limit measured by Welz et al. (2012) and slightly lower than the theoretical estimates of  $3\text{--}5 \times 10^{-15} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  reported by Anglada et al. (2011). However, this value is greater than the value of  $1.0 \times 10^{-17} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  used in MCMv3.2. For SCI2 + H<sub>2</sub>O and SCI3 + H<sub>2</sub>O we use rate constants of  $3.23 \times 10^{-18}$  and  $1.97 \times 10^{-18}$  respectively (Anglada et al., 2011). Our rate constant for SCI3 + H<sub>2</sub>O is similar to the values of  $2.0\text{--}6.0 \times 10^{-18} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  used in MCMv3.2.

We also implement the reactions of SCI1, SCI2, SCI3 with (H<sub>2</sub>O)<sub>2</sub>. Vereecken et al. (2012) reported a rate constant ratio of  $3.5 \times 10^5$  for

the reactions of SCI1 with (H<sub>2</sub>O)<sub>2</sub> and H<sub>2</sub>O,  $1.6 \times 10^5$  for the reactions of SCI2 with (H<sub>2</sub>O)<sub>2</sub> and H<sub>2</sub>O, and  $4.1 \times 10^2$  for the reactions of SCI3 with (H<sub>2</sub>O)<sub>2</sub> and H<sub>2</sub>O. We use these ratios to calculate rate constants for the reactions of SCI1, SCI2, and SCI3 with (H<sub>2</sub>O)<sub>2</sub>. Similar to Vereecken et al. (2012), we also constrain the estimated rate constant with a physical upper limit of  $1.0 \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ . We calculate (H<sub>2</sub>O)<sub>2</sub> using  $[(\text{H}_2\text{O})_2] = K_{\text{eq}} \times [\text{H}_2\text{O}]$  (Shillings et al., 2011), where  $K_{\text{eq}}$  ( $0.04 \text{ atm}^{-1}$ ) is the equilibrium constant for dimer formation (Vereecken et al., 2012). The model uses WRF predicted H<sub>2</sub>O mixing ratios. It should be noted that such reactions are not used in MCMv3.2. Previous modeling studies (Boy et al., 2013; Pierce et al., 2013; Sarwar et al., 2013; Li et al., 2013) did not use such reactions either.

While not important, we also implement the reaction of SCI1, SCI2, and SCI3 with NO<sub>2</sub> for completeness (rate constant taken from Welz et al., 2012). SCI can also react with other chemical species; however, they generally do not play substantial roles in affecting the fate of SCI in the atmosphere (Vereecken et al., 2012) and therefore are not considered in this study.

### 3. Results and discussions

#### 3.1. Impact of the SO<sub>2</sub> oxidation by SCI on SO<sub>4</sub><sup>2-</sup>

##### 3.1.1. Domain-wide mean SO<sub>4</sub><sup>2-</sup> concentrations without and with SCI initiated reaction

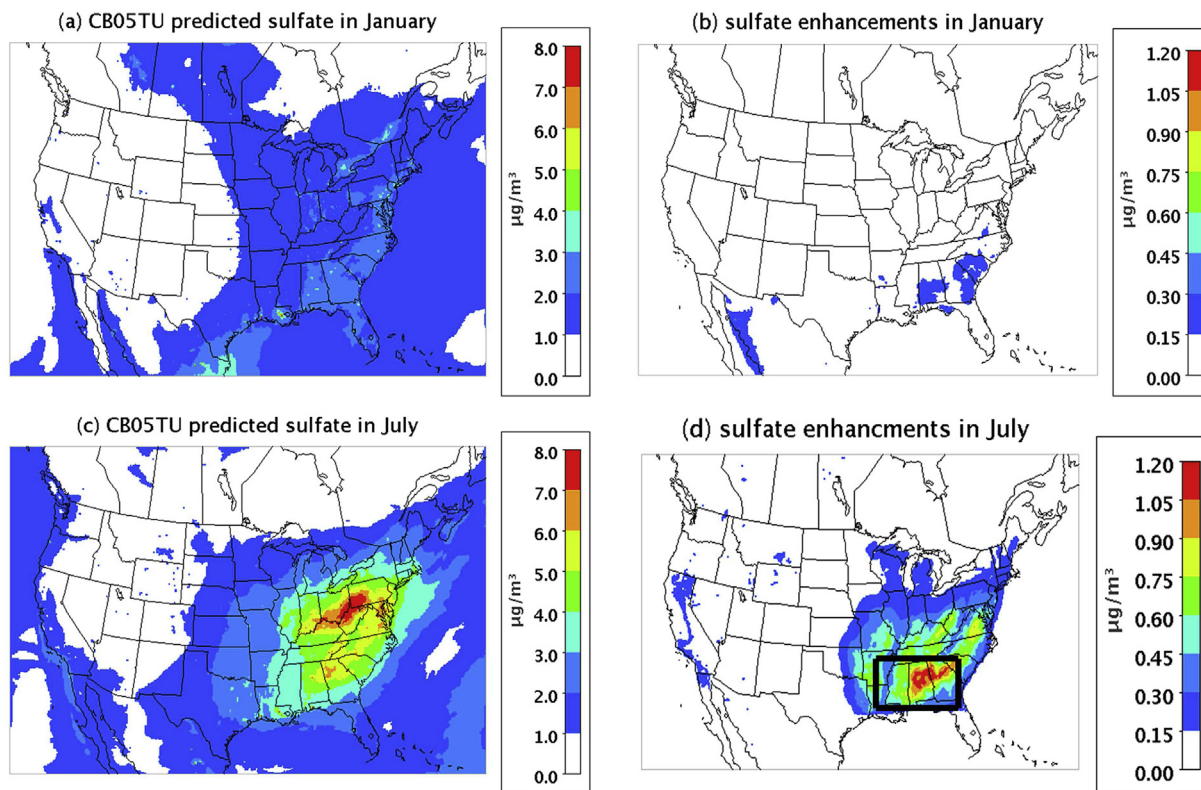
The surface-level domain-wide monthly mean SO<sub>4</sub><sup>2-</sup> concentration obtained without the SCI reactions is  $1.11 \mu\text{g}/\text{m}^3$  in January,  $1.60 \mu\text{g}/\text{m}^3$  in July, and  $1.59 \mu\text{g}/\text{m}^3$  in August. The oxidation of SO<sub>2</sub> by SCI enhances the domain-wide monthly mean SO<sub>4</sub><sup>2-</sup> concentration by  $0.05 \mu\text{g}/\text{m}^3$  in January,  $0.10 \mu\text{g}/\text{m}^3$  in July, and  $0.08 \mu\text{g}/\text{m}^3$  in August. While the SO<sub>2</sub> oxidation by SCI enhances SO<sub>4</sub><sup>2-</sup> both in winter and summer months, it produces more SO<sub>4</sub><sup>2-</sup> in summer than in winter.

##### 3.1.2. Spatial and seasonal variation of the SO<sub>4</sub><sup>2-</sup> enhancements due to SO<sub>2</sub> oxidation by SCI

Predicted monthly mean SO<sub>4</sub><sup>2-</sup> concentrations without the SCI initiated reactions and enhancements with the SCI initiated pathway are shown in Fig. 1. In winter, the SO<sub>2</sub> oxidation by SCI increases monthly mean SO<sub>4</sub><sup>2-</sup> in the southeastern U.S. and Mexico by  $0.15\text{--}0.30 \mu\text{g}/\text{m}^3$ . However, it increases SO<sub>4</sub><sup>2-</sup> by  $0.15\text{--}1.20 \mu\text{g}/\text{m}^3$  over a large area across the eastern U.S. during summer months. The impacts are especially pronounced in the southeastern U.S. where summertime enhancements exceed  $1.0 \mu\text{g}/\text{m}^3$ . Criegee chemistry leads to smaller increases in SO<sub>4</sub><sup>2-</sup> ( $0.15\text{--}0.3 \mu\text{g}/\text{m}^3$ ) in California and other areas in western U.S. during summer months. In addition to causing larger enhancements in SO<sub>4</sub><sup>2-</sup> in the summer than in the winter, Criegee chemistry also leads to increases over a more extensive geographic area during the summer than during the winter.

In the model simulations, SO<sub>4</sub><sup>2-</sup> enhancements are primarily the result of the SO<sub>2</sub> oxidation by SCI3 which is produced from the reactions of biogenic derived alkenes and O<sub>3</sub>. At 1.0 atm and 50% relative humidity, we calculate that most of SCI1 (>99%) and SCI2 (>90%) are lost by their reactions with H<sub>2</sub>O and (H<sub>2</sub>O)<sub>2</sub> and thus are unavailable for reacting with SO<sub>2</sub>. In contrast, only  $\sim 10\text{--}20\%$  of SCI3 is lost by its reactions with H<sub>2</sub>O and (H<sub>2</sub>O)<sub>2</sub> under similar conditions.

Although not shown here, predicted SCI3 concentrations in winter are small due to low emissions of biogenic precursor VOCs. In contrast during summer, larger biogenic emissions result in much higher simulated SCI3 concentrations. While predicted summertime SCI3 concentrations are lower than HO levels, the production rates of SO<sub>4</sub><sup>2-</sup> via the SCI initiated reaction are similar to



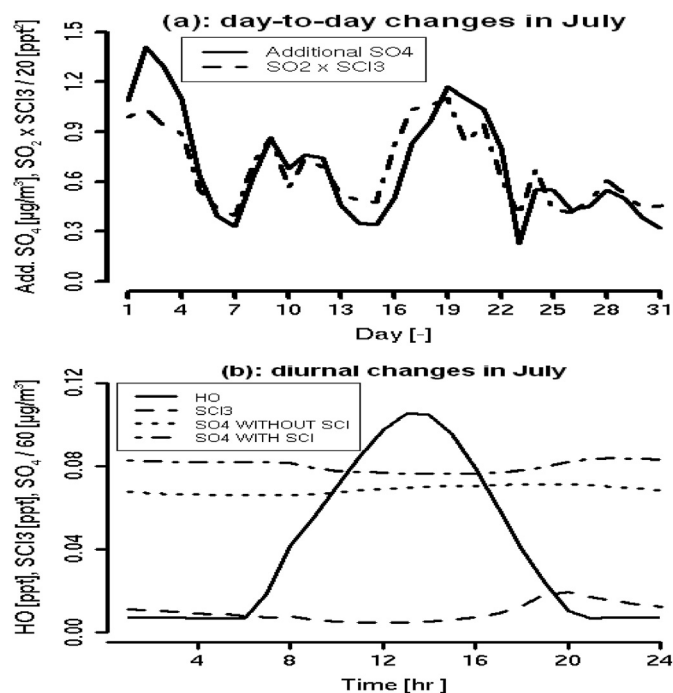
**Fig. 1.** (a) Predicted monthly mean  $\text{SO}_4^{2-}$  concentrations without SCI in January. (b) SCI initiated monthly mean enhancements in January. (c) predicted monthly mean  $\text{SO}_4^{2-}$  concentrations without SCI in July. (d) SCI initiated monthly mean enhancements in July. Biogenic emissions derived from BEIS. Predicted values occurring within the area outlined in Fig. 1(d) are averaged for Fig. 2. Observed values occurring within the area outlined in Fig. 1(d) are used for comparing predicted  $\text{SO}_4^{2-}$  (obtained with BEIS emissions) with observed data in Figs. 5 and 6.

or greater than those with the HO initiated pathway. As a reference, the rate constant for the reaction of  $\text{SO}_2 + \text{HO}$  at 1.0 atm and 298 K is  $9.5 \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ .

### 3.1.3. Temporal variation of the $\text{SO}_4^{2-}$ enhancements

We examine the day-to-day variability of the SCI initiated  $\text{SO}_4^{2-}$  enhancements by calculating an area-wide daily mean value over 490,000  $\text{km}^2$  in southeastern U.S. [see black rectangle in Fig. 1(d)]. Predicted area-wide day-to-day variations in daily mean  $\text{SO}_4^{2-}$  enhancements due to the SCI reaction are shown in Fig. 2a for July. Over this area of the Southeast, the SCI chemistry enhances daily mean summer  $\text{SO}_4^{2-}$  by 0.2–1.4  $\mu\text{g}/\text{m}^3$ . Day to day variation in  $\text{SO}_4^{2-}$  enhancements track the product of  $\text{SO}_2$  and SCI3 ( $r = 0.89$ ) (Fig. 2a) which supports the conclusion that the SCI3 initiated reaction is responsible for the  $\text{SO}_4^{2-}$  enhancements.

Monthly average diurnal variations are shown for the same region examined for daily variations (Fig. 2b). Predicted  $\text{SO}_4^{2-}$  concentrations without the SCI initiated pathway are relatively constant throughout the day. Although  $\text{SO}_4^{2-}$  concentrations are enhanced by Criegee chemistry at all hours, the enhancements are greater at night. This diurnal pattern is driven by the relative availability of the two oxidants. Predicted HO concentrations are relatively small at night and peak during the day while predicted SCI3 concentrations are relatively constant. Predicted SCI3 concentrations are greater than the nighttime HO values leading to greater nighttime production rates of  $\text{SO}_4^{2-}$  via the SCI initiated pathway than via the HO initiated pathway. Conversely, predicted SCI3 concentrations are substantially lower than the daytime HO values, causing daytime production rates of  $\text{SO}_4^{2-}$  to come predominantly from the HO initiated pathway.



**Fig. 2.** (a) Time series of predicted daily mean enhanced  $\text{SO}_4^{2-}$  due to the SCI chemistry and  $\text{SO}_2 \times \text{SCI3}/20$  for the area shown in Fig. 1(d). (b) diurnal changes of predicted  $\text{SO}_4^{2-}$  without and with the SCI chemistry along with HO and SCI3 for the same area. BEIS emissions were used.  $\text{SO}_2 \times \text{SCI3}$  has been divided by 20 and  $\text{SO}_4^{2-}$  by 60 to fit into scale.

### 3.2. Impact of the SCI initiated $\text{SO}_2$ oxidation on $\text{SO}_4^{2-}$ with alternate biogenic emissions estimates

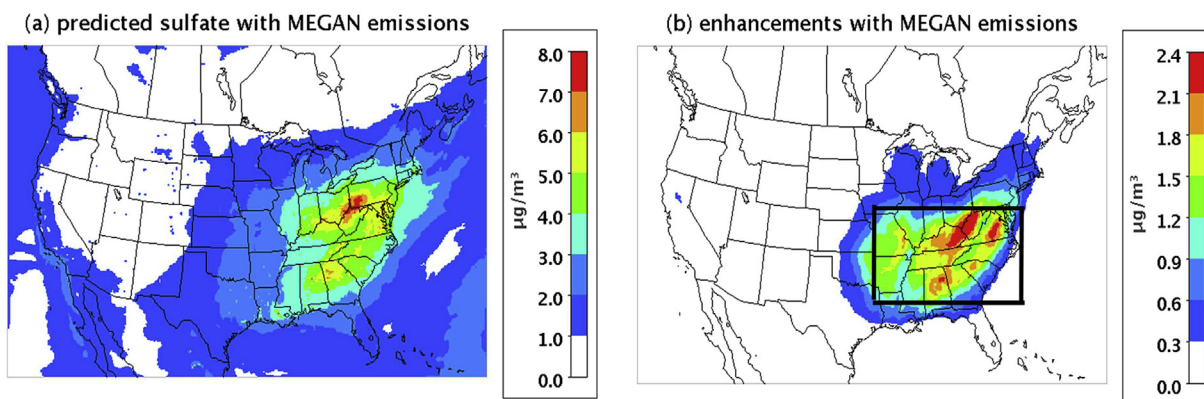
Since the SCI initiated  $\text{SO}_2$  oxidation enhances more  $\text{SO}_4^{2-}$  in summer, we performed two additional simulations in July using biogenic emissions inputs derived from the Model of Emissions of Gases and Aerosols from Nature (Guenther et al., 2012): one without the SCI initiated reaction and one with the SCI initiated reactions. Predicted monthly mean  $\text{SO}_4^{2-}$  concentrations from the MEGAN sensitivity without the SCI initiated reaction and related enhancements are presented in Fig. 3. The domain-wide monthly mean  $\text{SO}_4^{2-}$  concentration obtained without the SCI initiated reaction is  $1.53 \mu\text{g}/\text{m}^3$  (slightly lower than the  $1.6 \mu\text{g}/\text{m}^3$  obtained using BEIS emissions). The SCI initiated reaction enhances the domain-wide monthly mean  $\text{SO}_4^{2-}$  by  $0.20 \mu\text{g}/\text{m}^3$  (twice as much as the enhancement with BEIS emissions). With biogenic emissions estimates of MEGAN, the SCI initiated reaction increases  $\text{SO}_4^{2-}$  concentrations by  $1.2\text{--}2.4 \mu\text{g}/\text{m}^3$  in the eastern U.S., also about two times greater than the enhancements in the eastern U.S. with emissions estimates from BEIS. These differences are due to the much larger eastern U.S. biogenic emissions estimates from MEGAN than from BEIS. Pouliot and Pierce (2008) examined emissions from BEIS and MEGAN and reported that MEGAN produces 60% more isoprene emissions than those from BEIS. Carlton and Baker (2011) compared modeled isoprene concentrations to measurements in the Ozark mountains and reported that MEGAN emissions led to model over-predictions of surface isoprene while BEIS emissions led to model under-predictions of surface isoprene. Hogrefe et al. (2011) also studied the impact of biogenic emission uncertainties on ozone and fine particulate matter in eastern U.S. and reported that MEGAN estimated biogenic emissions are much greater than those estimated by BEIS. Predicted isoprene concentrations with MEGAN estimated emissions were much greater than the observed levels while predicted isoprene concentrations with BEIS estimated emissions were closer to the observed levels. The increased biogenic VOC concentrations affect  $\text{SO}_4^{2-}$  chemistry in several ways. First, HO levels are somewhat depressed in the MEGAN case due to more loss via  $\text{HO} + \text{VOC}$  reactions. Predicted  $\text{H}_2\text{O}_2$  levels are greater with the MEGAN case. These lead to slightly lower  $\text{SO}_4^{2-}$  concentrations when no Criegee chemistry was simulated. Second, and more significantly, increased biogenic emissions lead to enhanced SCI3 levels. Collectively, these suggest that the simulated relative importance of Criegee chemistry on  $\text{SO}_4^{2-}$  formation is heavily dependent on biogenic emissions estimates.

### 3.3. Impact of the $\text{SO}_2$ oxidation by SCI with alternative rate constants

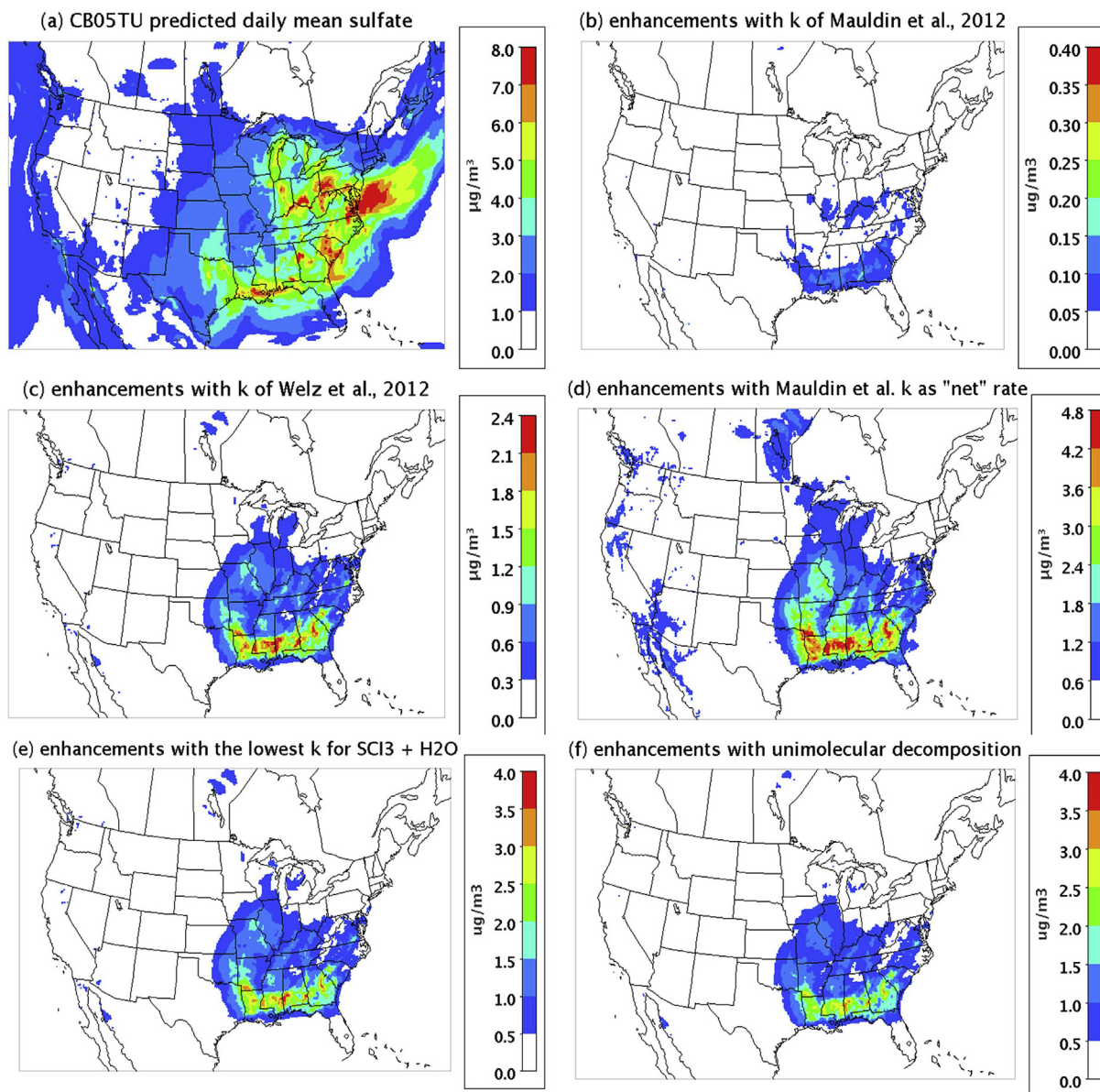
We performed a series of four sensitivity simulations to investigate the impact of uncertain rate constants involving SCIs. First, an additional simulation using BEIS estimated emissions was completed with the lower rate constant reported by Mauldin et al. (2012) for the  $\text{SCI3} + \text{SO}_2$  reaction (65 times slower than the Welz et al., 2012 value). The rate constants for  $\text{SCI1} + \text{SO}_2$  and  $\text{SCI2} + \text{SO}_2$  reactions are not changed for this simulation. Mauldin et al. (2012) did not report any rate constant for the reaction of SCI and  $\text{H}_2\text{O}$ ; thus, we assume the rate constants in Table 1 for this sensitivity. The use of the lower rate constant for the  $\text{SCI3} + \text{SO}_2$  reaction only marginally increases  $\text{SO}_4^{2-}$  concentrations. For example, daily mean  $\text{SO}_4^{2-}$  concentrations without the SCI initiated reaction and enhancements obtained with the SCI initiated reaction for July 1 are shown in Fig. 4(a–b). Daily mean enhancements obtained with the lower rate constant ranged from  $0.05$  to  $0.15 \mu\text{g}/\text{m}^3$ , compared to enhancements of up to  $0.3\text{--}2.6 \mu\text{g}/\text{m}^3$  in the original simulation (Fig. 4(c)).

Boy et al. (2013) implied that Mauldin et al. (2012) value is not an absolute rate constant for the reaction of SCI with  $\text{SO}_2$ , but rather an effective rate constant for  $\text{SO}_4^{2-}$  production by the SCI reaction that already accounts for the loss with other chemical compounds. Thus, we perform a second sensitivity simulation using  $\text{SCI3} + \text{SO}_2$  and without any reactions of  $\text{SCI3}$  with  $\text{H}_2\text{O}$ ,  $(\text{H}_2\text{O})_2$ , and  $\text{NO}_2$ . The resulting daily mean  $\text{SO}_4^{2-}$  enhancements for July 1 are shown in Fig. 4(d). This new “net” reaction rate produces  $\text{SO}_4^{2-}$  enhancements that are  $\sim 2$  times greater than the enhancements obtained with the higher rate constant of Welz et al. (2012). Thus, further clarification on the use of the lower rate constant reported by Mauldin et al. (2012) is needed.

Third, as indicated earlier, Anglada et al. (2011) calculated rate constants for the reactions of different SCIs and  $\text{H}_2\text{O}$ . The lowest calculated value was  $2.93 \times 10^{-19} \text{ molecules cm}^{-3} \text{ s}^{-1}$ . We performed another simulation by using this lowest value for the rate constant for the reaction of  $\text{SCI3}$  and  $\text{H}_2\text{O}$  and by additionally adjusting the rate constant for the reaction of  $\text{SCI3}$  and  $(\text{H}_2\text{O})_2$ . All other conditions were unchanged. Predicted daily mean sulfate enhanced by  $\sim 1.8\text{--}4.0 \mu\text{g}/\text{m}^3$  in the southeast U.S. (Fig. 4(e)) while the enhancements obtained with the higher rate constant for  $\text{SCI3}$  and  $\text{H}_2\text{O}$  were  $\sim 1.0\text{--}2.6 \mu\text{g}/\text{m}^3$  in the southeast U.S. (Fig. 4(c)). Thus, the use of the lower rate constant for  $\text{SCI3} + \text{H}_2\text{O}$  produces substantially greater sulfate which further emphasizes the role that the  $\text{SCI3}/\text{water}$  reaction plays in enhancing sulfate.



**Fig. 3.** (a) Predicted monthly mean  $\text{SO}_4^{2-}$  concentrations in July without SCI chemistry (MEGAN emissions) (b) SCI initiated monthly mean  $\text{SO}_4^{2-}$  enhancements in July (MEGAN emissions). Observed values occurring within the area outlined in Fig. 3(b) are used for comparing predicted  $\text{SO}_4^{2-}$  (obtained with MEGAN emissions) with observed data in Figs. 5 and 6.



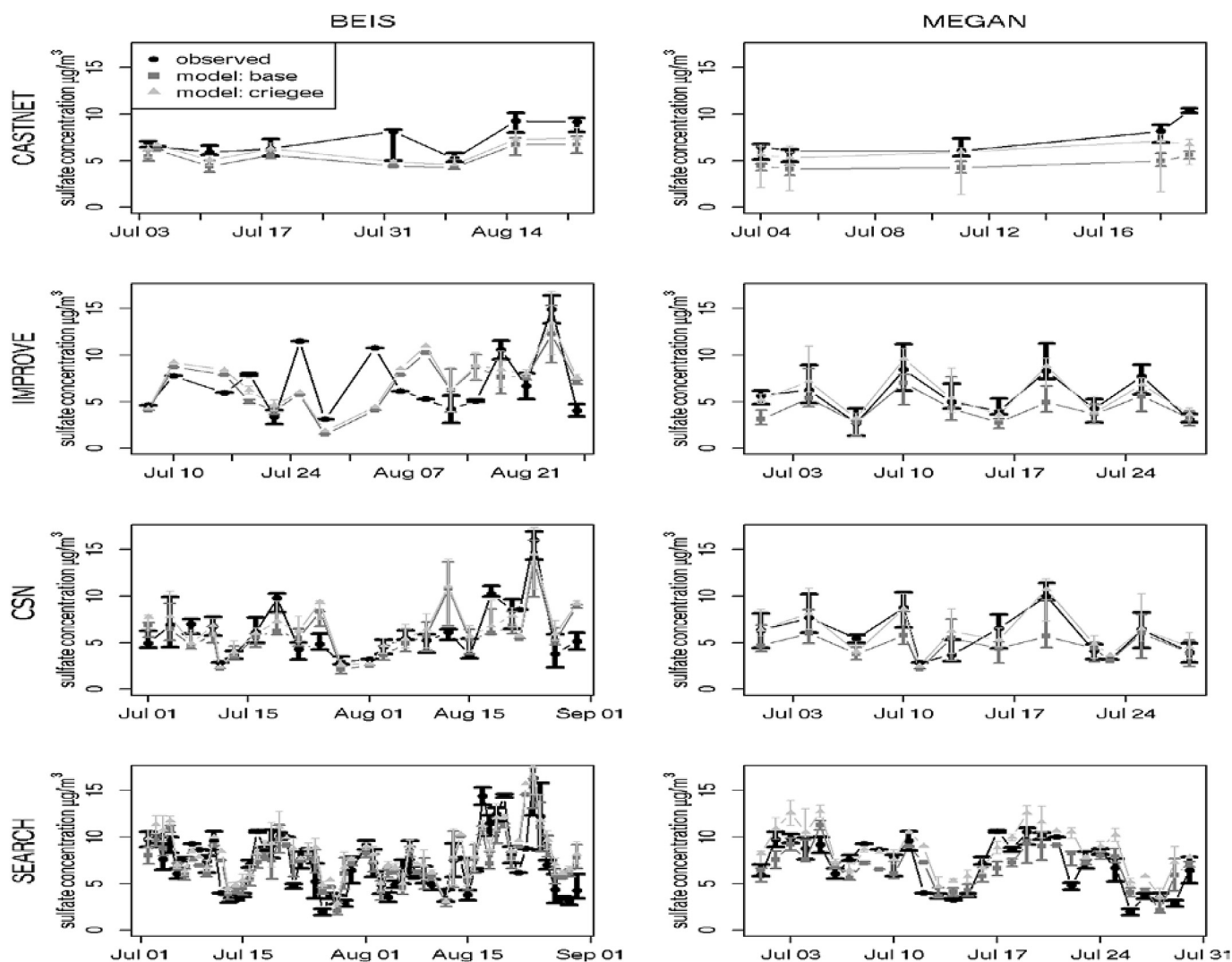
**Fig. 4.** (a) Predicted daily mean  $\text{SO}_4^{2-}$  concentration on July 1 without SCI chemistry. (b) SCI initiated daily mean enhancements with Mauldin et al. (2012) reported rate constant. (c) SCI initiated daily mean enhancement with Welz et al. (2012) reported rate constant. (d) SCI initiated daily mean enhancements obtained with the Mauldin et al. (2012) reported value as "net" rate constant [the rate constant reported by Mauldin et al., 2012 for the  $\text{SO}_2 + \text{SCI}$  reaction was used as "net" rate constant without any loss of SCI3 by reactions with  $\text{H}_2\text{O}$ ,  $(\text{H}_2\text{O})_2$ , and  $\text{NO}_2$ ]. (e) SCI initiated daily mean enhancement with Welz et al. (2012) reported rate constant for  $\text{SO}_2 + \text{SCI}$  reactions and the lowest rate constant for the  $\text{SCI3} + \text{H}_2\text{O}$  reaction. (f) SCI initiated daily mean enhancement with Welz et al. (2012) reported rate constant for  $\text{SO}_2 + \text{SCI}$  reactions, the lowest rate constant for the  $\text{SCI3} + \text{H}_2\text{O}$  reaction, and unimolecular decomposition of SCIs. Biogenic emissions are derived from BEIS.

Vereecken et al. (2012) suggested that SCIs can also undergo unimolecular decomposition and reported first order rate constants for their reactions. The fourth sensitivity simulation was performed by accounting for unimolecular decomposition of SCI1, SCI2, and SCI3 with the following first order rate constants:  $0.30 \text{ s}^{-1}$  for SCI1 (Fenske et al., 2000),  $0.388 \text{ s}^{-1}$  for SCI2 (Vereecken et al., 2012), and  $0.21 \text{ s}^{-1}$  for SCI3 (Vereecken et al., 2012). For this simulation, we used the lowest rate constant for the reaction of SCI3 and  $\text{H}_2\text{O}$  and appropriately adjusted the rate constant for the reaction of SCI3 and  $(\text{H}_2\text{O})_2$  as was done for the previous sensitivity simulation. Predicted daily mean sulfate enhancements are shown in Fig. 4(f) and ranged between  $\sim 1.2$  and  $3.5 \text{ µg/m}^3$  in the southeast U.S. Enhancements decreased by up to  $\sim 0.5 \text{ µg/m}^3$  compared to the enhancements obtained with the lower rate constant for the reaction

of SCI3 and  $\text{H}_2\text{O}$  alone as shown in Fig. 4(e) due to the loss of SCI3 via unimolecular decomposition. This further underscores the need for accounting all important loss pathways of SCI for accurately examining the impact of SCI initiated  $\text{SO}_2$  oxidation on sulfate.

#### 3.4. Comparison of predicted $\text{SO}_4^{2-}$ with observed data

Comparisons with ambient data are conducted to determine whether Criegee chemistry produces more realistic modeled  $\text{SO}_4^{2-}$  concentrations. Comparisons are made between modeled and observed values at monitoring locations in the Eastern U.S. defined by the black rectangles in Figs. 1(d) and 3(b) for the BEIS and MEGAN cases, respectively. Measurements came from the Clean Air Status and Trends Network (CASTNET), the Interagency Monitoring

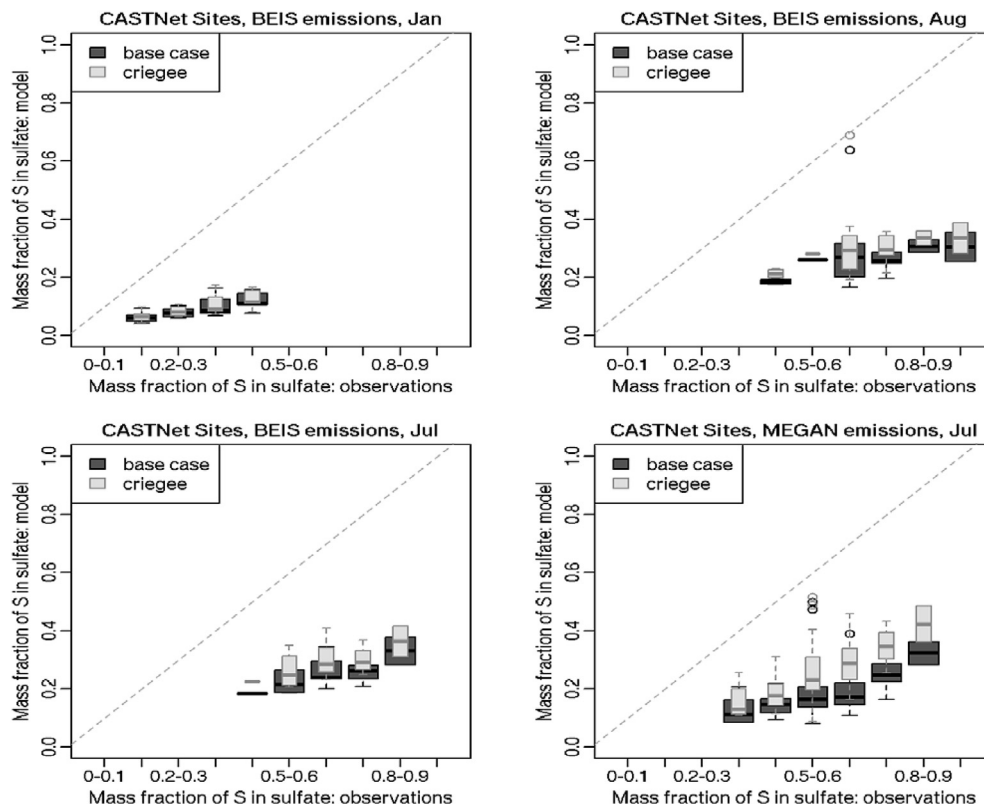


**Fig. 5.** A comparison of predicted  $\text{SO}_4^{2-}$  concentrations to observations from the CASTNET sites (top), the IMPROVE sites (second from top), the CSN sites (2nd from bottom), and the SEARCH sites (bottom). Results from model runs using BEIS emission are shown in left-hand panels and results from model runs using MEGAN emissions are shown in right-hand panels. Observed values occurring within the areas outlined in [Figures 1\(d\)](#) and [3\(b\)](#) are used for comparing predicted  $\text{SO}_4^{2-}$  with observed data in left and right-hand plots, respectively. Circle, square, and triangle symbols depict the median value across all sites for each date, while whiskers extend to the 25th and 75th percentile values at locations of monitoring sites for each date.

of Protected Visual Environments (IMPROVE), the Chemical Speciation Network (CSN), and the Southeastern Aerosol Research and Characterization (SEARCH) monitoring sites in southeastern U.S. It should be noted that CASTNET measurements are reported as weekly averages while IMPROVE and CSN measurements are reported as daily averages once every three days. SEARCH measurements are made hourly but were aggregated to 24-h averages for this analysis for comparison with other networks. [Fig. 5](#) shows that model predictions without the SCI initiated pathway are lower than the observed data for CASTNET, IMPROVE, and CSN monitoring networks (BEIS emissions) while predictions obtained with the SCI initiated pathway generally agree better with the observed concentrations. At the SEARCH sites, the results are mixed than for the measurements made in other networks. Although the  $\text{SO}_4^{2-}$  predicted in the base simulation (BEIS emissions) was generally lower than observed concentrations, there are a few time periods in which the model over-predicted  $\text{SO}_4^{2-}$ . During times of model under-predictions, the SCI initiated pathway tends to improve model predictions but during the less frequent period of model over-predictions, the Criegee chemistry degrade

performance slightly. Similar improvements in model performance are seen in the MEGAN case for CASTNET, IMPROVE, and CSN monitoring sites. At SEARCH sites, the Criegee chemistry sometime improved performance but also sometimes lead to model over-predictions for  $\text{SO}_4^{2-}$  similar in magnitude to the under-predictions in the base simulation. In the BEIS simulations, the model underestimation of  $\text{SO}_4^{2-}$  concentrations persists despite the Criegee enhancements. In contrast, this model underestimation in the MEGAN simulations is largely eliminated by the Criegee enhancements. As previously indicated, MEGAN estimated biogenic emissions are much higher than those obtained with BEIS and enhanced  $\text{SO}_4^{2-}$  predictions shown in [Fig. 5](#) are the direct result of these higher biogenic emissions estimates from MEGAN.

Availability of both  $\text{SO}_2$  and  $\text{SO}_4^{2-}$  measurements at the CASTNET and SEARCH sites allows an investigation into the model's ability to capture the amount of conversion from  $\text{SO}_2$  to  $\text{SO}_4^{2-}$ . [Figs. 6](#) and [7](#) compare the observed and predicted mass fraction of sulfur in  $\text{SO}_4^{2-}$  ( $(32 \times \text{SO}_4)/96$ ) /  $(((32 \times \text{SO}_2)/64) + ((32 \times \text{SO}_4)/96))$  at CASTNET and SEARCH sites, respectively. Mass fractions of sulfur in  $\text{SO}_4^{2-}$  without the SCI reaction are lower than the observed data



**Fig. 6.** A comparison of predicted mass fraction of sulfur in  $\text{SO}_4^{2-}$  (BEIS emissions) to observed data from CASTNET sites in January (top left), July (bottom left), and August (top right), and a comparison of predicted mass fraction of sulfur in  $\text{SO}_4^{2-}$  (MEGAN emissions) to observed data from CASTNET sites in July (bottom right). Observed values occurring within the areas outlined in Figs. 1(d) and 3(b) are used for comparing predicted  $\text{SO}_4^{2-}$  with observed data in BEIS emissions and MEGAN emissions panels, respectively. Centerline of the boxplots shows the mean modeled value for each bin of observed values. Boxes extend to 25th and 75th percentile values, whiskers extend to 1.5 times the interquartile range, and dots show outlier values.

which suggests missing  $\text{SO}_2$  oxidation pathways in the model. Mass fractions of sulfur in  $\text{SO}_4^{2-}$  with the SCI initiated  $\text{SO}_2$  reaction are slightly greater than those obtained without the SCI reaction in the BEIS case and substantially greater in the MEGAN case. For all simulations, the addition of Criegee chemistry brings the amount of  $\text{SO}_2$  conversion closer to observations. However, the modeled mass fraction is still lower than the measured fraction, suggesting either additional missing chemical pathways or underestimates of reaction rates or oxidant concentrations. Note that iron and manganese catalyzed aqueous  $\text{SO}_2$  oxidation is already included in the model, but uncertainty in this chemical pathway or underestimated cloud presence could also contribute to the underestimated mass fraction on cloudy days when aqueous-phase chemistry is important for  $\text{SO}_4^{2-}$  formation. Average cloud coverage was similar in July and August. However, cloud coverage was more prevalent in January than in July or August. In January, more cloudiness existed in north central area of the modeling domain. Predicted  $\text{SO}_2$  concentrations are generally higher than the observed values as shown by comparing the predictions of  $\text{SO}_4^{2-}$  in Fig. 5 with the under-predictions of the mass fraction of sulfur in Figs. 6 and 7.

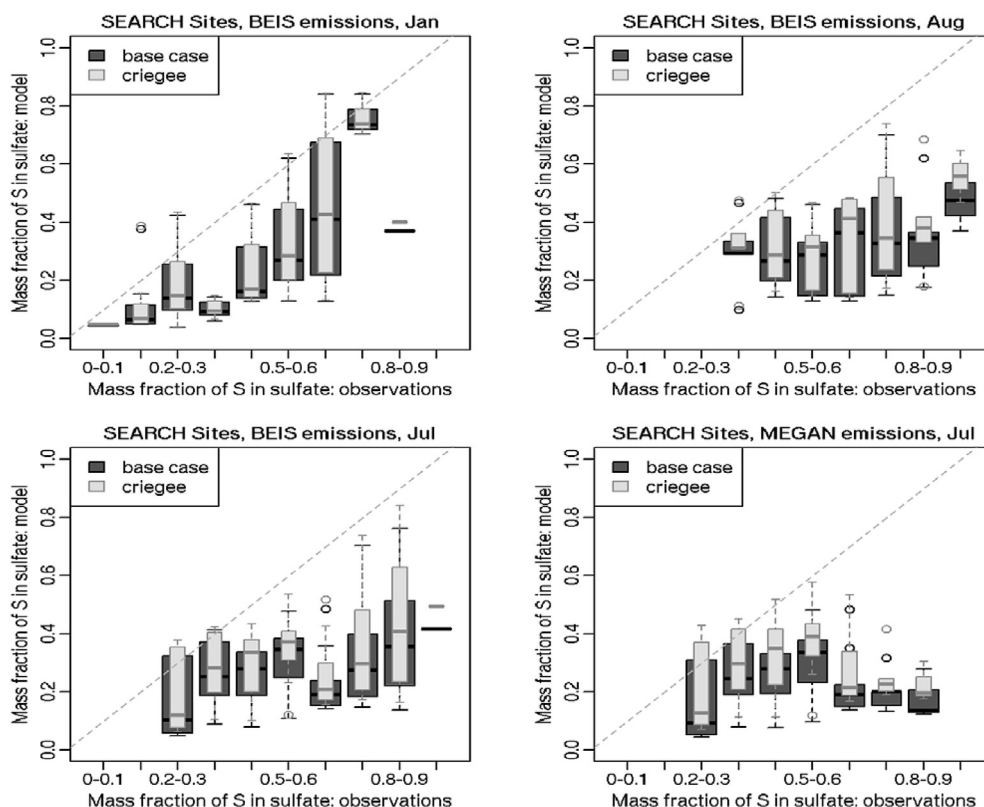
#### 4. Summary and conclusion

This work examines the impact of  $\text{SO}_2$  oxidation by SCI on  $\text{SO}_4^{2-}$  using two different rate constants and two different biogenic emissions estimates. When the higher rate constant is used, Criegee chemistry enhances the domain-wide monthly mean  $\text{SO}_4^{2-}$  by 4.5% in winter and 5–6% in summer. However, enhancements are much larger in regions with significant biogenic VOC emissions. The use of MEGAN estimated biogenic emissions results in larger

enhancements of  $\text{SO}_4^{2-}$  compared to simulations using BEIS estimated emissions which also suggests the need for further evaluation of emissions estimates from the two models. Substantial uncertainty in rate constants for both the SCI +  $\text{SO}_2$  and SCI +  $\text{H}_2\text{O}$  and SCI +  $(\text{H}_2\text{O})_2$  reactions lead to a wide range of possible impacts.

Our results obtained with the higher rate constant reported by Welz et al. (2012) for the  $\text{SO}_2$  + SCI reaction and the lower rate constant for the  $\text{H}_2\text{O}$  + SCI3 reaction reported by Anglada et al. (2011) are consistent with the suggestion of Welz et al. (2012) who noted that Criegee reactions can substantially enhance  $\text{SO}_4^{2-}$ . Our results are also similar to the findings of Pierce et al. (2013) who reported that it enhances  $\text{SO}_4^{2-}$  appreciably in forested regions but not in un-forested regions. Our results obtained with the BEIS emissions are consistent to the findings of Li et al. (2013) while impacts obtained with the MEGAN emissions are greater than the Li et al. (2013) results. However, these new findings contrast to those reported by Sarwar et al. (2013), who found that Criegee reactions minimally enhance  $\text{SO}_4^{2-}$ . The driver for these different findings is the use of different rate constant for SCI3 +  $\text{H}_2\text{O}$  reaction.

Our results with the lower rate constant reported by Mauldin et al. (2012) for the  $\text{SO}_2$  + SCI reaction and the lower rate constant for the  $\text{H}_2\text{O}$  + SCI3 reaction reported by Anglada et al. (2011) are different than the findings of Mauldin et al. (2012) and Boy et al. (2013) who reported that this reaction substantially enhances  $\text{SO}_4^{2-}$  in Finland and Germany. Possible reasons for such inconsistent results include differences in the model used in the two studies, differences in the rate constant used for the  $\text{H}_2\text{O}$  + SCI3 reaction, and not accounting for the loss of SCI3 by the reaction with  $(\text{H}_2\text{O})_2$ . When we use the lower rate constant reported by Mauldin et al. (2012) for the  $\text{SO}_2$  + SCI reaction without any loss of



**Fig. 7.** A comparison of predicted mass fraction of sulfur in  $\text{SO}_4^{2-}$  (BEIS emissions) to observed data from SEARCH sites in January (top left), July (bottom left), and August (top right), and a comparison of predicted mass fraction of sulfur in  $\text{SO}_4^{2-}$  (MEGAN emissions) to observed data from SEARCH sites in July (bottom right). Observed values occurring within the areas outlined in Figs. 1(d) and 3(b) are used for comparing predicted  $\text{SO}_4^{2-}$  with observed data in BEIS emissions and MEGAN emissions panels, respectively. Centerline of the boxplots shows the mean modeled value for each bin of observed values. Boxes extend to 25th and 75th percentile values, whiskers extend to 1.5 times the interquartile range, and dots show outlier values.

SCI3 by water, it enhances  $\text{SO}_4^{2-}$  which warrants clarification on the use of the lower rate constant reported by Mauldin et al. (2012).

Results of this and other recent studies suggest that the  $\text{SO}_2$  oxidation by SCI enhances  $\text{SO}_4^{2-}$  when both  $\text{SO}_2$  and biogenically derived SCI are simultaneously present. Such enhancements occur due to the use of the high rate constant for the  $\text{SO}_2 + \text{SCI}$  reaction and the low rate constant for the  $\text{H}_2\text{O} + \text{SCI3}$  reaction. While the high rate constant for the  $\text{SO}_2 + \text{SCI}$  reaction has been measured, the low rate constant for the  $\text{H}_2\text{O} + \text{SCI3}$  reaction is based on theoretical study (Anglada et al., 2011). We believe the results presented, herein, are the upper limit of the impact of the  $\text{SO}_2$  oxidation by SCI since a low rate constant for the  $\text{H}_2\text{O} + \text{SCI3}$  reaction was used and hope this study motivates others to measure rate constant for the  $\text{H}_2\text{O} + \text{SCI3}$  reaction.

## Disclaimer

Although this paper has been reviewed by EPA and approved for publication, it does not necessarily reflect EPA's policies or views.

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