Modeling natural emissions in the Community Multiscale Air Quality (CMAQ) model – Part 2: Modifications for simulating natural emissions

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Abstract

A recent version (4.6) of the Community Multiscale Air Quality (CMAQ) model was used as the basis for testing model revisions for including reactions involving chlorine (HCl, CINO₂) and reduced sulfur (dimethylsulfide, or DMS, and H₂S) species not normally treated in the CB05 gas chemical mechanism and cloud chemistry module. Model chemistry revisions were based on published reaction kinetic data and a recent cloud chemistry model that includes heterogeneous reactions of organic sulfur compounds. Testing of the revised model was conducted using a recently enhanced data base of natural emissions that includes ocean and continental sources of DMS, H₂S, chlorinated gases and lightning NOₓ for the continental United States and surrounding regions. Results using 2002 meteorology and emissions indicated that most simulated chemical and aerosol species exhibit the expected seasonal variations in grid-average surface concentrations. Ozone exhibits a winter and early spring maximum – reasonably consistent with ozone data and model results produced by others – in a pattern that reflects the influences of atmospheric dynamics and pollutant background levels imposed on the CMAQ simulation by boundary conditions derived from a global model. A series of experimental model simulations reveals that the addition of gas phase organic sulfur chemistry leads to sulfate aerosol increases over most of the continental United States. Modifications to the cloud chemistry module result in widespread decreases in SO₂ across the modeling domain and a mix of sulfate increases and decreases. Most cloud-mediated sulfate increases occurred over the Pacific Ocean (up to about 0.1 µg m⁻³) and at slightly lesser amounts over and downwind from the Gulf of Mexico (including portions of the Eastern US). Variations in the chemical response are due to the link between DMS/H₂S and their byproduct SO₂, the heterogeneity of cloud cover and precipitation (precipitating clouds act as net sinks for SO₂ and sulfate), and the persistence of cloud cover (the largest relative sulfate increases occurred over the persistently cloudy Gulf of Mexico and western Atlantic Ocean). Overall, the addition of organic sulfur chemistry increased surface hourly sulfate levels by as much as
1–2 µg m$^{-3}$ in selected grid cells. The added chemistry produced significantly less sulfate in the vicinity of high SO$_2$ emissions (e.g., wildfires), perhaps in response to lower OH from competing reactions with DMS and its derivatives. Simulated surface levels of DMS compare favorably with published observations made in the marine boundary layer. However, DMS derivatives are lower than observed implying either less chemical reactivity in the model or a low bias in the boundary conditions for DMS derivatives such as dimethylsulfoxide. The sensitivity of sulfate to cloud cover and the aqueous sulfate radical is also explored. This revised version of CMAQ provides a tool for more realistically evaluating the influence of natural emissions on air quality.

1 Introduction

A companion paper (Smith and Mueller, 2010) describes development of an expanded natural emissions data set for use in the United States Environmental Protection Agency (EPA) Community Multiscale Air Quality (CMAQ) Model. The rationale for doing so is the need for scientifically defensible estimates of naturally occurring levels of air pollutants. Natural contributions to air pollution play an important role in determining overall human and ecosystem exposures to potentially damaging pollutants, and set limits to and benchmarks for the pollutant reduction objectives at the heart of air pollution policy and regulations. Examples of the importance placed on naturally occurring pollutants include the guidelines for implementing the Regional Haze Rule (EPA, 2003), and the interest in background pollutant levels for their potential impact on achieving air quality standards (Lin et al., 2000; EPA, 2005).

This paper describes modifications in the CMAQ Model required so that it can fully use the natural emissions data developed by Smith and Mueller (2010). CMAQ is a widely used tool for estimating the association between pollutant emissions and downwind ambient concentrations. The most significant model changes were those needed to incorporate chemical reactions for organic sulfur compounds and associated reactive species in both the gas and aqueous (cloud) phases. The result is a model that
simulates the spatial and temporal variability in naturally-occurring ozone, fine particles and acid deposition. Tests of the revised model are described to illustrate the effects of the modified chemistry on simulated air quality. Work is underway to document more extensive simulations of the revised model and to provide insight into the contributions of different natural phenomena to air pollutant levels.

2 Previous work

2.1 Current treatment of natural emissions in CMAQ

This study used version 4.6 of the CMAQ model (CMAQ4.6 released October 2006) to examine natural levels of ozone and airborne particles. The EPA Models-3 air quality modeling system – including the SMOKE emissions and CMAQ air quality components – has long treated pollutant emissions from natural processes and systems (as distinguished from those that are created by human activity): (1) biogenic emissions of volatile organic compounds (VOCs) emitted by vegetation; (2) NO emissions from soils; (3) emissions from wildfires; (4) windblown dust; (5) animal-derived NH$_3$.

Recently, changes implemented in CMAQ4.6 enable internal computation of sea salt particle emissions. Thus, the SMOKE/CMAQ4.6 modeling system treats many primary particulate emissions and some ozone and secondary fine particle (PM$_{2.5}$, or particles <2.5 µm in size) precursor emissions.

2.2 Additions made to the standard SMOKE/CMAQ suite of natural emissions

Berntsen and Isaksen (1997) modeled global tropospheric photochemistry based on the Global Emissions Inventory Activity (GEIA) emissions data base (http://www.geiacenter.org/). This data base includes both anthropogenic and natural emissions, the latter including fluxes from biomass burning, biogenic sources (vegetation VOCs and soil NO), lightning NO$_x$ (LNO$_x$) and oceans [dimethylsulfide (DMS), NH$_3$, HCl and...
However, given the focus of Berntsen and Isaksen (1997) on ozone it is not clear to what extent their modeling used all the emissions species that are currently available.

Park et al. (2004) used GEOS-Chem to simulate atmospheric aerosols derived in part from natural sulfur emissions from oceans (DMS), volcanoes, NO$_x$ from lightning, vegetation, and soils, biomass burning emissions (including CO, NO$_x$ and VOCs), and ammonia emitted by animals. Likewise, Kaminski et al. (2007) used data from the EDGAR 2.0 and GEIA emissions inventories for their global air quality modeling effort including emissions from these same sources. They incorporated monthly mean totals of LNO$_x$ from the GEIA data base, scaling emission horizontally according to the modeled distribution of convective clouds and vertically following profiles reported by Pickering et al. (1993).

Koo et al. (2010) recently examined potential air quality impacts of selected natural emissions not normally treated in the CMAQ Model. They added lightning NO$_x$ and surrogates for organosulfur from oceans. Their approach to estimating LNO$_x$ emissions started with an annual estimate to total LNO$_x$ emitted across the United States followed by a spatial-temporal allocation scheme based on simulated convective precipitation. Organosulfur species DMS and methanesulfonic acid (MSA) were treated using ocean emissions estimates from the global GEOS-Chem model, and by using SO$_2$ as a surrogate for DMS and sulfate as a surrogate for MSA. This approach avoided the need for modifying the model chemistry but leaves questions about the validity of such an assumption. Koo et al. (2010) concluded that LNO$_x$ contributes significantly (1–6 ppbV) to annual average ozone levels, especially across the southeastern US. They also determined that their scheme for estimating organosulfur pollutants decreased ozone slightly (due to the added sulfur reacting with OH) in the vicinity of the emissions and increased fine particle mass by amounts generally $<0.25$ µg m$^{-3}$ on an annual average.

It is clear from the work cited here that there are natural emissions not treated in the standard SMOKE/CMAQ modeling package that are considered important on regional and global scales. Most notably, these emissions involve reduced sulfur (especially
DMS), NH₃ and soluble chlorine species from oceans, and LNOₓ. Despite the inherent uncertainty in quantifying these emissions, it is imperative to include them in any effort to examine a more complete picture of how natural emissions influence air quality. Smith and Mueller (2010) describe in detail the methodologies used to add natural emissions to the standard SMOKE/CMAQ inventory. Data from the National Lightning Detection Network along with recent work estimating NOₓ production from lightning strokes formed the basis of LNOₓ emission estimates. Ammonia emissions from populations of large wild animals were included using estimates from US and Canadian wildlife inventories and emissions estimates for Mexico in the GEIA data base. Atmospheric chlorine is believed to play a role in ozone formation in coastal areas (Knipping and Dabdub, 2003) and provides radicals that may also contribute to aerosol formation in clouds. Effective emissions rates for HCl and ClNO₂ in the marine boundary layer were incorporated from the GEIA data base, as were ammonia emissions from the oceans.

Reduced sulfur emissions from oceans and geogenic sources are also overlooked in CMAQ. Emissions of DMS, and to a lesser extent H₂S, are considered an important source of marine aerosols (Kreidenweis et al., 1991). Though relatively small compared to the oceans, inland lakes and coastal wetlands are also important sources of DMS and H₂S (National Acid Precipitation Assessment Program, 1991). Geogenic sources – especially the thermal vents of geologically active regions like Yellowstone National Park – emit H₂S that may be important contributors to downwind aerosols. Emissions from volcanoes were generally not included due to the sporadic nature of their emissions.

3 CMAQ modifications

Version 4.6 was the most recent release of CMAQ at the outset of this project. Because CMAQ is updated every 1–2 years it is impractical to try keeping up to date with the most current version, especially when independent model changes require
extensive testing. This study focused solely on version 4.6 although a more recent version (4.7) has since been released. A consequence of frequent code updates is that a more recent version often contains additional features or improvements that require further changes to ongoing work. Version 4.7 includes updates to the gas phase chemical mechanism that would have made unnecessary most of the chlorine reaction additions described later in this section. Also, CMAQ4.7 includes additional cloud chemistry reactions that enable some heterogeneous formation of organic aerosols. These reactions were not included in the current work but can easily be incorporated in the revised cloud chemistry module described below. Finally, secondary organic aerosol (SOA) formation in CMAQ4.6 (originally introduced into version 4.5.2) was updated from that in the original model version based on Morris et al. (2006) and further described in Sect. 4.1. It is important to note that the SOA treatment in CMAQ4.7 is somewhat different from that in CMAQ4.6.

3.1 Gas phase chemistry

This work uses the CMAQ optional configuration that includes an updated version of the carbon bond IV (CBIV) chemical mechanism called “CB05” (Yarwood et al., 2005). Changes made to the CMAQ4.6 CB05 gas phase chemical mechanism fall into three categories: (1) reactions added to treat chlorine species and/or involving chlorine radicals, (2) reactions added to treat DMS and its derivatives, and (3) reactions added to treat H$_2$S and its derivatives.

3.1.1 Chlorine reactions from CMAQ CBIV

Emissions of species HCl and ClNO$_2$ (nitryl chloride) require that gas- and aqueous-phase reactions be added that treat various chlorine species and their derivatives. CMAQ4.6 has an option to include a set of chlorine reactions in CB05, but it also includes reactions involving hazardous air pollutants (http://www.cmascenter.org/help/model_docs/cmaq/4.6/HAZARDOUS_AIR_POLLUTANTS.txt). This CB05 enhance-
ment was not used here because it required carrying a number of reactions that are not of interest for simulating natural ozone and aerosols. Instead, a subset of chlorine reactions originally added to the CMAQ4.6 CBIV reaction set were copied for use in CB05. This set of reactions (except for the last one), originally developed by Tanaka and Allen (2001), is listed in Table 1. These reactions produce radicals (Cl, ClO, OH, HO$_2$, XO$_2$) that react with VOCs, NO, H$_2$S, DMS and their oxidation products, and can play an important role in the chemistry of ocean coastal environments.

### 3.1.2 Nitryl chloride

Nighttime reactions of N$_2$O$_5$ on sea salt aerosols release ClNO$_2$ (Behnke et al., 1997) while other reactions involving sea salt aerosols release chlorine gas and HCl (Knipping and Dabdub, 2003). Chlorine gas photolyzes to atomic chlorine and ClNO$_2$ reacts with OH to form HOCl and NO$_2$. Thus, ClNO$_2$ is a reservoir of NO$_2$ in the marine boundary layer and provides reactive HOCl which further photolyzes to OH and Cl. Nitryl chloride is produced at levels roughly 100 times less than HCl (Erickson et al., 1999) and ambient concentrations of Cl are extremely low except in areas affected by anthropogenic chlorine and/or NO$_x$ emissions. Treating the dechlorination of sea salt aerosol explicitly in CMAQ requires a modification to the aerosol module and was beyond the scope of this project. Instead, we added ClNO$_2$ as an emitted species from the ocean following data provided in the GEIA global emissions data base (Graedel et al., 1993; Erickson et al., 1999). One reaction added to the Tanaka and Allen (2001) chlorine reaction set was

$$\text{OH} + \text{ClNO}_2 \rightarrow \text{HOCl} + \text{NO}_2 \quad \text{(R1)}$$

as presented in Atkinson et al. (2007). Note that HCl can be an important contributor to cloud droplet acidity in the marine environment. Also, aqueous Cl$^-$ plays a role in the droplet balance of various chlorine species that react with different organic sulfur species. Details of the heterogeneous chemistry modifications are provided in Sect. 3.2.
3.1.3 H$_2$S

Inorganic sulfur reactions added to CMAQ CB05 are listed in Table 2. Kinetic data exist for reactions of H$_2$S with OH, O, HO$_2$, Cl and NO$_3$. Each of the OH, O and Cl radicals is known to attack the S bond with H and produce the SH radical. Both HO$_2$ and NO$_3$ are likely to act similarly on H$_2$S although their reaction products have not been directly identified. The rate constant for H$_2$S+Cl has been measured to be the highest ($7.4 \times 10^{-11}$ cm$^3$ molecule$^{-1}$ s$^{-1}$ at 298 K) of this set of reactions. The next highest rate constants are for reactions involving OH and O (at 298 K): $k \approx 5 \times 10^{-12}$ cm$^3$ molecule$^{-1}$ s$^{-1}$ for the OH reaction is about two orders of magnitude greater than that for the O reaction (NASA, 1997). Upper limits to the rate constants for the reactions involving HO$_2$ and NO$_3$ are both $\sim 1 \times 10^{-15}$ cm$^3$ molecule$^{-1}$ s$^{-1}$ (Atkinson et al., 2004). During daytime, the reaction of H$_2$S with OH will dominate over that with O, while the reaction with Cl could be important over the ocean and in the presence of chlorine emissions. At night, the reaction with NO$_3$ will most likely be the dominant pathway for initiating the breakdown of H$_2$S with assumed products (by analogy with the other reactions) of SH and nitric acid. The reactions of H$_2$S with Cl, OH and NO$_3$ were added to the CB05 mechanism.

**SH Reactions:** The second step in oxidizing H$_2$S in the atmosphere involves reactions of SH with a variety of species. Data exist on the kinetics of SH reactions with O, O$_2$, O$_3$, NO, NO$_2$, Cl$_2$ and H$_2$O$_2$, as well as various bromine and fluorine species (NASA, 1997). At 298 K, rate constants $k_i$ for SH reactions with species $i$ are as follows (all have units of cm$^3$ molecule$^{-1}$ s$^{-1}$): $k_O = 1.6 \times 10^{-10}$; $k_O < 4 \times 10^{-19}$; $k_O = 3.7 \times 10^{-12}$; $k_{NO} = 6.5 \times 10^{-11}$; $k_{Cl} = 1.7 \times 10^{-10}$; $k_{H_2O_2} < 5 \times 10^{-15}$. The reaction SH+NO+M has a more complex rate constant expression that is a function of altitude (pressure) in the atmosphere. At sea level and 298 K $k_{NO} = 2.6 \times 10^{-12}$ cm$^3$ molecule$^{-1}$ s$^{-1}$. The slowest reaction is by far SH+O$_2$, but the abundance of O$_2$ as a reactant makes it competitive with most other trace species as an important pathway for SH removal. The reaction with H$_2$O$_2$ appears to be the least important overall and was dropped from consid-
eration (note that Friedl et al., 1985, reported finding little net production of product species HSO from this reaction). Reactions involving NO and NO₂ will be important only downwind of NOₓ emission sources. SH reactions with O and O₂ produce the SO radical whereas reaction with O₃ and NO₂ produce HSO. Reaction with NO produces HSN and reaction with Cl₂ produces CISH. Both HSN and CISH are treated as termination products.

**SO Reactions:** Data on reactions of SO with OH, O₂, O₃, NO₂ and ClO have been reported and all produce SO₂ (NASA, 1997). The reaction with O₂ is the slowest, but the abundance of O₂ makes it important relative to the other reactions. ClO is a product of the reaction between Cl and O₃. All of these reactions are included in the revision to CB05.

**HSO Reactions:** Atkinson et al. (2004) report kinetic rate constants for HSO reactions with O₂, O₃, NO and NO₂. As with other species, the reaction with O₂ is the slowest but the abundance of atmospheric O₂ makes it important. HSO reacting with NO is also very slow compared to the other reactions and was not included in this version of CB05. The reaction of HSO+NO₂ may produce HSO₂+NO (NASA, 1997) and these products were adopted for use here. HSO reacting with O₂ and O₃ are assumed to produce HSO₂ by analogy with the products of the NO₂ reaction. The only reaction identified for removing HSO₂ is that with O₂, but it is fairly rapid given the levels of O₂.

### 3.1.4 DMS and its derivatives

A realistic treatment of organic sulfur compounds must consider reactions between them and the various radicals present in the atmosphere. This is especially important in the case where “natural” pollutants are combined with anthropogenic pollutants because all pollutant reactions must compete for the available radicals. Finlayson-Pitts and Pitts (2000) provide a detailed overview of organic sulfur chemistry in the atmosphere. There is still much that needs to be learned about the reaction kinetics and reaction products that are involved. However, the level of detail described in the Finlayson-Pitts and Pitts (2000) overview is sufficient for constructing a treatment.
of DMS+products chemistry. Reactions added to CB05 are generally only those for which the products and kinetic rates are known and are sufficiently fast that they will have a significant impact on the evolution of atmospheric sulfur. Consideration was given to include those reactions that, although slow in comparison to competing daytime reactions, would be relatively important at night.

Table 3 lists the reactions added to CB05. Unless otherwise noted, details of reaction kinetics were taken from NASA (1997) and Atkinson et al. (2004). Reactions of DMS with various atmospheric constituents have been studied extensively because of the suspected role of DMS in aerosol formation and climate. A great deal has been learned within the past 10 years. The evolution of DMS in the atmosphere as described by Finlayson-Pitts and Pitts (2000) and as simulated in previous models was followed as a road map for modifying the CMAQ4.6 CB05 mechanism. Uncertainties in the chemistry of DMS and its byproducts are described in this section. Compromises and assumptions were necessary to treat some of the reactions and/or byproducts due to incomplete knowledge and the various assumptions are explained.

**DMS reactions:** Studies of DMS chemistry have revealed that it is relatively reactive with a broad spectrum of chemical species, including O_3, OH, HO_2, O, Cl, ClO, IO, BrO, F, NO_3, and N_2O_5. Halogen species are most likely to be found in the marine boundary layer. Ubiquitous O_3 would play an important role if its reaction rate was not so slow (rate constant \( k < 1 \times 10^{-18} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \)). A comparative analysis of the various reactions revealed that DMS reactions with O, Cl, OH, OH+O_2, and NO_3 were most likely to control the fate of DMS in the atmosphere. Reactions with other halogen compounds are probably also important in selected situations but little is known about naturally occurring emissions and atmospheric levels of species like IO and BrO. Reactions involving halogen species other than chlorine were not treated at this time to avoid guesswork about their emissions.

The fastest reaction considered was DMS+Cl. This reaction occurs by way of two channels with a rate constant of about \( 3.3 \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \) at 298 K (mea-
Cl + CH₃SCH₃ → HCl + CH₃SCH₂
→ CH₃S(Cl)CH₃

(F2)

(F3)

Finlayson-Pitts and Pitts (2000) report that although both channels appear to be equally important, the fate of the adduct CH₃S(Cl)CH₃ is unknown. Thus, only (R2) is included in CMAQ.

The reaction of OH with DMS is perhaps the most studied of all reactions involving DMS and it is one of the most complex. As with chlorine, the reaction occurs by way of two reaction channels:

OH + CH₃SCH₃ → CH₃SCH₂ + H₂O
OH + CH₃SCH₃ + M ↔ CH₃S(OH)CH₃ + M

(R4)

(R5)

At 298 K and 1 atm (R4) is predominant but the (R5) becomes more important as temperature decreases. The OH adduct itself may decompose back to its original reactants or it can react with O₂ to form dimethylsulfoxide (DMSO):

CH₃S(OH)CH₃ + O₂ → CH₃SOCH₃ + HO₂

(R6)

DMSO reacts rapidly with O₂ to form dimethylsulfone [DMSO₂: CH₃S(O)(O)CH₃]. In addition, CH₃SCH₂ (MSCH₂) reacts with O₂ as

CH₃SCH₂ + O₂ + M → CH₃SCH₂OO + M

(R7)

to form the peroxy radical CH₃SCH₂OO (MSP).

The CMAQ CB05 mechanism revision includes both (R6) and (R7). The first channel is modeled following Atkinson et al. (2004) with the product MSCH₂ treated explicitly along with its subsequent reaction to MSP. The chain of reactions that begins with formation of the OH adduct (by way of the second DMS+OH channel) is modeled following Zhu et al. (2006):

DMS + OH + O₂ → 0.5DMSO + 0.2DMSO₂ + 0.3MSIA

(R8)
where MSIA is methanesulfonic acid.

Another reaction treated in the revised CB05 is DMS+O which yields CH$_3$SO and a methyl radical (Atkinson et al., 2004). The final DMS reaction treated here, important at night, is DMS+NO$_3$. This reaction yields MSCH2 and nitric acid.

**MSCH$_2$ Reactions**: This radical is formed by three of the five DMS reactions. Its primary reaction pathways are with O$_2$ and NO$_3$. The reaction with O$_2$ is very rapid and produces the peroxyl radical MSP. Products of MSCH$_2$+NO$_3$ are not known and are assumed, analogous to the companion reaction with O$_2$, to be MSP and NO.

**MSP Reactions**: This mechanism includes three reactions involving MSP as a reagent. One is the reaction of MSP with itself. The other two are MSP with NO and MSP with HO$_2$. MSP reactions with itself and other species are believed to form CH$_3$SCH$_2$O which is very unstable and rapidly decomposes to CH$_3$S and HCHO. Thus, all reactions involving MSP are treated as yielding products CH$_3$S, HCHO and, in the case of MSP+NO, NO$_2$.

**CH$_3$S Reactions**: Finlayson-Pitts and Pitts (2000) report that the fate of CH$_3$S in the atmosphere is unclear. This is because there is evidence that it reacts with many different species in a variety of ways and in most cases the products are not well known. For example, CH$_3$S+O$_2$ produces CH$_3$SOO, but the latter has a short lifetime because it decomposes back to CH$_3$S. Reaction with NO$_2$ produces CH$_3$SO+NO. CH$_3$S+O$_3$ is another likely reaction but a large number of potential reaction channels exist. These include yields of CH$_3$SO+O$_2$ (the yield is low at low pressure while data at high pressure are nonexistent), CH$_3$+SO+O$_2$, CH$_2$SO+H+O$_2$, CH$_2$SO+HO$_2$, CH$_2$S+OH+O$_2$, and CH$_3$O+SO$_2$. The percent yields of many of these channels are estimated to be very small and species like CH$_2$SO and CH$_2$S are very short-lived. Consequently, Zhu et al. (2006) aggregated several reactions into a single net reaction for CH$_3$S with a host of ambient species as follows:

$$\text{CH}_3\text{S} \rightarrow 0.9\text{SO}_2 + 0.1\text{H}_2\text{SO}_4 \quad (R9)$$

In addition, they assigned this a rate constant of 5.0 cm$^3$ molecule$^{-1}$ s$^{-1}$ assuring
a near instantaneous reaction. In light of data summarized by Atkinson et al. (2004),
and given the thermal instability of the CH₃SOO product, we have chosen to ignore the
reaction of CH₃S with O₂ and include only reactions with O₃ and NO₂. The reaction
between CH₃S and NO produces CH₃SNO, but it was not included because it photodis-
sociates back to CH₃S+NO during the daytime resulting in a fairly short lifetime and
limited presence in the atmosphere. Clearly, this is one area where future advances
may require significant revision to the mechanism. The reaction with O₃ follows the net
yield modeled in Zhu et al. (2006), but applies the measured rate constant in Atkinson
et al. (2004).

**MSO Reactions:** MSO+O₃ has been observed to yield a variety of products. One,
CH₂SO₂, is a relative enigma because neither NASA (1997), Finlayson-Pitts and Pitts
(2000) nor Atkinson et al. (2004) provide any information on its reactivity or fate. The
two remaining noteworthy reaction channels – yielding CH₃S+2O₂ and CH₃+SO₂+O₂
– were added to CMAQ4.6 with percent yields based on data cited by Finlayson-Pitts
and Pitts (2000). Finally, MSO+NO₂ was included because it is well characterized and
relatively fast.

**DMSO & MSIA Reactions:** Zhu et al. (2006) relied on data from Kukui et al. (2003)
to model the reactions of DMSO and MSIA with OH. Their simplifications reduce
a complex set of reactions into two simplified reactions that were adopted in this study
(k=9.0×10⁻¹¹ cm³ molecule⁻¹ s⁻¹ for both):

\[
\begin{align*}
\text{DMSO} + \text{OH} & \rightarrow 0.9\text{MSIA} + 0.1\text{DMSO2} \\
\text{MSIA} + \text{OH} & \rightarrow 0.9\text{SO}_2 + 0.1\text{MSA}
\end{align*}
\]

The net effect of the organic sulfur reaction set that starts with DMS is the production of
inorganic species SO₂ and H₂SO₄, along with organic species DMSO, DMSO₂, MSIA
and MSA. A number of reactions involving DMS, DMSO, DMSO₂ and MSIA occur in
clouds.

**CH₃ and CH₃O Reactions:** Closure to the revised CB05 mechanism requires inclu-
sion of reactions involving the radicals CH₃ and CH₃O. Fortunately, the chemistry of
these species is well characterized. CH₃ reacts fairly quickly with O and O₃ to produce HCHO or CH₃O. CH₃O reacts with O₂ to produce HCHO and HO₂, and with NO₂ to yield HCHO and HONO.

3.1.5 Comparison with other gas phase DMS mechanisms

Our comparison here with previous organic sulfur mechanisms is not meant to be a complete compilation of other work but serves as a reference point for putting this work into perspective relative to other models. Kreidenweis et al. (1991) used a photochemical model with 72 chemical reactions (and 12 photolysis reactions) to examine sulfate aerosol formation in the marine environment. However, their model contained only one reaction involving DMS oxidation by OH with SO₂ and MSA as products. This highly simplified approach was sufficient to produce a latitudinal gradient in marine sulfate similar to that reported from some measurement studies. No reactions were included that treated H₂S.

Yin et al. (1990) developed a comprehensive model of DMS and its derivatives. Their mechanism included 40 sulfur species and 140 reactions. Zaveri (1997) simplified the Yin et al. mechanism (10 organic sulfur species and 30 reactions) for use in a large-scale atmospheric model. The Zaveri model retained the major oxidation pathways from its more complex progenitor, but several reactions were combined and/or simplified to reduce computational requirements. Zaveri’s work focused most attention on the fate of two radicals formed as part of the DMS-to-sulfate channels: CH₃SO₂ and CH₃SO₃. The reason for this is that CH₃SO₂ is formed as part of several reaction channels (while CH₃SO₃ is produced from some reactions involving CH₃SO₂) but its fate has been less certain than other intermediate species. The uncertainty is due to the relative importance of the thermal decomposition

\[ \text{CH}_3\text{SO}_2 \rightarrow \text{CH}_3 + \text{SO}_2 \]  \hspace{1cm} (R12)

versus reactions of CH₃SO₂ with species such as NO₂, O₃ and HO₂. Prior to Zaveri’s work, different laboratory studies of this decomposition yielded rates that differed by
a factor of $3 \times 10^5$. Clearly, this uncertainty – plus the uncertainty of the rate constants for chemical reactions involving CH$_3$SO$_2$ – made it difficult to know whether these reactions were of sufficient significance to include in a mechanism for marine sulfate. Zaveri concluded that the competing reactions were important and included them (plus reactions involving CH$_3$SO$_3$) in his mechanism.

The primary features of the Yin et al. mechanism, the Zaveri mechanism, and mechanisms used by Lucas and Prinn (2005) and Zhu et al. (2006), are essentially the same (although differences exist in the rate constants and branching or partitioning ratios for some of the reactions). DMS is initially attacked by OH with two reaction channels (all mechanisms), NO$_3$ (all mechanisms) and O (Yin et al. and Zaveri mechanisms). One DMS+OH channel produces DMSO, DMSO$_2$, MSIA and MSA (all mechanisms, except Lucas and Prinn do not include DMSO$_2$). The other OH channel leads to the formation of the hydroperoxy radical CH$_3$SCH$_2$OO which undergoes further reactions that produce CH$_3$S and, ultimately, SO$_2$ and H$_2$SO$_4$ (all but the Lucas and Prinn mechanism).

Only the Yin et al. and Zaveri mechanisms include reactions involving CH$_3$SO$_2$ and CH$_3$SO$_3$.

The modified CB05 mechanism outlined here shares many similarities with, and borrows from, the previous work. As described earlier, both DMS+OH reaction channels, the DMS+NO$_3$ reaction and the DMS+O reactions are all included. We have added the DMS+Cl reaction. Rate constants have been updated using the most recent information available in the peer-reviewed literature. Our major deviation from the Yin et al. and Zaveri mechanisms is in leaving out the CH$_3$SO$_2$ and CH$_3$SO$_3$ species and their reactions. The rationale for this is as follows. The simpler Zaveri mechanism has 11 reactions with CH$_3$SO$_2$ as a product. In addition, it includes 12 reactions that involve CH$_3$SO$_2$ or CH$_3$SO$_3$ as reactants. Thus, 23 reactions are used by Zaveri (1997) to handle these two species. It is not possible to eliminate all these reactions (some are slow enough to neglect), but in all cases reactions forming CH$_3$SO$_2$ can be replaced by reactions that yield CH$_3$+SO$_2$ if we assume the thermal decomposition of CH$_3$SO$_2$ is fast in comparison with CH$_3$SO$_2$ chemical reactions.
A study by Kukui et al. (2000) – published after Yin et al. (1990) and Zaveri (1997), and too late to be included in the overview of Finlayson-Pitts and Pitts (2000) – examined in detail the issue of CH$_3$SO$_2$ thermal decomposition. Kukui et al. (2000) measured CH$_3$SO$_2$ behavior and their data, coupled with theory, were used to develop a mathematical expression for CH$_3$SO$_2$ thermal decomposition as a function of temperature and pressure. This expression represents the CH$_3$SO$_2$ loss rate throughout the troposphere for comparison with CH$_3$SO$_2$ loss rates for its reactions with NO$_2$, O$_3$ and HO$_2$ at realistic concentrations based on the rate constants used by Zaveri (1997). The pressure/temperature effect on thermal decomposition was examined for a range of conditions that can occur between the ground and the top of the troposphere. Colder temperatures in the upper troposphere significantly reduce CH$_3$SO$_2$ decomposition. However, the loss rate due to decomposition in the troposphere is almost always a factor of ten or more greater than loss rates from reactions with NO$_2$, O$_3$ and HO$_2$. Based on this, it seems that including reactions involving CH$_3$SO$_2$ and CH$_3$SO$_3$ in a modified CB05 mechanism is likely a computational luxury that cannot be afforded at this time. Future research may further clarify the relative importance of various reaction pathways for DMS derivatives and require modifications to the approach outlined here. The current work mirrors fairly closely the mechanistic studies done previously by others.

### 3.2 Heterogeneous chemistry

#### 3.2.1 Background

Modifying the gas phase chemistry in CMAQ4.6 is straightforward because the model is designed with a feature that facilitates such changes. However, the model has no such feature regarding its heterogeneous cloud chemistry module which has remained mostly unchanged from the initial version. It is based on the module used in the RADM model developed for use in acid deposition analyses conducted by the National Acid Precipitation Assessment Program of the 1980s (NAPAP, 1991). The RADM cloud chemistry module treats 5 reactions involving SO$_2$ oxidation by H$_2$O$_2$,
S(IV) (=SO$_2$(aq) + HSO$_3^-$ + SO$_2^{2-}$) oxidation by O$_3$, HSO$_3^-$ oxidation by peroxyacetic acid (PAA) and methylhydrogen peroxide (MHP), and S(IV) catalytic oxidation by Fe$^{2+}$ and Mn$^{2+}$.

The standard CMAQ module assumes steady-state conditions within a cloud during the time integration of the kinetic equations, with gas-aqueous equilibria computed using Henry’s Law constants for the following gases: SO$_2$, H$_2$SO$_4$, CO$_2$, NH$_3$, HNO$_3$, O$_3$, H$_2$CO$_2$ (formic acid), H$_2$O$_2$, HCl, PAA, and MHP. The dissociation of dissolved acids and bases – plus the presence of soluble salts (ammonium nitrate, sodium and potassium chloride, and magnesium and calcium carbonate) from airborne particles – contribute to an ion balance that determines droplet pH. Ion activity coefficients are computed to calculate the activities of all dissolved ionic species. The total rate of heterogeneous sulfate formation is computed as the sum of the rates of formation from the individual kinetic equations. Rate (transient) equations are integrated for 6- or 12-min periods followed by adjustments made to equilibrium concentrations of interstitial gases and aerosol species consumed or produced during the integration. The CMAQ cloud module is executed in a quasi steady-state manner with cloud chemistry pausing to allow gas chemistry to proceed before resuming the heterogeneous reactions. This method is used because it is simple to program, has low computational overhead and is easily modified. A disadvantage of this approach is that, by suspending gas phase chemistry and diffusion during integration of the heterogeneous cloud reactions, it is likely that fast-reacting species will be depleted from the gas phase within the cloud, thereby stopping some heterogeneous reactions (hence, the reason for CMAQ reducing the cloud integration time step from 12 to 6 min).

Karamchandani and Venkatram (1992) used a similar approach in their ADOM model. The ADOM heterogeneous chemical reactions are essentially the same as in RADM/CMAQ although their treatment of cloud microphysics is more sophisticated. A cloud model developed by de Valk and van der Hage (1994) for use in long range transport models also used relatively sophisticated cloud microphysics but its chemistry only treated the oxidation reactions of S(IV) by O$_3$ and H$_2$O$_2$. Möller and Mauers-
berger (1992) examined cloud chemistry from the opposite perspective, using sophisticated heterogeneous chemistry (57 aqueous reactions and equilibria) in a flow-through reactor-type model to examine the roles of various inorganic and organic reactants in sulfur oxidation and radical cycling. Their sulfur chemistry included S(IV) oxidation by O₃, H₂O₂, organic peroxides, OH, NO₃ and metal ion catalysis, but no organic sulfur reactions. In addition, they simulated the interplay between OH, H₂O₂, HO₂, O₃, NO₃ and soluble organic species in cloud droplets. Under certain conditions (especially low SO₂), clouds can be a net source of H₂O₂ which can be transferred into the gas phase from the droplets. At very low SO₂ (<0.1 ppbV) no net H₂O₂ destruction (because of in-cloud H₂O₂ formation) was computed, although clouds become a very effective sink for H₂O₂ when SO₂>0.5 ppbV. Möller and Mauersberger (1992) concluded that, in low SO₂ conditions, clouds play an important role in photooxidant dynamics.

Williams et al. (2002) used a one-dimensional cloud model to investigate the role of marine stratocumulus clouds as a possible source of HONO. Their calculations, based on a cloud model originated by Van den Berg et al. (2000), simulated aqueous chemistry following the CAPRAM reaction mechanism (Herrmann et al., 2000) involving 86 species and 178 reactions. Williams et al. (2002) added 26 reactions treating reactive halogen species but simplified other reactions involving peroxy radicals. Their results indicated that in-cloud HONO formation, and its effects on droplet acidity and ozone chemistry, is most likely to be important in a moderately-polluted marine environment. However, due to large uncertainties in the aqueous chemistry involved, the modest impact on photochemistry and the high computational requirements of the modified mechanism, they recommended against trying to incorporate HNO₄/HONO chemistry into larger-scale three-dimensional atmospheric chemistry models.

Global modeling of sulfate and nitrate aerosols by Park et al. (2004) using their GEOS-Chem model computed in-cloud SO₂ oxidation by O₃ and H₂O₂ and an assumed droplet pH of 4.5. They computed gas phase oxidation of DMS with yields of MSA and SO₂, but did not include DMS or MSA in the heterogeneous reactions. An aqueous chemistry model that combined oxidation of S(IV) and DMS in a relatively sim-
ple set of kinetic reactions was presented by Zhu (2004) and again in Zhu et al. (2006). This model included the usual reactions involving the oxidation of S(IV) species by H$_2$O$_2$ and O$_3$, plus reactions of DMS, DMSO, MSIA and MSA with various oxidants (O$_3$, OH, SO$_4^-$, Cl and Cl$^-$) and is based in part on new laboratory measurements of several organic sulfur species that provided a more complete kinetic mechanism for heterogeneous reactions.

Henze and Seinfeld (2006) reported major increases in secondary organic aerosol (SOA) formation from isoprene when using a parameterized aerosol formation mechanism in GEOS-Chem. Recently, Ervens et al. (2008) examined the formation of SOA by way of heterogeneous reactions involving organic compounds derived from isoprene. Two processes were modeled for producing aerosol mass from isoprene oxidation products by partitioning semivolatile organics between the gas and condensed phases using empirical partitioning ratios and modeling heterogeneous chemical reactions involving water-soluble isoprene oxidation products. The carbon aerosol yield was significant (to greater than 10 percent on the initial isoprene carbon mass in boundary layer cycling through clouds) and was dependent on the VOC/NO$_x$ ratio. Their heterogeneous chemistry model included over 40 reactions to simulate the evolution of inorganic sulfur and organic reactants that lead to sulfate and water soluble SOA products. The release of CMAQ4.7 includes an update to the cloud chemistry that incorporates in-cloud SOA formation pathways originating with glyoxal and methylglyoxal (http://www.cmascenter.org/help/documentation.cfm?MODEL=cmaq&VERSION=4.7&temp_id=99999). Clearly, there is a need to follow up this current effort (based on version 4.6) by selectively adding organic reactions that produce SOA.

Given previous work on heterogeneous chemistry in clouds and the goal of incorporating organic sulfur reactions into CMAQ, we opted to incorporate reactions from the model of Zhu (2004) and Zhu et al. (2006) keeping many features of the old module for computational efficiency while adding new features that provide a more realistic approach to cloud chemistry. This is an incremental step in updating a model that is
widely used in regulatory settings and, therefore, must maintain some computational
shortcuts.

3.2.2 Equilibrium species used to determine droplet acidity

Table 4 lists the gas and aerosol species used to compute droplet acidity for both the
CMAQ standard and revised versions of the cloud chemistry module. The revised mod-
ule adds the effects of MSIA and MSA on droplet acidity. Incorporating the reactions
used by Zhu (2004) also requires the addition of Cl, Cl\(^{-}\), SO\(^{-}\)\(_4\) and OH as reactants in
the revised cloud module. As shown in the next section, Cl and Cl\(^{-}\) are in equilibrium
with Cl\(^{-}\) and this relationship is included in the initial equilibrium calculation. The vapor
pressure of H\(_2\)SO\(_4\) over water is so low that it is assumed to be entirely absorbed by
cloud droplets. Initial cloud droplet equilibrium concentrations are computed by calcu-
lating the Henry’s Law aqueous concentrations of atmospheric gases (adjusting gas
phase mixing ratios for highly soluble species), and solving a fourth-order equation in
[H\(^{+}\)]\(_{aq}\). Ion activity coefficients are subsequently calculated and ion aqueous activities
are adjusted accordingly.

3.2.3 Modifications to the CMAQ set of heterogeneous reactions

The most likely source of Cl and Cl\(^{-}\) in cloud droplets is not from gas phase Cl – which
is highly reactive and only expected to exist in air at extremely low concentrations – but
HCl. The latter goes readily into solution where it dissociates as HCl → H\(^{+}\)+Cl\(^{-}\). In the
presence of the sulfate radical,

\[
\text{SO}_4^{2-} + \text{Cl}^- \rightarrow \text{SO}_4^{2-} + \text{Cl}^- \quad (R13)
\]

(Zhu, 2004) and [Cl]\(_{aq}\) reacts with [Cl\(^{-}\)]\(_{aq}\) to produce [Cl\(^{2-}\)]\(_{aq}\). Properties of SO\(^{-}\)\(_4\) have
been measured in the laboratory (Chawla and Fessenden, 1975; Huie and Clifton,
1990), and its role in heterogeneous chemistry is described later. Also important are
the aqueous reactions

\[ \text{OH} + \text{Cl}^- \rightarrow \text{HOCl}^- \quad \text{(R14)} \]
\[ \text{HOCl}^- + \text{H}^+ \rightarrow \text{Cl}^- + \text{H}_2\text{O} \quad \text{(R15)} \]

Thus, [Cl]_{aq} is strongly controlled by [SO}_4^{2-} \text{]}_{aq} and [Cl^-]_{aq}. Zhu (2004) set [SO}_4^{2-} \text{]}_{aq}, [Cl]_{aq} and [Cl^-]_{aq} to constant values in his model.

Reactions not included in Zhu’s model (i.e., SO_2 oxidation by organic peroxides) are retained from the original CMAQ cloud chemistry module. Table 5 lists the set of all heterogeneous reactions included in the revised cloud chemistry module. Rate constants are those taken from Zhu (2004) and Zhu et al. (2006) or are currently used in CMAQ. Besides the added reactions involving MHP and PAA, the other differences between the CMAQ revisions and the Zhu’s model are in the treatment of the sulfate radical, Cl and Cl^- . Zhu set [SO}_4^{2-} \text{]}_{aq}=1 \times 10^{-12} \text{ M}. This served the purposes of his test for the relative importance of various sulfur oxidation reactions. However, using a constant for aqueous SO_4^- in CMAQ could introduce an artificial source of sulfur into the model. Zhu (2004) includes reactions with SO_4^- in his study because it was found to be important during his laboratory measurements of DMSO and CH_3SO_2^- oxidation. He describes three theories of the origin of SO_4^{-} in aqueous solution, including (1) a hypothetical reaction chain initiated by OH reacting with HSO_3^- that leads to formation of SO_5^- and eventually SO_4^2-, and (2) OH reacting with HSO_4^- . The value Zhu uses for [SO}_4^{2-} \text{]}_{aq} is many orders of magnitude less than the typical concentrations expected for both HSO_3^- and HSO_4^- based on reasonable atmospheric concentrations of SO_2 and H_2SO_4. A working assumption is to link [SO}_4^{2-} \text{]}_{aq} to computed levels of [HSO}_3^- \text{]}_{aq} and [HSO}_4^- \text{]}_{aq} by applying a small proportionality factor to computed ion levels (based on equilibrium considerations). This is what is done in the revised CMAQ module with [SO}_4^{2-}]=\alpha ([HSO}_3^-] + [HSO}_4^-), \alpha \leq 1 \times 10^{-3}.

Figure 1 illustrates the sensitivity of heterogeneous [SO_4^{2-}]_{aq} formation to \alpha and cloud droplet pH at a temperature of 298 K and pressure of 1 atm. In this example at-
Atmospheric mixing ratios were SO$_2$=0.4 ppbV, DMSO=DMSO$_2$=MSIA=MSA=0.1 ppbV, O$_3$=30 ppbV, H$_2$O$_2$=MHP=PAA=0.1 ppbV and OH=1×10$^{-10}$ ppbV, and cloud liquid water content ($W_c$) was 0.5 g m$^{-3}$. When pH is extremely low (≤1.5), steady-state sulfate formation rates from organic and inorganic sulfur oxidation are within a factor of 10. However, the rates diverge rapidly as pH increases for all values of $\alpha$ so that at pH=7 sulfate formation from oxidized organic sulfur compounds exceeds that from SO$_2$ by 5 orders of magnitude in the absence of [SO$_4^{2-}$]$_{aq}$ and much more when [SO$_4^{2-}$]$_{aq}$>0. Note that, in the presence of anthropogenic sources, atmospheric levels of DMS and its oxidation products are much lower than SO$_2$ but this is not necessarily the case in a simulation that examines the chemistry of “natural emissions” only. In addition, droplet pH is usually <5.6 unless there is a major nearby source of alkaline emissions. Thus, for expected droplet acidities, the influence of [SO$_4^{2-}$]$_{aq}$ is small when its magnitude compared to HSO$_3^-$+HSO$_4^-$ is one ppm or less, but its importance grows rapidly with pH and for $\alpha$ above 1×10$^{-6}$. Model sensitivity to $\alpha$ is explored further in Sect. 4.2.

Chlorine’s role in the heterogeneous chemistry of sulfate formation depends on the presence of the chloride ion. During his model testing, Zhu (2004) assumed [Cl]$_{aq}$=1×10$^{-13}$ M, or a factor of 10 less than the value for [SO$_4^{2-}$]$_{aq}$. In this work [Cl]$_{aq}$ is derived using Henry’s Law and the gaseous mixing ratio of ambient Cl. It follows that [Cl$^-$]$_{aq}$ is then computed from [Cl]$_{aq}$ and [Cl$^-$]$_{aq}$ using the equilibrium relation

$$\frac{[\text{Cl}][\text{Cl}^-]}{[\text{Cl}_2^-]} = 7.14 \times 10^{-6} \text{M}. \quad \text{(R16)}$$

Of the five DMSO oxidation reactions, those involving reactions with [Cl]$_{aq}$ and [Cl$^-$]$_{aq}$ are 2 to 4 orders of magnitude slower than those in which [OH]$_{aq}$ and [SO$_4^{2-}$]$_{aq}$ are reactants. Chlorine as Cl$^-$ can play a larger – though not dominant – role in reactions involving CH$_3$SO$_2^-$. Hence, the role of chlorine in heterogeneous organic sulfur chemistry is of minor importance most of the time.
Of the two reactions involving DMS, the one with OH is more than a factor of 20 faster than that with O$_3$, but O$_3$ concentrations are far greater than OH making the ozone reaction the dominant pathway. For reactions with DMSO, the hierarchy of rate constants is $k_{\text{OH}} \approx k_{\text{Cl}} > k_{\text{SO}_4} \gg k_{\text{Cl}_2} \gg k_{\text{O}_3}$. Ozone is the most abundant reactant to attack DMSO by at least 2 to 3 orders of magnitude. Nevertheless, the benefit of a higher concentration is still not sufficient to make up for its lower rate constant and the OH and SO$_4^-$ reactions will usually be the most important.

### 3.2.4 Generic chemical transient equation

The rate at which droplets take up gaseous pollutants can be limited by gaseous diffusion toward the droplets and by the efficiency with which molecules of certain species pass through the gas-droplet interface. These rate-limiting processes are not treated by the default CMAQ cloud chemistry module and have been added to the revised version. The following treatment is based on Seinfeld and Pandis (1998). Let the activity of water-soluble gas species $i$ at the surface of a cloud droplet be denoted $C_{s(i)}$. Diffusion limits both outside and within the droplet and variations in chemical reaction times can result in non-uniform $C_i$ throughout the droplet. This characteristic of reactant $C_i$ directly affects the temporal evolution of some species and must be treated in the chemical transient equations. The rate of change of the average $C_i$ in a droplet of radius $r_d$ is given by

$$\frac{dC_i}{dt} = \frac{x_{\text{mt}}}{RT} \left( p_i - \frac{C_{s(i)}}{(H_A)_i} \right) + X$$

(1)

where $x_{\text{mt}}$ is the mass transfer coefficient, $R$ is the universal gas constant, $T$ is temperature, $(H_A)_i$ is the Henry’s Law constant, $p_i$ is the atmospheric partial pressure of the species at a large distance from the droplet, and $X$ is an aqueous chemical reaction term representing any change due to chemical reactivity. To make (1) generic we replace $X$ with $\sum_k (Q_k P_{kl}) - \sum_j (Q_j L_{ij})$ with $P_{kl}$ representing the production rate of
species $i$ from a reaction between species $k$ and $l$, and $L_{ij}$ representing the loss rate of species $i$ through its reaction with species $j$. Parameter $Q$ (defined below) is an adjustment factor to account for the non-uniformity of a species activity, $C_i$ or $C_k$, within the droplet. Note that this assumes co-reactant species $C_j$ and $C_l$ are uniform within the drop. The transient equation then becomes

$$\frac{dC_i}{dt} = \frac{x_{mt}(i)}{RT} \left( p_i - \frac{C_i}{(H_A)_i} \right) + \sum_{kl} (Q_k P_{kl}) - \sum_j (Q_i L_{ij})$$

(2)

where $x_{mt}$ is given by

$$x_{mt}(i) = \left[ \frac{r_d^2 RT}{3 \kappa_g} + \frac{r_d (2 \pi M_i RT)^{1/2}}{3 a_i} \right]^{-1}$$

(3)

with $\kappa_g$ as the gas diffusivity, $M_i$ the molecular weight, and $a_i$ the accommodation coefficient. The first product term on the right hand side of (2) represents the diffusion and “sticking” tendency of species $i$ from the air surrounding a droplet (with partial pressure difference $p_i - C_i / H_A$) to the droplet surface. The parameter $a_i$ is the ratio of the molecules of species $i$ that adhere to the droplet surface to the total number of molecules that impact the droplet.

In (2), $Q$ is the ratio of the average droplet activity of the non-uniform species to its activity at the droplet surface. When $Q=1$ the activity (concentration) is uniform. Chemical production and loss terms are derived from the appropriate kinetic rate equations. The backward Euler implicit method is used to solve for $\frac{dC_i}{dt}$:

$$C_i^{n+1} = C_i^n + (P_i^{n+1} - C_i^{n+1} L_i^{n+1}) \Delta t$$

(4)

(Seinfeld and Pandis, 1998). Function $Q$ is given by

$$Q = 3 \left( \frac{\coth(q)}{q} - \frac{1}{q^2} \right), \quad q = r_d \left( \frac{kC_U}{k_w} \right)^{1/2}$$

(5)
where $k$ is the reaction rate constant, $C_U$ represents the uniform species activity, and $\kappa_w$ is the water diffusivity ($q$ and $Q$ are dimensionless). In general, $Q<1$ when $kC_U>10^8\text{ m}^{-2}\text{ s}^{-1}$ $\kappa_w$. If $\kappa_w=1\times10^{-9}\text{ m}^2\text{ s}^{-1}$ ($1\times10^{-5}\text{ cm}^2\text{ s}^{-1}$), then the co-reactant is non-uniform when $kC_U>0.1\text{ s}^{-1}$. This implies that the non-uniform species is consumed by chemical reaction at a rate $>10$ percent per second.

Unlike in the default CMAQ module, this approach requires that droplet size be defined. Cloud droplets are assumed to be monodisperse (uniform in size) to minimize computer execution time. Measured droplet size distributions described by Byers (1965) for different cloud types — ranging from fog to stratus and convectively-growing cumulus and for $0.02\text{ g m}^{-3}<W_c<0.8\text{ g m}^{-3}$ — were analyzed to estimate their median size characteristics. Median diameters for the analyzed droplet spectra ranged from 5 to 12 $\mu$m. Most values of $W_c$ provided to the cloud chemistry module are in the range represented by these median diameters, but higher $W_c$ are certainly possible. As used here, when $W_c\leq1\text{ g m}^{-3}$ the cloud module calculated $r_d$ as based on the information provided in Byers (1965). For $W_c>1$ radius was set equal to a constant ($r_d=6.15\mu$m) corresponding to the maximum value derived from this empirical formula. By introducing droplet size the cloud module is enabled to accommodate size-specific droplet chemistry in the future.

### 3.2.5 Transient and steady-state species in cloud chemical mechanism

Unlike the original CMAQ cloud chemistry module, some chemical species other than sulfate are not assumed to be steady-state. A species is assumed to be steady-state if its droplet concentration is likely to remain nearly constant during the relatively short temporal integration of the transient equations. This is true if a species is not a reactant and is usually a good assumption for reactive species if their concentrations are controlled by a large reservoir in the gas phase (i.e., the species is only partially soluble). For example, $[\text{SO}_2]_{aq}$, $[\text{HSO}_3^-]_{aq}$ and $[\text{SO}_3^{2-}]_{aq}$ are dependent on $p_{\text{SO}_2}$, the partial pressure of $\text{SO}_2$ in air. $\text{SO}_2$ is moderately soluble in water so that some dissolves into
the aqueous phase but a considerable amount remains in the gas phase. In addition, 
\([\text{HSO}_3^-]_{aq}\) and \([\text{SO}_3^{2-}]_{aq}\) are partly dependent on pH which tends to vary little during
the period of integration (\([\text{H}^+]_{aq}\) is treated as a steady-state species). Thus, for the 
short time interval when the transient equations are integrated any \(\text{SO}_2\) and its deriva-
tive ions consumed by chemical reactions are replaced by more \(\text{SO}_2\) from outside the 
cloud droplets. This allows the assumption that \([\text{SO}_2]_{aq}\), \([\text{HSO}_3^-]_{aq}\) and \([\text{SO}_3^{2-}]_{aq}\) are 
steady-state.

The steady-state assumption is strengthened by keeping the temporal integration interval short – currently \(\leq 4\) min. The original version of the CMAQ cloud module per-
forms the temporal integration over periods of 6 to 12 min. This time period is long com-
pared to some of the reaction rates in the module but allowed for more computational 
efficiency. With faster computer processors it is now feasible to shorten the integration 
interval. The revised module uses a minimum integration step of one minute, the ex-
act interval depending on the consumption rate of certain key species in the reaction 
set. The maximum interval of four minutes also allows for more frequent updating of 
gas phase chemistry so that some depleted reactive species in the air are allowed to 
recover more quickly between cloud chemical integrations than before.

Table 6 lists all the species in the revised cloud chemistry module, indicates which 
are treated as steady-state, which are reactive, and which are most likely to have non-
uniform droplet concentrations. There are eight species that are not steady-state and 
whose temporal changes are represented by transient equations. An analytical solution 
to this set of equations (see Appendix) is used to calculate temporal changes in cloud 
chemistry.

4 Behavior of the modified CMAQ model

Comparisons between the old and new cloud chemistry modules, and between 
different chemical pathways in the new module, provide insight into the effects 
of the new module on air quality simulations. All comparisons described here
were done using the natural emissions data set described by Smith and Mueller (2010), i.e., in the absence of anthropogenic emissions. CMAQ behavior in simulating sulfate aerosol was investigated by exercising the model in various chemical configurations to identify its sensitivity to the gas phase organic sulfur chemistry \( S_{\text{org}} = \text{DMS} + \text{DMSO} + \text{DMSO}_2 + \text{MSIA} + \text{MSA} \), cloud \( S_{\text{org}} \) chemistry, cloud cover bias, and selected cloud module parameters.

Aside from chemistry, the CMAQ configuration applied here followed that used by the VISTAS Regional Planning Organization (see http://vistas-sesarm.org/) as described in Tesche et al. (2008). The VISTAS modeling domain covers all of the continental United States, large portions of Canada, Mexico, and adjacent ocean waters. The CMAQ parent grid over this domain is 4032 km (west-east) \( \times \) 5328 km (north-south) and composed of 36 \( \times \) 36 km grid cells. Meteorological fields used by CMAQ are from simulations of the MM5 meteorological model (Grell et al., 1994). Chemical boundary conditions were derived from a 2002 global simulation using the GEOS-Chem model (Jacob et al., 2005). A deviation from Tesche et al. (2008) was our use of the SMVGEAR chemical solver in place of the optimized solver available in CMAQ for use with the CBIV and CB05 mechanisms. This was necessitated by changes in the gas phase chemical reaction set that preclude use of the optimized solvers, thereby increasing substantially the execution time for the model.

### 4.1 Grid-averaged model time series

Time series of simulated hourly natural pollutant concentrations for 2002, when averaged over the entire modeling domain, provide insight into the joint behavior of emissions and secondary pollutants. Surface layer mixing ratios of selected gas species and aerosol concentrations were averaged for each hour and then a 24-h smoothing filter applied to suppress diurnal noise. Model output for 29 December 2001 through 10 January 2002 was dropped from the analysis due to chemical spin-up issues. The simulation ended at 00 UTC on 1 January 2003 making 31 December incomplete (based on local time). Therefore, all 2002 results are presented for 354 days. Note that all
time series plots include “background” contributions from pollutants advected into the domain from the boundaries.

Figure 2 plots grid-averaged surface layer annual time series of ozone, NO$_y$ (=sum of NO, NO$_2$ and all other model oxidized nitrogen species) and formaldehyde (CH$_2$O). Both NO$_y$ and CH$_2$O exhibit a clear winter minimum and summer maximum consistent with the expected seasonally-driven photochemical cycle. However, ozone is nearly constant for the first four months, declines slightly May through September, and then levels off for the remainder of the year. Simulations made by removing lightning and wildfire NO$_x$ emissions revealed that the seasonal patterns of both sources favor higher summer ozone and in no way contribute to the observed ozone pattern (the other source of natural NO$_x$ – soils – is too small to have a significant effect on the grid average). Thus, the winter/early spring peak in grid-average ozone is imposed on the grid from outside the modeling domain, i.e., from the boundary conditions.

The global GEOS-Chem model, the source of these boundary conditions, appears to produce a pattern of background ozone that is similar to that produced by Berntsen et al. (1999) except that their modeling also produced a summer minimum in background air arriving in the US from across the Pacific Ocean. They concluded that the higher spring ozone was attributable to Asian emissions having a greater impact at long distances in spring because of enhanced trans-Pacific transport during that time of year. Vingarzan (2004) also found a spring (May) maximum in measured background ozone at “clean” sites in Canada and the US. Finally, Oltmans et al. (2008) analyzed ozone measured at west coast sites usually uninfluenced by air from the mainland, reporting an annual pattern for 2004 that looks a lot like the ozone pattern in Fig. 2 with a March–May peak. These similarities suggest that the CMAQ grid-average seasonal ozone pattern reflects a known phenomenon.

Time series of modeled sulfur (S) species are illustrated in Fig. 3. Inorganic S (S$_{\text{inorg}}$=SO$_2$+H$_2$S+sulfuric acid) represents the most abundant class of gaseous sulfur compounds. Grid-average values peak above 100 pptV during several periods throughout the year. Grid-average S$_{\text{org}}$ stays below 100 pptV, peaking in summer and falling
to levels well below those of $S_{\text{inorg}}$ in winter. The S radicals (labeled “S-rad” in Fig. 3) time series is the sum of organic and inorganic gaseous S intermediate species (e.g., SH, HSO, CH$_3$S and CH$_3$SCH$_2$) that are very reactive, have relatively short lifetimes and represent intermediate oxidation steps between DMS and H$_2$S on one hand and MSIA, MSA, H$_2$SO$_4$ and sulfate on the other. S radical values peak in summer. The total gaseous S time series (“S-gas”) plotted in Fig. 3 indicates that the sum of all natural gaseous species tends to remain fairly constant throughout the year with values in the 100–300 pptV range. Sulfate aerosol concentrations follow the expected seasonal cycle with grid-average values peaking near 0.3 µg m$^{-3}$ in summer.

Ammonia, NO$_z$ (=NO$_y$−NO$_x$) and ammonium nitrate aerosol time series are plotted in Fig. 4. NO$_z$, which includes nitric acid, represents the more oxidized of the nitrogen compounds and is a better indicator than NO$_x$ of precursors to nitrate aerosol formation. All these species follow a seasonal cycle with a grid-averaged summertime maxima. For NH$_4$NO$_3$ this represents a departure from the expectation that thermodynamics are more favorable for winter formation of the aerosol. In both winter and summer, simulated natural nitrate aerosol concentrations were primarily centered on areas with relatively high ammonia emissions. These areas were over the Pacific and Atlantic Oceans and the Gulf of Mexico, as well as in the vicinity of wildfires in the western US, Florida (winter), and eastern Canada (summer).

Secondary organic aerosols formed from precursor VOCs such as isoprene and terpene compounds, and from organic aerosol polymerization that results in non-volatile aerosols, were simulated in CMAQ4.6 using an approach developed for regional haze modeling (Morris et al., 2006) and implemented in the previous version of CMAQ. The changes introduced by Morris et al. were transferred to CMAQ4.6.

Figure 5 illustrates grid-averaged time series for all simulated natural particulate matter: sulfate, nitrate, estimated organic carbon (OC), elemental carbon (EC), fine soil dust, coarse particle mass (PM$_C$=particles in the 2.5–10 µm diameter range, fine sea salt and PM$_{2.5}$. All appeared consistent with expectations based on seasonal emissions behavior and the dependence of atmospheric chemistry on meteorology. Am-
monium sulfate/bisulfate, ammonium nitrate, and carbonaceous particles all peak in summer as does total PM$_{2.5}$ mass. Both fine dust and sea salt are highest in late winter and spring when winds are strongest. Coarse particles follow a similar pattern to that of fine dust.

Winter and summer grid-average natural ozone mixing ratios and aerosol concentrations are compared in Table 7. The difference between winter and summer “background” ozone is apparent. In the absence of anthropogenic emissions, a west-east ozone gradient is expected in winter due to the transport of anthropogenic emissions from Asia. Sulfate aerosol (including the associated ammonium component) is over a factor of two greater in summer than winter. Organic carbon aerosol mass is more than 6 times greater in summer than winter because of the combined contributions from wildfires and biogenic precursor emissions. Natural coarse particle mass is computed to be less in summer but PM$_{2.5}$ mass levels are much higher. These averages mask a great deal of spatial and temporal variability that is addressed by a future paper.

4.2 Influences of different gas and cloud chemistry treatments

Special CMAQ simulations for June 2002 investigated the influence of different gas and cloud chemistry options. June was selected because its high levels of photochemistry were expected to strongly differentiate among the different chemistry treatments. June test simulations were initiated following a common set of initial conditions derived from a preceding simulation of January–May 2002. The January–May simulation that produced the initial conditions was made using CMAQ4.6 with both revised gas and cloud chemistry options activated. Test results from the first week of June were not analyzed to allow the model to adjust to an abrupt change in internal parameters on 1 June. The various tests are summarized in Table 8. Comparisons of test results from 8–30 June are provided in the following sections.
4.2.1 Effect of adding reduced sulfur and chlorine gas phase chemistry: tests A and B compared

Differences between tests A and B reveal the impact of adding reduced sulfur and chlorine gas phase chemical reactions to the standard CB05 mechanism. Changes are quantified as the mean change, $\bar{\Delta}$, in variable $x$ relative to reference variable $x_0$ where $\Delta = \frac{x - x_0}{x_0}$ and the average is computed at each grid cell over the time period of the test simulations. The pattern in OH showed little change during the day with more significant changes at night. The resulting average over 8–30 June (Fig. 6, top) produced decreases over land as large as 60 percent and increases over the oceans of up to 60 percent. Nighttime increases over the water are almost certainly caused by the introduction of DMS and its derivatives. These species react with many other species that also react to remove OH. Thus, $S_{\text{org}}$ compounds act as an additional sink for species that remove OH thereby slowing the nocturnal depletion and resulting in higher nighttime levels. Widespread inland decreases in OH are the expected response to “aged $S_{\text{org}}$” (less DMS and more DMSO, etc.) in air advected across the continent from the west. Note that the aging of $S_{\text{org}}$ includes formation of $SO_2$.

The only source of secondary sulfate aerosols in standard CMAQ4.6 is $SO_2$ oxidation. The relative change in $SO_2$ due to the change in chemistry treatment is illustrated in Fig. 6 (middle). With meteorology fixed, the $SO_2$ response is determined by $SO_2$ formation from $S_{\text{org}}$ oxidation and to a lesser extent by changes in OH, peroxides, and ozone. Domain-wide $SO_2$ increases occurred because of the organic sulfur chemistry added to the model. The largest increases – often 3 orders of magnitude and more – occurred over and downwind of grid cells experiencing the highest emission rates of DMS and $H_2S$. However, these dramatic increases are due in large part because many of the most affected grid cells have little or no $SO_2$ emissions.

Aerosol sulfate is enhanced everywhere by the chemistry changes (Fig. 6, bottom) but the greatest increases occurred near sources of DMS and $H_2S$. Over many cells the increases exceeded a factor of 10. For ocean cells sulfate averages increased by
nearly 2 µg m\(^{-3}\) in some places. Inland sulfate increases averaged 0.1–0.2 µg m\(^{-3}\) over south Texas and Florida with smaller increases elsewhere.

### 4.2.2 Effect of adding organic sulfur cloud chemistry: tests B and C compared

Test C replaced the default CMAQ cloud chemistry module with one that included \(S_{\text{org}}\) reactions. The OH radical responded with mostly small increases over most of the domain (Fig. 7, top). Overall, changes in OH were far smaller than those attributable to the change in gas phase chemistry and were generally in response to the consumption of \(S_{\text{org}}\) by the heterogeneous reactions. Changes in \(SO_2\) (Fig. 7, middle) were negative over most of the domain. The \(SO_2\) response to cloud chemistry changes is caused partly by moving \(S_{\text{org}}\) from the gas phase, where it oxidizes to \(SO_2\), to the aqueous phase in which \(SO_2\) does not form. However, changes in the timing between cloud chemistry integration and the gas-phase chemistry may also play a role (see Sect. 4.2.3).

Changes in aerosol sulfate in response to cloud chemistry changes (Fig. 7, bottom) occurred primarily where clouds were most prevalent. Significant reductions in sulfate from reduced \(SO_2\) gas phase oxidation were offset by enhanced sulfate formation in clouds. Widespread sulfate increases occurred over the Gulf of Mexico, Florida and the western Atlantic east of Florida where diagnostics indicate a persistent cloud cover for the month. Generally, the cloud chemistry changes resulted in higher sulfate across the eastern half of the US. Sulfate increased over the Pacific Ocean off the North American coast by an average of 0.05–0.1 µg m\(^{-3}\) due to cloud chemistry but inland cloud effects were much smaller.

### 4.2.3 Effect of cloud OH uptake: tests D and B compared

Test D was done to determine the relative influence of the \(S_{\text{org}}\) versus \(SO_2\) cloud chemistry as well as the differences between the old and new cloud module \(SO_2\) chemistry. The former comparison, enabled by not allowing OH to enter the clouds, was facili-
tated because aqueous OH reactions involving $S_{\text{org}}$ are the dominant reactions in the clouds (reactions involving the sulfate radical and chlorine species were of much less significance because of the low value for $\alpha$ – see later comparison of tests E and F). With both tests B and D using the modified gas phase chemical mechanism, their differences illustrate how the original and modified $SO_2$ cloud chemistry differentially influence sulfate formation.

Differences in air concentrations of $SO_2$ and sulfate were generally small across the model domain. This is partly because cloudy cells accounted for only 5 percent of all grid cells. However, even in cells that experienced significant cloud cover, $f_{cc}$, (i.e., whenever $f_{cc}>10$ percent for a given hour) the differences in hourly averaged $SO_2$ and sulfate were usually small. Surface $SO_2$ mixing ratios beneath cloudy cell columns with $f_{cc}>0.1$ had a tendency to have somewhat higher values in test D compared to test B but the result is misleading. More cells experienced higher $SO_2$ in test D but the differences were generally <20 percent and were associated with those cells experiencing mixing ratios $<1$ ppbV. $SO_2$ decreases were larger – some exceeding 75 percent – but those tended to occur in the cells with mixing ratios $>1$ ppbV. The net effect was for higher $SO_2$ in test D with the domain-averaged value (under clouds) increasing from 0.02 ppbV to 0.23 ppbV. Sulfate also responded in test D with higher values under clouds. The pattern in sulfate differences as seen in Fig. 8 mimicked that in $SO_2$ with small increases occurring in cells with low sulfate and larger decreases occurring in cells with higher sulfate. The net result across the domain was for an increase in sulfate under cloudy conditions from 0.01 to 0.29 µg m$^{-3}$. The effect on all cells was far smaller, however, due to the low spatial coverage of simulated clouds.

The different results between tests D and B are associated with differences in the behavior of the original and modified cloud chemistry modules in their treatment of $SO_2$ chemistry (although some minor differences are caused by the reactions of $S_{\text{org}}$ as previously mentioned). The revised cloud module slows down $SO_2$ reactions by putting rate limits on droplet uptake of gaseous reactants and by computing average droplet concentrations (for fast-reacting species like $H_2O_2$) that are below the idealized
concentrations computed in the original cloud module. However, the effect of shortening the integration time step for droplet chemistry from 6–12 min down to 1–4 min can have an additional effect of increasing sulfate production under certain conditions (e.g., when reactants would otherwise be depleted for longer time steps) by allowing the gas chemistry to better keep pace with the droplet chemistry. The net effect as illustrated in Fig. 8 appears to be sulfate concentration differences that depend on which cloud module characteristic is more important for a particular situation. Note that comparisons of test results showed that the changes to \( \text{SO}_2 \) and sulfate concentrations were not caused by differences in calculated wet deposition scavenging.

### 4.2.4 Effect of enhancing cloud cover: tests E and C compared

There is evidence that cloud cover is underestimated in CMAQ. This issue has been addressed before (Mueller et al., 2006). For the current modeling, total sky cloud cover was examined using observations from 7 surface stations across the US\(^1\) and three in the Bahamas.\(^2\) Data were compared with CMAQ output. This allows for a test of how well CMAQ replicates cloud cover by combining cloud output from MM5 with its own sub-grid scale diagnostic cloud module. The comparison suffers from imperfect observations (they are all automated and do not include clouds above 3700 m) but is believed to be at least as representative of model performance as would be a comparison based on satellite imagery (the latter suffers from an inability to detect lower clouds beneath elevated cloud cover). CMAQ underestimated cloud cover for 2002 at all 7 US stations, with “clear” (<1/8 cover) being the predominant condition in the model for all but Tampa, Florida. However, for the Bahamian stations the model actually overestimated cloud cover. This appears symptomatic of a CMAQ diagnostic issue over warm waters, including the Gulf of Mexico, where persistent cloud cover was a characteristic problem.

\(^1\)Los Angeles, Denver, Houston, Atlanta, Tampa, Chicago and Boston.
\(^2\)Freeport, George Town and Nassau.
A low cloud cover bias across most of the CMAQ domain suggests that the role of clouds in $S_{\text{org}}$ and $SO_2$ oxidation may be underestimated. This may potentially underestimate natural sulfate aerosol levels. Test E examined the potential impact of this problem on sulfate by simulating enhanced cloud cover over Pacific Ocean grid cells. This was done by inserting clouds into model layers between 250 and 750 m above sea level when clouds were absent. In addition, minimum cloud liquid water content was arbitrarily set to 0.5 g m$^{-3}$, a value that is roughly half of the highest values used in CMAQ (and output from MM5). This ensured that clouds were able to process air at lower levels moving into the domain from the west throughout the period. Differences between test E and test C were used to estimate the upper limit to model sensitivity to clouds. Unlike previous tests, the effect on OH was fairly small ($-0.1 \leq \Delta_{\text{OH}} \leq 0.05$) with most changes being negative over the Pacific Ocean.

Responses of $SO_2$ and aerosol sulfate are plotted in Fig. 9. Decreases in $SO_2$ in response to increased cloud cover (Fig. 9, top) occurred over the Pacific Ocean, mostly in the range of $-40$ to $-80$ percent. Inland over the continent – and downwind from the artificially enhanced cloud cover – $SO_2$ changes were $\pm 20$ percent and generally decreased as expected from west to east. Sulfate changes (Fig. 9, bottom) were likewise positive over the Pacific Ocean and decreased going eastward. Most ocean grid cells had increases of 20–30 percent but some isolated areas experienced increases in excess of $10^4$. These latter cells were those that had extremely low sulfate values in the reference simulation and the large relative changes did not indicate a problem with excessively high values. Absolute sulfate changes were no more than 0.15 µg m$^{-3}$ in cells experiencing the highest relative sulfate increases, and the highest simulated concentrations over water were about 2 µg m$^{-3}$.

4.2.5 Model sensitivity to the aqueous sulfate radical: tests F and C compared

The aqueous sulfate radical, $SO_4^-$, is an integral part of the revised cloud chemistry model as implemented from Zhu (2004). The parameter $\alpha$ used in the revised CMAQ cloud module determines the magnitude of $[SO_4^+]_{\text{aq}}$ that reacts with $\text{DMSO}_{\text{aq}}$ and...
MSIA\textsubscript{aq} (as dissociated to [CH\textsubscript{3}SO\textsubscript{2}\textsuperscript{-}]\textsubscript{aq}). Zhu (2004) set [SO\textsubscript{4}\textsuperscript{-}]\textsubscript{aq}=1\times10^{-12} \text{ M}. His modeling used an atmospheric SO\textsubscript{2} mixing ratio at cloud height of about 6 pptV (CMAQ values for June were \leq20 pptV over the Pacific) and he assumed a cloud droplet pH of 5. Using published Henry’s Law and dissociation constants for SO\textsubscript{2} yields [HSO\textsubscript{3}\textsuperscript{-}]\textsubscript{aq}=1\times10^{-8} \text{ M} at 298 K near sea level. This is equivalent to \( \alpha=1\times10^{-4} \) in the absence of sulfuric acid. The rate constants for reactions involving the sulfate radical made it the second most important reactant in his model after OH (Zhu, 2004). Based on this, we conservatively assumed \( \alpha=1\times10^{-6} \) for all but test F thereby maximizing the contribution from OH relative to SO\textsubscript{4}\textsuperscript{-}. However, at a realistic cloud droplet pH of 4 the value of \( \alpha \) would be \( 1\times10^{-3} \) and the sulfate radical would make a much larger contribution to the cloud S\textsubscript{org} chemistry, rivaling OH as the primary reactant oxidizing DMSO. We tested the sensitivity of CMAQ to \( \alpha \) by increasing it to \( 1\times10^{-3} \). Thus, test F results represent an upper limit to the model’s sensitivity to sulfate radical in-cloud reactions.

Figure 10 illustrates the relative sensitivity of SO\textsubscript{2} and sulfate to \( \alpha \). The average change \( \bar{\Delta}_{\text{SO}_2} \) (Fig. 10, top) produced by increasing \( \alpha \) was a net SO\textsubscript{2} reduction over the model domain of only 2.4 percent. However, SO\textsubscript{2} reductions averaged >5 percent over the Pacific Ocean where S\textsubscript{org} was more prevalent. In Fig. 10 (bottom) \( \bar{\Delta}_{\text{SO}_4} \) is seen to be positive across the domain (+5 percent) but especially over the Gulf of Mexico and southeastern US (+26 percent). The relative increase in sulfate is larger where sulfate concentrations are originally smaller and where more persistent cloud cover has a greater influence on sulfate formation. We conclude that modeled sulfate sensitivity to \( \alpha \) is small on average but can be significant in regions with persistent cloud cover. Note that the relatively large change over the southeastern US and adjacent ocean is only about 0.035 \text{ µg m}^{-3} in absolute terms.
4.2.6 Ozone and OC sensitivity to different CMAQ chemistry configurations

The influence of different CMAQ chemistry configurations on ozone was also examined. The case can be made that model O₃ results from tests B, C and D were very similar to each other and were significantly different from test A. Test A (original model) produced higher O₃ across most of the grid for most hours with a grid-average difference of about 3.5 ppbV compared to test B in which the gas-phase chemistry was modified to include chlorine, S_{org} and H₂S reactions. This difference is likely due mainly to the extra sink for various radicals included in the gas chemistry for S_{org} and H₂S. Test C (implementation of revised cloud model with S_{org} chemistry) produced on average 1.5 ppbV more O₃ than test B. Blocking OH uptake in clouds in test D resulted in an average reduction in O₃ (from test C) of only 0.25 ppbV.

Differences in OC between tests A and C were also minor. This is primarily because organic aerosol mass is dominated by wildfire emissions that are unaffected by the model chemical schemes. However, SOA is somewhat sensitive to the model chemistry because of the role played by OH in oxidizing VOCs. Thus, in areas where total organic aerosol mass is primarily composed of SOA mass, the influence of chemical schemes may be important. Average relative differences in SOA (and OC) for tests A and C were nearly nonexistent over the Pacific Ocean but this is not surprising given the nearly total absence of precursor VOC species there. The largest differences occurred over the Gulf of Mexico with decreases averaging about 7 percent (Atlantic Ocean decreases were only about 2–3 percent). SOA decreases were driven by OH consumption by S_{org} both in the gas and aqueous phases. Inland, the largest SOA effects occurred over the Southeast US with SOA decreases averaging nearly 5 percent. Across the northern US and Canada SOA increases averaging about 3–4 percent were modeled, perhaps due to transport from the south of more unreacted VOCs. Thus, the introduction of S_{org} chemistry has a small negative impact on SOA – and total OC – mass over the Atlantic Ocean/Gulf of Mexico and adjacent inland areas, and a compensating effect farther north.
In certain grid cells influenced by wildfire emissions, hourly OC differences as large as \( \pm 400 \mu g \, m^{-3} \) or more occurred during the 8–30 June test A overlap with test C. Typically, offsetting differences of opposite sign and nearly equal magnitude occurred in adjacent grid cells. The mechanism for this effect is not clear but could be associated with the interaction of \( S_{org} \) with OH. In any event, the net effect when averaged over several hours and across large regions was miniscule.

### 4.3 Simulated concentrations in the marine boundary layer

Table 9 compares average simulated \( S_{org} \), SO\(_2\) and sulfate concentrations in the Pacific Ocean marine boundary layer with average values measured globally by various researchers. The observations represent a variety of measurement techniques, locations and seasons. Reported values were averaged for comparison with the CMAQ June 2002 results from test C (revised model). Simulated DMS values are consistent with and slightly lower than those reported from field data, the latter usually based on summer season measurement campaigns. Simulated DMSO, MSA and SO\(_2\) levels are also lower than the mean observations. This implies that the test C model configuration may underestimate DMS oxidation rates and, thus, oxidation products. The exception is sulfate with model values being somewhat higher than those measured by several investigators.

A second comparison was made (Table 9) with observations using model results from test F in which DMS oxidation and sulfate formation were maximized by increasing the role of the sulfate radical in cloud oxidation of DMSO. As expected, this reduced DMS concentrations about 10 percent, and decreased DMSO by nearly 50 percent. It also increased MSA by 50–60 percent. However, \( S_{org} \) oxidation product SO\(_2\) decreased about 5 percent and average sulfate aerosol increased slightly. It is possible that, in test F over the Pacific Ocean, enhanced cloud oxidation of \( S_{org} \) was mostly offset by lower gas-phase oxidation leading to little net change in SO\(_2\) and only a small increase in sulfate.
Another way to examine these data is to normalize DMSO, MSA, SO$_2$ and sulfate by DMS concentrations to determine how closely the relative abundance of simulated DMS oxidation products mimic the observed relative levels thereby providing a better way to evaluate the model’s S$_{org}$ chemistry. Using results from tests C and F, CMAQ values of DMSO/DMS over the Pacific Ocean were 0.005–0.008 compared to an observed ratio of about 0.01. Likewise, normalized MSA in CMAQ was 0.030–0.067 compared to observe values of 0.067–0.560, and normalized CMAQ SO$_2$ was 0.076–0.080 compared with ~0.40 observed. Finally, normalized sulfate from CMAQ was 0.31–0.46 compared with 0.23–1.60 observed. The only simulated species whose normalized concentrations were clearly not consistent with observed normalized values was SO$_2$. However, observed maritime SO$_2$ is represented here by data from only one study which may not be representative of the larger population of actual conditions.

These results suggest that the revised CMAQ model chemistry, acting on the new ocean emissions of DMS, does a reasonable job simulating the behavior of organic sulfur. Intermediate products DMSO, MSA and SO$_2$ (and, by implication, DMSO$_2$ and MSIA) tend to fall on the low side of observed values when normalized by DMS. Simulated sulfate levels seem to be relatively unbiased compared to observations made over the oceans.

5 Summary

A revised cloud chemistry module and modifications to the CMAQ4.6 CB05 gas phase chemical mechanism have been tested as a prelude to detailed modeling of natural air pollutant levels. This model, coupled with a natural emissions data base, provides a means of exploring contributions from natural systems/processes to total air quality over the US. Simulated natural+background ozone across the modeling domain has a winter-spring maximum consistent with observations at background sites along the western edge of North America. Various aerosol components have either summer or winter-spring maxima depending on their means of formation.
The most notable effects of introducing gas-phase and cloud S$_{org}$ and gas-phase H$_2$S chemistry changes in CMAQ4.6 are:

- Slight overall decreases in natural ozone – averaging 2 ppbV in summer – and attributable to decreases in OH and other oxidant radicals.

- Sulfate increases of up to 2 µg m$^{-3}$ on an hourly basis were found over the Pacific Ocean in areas far removed from SO$_2$ sources, and increases of nearly 1 µg m$^{-3}$ occurred over the Gulf of Mexico. The largest inland increases occurred over the Southeast US along coastal areas. In the vicinity of high SO$_2$ emissions (e.g., wildfires), the revised chemistry occasionally reduced sulfate levels, sometimes considerably.

- One hour changes in natural organic aerosol mass in response to the added sulfur chemistry were generally moderate except in the vicinity of wildfires where variations of ± several hundred µg m$^{-3}$ sometimes occurred during a few hours. However, across the domain, natural organic aerosol mass changes averaged <±0.1 µg m$^{-3}$ in June.

- In locations over the Pacific Ocean where continuous cloud cover was added to test model sensitivity to cloud presence, modeled sulfate concentrations at the surface increased as much as 0.15 µg m$^{-3}$ and total sulfate concentrations of up to 2 µg m$^{-3}$ occurred. Modeled sulfate sensitivity to the aqueous sulfate radical was smaller, with sulfate increasing by 26 percent over the Gulf of Mexico but totaling <0.04 µg m$^{-3}$ at most.

- Simulated levels of DMS are realistic compared with observations for similar marine environments. Modeled levels of DMS oxidation products (DMSO, MSA and SO$_2$) are generally lower, on average, than observations but DMSO and MSA concentrations normalized by DMS are on the lower end of the range in observed normalized values. Sulfate responded positively to increased cloud cover and in-
clouds levels of the sulfate radical, and simulated sulfate concentrations over the Pacific Ocean were similar to those reported by field measurements.

As for the sulfate radical scaling factor $\alpha$, model results for sulfate do not appear to be very sensitive overall to its magnitude between $1 \times 10^{-6}$ and $1 \times 10^{-3}$ although the model response could be greater when the model is run with a combined natural and anthropogenic emissions data set. The importance of $\alpha$ depends on the presence of substantial cloud cover. A scaling factor toward the upper end of this range, given the tendency for the model to underestimate DMS oxidation products, may produce more realistic effects from the sulfate radical but its importance will depend on the availability of SO$_2$. The effects of the sulfate radical will be most important in coastal areas where DMS oxidation products are most abundant.

One potential consequence of the revised set of chemical reactions, requiring further testing to verify, is the decrease in SO$_2$ → sulfate oxidation efficiency in some anthropogenic SO$_2$ plumes when the enhanced natural emissions and “standard” anthropogenic emissions inventories are combined. This effect was seen in natural SO$_2$ plumes from wildfires and is likely associated with the increased competition for OH cited above. The revised model (with implementation of an updated SOA formation scheme) described here represents a new tool for air quality management because it provides a means of evaluating more realistically the influence of natural trace gas emissions on total air pollutant levels.

Appendix A

Analytical solution to the heterogeneous chemical transient equations

The equations in this appendix use subscripts to denote the various chemical species. Table A1 is a key that defines the subscript values in terms of the species they represent. The set of heterogeneous chemical transient equations in the modified CMAQ4.6 cloud chemistry module consists of the following:
Sulfate:

\[
\frac{dC_4}{dt} = \frac{1}{Y_2} \left[ \gamma_1 k_{21,23} Q_{21(23)} \tilde{C}_{23} C_{21} + 0.7 k_{22,31} \tilde{C}_{31} C_{22} + \gamma_1^2 k_{16,23} \tilde{C}_{23} C_{16} + \gamma_1 k_{17,31} \tilde{C}_{31} C_{17} + \gamma_1 k_{5,7} Q_{7(5)} \tilde{C}_{5} C_{7} + (k_{1,24} \tilde{C}_1 \tilde{C}_{24} + \gamma_1 k_{5,24} \tilde{C}_5 \tilde{C}_{24} + \gamma_2 k_{6,24} \tilde{C}_6 \tilde{C}_{24} + \gamma_1 k_{5,25} Q_{25(5)} \tilde{C}_5 \tilde{C}_{25} + \gamma_1 k_{5,26} \tilde{C}_5 \tilde{C}_{26}) \right] \tag{A1}
\]

\[
H_2O_2:
\frac{dC_7}{dt} = g(7,T) \left[ p_7 - \frac{C_7}{(H_A)_7} \right] - \gamma_1 k_{5,7} Q_{7(5)} \tilde{C}_5 C_7 \tag{A2}
\]

\[
CH_3SO^-:
\frac{dC_{16}}{dt} = (k_{21,23} Q_{21(23)} \tilde{C}_{23} + k_{21,32} Q_{21(32)} \tilde{C}_{32} + k_{21,33} \tilde{C}_{33}) C_{21} - (k_{16,31} \tilde{C}_{31} + k_{16,23} \tilde{C}_{23} + k_{16,33} \tilde{C}_{33}) C_{16} \tag{A3}
\]

\[
CH_3SO_3^-:
\frac{dC_{17}}{dt} = (k_{16,31} \tilde{C}_{31} + k_{16,23} \tilde{C}_{23} + k_{16,33} \tilde{C}_{33}) C_{16} - k_{17,31} \tilde{C}_{31} C_{17} \tag{A4}
\]

MSIA:

\[
\frac{dC_{18}}{dt} = g(18,T) \left[ p_{18} - \frac{C_{18}}{(H_A)_{18}} \right] C_{18} + k_{21,31} Q_{21(31)} \tilde{C}_{31} C_{21} + \frac{\tilde{C}_{11}}{k_{18}} \frac{dC_{16}}{dt} \tag{A5}
\]

MSA:

\[
\frac{dC_{19}}{dt} = g(19,T) \left[ p_{19} - \frac{C_{19}}{(H_A)_{19}} \right] C_{19} + 0.3 k_{22,31} \tilde{C}_{31} C_{22} + \frac{\tilde{C}_{11}}{k_{19}} \frac{dC_{17}}{dt} \tag{A6}
\]

DMSO:

\[
\frac{dC_{21}}{dt} = g(21,T) \left[ p_{21} - \frac{C_{21}}{(H_A)_{21}} \right] + k_{20,24} Q_{20,24} \tilde{C}_{20} \tilde{C}_{24} + k_{20,31} Q_{20(31)} \tilde{C}_{20} \tilde{C}_{31} - k_{21,24} C_{21} \tilde{C}_{24} - k_{21,31} Q_{21(31)} C_{21} \tilde{C}_{31} - k_{21,23} Q_{21(23)} C_{21} \tilde{C}_{23} - k_{21,32} Q_{21(32)} C_{21} \tilde{C}_{32} - k_{21,33} C_{21} \tilde{C}_{33} \tag{A7}
\]
DMSO$_2$:

\[
\frac{dC_{22}}{dt} = g(22,T) \left[ p_{22} - \frac{C_{22}}{(H_A)_{22}} \right] + k_{21,24} \tilde{C}_{24} C_{21} - k_{22,31} \tilde{C}_{31} C_{22} \tag{A8}
\]

where individual variables (activities) are denoted by $C_j$ with subscript $j$ indicating the species index number (Table A1). $\gamma_1$ and $\gamma_2$ are ion activity coefficients. Parameters $k$, $Q$, $\tilde{C}$, $g$, $p$, and $H_A$ with subscripts omitted are all known constants at temperature $T$ and are defined as follows:

- $k_{ij}$: rate constant for reaction between species $i$ and $j$
- $Q_{i(j)}$: concentration adjustment coefficient for non-uniform species $i$ reacting with uniform species $j$ ($Q_{20,24}$ is an exception; see below).
- $Q_{20,24}$: Both species 20 and 24 may be non-uniform and this quantity must be computed following (5) in the main text, $Q_{20,24} = f(q), q = r_d \left( \frac{k_{20,04} \max(C_{20},C_{24})}{k_w} \right)^{1/2}$
- $\tilde{C}_i$: activity of steady-state species $i$ (=concentration for non-ionic species)
- $g(i,T)$: mass transfer function for gas species $i$ at temperature $T$; [representing $\frac{x_m(i)}{RT}$ (see paper Eq. 3)]
- $p_i$: gas partial pressure of species $i$
- $H_{A(i)}$: Henry’s Law constant for species $i$.

Equations (A1) through (A8) are linear. Their solutions can be obtained by integrating these equations with time. Since the solutions of some equations are dependent on those of others, the procedure for solving equations (A1) through (A8) is given in this order: $C_{21}$, $C_{22}$, $C_{16}$, $C_{17}$, $C_7$, $C_{18}$, $C_{19}$, and $C_4$. The initial conditions are $C_i(t=0) = B_i$, where $i = 21, 22, 16, 17, 7, 18, 19,$ and $4$.

Integrating (A7) with time after proper manipulation and simplification leads to

\[
C_{21}(t) = \frac{\beta_{21} B_{21} - \alpha_{21}}{\beta_{21}} e^{-\beta_{21} t} + \frac{\alpha_{21}}{\beta_{21}}, \tag{A9}
\]

with coefficients

\[
\alpha_{21} = g(21,T)p_{21} + k_{20,24} Q_{20,24} \tilde{C}_{20} \tilde{C}_{24} + k_{20,31} Q_{20(31)} \tilde{C}_{20} \tilde{C}_{31}, \tag{A10}
\]

\[15854\]
\[ \beta_{21} = \frac{g(21, T)}{(H_A)_{21}} + k_{21,24} \bar{C}_{24} + k_{21,31} Q_{21(31)} \bar{C}_{31} + k_{21,23} Q_{21(23)} \bar{C}_{23} + k_{21,32} Q_{21(32)} \bar{C}_{32} + k_{21,33} \bar{C}_{33}. \]  
(A11)

Similarly, the solution for (A8) after substituting \( C_{21} \) with (A9) is given by
\[ C_{22}(t) = \frac{n_{22}}{\beta_{22} - \beta_{21}} e^{-\beta_{21} t} + \left( B_{22} - \frac{n_{22}}{\beta_{22} - \beta_{21}} - \frac{a_{22}}{\beta_{22}} \right) e^{-\beta_{22} t} + \frac{a_{22}}{\beta_{22}}, \]  
(A12)

where
\[ \begin{cases} 
\alpha_{22} = g(22, T) \rho_{22} + \frac{a_{21}}{\beta_{21}} k_{21,24} \bar{C}_{24}, \\
\beta_{22} = \frac{g(22, T)}{(H_A)_{22}} + k_{22,31} \bar{C}_{31}, \\
n_{22} = k_{21,24} \bar{C}_{24} - \frac{\beta_{21} B_{21} - a_{21}}{\beta_{21}}. 
\end{cases} \]  
(A13)

Substituting (A9) into (A3) and integrating with time results in
\[ C_{16}(t) = \frac{n_{16}}{\beta_{16} - \beta_{21}} e^{-\beta_{21} t} + \left( B_{16} - \frac{n_{16}}{\beta_{16} - \beta_{21}} - \frac{a_{16}}{\beta_{16}} \right) e^{-\beta_{16} t} + \frac{a_{16}}{\beta_{16}}, \]  
(A14)

where
\[ \begin{cases} 
\alpha_{16} = \frac{a_{21}}{\beta_{21}} (k_{21,23} Q_{21(23)} \bar{C}_{23} + k_{21,32} Q_{21(32)} \bar{C}_{32} + k_{21,33} \bar{C}_{33}), \\
\beta_{16} = k_{16,31} \bar{C}_{31} + k_{16,23} \bar{C}_{23} + k_{16,33} \bar{C}_{33}, \\
n_{16} = \frac{a_{16}}{a_{21}} (\beta_{21} B_{21} - a_{21}). 
\end{cases} \]  
(A15)

Substituting (A14) into (A4) and integrating with time yields
\[ C_{17}(t) = \frac{n_{17}}{\beta_{17} - \beta_{21}} e^{-\beta_{21} t} + \left( B_{17} - \frac{n_{17}}{\beta_{17} - \beta_{21}} - \frac{\delta_{17}}{\beta_{17}} - \frac{a_{17}}{\beta_{17}} \right) e^{-\beta_{17} t} + \frac{\delta_{17}}{\beta_{17}} e^{-\beta_{16} t} + \frac{a_{17}}{\beta_{17}}, \]  
(A16)
where

\[
\begin{aligned}
\alpha_{17} &= \frac{\alpha_{16}}{\beta_{16}} (k_{16,31} \tilde{C}_{31} + k_{16,23} \tilde{C}_{23} + k_{16,33} \tilde{C}_{33}), \\
\beta_{17} &= k_{17,31} \tilde{C}_{31}, \\
\eta_{17} &= \frac{\eta_{16}}{\beta_{16}-\beta_{21}} (k_{16,31} \tilde{C}_{31} + k_{16,23} \tilde{C}_{23} + k_{16,33} \tilde{C}_{33}), \\
\delta_{17} &= \left( B_{16} - \frac{\eta_{16}}{\beta_{16}-\beta_{21}} - \frac{\alpha_{16}}{\beta_{16}} \right) (k_{16,31} \tilde{C}_{31} + k_{16,23} \tilde{C}_{23} + k_{16,33} \tilde{C}_{33}).
\end{aligned}
\] (A17)

Next, integrating (A2) gives

\[
C_7(t) = \frac{\beta_7 B_7 - \alpha_7}{\beta_7} e^{-\beta_7 t} + \frac{\alpha_7}{\beta_7} \tag{A18}
\]

where

\[
\alpha_7 = g(7,T)p_7, \\
\beta_7 = \frac{g(7,T)}{(H_A)_7} + \gamma_1 k_{5,7}Q_{7(5)} \tilde{C}_5. \tag{A19}
\]

Substituting (A9) and (A14) into (A5) and integrating with time leads to

\[
C_{18}(t) = \frac{\delta_{18}}{\beta_{18}-\beta_{16}} e^{-\beta_{16} t} + \left( B_{18} - \frac{\eta_{18}}{\beta_{18}-\beta_{21}} - \frac{\delta_{18}}{\beta_{18}-\beta_{16}} - \frac{\alpha_{18}}{\beta_{18}} \right) e^{-\beta_{18} t} \\
+ \frac{\eta_{18}}{\beta_{18}-\beta_{21}} e^{-\beta_{21} t} + \frac{\alpha_{18}}{\beta_{18}}, \tag{A21}
\]

where

\[
\begin{aligned}
\alpha_{18} &= g(18,T)p_{18} + \frac{\alpha_{21}}{\beta_{21}} k_{21,31} Q_{21(31)} \tilde{C}_{31}, \\
\beta_{18} &= \frac{g(18,T)}{(H_A)_{18}}, \\
\eta_{18} &= k_{21,31} Q_{21(31)} \tilde{C}_{31} \left( \frac{\beta_{21} B_{21} - \alpha_{21}}{\beta_{21}} \right) - \frac{\tilde{C}_{11}}{k_{18}} \frac{\beta_{21} \eta_{16}}{\beta_{16}-\beta_{21}}, \\
\delta_{18} &= -\frac{\beta_{16} \tilde{C}_{11}}{k_{18}} \left( B_{16} - \frac{\eta_{16}}{\beta_{16}-\beta_{21}} - \frac{\alpha_{16}}{\beta_{16}} \right).
\end{aligned} \tag{A22}
\]
Next, substituting (A12) and (A16) into (A6) and integrating with time results in

\[
C_{19}(t) = \frac{\theta_{19}}{\beta_{19} - \beta_{16}} e^{-\beta_{16} t} + \frac{\lambda_{19}}{\beta_{19} - \beta_{17}} e^{-\beta_{17} t} + \frac{\delta_{19}}{\beta_{19} - \beta_{21}} e^{-\beta_{21} t} + \frac{n_{19}}{\beta_{19} - \beta_{22}} e^{-\beta_{22} t} \\
+ \left( B_{19} - \frac{n_{19}}{\beta_{19} - \beta_{22}} - \frac{\delta_{19}}{\beta_{19} - \beta_{21}} - \frac{\lambda_{19}}{\beta_{19} - \beta_{17}} - \frac{\theta_{19}}{\beta_{19} - \beta_{16}} - \frac{\alpha_{19}}{\beta_{19}} \right) e^{-\beta_{19} t} + \frac{\alpha_{19}}{\beta_{19}},
\]

(A23)

where

\[
\begin{align*}
\alpha_{19} &= g(19, T) \rho_{19} + 0.3 k_{22,31} \bar{C}_{31} \frac{a_{22}}{\beta_{22}}, \\
\beta_{19} &= \frac{g(19, T)}{(H_{A})_{19}}, \\
n_{19} &= 0.3 k_{22,31} \bar{C}_{31} \left( B_{22} - \frac{n_{22}}{\beta_{22} - \beta_{21}} - \frac{a_{22}}{\beta_{22}} \right), \\
\delta_{19} &= 0.3 k_{22,31} \bar{C}_{31} \left( \frac{n_{22}}{\beta_{22} - \beta_{21}} - \frac{\bar{C}_{11}}{k_{19}} \left( \beta_{21} \frac{B_{19}}{\beta_{17}} - \frac{\beta_{17}}{\beta_{16}} \right) \right), \\
\lambda_{19} &= -\frac{\beta_{17} \bar{C}_{11}}{k_{19}} \left( B_{17} - \frac{n_{17}}{\beta_{17} - \beta_{21}} - \frac{\delta_{17}}{\beta_{17} - \beta_{16}} - \frac{\delta_{17}}{\beta_{16}} \right), \\
\theta_{19} &= -\frac{\bar{C}_{11}}{k_{19}} \left( \beta_{16} \frac{\delta_{17}}{\beta_{17} - \beta_{16}} \right).
\end{align*}
\]

(A24)

Finally, integrating equation (A1) with time and substituting (A9), (A12), (A14), (A16), and (A18) for \(C_{21}, C_{22}, C_{16}, C_{17},\) and \(C_{7},\) we obtain

\[
C_{4}(t) = \alpha_{4} t - \frac{\beta_{4}}{\beta_{21}} e^{-\beta_{21} t} - \frac{n_{4}}{\beta_{7}} e^{-\beta_{7} t} - \frac{\delta_{4}}{\beta_{22}} e^{-\beta_{22} t} - \frac{\lambda_{4}}{\beta_{16}} e^{-\beta_{16} t} - \frac{\theta_{4}}{\beta_{17}} e^{-\beta_{17} t} \\
+ \left( B_{4} + \frac{\beta_{4}}{\beta_{21}} + \frac{n_{4}}{\beta_{7}} + \frac{\delta_{4}}{\beta_{22}} + \frac{\lambda_{4}}{\beta_{16}} + \frac{\theta_{4}}{\beta_{17}} \right),
\]

(A25)

where

\[
\alpha_{4} = \frac{y_{1}}{y_{2}} k_{21,23} Q_{21(23)} \bar{C}_{23} \frac{a_{21}}{\beta_{21}} + \frac{0.7}{y_{2}} k_{22,31} \bar{C}_{31} \frac{a_{22}}{\beta_{22}} \\
+ \frac{y_{2}^{2}}{y_{2}} k_{16,23} \bar{C}_{23} \frac{a_{16}}{\beta_{16}} + \frac{y_{1}}{y_{2}} k_{17,31} \bar{C}_{31} \frac{a_{17}}{\beta_{17}}.
\]

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\[ \begin{align*}
\beta_4 &= \frac{\gamma_1}{\gamma_2} k_{21,23} Q_{21(23)} \bar{C}_{23} \frac{\beta_{21}}{\bar{C}_{21}} B_{21} - \alpha_{21} \\
&+ \frac{0.7}{\gamma_2} k_{22,31} \bar{C}_{31} \frac{\eta_{22}}{\beta_{22} - \beta_{21}} \\
&+ \frac{\gamma_1^2}{\gamma_2} k_{16,23} \bar{C}_{23} \frac{n_{16}}{\beta_{16} - \beta_{21}} \\
&+ \frac{\gamma_1}{\gamma_2} k_{17,31} \bar{C}_{31} \frac{n_{17}}{\beta_{17} - \beta_{21}},
\end{align*} \]  
(A27)

\[ \begin{align*}
\eta_4 &= \frac{\gamma_1}{\gamma_2} k_{5,7} Q_{7(5)} \bar{C}_{5} \frac{\beta_7 B_7 - \alpha_7}{\beta_7},
\end{align*} \]  
(A28)

\[ \begin{align*}
\delta_4 &= \frac{0.7}{\gamma_2} k_{22,31} \bar{C}_{31} \left( B_{22} - \frac{\eta_{22}}{\beta_{22} - \beta_{21}} - \alpha_{22} \right),
\end{align*} \]  
(A29)

\[ \begin{align*}
\lambda_4 &= \frac{\gamma_1^2}{\gamma_2} k_{16,23} \bar{C}_{23} \left( B_{16} - \frac{n_{16}}{\beta_{16} - \beta_{21}} - \alpha_{16} \right) + \frac{\gamma_1}{\gamma_2} k_{17,31} \bar{C}_{31} \frac{\delta_{17}}{\beta_{17} - \beta_{16}},
\end{align*} \]  
(A30)

\[ \begin{align*}
\theta_4 &= \frac{\gamma_1}{\gamma_2} k_{17,31} \bar{C}_{31} \left( B_{17} - \frac{n_{17}}{\beta_{17} - \beta_{21}} - \frac{\delta_{17}}{\beta_{17} - \beta_{16}} - \alpha_{17} \right).
\end{align*} \]  
(A31)
Acknowledgements. This work was funded by the environmental research program of the Tennessee Valley Authority (TVA) and the Electric Power Research Institute (EPRI). The authors are indebted to the efforts of our colleague, Shandon Smith, who prepared the natural emissions data base used in this project. We are also grateful for the constructive feedback provided by Roger Tanner (TVA) and Eladio Knipping (EPRI) during the course of this work.

References


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Table 1. Chlorine reactions added to CB05 in CMAQ4.6.\(^a\)

<table>
<thead>
<tr>
<th>Reaction</th>
<th>Rate constant(^b), (k) ((cm^3\text{ molecule}^{-1}\text{s}^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>(Cl_2 + h\nu \rightarrow 2Cl)</td>
<td>(0.264k_{NO_2})</td>
</tr>
<tr>
<td>(HOCl + h\nu \rightarrow OH + Cl)</td>
<td>(0.51k_{ACRO})</td>
</tr>
<tr>
<td>(PAR + Cl \rightarrow HCl + 0.87XO_2 + 0.13XO_2N + 0.11HO_2 + 0.11ALD2 + 0.76ROR - 0.11PAR)</td>
<td>(78k_{OH+PAR})</td>
</tr>
<tr>
<td>(OLE + Cl \rightarrow FMCL + ALD2 + 2XO_2 + HO_2 - PAR)</td>
<td>(20k_{OH+OLE})</td>
</tr>
<tr>
<td>(CH_4 + Cl \rightarrow HCl + XO_2 + HCHO + HO_2)</td>
<td>(6.6 \times 10^{-12}\exp(-1240/T))</td>
</tr>
<tr>
<td>(ETH + Cl \rightarrow 2XO_2 + HCHO + FMCL + HO_2)</td>
<td>(12.6k_{OH+ETH})</td>
</tr>
<tr>
<td>ISOP + Cl \rightarrow 0.15HCl + XO_2 + HO_2 + 0.28ICL1</td>
<td>(4.5k_{OH+ISOP})</td>
</tr>
<tr>
<td>ICL1 + OH \rightarrow ICL2</td>
<td>(0.19k_{OH+ISOP})</td>
</tr>
<tr>
<td>Cl + O_3 \rightarrow ClO + O_2</td>
<td>(2.9 \times 10^{-11}\exp(-260/T))</td>
</tr>
<tr>
<td>ClO + NO \rightarrow Cl + NO_2</td>
<td>(6.2 \times 10^{-12}\exp(295/T))</td>
</tr>
<tr>
<td>ClO + HO_2 \rightarrow HOCl + O_2</td>
<td>(4.6 \times 10^{-13}\exp(710/T))</td>
</tr>
<tr>
<td>ClNO_2 + OH \rightarrow HOCl + NO_2</td>
<td>(2.4 \times 10^{-12}\exp(-1250/T))</td>
</tr>
</tbody>
</table>

\(^a\) All but the last reaction are based on Tanaka and Allen (2001). The reaction of ClNO_2 with OH is from Atkinson et al. (2007).

\(^b\) CMAQ species abbreviations: ACRO=acrolein (in reference to the SAPRC99 mechanism); PAR=paraffin lumped group; OLE=olefin lumped group; ETH=ethene; ISOP=isoprene; XO2N=NO converted to organic nitrate; ALD2=acetaldehyde carbonyl lumped group; ROR=secondary alkoxy radical; FMCL=formyl chloride; ICL1=1-chloro-3-methyl-3-butene-2-one; ICL2=derivative of ICL1.

\(^c\) Constants that are defined in terms of other rate constants are denoted with “\(nk_{\text{reaction}}\)” where “reaction” denotes a pre-existing CMAQ chemical or photolysis rate constant with \(n\) proportionality factor.
Table 2. Reactions added to CB05 for inorganic sulfur species and their reaction products.

<table>
<thead>
<tr>
<th>Reactants</th>
<th>Products</th>
<th>Rate constant (cm$^3$ molecule$^{-1}$ s$^{-1}$)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>H$_2$S+OH</td>
<td>SH+H$_2$O</td>
<td>6.0×10$^{-12}$ exp(-80/T)</td>
<td>Atkinson et al., 2004</td>
</tr>
<tr>
<td>H$_2$S+NO$_3$</td>
<td>SH+HNO$_3$</td>
<td>1.0×10$^{-15}$</td>
<td>Atkinson et al., 2004</td>
</tr>
<tr>
<td>H$_2$S+Cl</td>
<td>SH+HCl</td>
<td>3.7×10$^{-11}$ exp(208/T)</td>
<td>Atkinson et al., 2004</td>
</tr>
<tr>
<td>SH+O</td>
<td>SO+H</td>
<td>1.6×10$^{-10}$</td>
<td>NASA, 1997</td>
</tr>
<tr>
<td>SH+O$_2$</td>
<td>SO+OH</td>
<td>4.0×10$^{-19}$</td>
<td>NASA, 1997</td>
</tr>
<tr>
<td>SH+O$_3$</td>
<td>HSO+O$_2$</td>
<td>9.5×10$^{-12}$ exp(-280/T)</td>
<td>Atkinson et al., 2004</td>
</tr>
<tr>
<td>SH+NO$_2$</td>
<td>HSO+NO</td>
<td>2.9×10$^{-11}$ exp(240/T)</td>
<td>Atkinson et al., 2004</td>
</tr>
<tr>
<td>SH+NO+M</td>
<td>HSN+O+M</td>
<td>$k_0=2.4×10^{-31}(T/300)^{-3}[M]$</td>
<td>Atkinson et al., 2004</td>
</tr>
<tr>
<td></td>
<td></td>
<td>$k_\infty=2.7×10^{-11}$</td>
<td></td>
</tr>
<tr>
<td>SH+Cl$_2$</td>
<td>CISH+Cl</td>
<td>1.7×10$^{-11}$ exp(690/T)</td>
<td>NASA, 1997</td>
</tr>
<tr>
<td>HSO+NO$_2$</td>
<td>HSO$_2$+NO</td>
<td>9.6×10$^{-12}$</td>
<td>NASA, 1997</td>
</tr>
<tr>
<td>HSO+O$_2$</td>
<td>HSO$_2$+O</td>
<td>2.0×10$^{-17}$</td>
<td>Atkinson et al., 2004</td>
</tr>
<tr>
<td>HSO+O$_3$</td>
<td>HSO$_2$+O$_2$</td>
<td>1.1×10$^{-13}$</td>
<td>Atkinson et al., 2004</td>
</tr>
<tr>
<td>SO+OH</td>
<td>SO$_2$+H</td>
<td>8.6×10$^{-11}$</td>
<td>NASA, 1997</td>
</tr>
<tr>
<td>SO+O$_2$</td>
<td>SO$_2$+O</td>
<td>1.6×10$^{-13}$ exp(-2280/T)</td>
<td>Atkinson et al., 2004</td>
</tr>
<tr>
<td>SO+O$_3$</td>
<td>SO$_2$+O$_2$</td>
<td>4.5×10$^{-12}$ exp(-1170/T)</td>
<td>Atkinson et al., 2004</td>
</tr>
<tr>
<td>SO+NO$_2$</td>
<td>SO$_2$+NO</td>
<td>1.4×10$^{-11}$</td>
<td>Atkinson et al., 2004</td>
</tr>
<tr>
<td>SO+ClO</td>
<td>SO$_2$+Cl</td>
<td>2.8×10$^{-11}$</td>
<td>NASA, 1997</td>
</tr>
<tr>
<td>HSO$_2$+O$_2$</td>
<td>HO$_2$+SO$_2$</td>
<td>3.0×10$^{-13}$</td>
<td>NASA, 1997</td>
</tr>
</tbody>
</table>

$^a$ Termolecular rate constant expression:

$$k = \left[ \frac{k_0}{1 + (k_0/k_\infty)} \right] 0.6^{(1 + \log_{10}(k_0/k_\infty))^2}$$
Table 3. Reactions added to CB05 for organic sulfur species and their reaction products.\textsuperscript{a}

<table>
<thead>
<tr>
<th>Reactants</th>
<th>Products</th>
<th>Rate constant (cm\textsuperscript{3} molecule\textsuperscript{-1} s\textsuperscript{-1})\textsuperscript{b}</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>DMS+O</td>
<td>MSO+CH\textsubscript{3}</td>
<td>1.34×10\textsuperscript{-11} exp(409/T)</td>
<td>Atkinson et al., 2004</td>
</tr>
<tr>
<td>DMS+NO\textsubscript{3}</td>
<td>MSCH\textsubscript{3}+HNO\textsubscript{3}</td>
<td>1.9×10\textsuperscript{-13} exp(520/T)</td>
<td>Atkinson et al., 2004</td>
</tr>
<tr>
<td>DMS+OH</td>
<td>MSCH\textsubscript{3}+H\textsubscript{2}O</td>
<td>1.1×10\textsuperscript{-11} exp(−253/T)</td>
<td>Atkinson et al., 2004</td>
</tr>
<tr>
<td>DMS+OH+O\textsubscript{2}</td>
<td>0.5DMSO\textsubscript{2}+0.2DMSO2+0.3MSIA</td>
<td>{1×10\textsuperscript{-39} exp(5820/T)/O\textsubscript{2}}/{1+5×10\textsuperscript{-39} exp(6280/T)/[O\textsubscript{2}]}</td>
<td>Zhu et al., 2006</td>
</tr>
<tr>
<td>DMS+Cl</td>
<td>MSCH\textsubscript{3}+HCl</td>
<td>3.3×10\textsuperscript{-10}</td>
<td>Atkinson et al., 2004</td>
</tr>
<tr>
<td>MSCH\textsubscript{2}+O\textsubscript{2}+M</td>
<td>MSP+M</td>
<td>5.7×10\textsuperscript{-12}</td>
<td>Atkinson et al., 2004</td>
</tr>
<tr>
<td>MSCH\textsubscript{3}+NO\textsubscript{3}</td>
<td>MSP+NO</td>
<td>3.0×10\textsuperscript{-10}</td>
<td>NASA, 1997</td>
</tr>
<tr>
<td>MSP+NO</td>
<td>CH\textsubscript{3}S+HCHO+NO\textsubscript{2}</td>
<td>4.9×10\textsuperscript{-12} exp(260/T)</td>
<td>Atkinson et al., 2004; Zhu et al., 2006</td>
</tr>
<tr>
<td>MSP+MSP</td>
<td>2CH\textsubscript{2}S+2HCHO+O\textsubscript{2}</td>
<td>1.0×10\textsuperscript{-11}</td>
<td>Atkinson et al., 2004; Zhu et al., 2006</td>
</tr>
<tr>
<td>MSP+H\textsubscript{2}O</td>
<td>CH\textsubscript{3}S+HCHO+OH+O\textsubscript{2}</td>
<td>3.8×10\textsuperscript{-13} exp(780/T)</td>
<td>Zhu et al., 2006; following Tyndall et al., 2001</td>
</tr>
<tr>
<td>CH\textsubscript{3}S+O\textsubscript{3}</td>
<td>0.9SO\textsubscript{2}+0.1H\textsubscript{2}SO\textsubscript{4}+0.9CH\textsubscript{3}OH+0.1CH\textsubscript{3}S\textsuperscript{a}</td>
<td>1.15×10\textsuperscript{-12} exp(430/T)\textsuperscript{c}</td>
<td>Atkinson et al., 2004; Zhu et al., 2006</td>
</tr>
<tr>
<td>CH\textsubscript{3}S+NO\textsubscript{2}</td>
<td>MSO+NO</td>
<td>3.0×10\textsuperscript{-11} exp(210/T)</td>
<td>Atkinson et al., 2004</td>
</tr>
<tr>
<td>MSO+O\textsubscript{3}</td>
<td>0.14CH\textsubscript{3}S+0.86CH\textsubscript{3}+0.86SO\textsubscript{2}+O\textsubscript{2}</td>
<td>6.0×10\textsuperscript{-13}</td>
<td>Finlayson-Pitts and Pitts, 2000; Atkinson et al., 2004</td>
</tr>
<tr>
<td>MSO+NO\textsubscript{2}</td>
<td>CH\textsubscript{3}S+SO\textsubscript{2}+NO</td>
<td>1.2×10\textsuperscript{-11}</td>
<td>Finlayson-Pitts and Pitts, 2000; Atkinson et al., 2004</td>
</tr>
<tr>
<td>DMSO+OH</td>
<td>0.9MSIA+0.1DMSO\textsubscript{2}</td>
<td>9.0×10\textsuperscript{-11}</td>
<td>Kukui et al., 2003; Zhu et al., 2006</td>
</tr>
<tr>
<td>MSIA+OH</td>
<td>0.9SO\textsubscript{2}+0.1MSA</td>
<td>9.0×10\textsuperscript{-11}</td>
<td>Kukui et al., 2003; Zhu et al., 2006</td>
</tr>
<tr>
<td>CH\textsubscript{3}O\textsubscript{3}</td>
<td>CH\textsubscript{3}O+O\textsubscript{2}</td>
<td>4.7×10\textsuperscript{-12} exp(−210/T)</td>
<td>Atkinson et al., 2004, 2006</td>
</tr>
<tr>
<td>CH\textsubscript{3}O</td>
<td>HCHO+H</td>
<td>1.3×10\textsuperscript{-10}</td>
<td>Atkinson et al., 2006</td>
</tr>
<tr>
<td>CH\textsubscript{3}O+O\textsubscript{2}</td>
<td>HCHO+HO\textsubscript{2}</td>
<td>7.2×10\textsuperscript{-14} exp(−1080/T)</td>
<td>Atkinson et al., 2004, 2006</td>
</tr>
<tr>
<td>CH\textsubscript{3}O+NO\textsubscript{2}</td>
<td>HCHO+HO\textsubscript{2}</td>
<td>9.6×10\textsuperscript{-12} exp(−1150/T)</td>
<td>Atkinson et al., 2004, 2006</td>
</tr>
</tbody>
</table>

\textsuperscript{a} Abbreviations: DMS=dimethylsulfide, \textsubscript{CH\textsubscript{3}}SCH\textsubscript{3}; DMSO=dimethylsulfoxide, \textsubscript{CH\textsubscript{3}}Si(\textsubscript{CH\textsubscript{3}})Si(\textsubscript{CH\textsubscript{3}}); DMSO\textsubscript{2}=dimethylsulfone, \textsubscript{CH\textsubscript{3}}S(\textsubscript{O})(\textsubscript{O})\textsubscript{CH\textsubscript{3}}; MSCH\textsubscript{3}=methylthiomethyl radical, \textsubscript{CH\textsubscript{3}}SCH\textsubscript{2}; MSP=methylthiomethylperoxy radical, \textsubscript{CH\textsubscript{3}}SCH\textsubscript{2}O\textsubscript{2}; MSO=methylsuloxide radical, \textsubscript{CH\textsubscript{3}}SO; MSIA=methanesulfinic acid, \textsubscript{CH\textsubscript{3}}SOOH; MSA=methanesulfonic acid, \textsubscript{CH\textsubscript{3}}S(\textsubscript{O})(\textsubscript{O})\textsubscript{OH}.

\textsuperscript{b} The exception is for termolecular rate constants that have units of cm\textsuperscript{6} molecule\textsuperscript{-2} s\textsuperscript{-1}.

\textsuperscript{c} The mechanism of Zhu et al. (2006) treats the reaction of CH\textsubscript{3}S with a variety of species as one reaction producing sulfur dioxide and sulfuric acid with no additional products specified. As implemented in CMAQ, the additional products are assumed to be species needed to achieve stoichiometric closure to the reaction in the presence of H\textsubscript{2}O.

\textsuperscript{d} This is believed to be a termolecular reaction (Atkinson et al., 2004) but the rate constant at different pressures has not been determined. See Sect. 3.1.4 for more information.
Table 4. Airborne chemical species ingested by clouds and used to compute droplet acidity.

<table>
<thead>
<tr>
<th>Species</th>
<th>CMAQ cloud module</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Original</td>
</tr>
<tr>
<td>H$_2$SO$_4$ (gas)</td>
<td>X</td>
</tr>
<tr>
<td>SO$_2$ (gas)</td>
<td>X</td>
</tr>
<tr>
<td>H$_2$O$_2$ (gas)</td>
<td>X</td>
</tr>
<tr>
<td>CO$_2$ (gas)</td>
<td>X</td>
</tr>
<tr>
<td>NH$_3$ (gas)</td>
<td>X</td>
</tr>
<tr>
<td>MSIA (gas)</td>
<td>X</td>
</tr>
<tr>
<td>MSA (gas)</td>
<td>X</td>
</tr>
<tr>
<td>HCl (gas)</td>
<td>X</td>
</tr>
<tr>
<td>HNO$_3$ (gas)</td>
<td>X</td>
</tr>
<tr>
<td>H$_2$CO$_2$ (gas)</td>
<td>X</td>
</tr>
<tr>
<td>NaCl (aerosol)</td>
<td>X</td>
</tr>
<tr>
<td>KCl (aerosol)</td>
<td>X</td>
</tr>
<tr>
<td>CaCl$_2$ (aerosol)</td>
<td>X</td>
</tr>
<tr>
<td>MgCl$_2$ (aerosol)</td>
<td>X</td>
</tr>
<tr>
<td>NH$_3$NO$_3$ (aerosol)</td>
<td>X</td>
</tr>
</tbody>
</table>
Table 5. Revised set of heterogeneous cloud reactions in CMAQ4.6.\(^a\)

<table>
<thead>
<tr>
<th>Reaction</th>
<th>Rate constant, (k) (M(^{-1}) s(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>(\text{DMS}+\text{O}_3 \rightarrow \text{DMSO}+\text{O}_2)</td>
<td>(5.3 \times 10^{12}\exp(-2600/T)) (^c)</td>
</tr>
<tr>
<td>(\text{DMS}+\text{OH} \rightarrow \text{DMSO}+\text{HO}_2)</td>
<td>(1.9 \times 10^{10}) (^d)</td>
</tr>
<tr>
<td>(\text{DMSO}+\text{O}_3 \rightarrow \text{DMSO}_2+\text{O}_2)</td>
<td>(5.7 \times 10^0) (^e)</td>
</tr>
<tr>
<td>(\text{DMSO}+\text{OH} \rightarrow \text{MSIA}+\text{CH}_3)</td>
<td>(4.7 \times 10^{11}\exp(-1270/T)) (^f)</td>
</tr>
<tr>
<td>(\text{DMSO}+\text{SO}^- \rightarrow \text{CH}_3\text{SO}_2^-+\text{SO}_4^{2-}+2\text{H}^+)</td>
<td>(3.7 \times 10^{11}\exp(-1440/T)) (^f)</td>
</tr>
<tr>
<td>(\text{DMSO}+\text{Cl} \rightarrow \text{CH}_3\text{SO}_2^-+2\text{H}^++\text{Cl}^-)</td>
<td>(6.3 \times 10^9) (^f)</td>
</tr>
<tr>
<td>(\text{DMSO}+\text{Cl}_2^- \rightarrow \text{CH}_3\text{SO}_2^-+\text{Cl}_2)</td>
<td>(1.7 \times 10^7) (^f)</td>
</tr>
<tr>
<td>(\text{DMSO}_2+\text{OH} \rightarrow 0.3\text{MSA}+0.7\text{SO}_4^{2-}+1.4\text{H}^+)</td>
<td>(5.1 \times 10^9\exp(-1690/T)) (^f)</td>
</tr>
<tr>
<td>(\text{CH}_3\text{SO}_2^-+\text{OH} \rightarrow \text{CH}_3\text{SO}_2^-+\text{H}^++\text{O}_2^-)</td>
<td>(7.7 \times 10^9) (^f)</td>
</tr>
<tr>
<td>(\text{CH}_3\text{SO}_2^-+\text{SO}_4^- \rightarrow \text{CH}_3\text{SO}_3^-+\text{SO}_4^{2-}+\text{H}^+)</td>
<td>(1.0 \times 10^9) (^f)</td>
</tr>
<tr>
<td>(\text{CH}_3\text{SO}_2^-+\text{Cl}^- \rightarrow \text{CH}_3\text{SO}_2^-+2\text{Cl}^-+\text{H}^+)</td>
<td>(8.0 \times 10^8) (^f)</td>
</tr>
<tr>
<td>(\text{CH}_3\text{SO}_2^-+\text{OH} \rightarrow \text{SO}_4^{2-}+\text{H}^+)</td>
<td>(8.8 \times 10^{10}\exp(-2630/T)) (^f)</td>
</tr>
<tr>
<td>(\text{SO}_2+\text{O}_3 \rightarrow \text{SO}_4^{2-}+2\text{H}^+)</td>
<td>(2.4 \times 10^4) (^g)</td>
</tr>
<tr>
<td>(\text{HSO}_3^-+\text{O}_3 \rightarrow \text{SO}_4^{2-}+\text{H}^+)</td>
<td>(3.5 \times 10^5\exp[-5530(1/T-1/298)]) (^h)</td>
</tr>
<tr>
<td>(\text{SO}_3^{2-}+\text{O}_3 \rightarrow \text{SO}_4^{2-})</td>
<td>(1.5 \times 10^9\exp[-5280(1/T-1/298)]) (^h)</td>
</tr>
<tr>
<td>(\text{HSO}_3^-+\text{H}_2\text{O}_2 \rightarrow \text{SO}_4^{2-}+\text{H}^+)</td>
<td>(7.45 \times 10^7\exp[-4430(1/T-1/298)]) (^{7+13[H^+]\text{}}) (^h)</td>
</tr>
<tr>
<td>(\text{HSO}_3^-+\text{MHP} \rightarrow \text{SO}_4^{2-}+\text{H}^+)</td>
<td>(1.75 \times 10^7\exp[-3801(1/T-1/298)])</td>
</tr>
<tr>
<td>(\text{HSO}_3^-+\text{PAA} \rightarrow \text{SO}_4^{2-}+\text{H}^+)</td>
<td>(3.64 \times 10^7{[\text{H}^+]\text{}}+1.65 \times 10^{-5}\exp[-3994(1/T-1/298)])</td>
</tr>
</tbody>
</table>

---

\(^{a}\) CMAQ species abbreviations: MHP=methylhydrogen peroxide; PAA=peroxyacetyl acid.

\(^{b}\) The last six reactions are essentially those treated in the standard version of CMAQ, although their rate constants were taken from other sources except for the last two which are the expressions for \(k\) used in CMAQ.

\(^{c}\) Zhu (2004), Zhu et al. (2006), Gershenzon et al. (2001).

\(^{d}\) Zhu (2004), Zhu et al. (2006), Bonifacic et al. (1975).


\(^{f}\) Zhu (2004), Zhu et al. (2006).

\(^{g}\) Zhu (2004), Zhu et al. (2006), Kreidenweis et al. (2003).

**Table 6.** Species treated in the revised CMAQ cloud module.

<table>
<thead>
<tr>
<th>Index number&lt;sup&gt;a&lt;/sup&gt;</th>
<th>Species</th>
<th>Steady-state</th>
<th>Reactive</th>
<th>Likely to be non-uniform</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>SO&lt;sub&gt;2&lt;/sub&gt;</td>
<td>X</td>
<td>X</td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>H&lt;sub&gt;2&lt;/sub&gt;SO&lt;sub&gt;4&lt;/sub&gt;</td>
<td>X</td>
<td></td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>HSO&lt;sub&gt;3&lt;/sub&gt;</td>
<td>X</td>
<td></td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>SO&lt;sub&gt;3&lt;/sub&gt;</td>
<td>X</td>
<td></td>
<td></td>
</tr>
<tr>
<td>5</td>
<td>HSO&lt;sub&gt;2&lt;/sub&gt;</td>
<td>X</td>
<td>X</td>
<td></td>
</tr>
<tr>
<td>6</td>
<td>SO&lt;sub&gt;3&lt;/sub&gt;</td>
<td>X</td>
<td>X</td>
<td></td>
</tr>
<tr>
<td>7</td>
<td>H&lt;sub&gt;2&lt;/sub&gt;O&lt;sub&gt;2&lt;/sub&gt;</td>
<td>X</td>
<td>X</td>
<td></td>
</tr>
<tr>
<td>8</td>
<td>HO&lt;sub&gt;2&lt;/sub&gt;</td>
<td>X</td>
<td></td>
<td></td>
</tr>
<tr>
<td>9</td>
<td>CO&lt;sub&gt;2&lt;/sub&gt;</td>
<td>X</td>
<td></td>
<td></td>
</tr>
<tr>
<td>10</td>
<td>HCO&lt;sub&gt;3&lt;/sub&gt;</td>
<td>X</td>
<td></td>
<td></td>
</tr>
<tr>
<td>11</td>
<td>H&lt;sup&gt;+&lt;/sup&gt;</td>
<td>X</td>
<td></td>
<td></td>
</tr>
<tr>
<td>12</td>
<td>CO&lt;sub&gt;3&lt;/sub&gt;</td>
<td>X</td>
<td></td>
<td></td>
</tr>
<tr>
<td>13</td>
<td>NH&lt;sub&gt;3&lt;/sub&gt;</td>
<td>X</td>
<td></td>
<td></td>
</tr>
<tr>
<td>14</td>
<td>NH&lt;sub&gt;4&lt;/sub&gt;</td>
<td>X</td>
<td></td>
<td></td>
</tr>
<tr>
<td>15</td>
<td>OH&lt;sup&gt;-&lt;/sup&gt;</td>
<td>X</td>
<td></td>
<td></td>
</tr>
<tr>
<td>16</td>
<td>CH&lt;sub&gt;3&lt;/sub&gt;SO&lt;sub&gt;3&lt;/sub&gt;</td>
<td>X</td>
<td></td>
<td></td>
</tr>
<tr>
<td>17</td>
<td>CH&lt;sub&gt;3&lt;/sub&gt;SO&lt;sub&gt;3&lt;/sub&gt;</td>
<td>X</td>
<td></td>
<td></td>
</tr>
<tr>
<td>18</td>
<td>MSIA&lt;sup&gt;c&lt;/sup&gt;</td>
<td>X</td>
<td></td>
<td></td>
</tr>
<tr>
<td>19</td>
<td>MSA&lt;sup&gt;c&lt;/sup&gt;</td>
<td>X</td>
<td></td>
<td></td>
</tr>
<tr>
<td>20</td>
<td>DMS</td>
<td>X</td>
<td>X</td>
<td>X</td>
</tr>
<tr>
<td>21</td>
<td>DMSO</td>
<td>X</td>
<td>X</td>
<td></td>
</tr>
<tr>
<td>22</td>
<td>DMSO&lt;sub&gt;2&lt;/sub&gt;</td>
<td>X</td>
<td></td>
<td></td>
</tr>
<tr>
<td>23</td>
<td>SO&lt;sub&gt;4&lt;/sub&gt;</td>
<td>X</td>
<td>X</td>
<td></td>
</tr>
<tr>
<td>24</td>
<td>O&lt;sub&gt;3&lt;/sub&gt;</td>
<td>X</td>
<td>X</td>
<td></td>
</tr>
<tr>
<td>25</td>
<td>MHP</td>
<td>X</td>
<td>X</td>
<td>X</td>
</tr>
<tr>
<td>26</td>
<td>PAA</td>
<td>X</td>
<td>X</td>
<td></td>
</tr>
<tr>
<td>27</td>
<td>HCl</td>
<td>X</td>
<td></td>
<td></td>
</tr>
<tr>
<td>28</td>
<td>Cl&lt;sup&gt;-&lt;/sup&gt;</td>
<td>X</td>
<td></td>
<td></td>
</tr>
<tr>
<td>29</td>
<td>HNO&lt;sub&gt;3&lt;/sub&gt;</td>
<td>X</td>
<td></td>
<td></td>
</tr>
<tr>
<td>30</td>
<td>NO&lt;sub&gt;2&lt;/sub&gt;</td>
<td>X</td>
<td></td>
<td></td>
</tr>
<tr>
<td>31</td>
<td>OH&lt;sup&gt;-&lt;/sup&gt;</td>
<td>X</td>
<td>X</td>
<td></td>
</tr>
<tr>
<td>32</td>
<td>Cl&lt;sup&gt;-&lt;/sup&gt;</td>
<td>X</td>
<td>X</td>
<td></td>
</tr>
<tr>
<td>33</td>
<td>Cl&lt;sub&gt;2&lt;/sub&gt;</td>
<td>X</td>
<td>X</td>
<td></td>
</tr>
<tr>
<td>34</td>
<td>Na&lt;sup&gt;+&lt;/sup&gt;</td>
<td>X</td>
<td></td>
<td></td>
</tr>
<tr>
<td>35</td>
<td>K&lt;sup&gt;+&lt;/sup&gt;</td>
<td>X</td>
<td></td>
<td></td>
</tr>
<tr>
<td>36</td>
<td>Mg&lt;sup&gt;2+&lt;/sup&gt;</td>
<td>X</td>
<td></td>
<td></td>
</tr>
<tr>
<td>37</td>
<td>Ca&lt;sup&gt;2+&lt;/sup&gt;</td>
<td>X</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

<sup>a</sup> Used as a subscript to identify species in the transient equations.

<sup>b</sup> Although linked to a species that is not steady-state, the activity of this species is only determined for the purpose of computing the initial equilibrium cloud droplet acidity.

<sup>c</sup> These species are not themselves reactive but dissociate to ions that are reactive.
**Table 7.** Average simulated winter and summer natural pollutant levels for the modeling domain.

<table>
<thead>
<tr>
<th>Pollutant</th>
<th>Winter (Dec–Feb)</th>
<th>Summer (Jun–Aug)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ozone (ppbV)</td>
<td>27.3</td>
<td>23.5</td>
</tr>
<tr>
<td>Ammonium + sulfate&lt;sup&gt;a&lt;/sup&gt; (µg m&lt;sup&gt;−3&lt;/sup&gt;)</td>
<td>0.12</td>
<td>0.27</td>
</tr>
<tr>
<td>Ammonium nitrate&lt;sup&gt;a&lt;/sup&gt; (µg m&lt;sup&gt;−3&lt;/sup&gt;)</td>
<td>0.01</td>
<td>0.02</td>
</tr>
<tr>
<td>Organic carbon&lt;sup&gt;a&lt;/sup&gt; (µg m&lt;sup&gt;−3&lt;/sup&gt;)</td>
<td>0.35</td>
<td>2.22</td>
</tr>
<tr>
<td>Elemental carbon&lt;sup&gt;a&lt;/sup&gt; (µg m&lt;sup&gt;−3&lt;/sup&gt;)</td>
<td>0.004</td>
<td>0.23</td>
</tr>
<tr>
<td>Windblown dust&lt;sup&gt;a&lt;/sup&gt; (µg m&lt;sup&gt;−3&lt;/sup&gt;)</td>
<td>0.12</td>
<td>0.14</td>
</tr>
<tr>
<td>Sea salt&lt;sup&gt;a&lt;/sup&gt; (µg m&lt;sup&gt;−3&lt;/sup&gt;)</td>
<td>0.02</td>
<td>0.02</td>
</tr>
<tr>
<td>Total PM&lt;sub&gt;2.5&lt;/sub&gt;&lt;sup&gt;b&lt;/sup&gt; (µg m&lt;sup&gt;−3&lt;/sup&gt;)</td>
<td>0.91</td>
<td>4.66</td>
</tr>
<tr>
<td>PM&lt;sub&gt;c&lt;/sub&gt; (µg m&lt;sup&gt;−3&lt;/sup&gt;)</td>
<td>1.69</td>
<td>1.05</td>
</tr>
</tbody>
</table>

<sup>a</sup> In the fine particle size fraction (i.e., below 2.5 µm).

<sup>b</sup> Assumes organic aerosol mass equal to 1.8 × OC.
**Table 8.** CMAQ configurations and assumptions used in model test simulations.

<table>
<thead>
<tr>
<th>Test</th>
<th>CMAQ Configuration and Assumptions&lt;sup&gt;a&lt;/sup&gt;</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>Unmodified CMAQ4.6 using CB05 mechanism</td>
</tr>
<tr>
<td>B</td>
<td>Test A configuration with CB05 mechanism modified to include DMS and H₂S gas phase chemistry</td>
</tr>
<tr>
<td>C</td>
<td>Test B configuration with standard cloud module replaced by module that includes organic sulfur chemistry</td>
</tr>
<tr>
<td>D</td>
<td>Test C configuration but with OH cloud uptake blocked</td>
</tr>
<tr>
<td>E</td>
<td>Test C configuration but with Pacific Ocean clouds enhanced between 250 and 750 m&lt;sup&gt;b&lt;/sup&gt;</td>
</tr>
<tr>
<td>F</td>
<td>Test C configuration with α=0.001&lt;sup&gt;c&lt;/sup&gt;</td>
</tr>
</tbody>
</table>

<sup>a</sup> All tests were run for the entire month of June.

<sup>b</sup> All model layers in 250–750 m range included clouds with minimum cloud water content of 0.5 g m<sup>−3</sup>.

<sup>c</sup> The proportion, α, of [HSO₃<sup>−</sup>]<sub>aq</sub>+[HSO₄<sup>−</sup>]<sub>aq</sub> in cloud droplets that is assumed to convert to the sulfate radical, SO₄<sup>−</sup>. All other tests assumed α=1×10<sup>−6</sup>.
Table 9. Modified CMAQ4.6 simulated levels of sulfur compounds in the marine boundary layer compared with values from other sources.

<table>
<thead>
<tr>
<th>Species</th>
<th>Metric</th>
<th>CMAQ Test C</th>
<th>CMAQ Test F</th>
<th>Measured</th>
<th>Citation source</th>
</tr>
</thead>
<tbody>
<tr>
<td>DMS</td>
<td>nanomoles m⁻³</td>
<td>10</td>
<td>9</td>
<td>5</td>
<td>Yang et al. (2009)</td>
</tr>
<tr>
<td>DMSO</td>
<td>pptV</td>
<td>2</td>
<td>1.1</td>
<td>5</td>
<td>Sciare et al. (2000), Sciare et al. (2001), Jourdain et al. (2003)</td>
</tr>
<tr>
<td>MSA</td>
<td>nanomoles m⁻³</td>
<td>0.3–0.4</td>
<td>0.5–0.6</td>
<td>2.8</td>
<td>Watts et al. (1987), Yang et al. (2009)</td>
</tr>
<tr>
<td>SO₂</td>
<td>pptV</td>
<td>19</td>
<td>18</td>
<td>114</td>
<td>Sciare et al. (2001)</td>
</tr>
<tr>
<td>Sulfate</td>
<td>µg m⁻³</td>
<td>0.3</td>
<td>0.4</td>
<td>8</td>
<td>Yvon and Saltzman (1996), Sciare et al. (2001), Jourdain et al. (2003)</td>
</tr>
<tr>
<td></td>
<td>pptV</td>
<td>90</td>
<td>100</td>
<td>70</td>
<td></td>
</tr>
</tbody>
</table>

a Maximum mass concentrations and mixing ratios do not usually occur in the same locations or at the same times.
b Average for June 2002 over the Pacific Ocean portion of the modeling domain.
c Averages over multiple samples, locations and seasons.
d It is not clear to what extent MSIA contributes to measured values of MSA given the similarities in the two species and the fact that MSIA can convert to MSA in aqueous solution. Model results presented here include a range of values that reflect this uncertainty and the fact that the model makes a clear distinction between the two S₉org components.
Table A1. Index list for aqueous species included in the revised cloud chemistry module.\(^a\)

<table>
<thead>
<tr>
<th>Species</th>
<th>Index</th>
<th>Species</th>
<th>Index</th>
</tr>
</thead>
<tbody>
<tr>
<td>SO(_2)</td>
<td>1</td>
<td>DMS</td>
<td>20</td>
</tr>
<tr>
<td>H(_2)SO(_4)</td>
<td>2</td>
<td>DMSO</td>
<td>21</td>
</tr>
<tr>
<td>HSO(_4)(^-)</td>
<td>3</td>
<td>DMSO2</td>
<td>22</td>
</tr>
<tr>
<td>SO(_4)^2-</td>
<td>4</td>
<td>SO(_4)^-</td>
<td>23</td>
</tr>
<tr>
<td>HSO(_3)^-</td>
<td>5</td>
<td>O(_3)</td>
<td>24</td>
</tr>
<tr>
<td>SO(_2)^2-</td>
<td>6</td>
<td>MHP</td>
<td>25</td>
</tr>
<tr>
<td>H(_2)O(_2)</td>
<td>7</td>
<td>PAA</td>
<td>26</td>
</tr>
<tr>
<td>HO(_2)</td>
<td>8</td>
<td>HCl</td>
<td>27</td>
</tr>
<tr>
<td>CO(_2)</td>
<td>9</td>
<td>Cl(^-)</td>
<td>28</td>
</tr>
<tr>
<td>HCO(_3)^-</td>
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<tr>
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<td>Cl(^-)</td>
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<tr>
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<td>Cl(_2)^+</td>
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<tr>
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<tr>
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<td>MSA</td>
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\(^a\) Abbreviations: DMS=dimethylsulfide, DMSO=dimethylsulfoxide, DMSO2=dimethylsulfone, MSIA=methanesulfinic acid, MSA=methanesulfonic acid, MHP=methylhydrogen peroxide, PAA=peroxyacetic acid
Fig. 1. Comparative steady-state heterogeneous sulfate formation rates in the presence of SO$_2$ and equal parts DMSO and DMSO2 for different levels of [SO$_4^{2-}$]$_{aq}$ as determined from the parameter $\alpha$. Atmospheric conditions are: 298 K, 1 atm, 0.5 µg m$^{-3}$ cloud liquid water content, $X_{SO_2}$=0.4 ppbV, $X_{DMSO}$=0.2 ppbV, $X_{DMSO_2}$=0.2 ppbV, $X_{O_3}$=30 ppbV, $X_{OH}$=$1\times10^{-10}$ ppbV, total peroxide=0.3 ppbV.
Fig. 2. Grid-averaged time series of three photochemically active species for the natural emissions simulation of 2002. Diurnal noise was removed by applying a 24-h averaging filter.
Fig. 3. Grid-averaged time series of various gas and aerosol sulfur species for the natural emissions simulation of 2002. Diurnal noise was removed by applying a 24-h averaging filter.
Fig. 4. Grid-averaged time series of NO$_2$, NH$_3$ and ammonium nitrate aerosol for the natural emissions simulation of 2002. Diurnal noise was removed by applying a 24-h averaging filter.
Fig. 5. Grid-averaged time series of simulated particle concentrations for the natural emissions simulation of 2002. Diurnal noise was removed by applying a 24-h averaging filter.
Fig. 6. Mean simulated relative changes, $\bar{\Delta}$, during June in natural levels of airborne pollutants (top: OH; middle: SO$_2$; bottom: aerosol sulfate) due to the introduction of reduced sulfur and chlorine gas chemistry into CMAQv4.6 (i.e., test B changes relative to test A). Model output is for the surface layer.
Fig. 7. Same as in Fig. 6 except the changes represent the impacts from adding organic sulfur chemistry to the cloud chemistry module (i.e., test C changes relative to test B).
Fig. 8. Comparison of CMAQ hourly sulfate aerosol mass concentrations in the surface layer using the revised (with $S_{\text{org}}$ chemistry turned off) and default (original) cloud chemistry models. The new cloud model produces lower values for some of the higher original cases and higher values for most of the lower original cases. Model differences are a result of differences in the treatment of gaseous reactant uptake by cloud droplets and the timing of cloud and gas-phase chemistry.
Fig. 9. Average relative changes ($\Delta$) for June in surface layer SO$_2$ mixing ratio (top) and sulfate concentration (bottom) incurred by enhancing cloud cover over the Pacific Ocean portion of the modeling domain (i.e., test E). The reference case is test C.
Fig. 10. Average relative changes (Δ) for June in surface layer SO₂ mixing ratio (top) and sulfate concentration (bottom) incurred by increasing the fraction of sulfate radical formed from aqueous SO₂ and H₂SO₄ in clouds (i.e., test F). The reference case is test E results.