CESM/CAM5 Improvement and Application: Comparison and Evaluation of Updated CB05_GE and MOZART-4 Gas-Phase Mechanisms and Associated Impacts on Global Air Quality and Climate

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Abstract: Atmospheric chemistry plays a key role in determining the amounts and distributions of oxidants and gaseous precursors that control the formation of secondary gaseous and aerosol pollutants; all of those species can interact with the climate system. To understand the impacts of different gas-phase mechanisms on global air quality and climate predictions, in this work, a comprehensive comparative evaluation is performed using the Community Atmosphere Model (CAM) Version 5 with comprehensive tropospheric and stratospheric chemistry (CAM5-chem) within the Community Earth System Model (CESM) with two most commonly-used gas-phase chemical mechanisms: the 2005 Carbon Bond mechanism with Global Extension (CB05_GE) and the Model of OZone and Related chemical Tracers version 4 (MOZART-4) mechanism with additional updates (MOZART-4x). MOZART-4x and CB05_GE use different approaches to represent volatile organic compounds (VOCs) and different surrogates for secondary organic aerosol (SOA) precursors. MOZART-4x includes a more detailed representation of isoprene chemistry compared to CB05_GE. CB05_GE includes additional oxidation of

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SO$_2$ by O$_3$ over the surface of dust particles, which is not included in MOZART-4x. The results show that the two CAM5-chem simulations with CB05_GE and MOZART-4x predict similar chemical profiles for major gases (e.g., O$_3$, CO, and NO$_x$) compared to the aircraft measurements, with generally better agreement for NO$_x$ profile by CB05_GE than MOZART-4x. The concentrations of SOA at four sites in continental U.S. (CONUS) and organic carbon (OC) over the IMPROVE sites are well predicted by MOZART-4x (with NMBs of -1.9% and 2.1%, respectively) but moderately underpredicted by CB05_GE (with NMBs of -23.1% and -20.7%, respectively). This is mainly due to the higher biogenic emissions and OH levels simulated with MOZART-4x than with CB05_GE. The concentrations of OC over Europe are largely underpredicted by both MOZART-4x and CB05_GE, with NMBs of -73.0% and -75.1%, respectively, indicating the uncertainties in the emissions of precursors and primary OC and relevant model treatments such as the oxidations of VOCs and SOA formation. Uncertainties in the emissions and convection scheme can contribute to the large bias in the model predictions (e.g., SO$_2$, CO, black carbon, and aerosol optical depth). The two simulations also have similar cloud/radiative predictions, with slightly better performance of domain average cloud condensation nuclei (CCN) at supersaturation of 0.5% by CB05_GE, but slightly better agreement with observed CCN (at supersaturation of 0.2%) profile over Beijing by MOZART-4x. The two gas-phase mechanisms result in a global average difference of 0.5 W m$^{-2}$ in simulated shortwave cloud radiative forcing, with significant differences (e.g.,
up to 13.6 W m\(^{-2}\)) over subtropical regions.

**Keywords**: CB05 GE, MOZART-4, CAM5-chem, atmospheric gas-phase chemistry, secondary organic aerosol, model evaluation

1. Introduction

Atmospheric chemistry plays an important role in the perturbation of climate system by determining the amounts and distributions of important oxidants and gaseous precursors for secondary air pollutants such as ozone (O\(_3\)) and aerosols (IPCC, 2013). Aerosols can influence the Earth’s radiative balance by directly scattering and absorbing radiation and indirectly affecting cloud properties through acting as cloud condensation nuclei (CCN) and ice nuclei (IPCC, 2013). The aerosol effects on radiation depend critically on their chemical composition and physical properties. Therefore, atmospheric chemistry is an important component for atmospheric and Earth system models. Different chemical mechanisms (e.g., different chemical reactions and kinetic parameters) can lead to differences in the predictions of gases, secondary aerosols, as well as climatic variables such as CCN, cloud droplet number concentration (CDNC), and radiative forcings (Luecken et al., 2008; Sarwar et al., 2008; Zhang et al., 2012a; Lamarque et al., 2013).

There are generally two types of species in the gas-phase mechanisms: inorganic and organic. Although most mechanisms include the same important inorganic species (e.g., O\(_3\), carbon monoxide (CO), HO\(_x\) (odd hydrogen = hydroxyl radical (+) +
human hydroperoxyl radical (HO$_2$) and nitrogen oxides (NO$_x$), the predicted amounts can vary greatly among different mechanisms (Knote et al., 2014a). Some mechanisms ignore reactions with very low reaction rates since they do not affect results significantly. Also, some reactions may use different rate coefficients with different dependence on atmospheric temperature and pressure due to the uncertainties in the laboratory measurements or the use of mechanisms that have not been updated in time. Unlike inorganic species, there are more significant differences in the representation of organic species. Light organic species with low molecular weight are often explicitly treated (e.g., methane, formaldehyde (HCHO)), whereas lumped or surrogate species are used to represent more complex mixtures of heavy organic compounds with high molecular weight (e.g., aromatics, organic nitrates). There are three most common representations of organic chemistry, including the lumped structure technique, the surrogate species approach, and the lumped species method (Zhang et al., 2004). For example, the Carbon Bond mechanism version IV (CB-IV, Gery et al., 1989), which uses the lumped structure approach for volatile organic compounds (VOCs), has been widely used in air quality modeling systems through urban to regional scales for many years. This mechanism has later been extensively updated in 2005 (CB05, Yarwood et al., 2005), and has been implemented into the Community Multiscale Air Quality model (CMAQ, Sarwar et al., 2008) and the Weather Research and Forecasting model with Chemistry (WRF-Chem, Wang et al., 2014). CB05 has been further expanded to include more than 120 reactions
that are important on global scale (CB05 with global extension (CB05 GE),
Karamchandani et al., 2012) and implemented into global models, such as the Global-
through-Urban WRF/Chem (GU-WRF/Chem, Zhang et al., 2012a) and the Community
Atmosphere Model version 5 (CAM5), the atmospheric component of the Community
Earth System Model (CESM/CAM5, He and Zhang, 2014). The Model of OZone and
Related chemical Tracers version 4 (MOZART-4, Emmons et al., 2010) mechanism,
which uses the lumped species approach for VOCs, has also been used in WRF-Chem
(Knote et al., 2014b), and CAM with extensive tropospheric and stratospheric chemistry
(CAM-chem) Versions 4 and 5 (Lamarque et al., 2012; Tilmes et al., 2015). Different gas-
phase mechanisms have also been compared in several studies, however, most of which
are conducted in box models or using regional models (Kim et al., 2009; Kim et al.,
2011a, b; Yu et al., 2010). For example, using WRF-Chem, Zhang et al. (2012b) found
that three different mechanisms (i.e., the Carbon Bond Mechanism-Z (CBM-Z), the 1999
Statewide Air Pollution Research Center Mechanism (SAPRC99), and the CB05) can
predict different O\textsubscript{3} concentrations up to 5 ppb at surface in July, 2001. Yu et al. (2010)
compared the O\textsubscript{3} predictions from three different mechanisms (i.e., CB4, CB05, and
SAPRC99) using Eta-CMAQ and found that at the AIRNow surface sites, CB05 gives the
best O\textsubscript{3} performance followed by CB4 and SAPRC-99 for observed O\textsubscript{3} \textgeq 75 ppb, whereas
CB4 gives the best O\textsubscript{3} performance for observed O\textsubscript{3} < 75 ppb. Knote et al. (2014a) also
compared seven chemical mechanisms using a box model and found that the differences

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in daytime OH radical concentrations can be up to 40%.

Climate change can also strongly influence atmospheric chemistry and aerosols and therefore air quality. For example, photolysis and temperature-dependent reactions can be directly impacted by climate change (Jacob and Winner, 2009). Due to the nonlinear relationships between chemistry, aerosols, and climate, it is important to accurately represent their interactions in a three-dimensional global model. Several studies have demonstrated the capability of CAM-chem to represent tropospheric (Aghedo et al., 2011; Lamarque et al., 2010, 2011a, b; Tilmes et al., 2015) and stratospheric (Lamarque et al., 2008; Lamarque and Solomon, 2010) conditions. The chemical mechanism used in CAM-chem is based on MOZART-4, with detailed stratospheric chemistry of Kinnison et al. (2007). In this work, two most commonly used gas-phase mechanisms: the extended MOZART-4 (with updates as described by Knote et al. (2014b) and additional updates in this work) (referred to as MOZART-4x) and the CB05_GE chemical mechanisms are compared using the latest CESM/CAM5. The objectives are to examine the differences in the secondary organic aerosols (SOA) predictions resulted from the two gas-phase chemical mechanisms and study the sensitivity of air quality and climate predictions to different gas-phase chemical mechanisms.

2. Model Descriptions
The CESM/CAM5 used in this work is based on CAM version 5.3 of CESM version 1.2.2, coupled to comprehensive tropospheric and stratospheric chemistry (CAM5-chem, Tilmes et al., 2015) using the 7-mode Modal Aerosol Model (MAM7) (Liu et al., 2012). This version of CAM5-chem was further developed and improved at North Carolina State University (NCSU) in collaboration with NCAR, as described below. A more detailed description of this version of CESM CAM5-chem (referred to as CAM5-NCSU hereafter) used in this study can be found in He and Zhang (2014) and He et al. (2015).

2.1 Chemical Mechanisms

In this study, CB05_GE has been updated to include additional kinetic reactions describing interactions between functionalization and fragmentation processes during gas-phase oxidation of anthropogenic and biogenic VOCs by OH (Glotfelty et al., 2015). The products of those reactions are linked with the organic gas/particle partitioning for SOA formation. Heterogeneous reactions on tropospheric aerosols and stratospheric clouds are also added as same as those in MOZART-4x (Tilmes et al., 2015) with one additional pathway in CB05_GE to simulate sulfate formation through oxidation of sulfur dioxide (SO$_2$) by O$_3$ on the surface of dust particles.

MOZART-4x used in this work extends the MOZART chemical mechanism used in Lamarque et al. (2012) and Tilmes et al. (2015) to include several updates as described
in Knote et al. (2014b). These updates include (1) detailed treatments of monoterpenes (α-pinene, β-pinene, and limonene) and 2-methyl-3-buten-2-ol (MBO); (2) detailed treatments of aromatics (e.g., benzene, toluene, and xylenes); (3) additional glyoxal \( (C_2H_2O_2)\) production from oxidized VOCs products; and (4) an updated isoprene (ISOP) oxidation scheme. In this work, the oxidation of anthropogenic and biogenic VOCs and subsequent aging processes are also included in MOZART-4x, and the products of those reactions are linked with the organic gas/particle partitioning for SOA formation.

Table 1 shows the gas-phase organic precursors for SOA formation treated in MOZART-4x and CB05_GE. For aromatic precursors of SOA, MOZART-4x includes benzene, toluene (TOL), xylenes, and cresol. Although CB05_GE does not include benzene, it includes polycyclic aromatic hydrocarbons (PAH) as a SOA precursor. For alkane precursors of SOA, MOZART-4x includes BIGALK (lumped alkanes with carbon number \( > 3 \)), whereas CB05_GE includes ALKH (long-chain alkanes, with \( C > 6 \)).

For anthropogenic alkene precursors of SOA, MOZART-4x includes propene \( (C_3H_6)\) and BIGENE (lumped alkenes with \( C > 3 \)), whereas CB05_GE includes terminal olefin (OLE) and internal olefin (IOLE). The emissions for biogenic alkene precursors are from the Model of Emissions of Gases and Aerosols from Nature version 2.1 (MEGAN2.1, Guenther et al., 2012). Both MOZART-4x and CB05_GE include α-pinene (APIN), β-pinene (BPIN), limonene, and ISOP as precursors for biogenic SOA. CB05_GE also includes additional biogenic precursors such as speciated ocimene (OCI), humulene
(HUM) and terpinene (TER). However, in MOZART-4x, the species mapping for MEGAN emission calculation is slightly different. For example, α-pinene and other compounds (e.g., α-thujene, p-cymene, and o-cymene) are mapped into APIN, β-pinene and other compounds (e.g., sabinene and camphene) are mapped into BPIN, limonene and other compounds (e.g.; phellandrene and terpinene) are mapped into LIMON, myrcene and other compounds (e.g., ocimene) are mapped into MYRC, and beta-caryophyllene and other sesquiterpenes (e.g., humulene and α-bergamotene) are mapped into BCARY. Due to the different mapping for MEGAN species, biogenic emissions between MOZART-4x and CB05_GE are different, which can result in different biogenic SOA predictions. On the other hand, the rate coefficients for the oxidations of biogenic VOCs (e.g., APIN, BPIN, and limonene) are constant in CB05_GE, whereas they are temperature dependent in MOZART-4x, such a difference can result in different SOA predictions as well. In addition, there are uncertainties in the HO_x recycling associated with isoprene chemistry in CB05_GE (Karamchandani et al., 2012), whereas MOZART-4x used in this work includes OH recycling from improved isoprene chemistry. For example, in CB05_GE, ISOP is oxidized by OH to generate 91.2% molar yield of HO_2. In MOZART-4x, the isoprene peroxy radical from the oxidation ISOP by OH (i.e., ISOPPO2) has different yields of HO_2 through reactions with nitrogen monoxide (NO), nitrate radical (NO_3), methylperoxy radical (CH_3O_2), and acetylperoxy radical (CH_3CO_3), and it can also consume HO_2 itself. These reactions have different reaction rates.
coefficients. These differences can affect O₃, OH, and NOₓ predictions, and thus the
oxidation of VOCs.

2.2 Aerosol/Cloud Treatments

In CAM5-NCSU, the aerosol module is based on MAM7 of Liu et al. (2012),
with improvements in terms of condensation, nucleation, aerosol thermodynamics, and
aerosol activation (He and Zhang, 2014; Gantt et al., 2014). The major updates include:
(1) the new particle formation treatments with a combination of the default nucleation
parameterizations of Vehkamaki et al. (2002), Merikanto et al. (2007), and a newly added
ion-mediated aerosol nucleation (Yu, 2010) above the planetary boundary layer (PBL),
and a combination of the three and an additional parameterization of Wang and Penner
(2009) in the PBL; (2) the inorganic aerosol thermodynamics based on ISORROPIA II of
Fountoukis and Nenes (2007), which explicitly simulates the thermodynamics of sulfate
(SO₄²⁻), ammonium (NH₄⁺), nitrate (NO₃⁻), sodium (Na⁺), and chloride (Cl⁻) in the
Aitken, accumulation, and fine sea-salt modes, as well as the impact of crustal species
associated with the fine dust mode; (3) an advanced aerosol activation scheme based on
Fountoukis and Nenes (2005) with additional updates based on Kumar et al. (2009) and
Barahona et al. (2010), which accounts for adsorption activation from insoluble CCN and
giant CCN equilibrium timescale on aerosol activation.

CAM5-NCSU also includes an advanced treatment for SOA formation based on a
volatility-basis-set (VBS) approach that has been coupled with CB05_GE by Glotfelty et al. (2015) and is also coupled with MOZART-4x in this work. This approach consists of two primary components: (1) volatile SOA (VSOA) formation from anthropogenic VOCs (AVOCs) and biogenic VOCs (BVOCs) and (2) the volatility and aging of primary organic aerosol (POA) and the repartitioning of the semi/intermediate volatility compounds (S/IVOC) into SOA. The VSOA treatment is based on the treatment of Tsimpidi et al. (2010). The products of VOC oxidation are mapped onto the volatility distribution using the aerosol mass yields listed in Tsimpidi et al. (2010) using the CB05_GE species that represent those precursor VOCs. An additional pathway for the formation of SOA from PAH is also added in CB05_GE. The SOA mass yields for PAHs are derived from the laboratory measurements of Chan et al. (2009) following the approach of Stainer et al. (2008), where the SOA mass yields for naphthalene, 1-methylnaphthalene, and 2-methylnaphthalene are averaged as surrogates for PAHs. The volatility of POA and the subsequent formation of SOA from POA vapors are based on the work of Robinson et al. (2007) and Shrivastava et al. (2008). POA emissions are distributed into nine logarithmically-spaced volatility bins with effective saturation (C*) values ranging from $10^{-2}$ to $10^6$ μg m$^{-3}$. An updated emission spectrum is used to distribute the POA emissions into the volatility bins as the emission spectrum used in Robinson et al. (2007) has been shown to be too volatile (Cappa and Jimenez, 2010; Hodzic et al., 2010; Jathar et al., 2011). This new emission spectrum maps the
anthropogenic POA emissions onto the volatility distribution based on thermodenuder measurements of gasoline exhaust and also contains separate emissions fractions for biomass burning aerosol which is less volatile than anthropogenic POA (May et al., 2013a, b). The emission spectrum of Robinson et al. (2007), also assumes that the emissions of SVOCs are fully captured by the original POA emissions and missing IVOCs are assumed to be equivalent to 1.5 times the POA emissions inventory with these additional emissions placed in the three highest volatility bins. However, because the estimations of the missing IVOC emissions are poorly constrained, the 1.5 times the POA mass for IVOCs is not included in this study.

In addition to the classic 1-D VBS treatment as described above, functionalization and fragmentation treatment described in Shrivastava et al. (2013) are included in this version of VBS for both VSOA and S/IVOCs (referred to as 1.5 D VBS). In this treatment, the VSOA and S/IVOCs in each volatility bin are split into three different species representing three generations of oxidation. During the first two generations of oxidation the mass of the VSOA and S/IVOCs grows by 15%, reflecting the addition of oxygen atoms. In this aging scheme not only do the masses of VSOA and S/IVOCs increase in generation when oxidized by OH (at a rate of $1.0 \times 10^{-11}$ and $4.0 \times 10^{-11}$ cm$^3$ molecule$^{-1}$ s$^{-1}$, respectively) but also their volatility decrease as they are moved into smaller volatility bins. Fragmentation occurs once the VSOA and S/IVOCs have aged to the third generation. This represents the breaking of carbon bonds, which can
increase volatility of the organic species thus reducing SOA formation. This is parameterized by allowing 17.25% of the organic mass to pass to the next lowest volatility bin but passing 75% of the VSOA and S/IVOC to the highest volatility bin in the VBS structure. The remaining mass is assumed to be lost to species of higher volatility than the VBS structure. There are several differences between the VBS used in this work and Shrivastava et al. (2015). For example, nine volatility bins are used in this work to represent the aging and gas-particle partitioning of POA, instead of five volatility bins used in Shrivastava et al. (2015). In addition, compared to the reaction (3) in Shrivastava et al. (2015), we do not have the third term, which denotes additional fragmentation where 10% of the mass results in low carbon number species with very high volatility that is eventually oxidized to CO/CO₂ and/or removed by dry deposition. In the model treatment used in this work, the remaining mass is assumed to be lost to species with a volatility higher than the volatility values in the VBS structure. A more detailed description of SOA formation from the VBS approach is summarized in Glotfelty et al. (2015).

3. Model Configurations and Evaluation Protocols

3.1 Model Setup and Inputs

The simulations are performed with specified dynamics configuration, of which winds and temperature are driven by the Goddard Earth Observing System Model,
Version 5 (GEOS-5) meteorology. The internally-derived meteorological fields are nudged every time step (30 min) by 10% towards analysis fields from GEOS-5. The nudged meteorological fields include surface pressure, meridional wind, zonal wind, zonal surface stress, meridional surface stress, snow height, solar flux at surface, soil moisture fraction, surface temperature, temperature, specific humidity, surface geopotential, orography flag, surface water flux, and surface sensible flux. The simulations are conducted for a 3-year period of 2008-2010 at a horizontal resolution of 0.9° × 1.25° and a vertical resolution of 56 layers for CAM5. The initial chemical conditions are generated with same configurations with 1-year spinup. The offline emissions used in this work are based on those used in Tilmes et al. (2015), of which the anthropogenic and biofuel emissions are from the Monitoring Atmospheric Composition and Climate/CityZen (MACCity) emission data set (Granier et al., 2011), and biomass burning emissions are taken from the Atmospheric Chemistry and Climate Model Intercomparison Project (ACCMIP) historical emissions dataset (Lamarque et al., 2010). The ACCMIP emissions are extrapolated for 2008-2010 with the Representative Concentration Pathway (RCP) 8.5 scenario and extended for VOCs and several other species for MOZART-4x species. MOZART-4x species are then mapped into CB05_GE species to generate emissions for CB05_GE species. Although both MOZART-4x and CB05_GE simulates bromine chemistry, no bromine emissions are included. For bromine/chlorine species (e.g., CF2CLBR, CF3BR, CFC11, CFC12, CH3BR, and
CH3CL), their surface concentrations are specified using the historical reconstruction from Meinshausen et al. (2011). No bromine emissions were included.

The online emissions include biogenic VOCs from MEGAN2.1 (Guenther et al., 2012), lightning NOx (Price and Rind, 1992; Price et al., 1997), mineral dust (Zender et al., 2003), and sea-salt (Martensson et al., 2003).

3.2 Available Measurements for Model Evaluation

A number of observational datasets from surface networks and satellites are used for model evaluation. They are summarized along with the variables to be evaluated in Table 2. The global surface network includes data sets from the National Oceanic and Atmospheric Administration Climate Diagnostics Center (NOAA/CDC). The satellite datasets include the Moderate Resolution Imaging Spectroradiometer (MODIS) for the retrievals of cloud properties, the Clouds and Earth's Radiant Energy System (CERES) Energy Balanced and Filled (EBAF) for the retrievals of radiation fluxes at surface and top of atmosphere, the Aura Ozone Monitoring Instrument in combination with Aura Microwave Limb Sounder (OMI/MLS) for the tropospheric ozone retrieval, the Measurements Of Pollution In The Troposphere (MOPITT) for tropospheric carbon monoxide (CO) retrieval, and the SCanning Imaging Absorption spectroMeter for Atmospheric CHartographY (SCIAMACHY) for the retrievals of tropospheric nitrogen dioxide (NO2), HCHO, and C2H2O2. Other satellite-based data include the MODIS-
derived CDNC and cloud liquid water path (LWP) by Bennartz (2007).

Regional observational networks include the Clean Air Status and Trends Network (CASTNET), the Interagency Monitoring of Protected Visual Environments (IMPROVE), the Speciation Trends Network (STN), and the Air Quality System (AQS) over CONUS; the European Monitoring and Evaluation Program (EMEP), the Base de Données sur la Qualité de l'Air (BDQA, France), and the European air quality database (AirBase) over Europe; the Ministry of Environmental Protection of China (MEPC), the National Institute for Environmental Studies of Japan (NIESJ), the Korean Ministry of Environment (KMOE), and Taiwan Air Quality Monitoring Network (TAQMN) over East Asia. In addition to the data from the above networks, SOA measurements collected by Lewandowski et al. (2013) at four field study sites including Cleveland and Medina, OH (July-August, 2009), and Bakersfield and Pasadena, CA (May-June, 2010) are used to evaluate SOA predictions.

Aircraft measurements include aircraft campaigns from Aerosol, Radiation, and Cloud Processes affecting Arctic Climate (ARCPAC), Stratosphere-Troposphere Analyses of Regional Transport in 2008 (START08), California Nexus 2010 (CalNex), Arctic Research of the Composition of the Troposphere from Aircraft and Satellites (ARCTAS), and CCN measurements in China (CCN_China). ARCPAC (Brock et al., 2011) was conducted during March-April 2008 in the troposphere of the Alaskan Arctic, including particle size distributions, composition, and optical properties. START08 (Pan
et al., 2010) was conducted during April-June 2008 to study the chemical and transport characteristics of the extratropical upper tropospheric and lower stratospheric region over central North America. CalNex (Ryerson et al., 2013) was conducted during May-July 2010 to provide improved scientific knowledge for emission control strategies to simultaneously address the interrelated issues of air quality and climate change. ARCTAS (Jacob et al., 2010) was conducted during April-June 2008 to investigate the chemistry of the Arctic's lower atmosphere. CCN_China (Zhang et al., 2011) was conducted over Beijing during July-September 2008, to investigate the impacts of aerosols on cloud formation.

3.3 Evaluation Protocol

The protocols for performance evaluation include spatial distributions and statistics, following the approach of Zhang et al. (2012b). The aircraft profile evaluation is based on the Atmospheric Model Working Group (AMWG) diagnostics package (Tilmes et al., 2015). Monthly-mean model results are compared for corresponding regions and seasons of the field campaign. The analysis of the performance statistics will focus on mean bias (MB), normalized mean bias (NMB), normalized mean error (NME), and root mean square error (RMSE) defined by Yu et al. (2006) and Zhang et al. (2006). The radiative/cloud variables are evaluated annually, including outgoing longwave radiation (OLR) from NOAA/CDC; downwelling shortwave radiation (FSDS),
downwelling longwave radiation (FLDS), shortwave cloud forcing (SWCF), and longwave cloud forcing (LWCF) from CERES-EBAF; cloud fraction (CF), aerosol optical depth (AOD), cloud optical thickness (COT), precipitating water vapor (PWV), and CCN from MODIS, as well as CDNC and LWP from Bennartz (2007). CDNC is calculated as an average value of layers between 850 and 960 hPa for comparison with the satellite-derived values. Chemical concentrations evaluated include CO, O₃, SO₂, ammonia (NH₃), NO₂, nitric acid (HNO₃), VOCs (i.e., formaldehyde, isoprene, and toluene), particulate matter (PM) with diameter less than and equal to 10 µm (PM₁₀) and 2.5 µm (PM₂.₅), and PM₂.₅ major components (e.g., SO₄²⁻, NH₄⁺, NO₃⁻, black carbon (BC), organic carbon (OC), and total carbon (TC)) for CONUS and Europe. The chemical observations over East Asia are very limited, which only include surface observations of CO, SO₂, NO₂, and O₃ from Hong Kong, South Korea, and Japan, and PM₁₀ over mainland China (derived from air pollution index), Hong Kong, South Korea, and Japan. Since PM₂.₅ and PM₁₀ are not explicit species simulated in MAM7, their concentrations are estimated based on size distributions of dry particles used in MAM7.

The properties of the particle size distribution for MAM7 are summarized in Table S1 in the supplementary material.

Column concentrations of tropospheric CO, NO₂, HCHO, C₂H₂O₂, and tropospheric O₃ residual (TOR) are evaluated for globe. The CO column evaluation follows the AMWG diagnostics approach, which applies 1° × 1° monthly mean Level 3
MOPITT a priori and averaging kernels to monthly mean model results to account for the a priori dependence and vertical resolution of the MOPITT data. The measured NO_2 and HCHO columns are derived from the satellite retrievals from SCIAMACHY, which are monthly mean gridded data on a 0.25° × 0.25° horizontal grid resolution for the period of 2008-2010. The measured glyoxal column is derived from the satellite retrievals from SCIAMACHY, which are monthly mean gridded data on a 0.125° × 0.125° horizontal grid resolution for the period of 2008. The measured O_3 is derived from the combing retrievals from the Aura Ozone Monitoring Instrument and Microwave Limb Sounder observations, which are monthly mean gridded data on a 1.25° × 1.25° horizontal grid resolution for the period of 2008-2010.

All surface observational data used for evaluating 2008-2010 simulations are available throughout 2008-2010 except for several variables with data during a limited time period of 2001-2010 including OC from EMEP, SOA from Lewandowski et al. (2013), and OA from Zhang et al. (2007) and Jimenez et al. (2009). For one grid cell containing multiple observational sites, all the observations within the grid cell are averaged and compared to the simulated results in that grid cell. While using grid averaged observations helps reduce, to some extent, the uncertainties in comparing grid averaged model output with pointwise observations, this approach cannot address the inherent uncertainties associated with the evaluation of the model results obtained at a coarse grid resolution.
4 Model Evaluations

4.1 Surface Evaluation

4.1.1 Inorganic Gases and Aerosols

Table 3 summarizes the performance statistics for major chemical species for CAM5-NCSU simulations with MOZART-4x and CB05_GE. Figure 1 shows the scatter plots between observations and model results. The statistical performance of MOZART-4x and CB05_GE are similar for most chemical species. As shown in Table 3, CO is underpredicted over East Asia by both MOZART-4x and CB05_GE, with NMBs of -65.6% and -65.7%, respectively. The underprediction of CO is mainly due to the underestimation of CO emissions from biomass burning (Tilmes et al., 2015). The underestimations in CO emissions lead to underpredictions of column CO concentrations, with NMBs of -25.8% and -24.4% for MOZART-4x and CB05_GE, respectively. Both MOZART-4x and CB05_GE largely overpredict the concentrations of SO$_2$ over CONUS (with NMBs of 580.2% and 561.6%, respectively), East Asia (with NMBs of 47.0% and 35.5%, respectively), and Europe (with NMBs of 100.9% and 94.1%, respectively), likely due to the overestimation of SO$_2$ emissions, the uncertainties in the emission injection heights as well as the vertical mixing scheme used. For example, several modeling studies over East Asia reported the underestimates of emissions of SO$_2$ and NO$_x$ are a main cause for poor model performance (e.g., Liu et al., 2010; Zhang et al.,
The overpredictions of surface SO$_2$ concentrations result in the overpredictions of the concentrations of SO$_4^{2-}$ at the surface. The overpredictions of surface SO$_4^{2-}$ concentrations can also be attributed to the uncertainties in the OH predictions. The air-mass weighted tropospheric mean OH concentrations predicted by MOZART-4x and CB05_GE are both $13.1 \times 10^5$ molec cm$^{-3}$, which is slightly higher than the present-day tropospheric mean OH level of $11.1 \pm 1.6$ molec cm$^{-3}$ of Naik et al. (2013). The higher OH level can result in higher oxidation of SO$_2$ to produce more SO$_4^{2-}$. Surface NH$_3$ concentrations from MOZART-4x and CB05_GE are overpredicted over Europe (with NMBs of 112.4% and 104.3%, respectively), likely due to the overestimation of NH$_3$ emissions. The overpredictions of the NH$_3$ concentrations can potentially result in the overpredictions of the NH$_4^+$ concentrations at the surface. On the other hand, the overpredictions of the NH$_4^+$ concentrations at the surface are also related to the overpredictions of the concentrations of SO$_4^{2-}$ at the surface. The concentrations of NO$_2$ from MOZART-4x and CB05_GE are largely underpredicted over CONUS (with NMBs of -51.4% and -52.2%, respectively), Europe (with NMBs of -61.4% and -62.1%, respectively), and East Asia (with NMBs of -74.1% and -74.8%, respectively), which is likely due to the uncertainties in estimating total NO$_x$ emissions and emission injection heights as well. As shown in Figure 1, the concentrations of O$_3$ from MOZART-4x and CB05_GE are overpredicted over CONUS (with NMBs of 29.0% and 28.2% over the CASTNET sites, respectively), Europe (with NMBs of 19.3% and 22.2% over the EMEP
sites, respectively) and East Asia (with NMBs of 68.8% and 65.7% over the KMOE sites, respectively). This is likely due to less O₃ titration resulted from the underpredictions of NOₓ, the dilution of NOₓ emissions resulted from the use of a coarse grid resolution, as well as possible underestimates in O₃ dry deposition. Martin et al. (2014) reported the uncertainties in O₃ dry deposition associated with vegetation phenology in CAM-chem, which led to positive biases of 16 ppb over eastern U.S. and 8 ppb over Europe, respectively, for summertime surface O₃. The overpredictions of SO₄²⁻ result in the underpredictions of NO₃⁻ and Cl⁻, through thermodynamic equilibrium, and therefore overpredictions of HNO₃ over CONUS. As more NH₄⁺ are needed to neutralize SO₄²⁻, less NH₄⁺ are available to neutralize NO₃⁻ and Cl⁻, driving total nitrate and total chlorine to partition into the gas-phase to produce more HNO₃ and HCl. Yu et al. (2005) also found that the model biases in total nitrate (TNO₃ = HNO₃ + NO₃⁻) predictions can be attributed to measurement errors in SO₄²⁻ and total ammonium (TNH₄ = NH₃ + NH₄⁺) as well as the inaccurate predictions in SO₄²⁻ and TNH₄. In addition, Reff et al. (2009) suggested several sources for Cl⁻ (e.g., biomass burning and wildfires), which are not included in this work. There are no anthropogenic Cl⁻ emissions included in this work except from sea-salt emissions, which is calculated online in CESM/CAM5. Omission of additional chlorine emissions may also partly explain the underpredictions of Cl⁻ over CONUS. HNO₃ is underpredicted over Europe, which is mainly due to the underpredictions of NOₓ. The concentration of Cl⁻ is overpredicted over Europe, which is
likely due to the uncertainties for the gas/particle partitioning over coarse modes (He and Zhang, 2014). Unlike the performance of Cl\(^{-}\) over CONUS, which is only for fine Cl\(^{-}\) (in Aitken, accumulation, fine sea-salt, and fine dust modes), the performance of Cl\(^{-}\) over Europe is for fine and coarse Cl\(^{-}\) (in all seven modes). As the thermodynamic equilibrium is not treated for coarse particles (the irreversible condensation of HCl is assumed to occur on the surface of coarse particles), it is likely that the model overpredicts coarse Cl\(^{-}\), but underpredicts fine Cl\(^{-}\) due to the missing sources. Both MOZART-4x and CB05_GE overpredict PM\(_{2.5}\) over CONUS, however, they underpredict PM\(_{10}\) over the AQS sites, with NMBs of -38.6% and -38.9%, respectively. The underpredictions of PM\(_{10}\) are mainly due to the inaccurate predictions of coarse particles. Both MOZART-4x and CB05_GE underpredict PM\(_{2.5}\) and PM\(_{10}\) over Airbase and BDQA sites, however, they overpredict PM\(_{10}\) by 3.14 μg m\(^{-3}\) (or by 22.2%) and 3.43 μg m\(^{-3}\) (or by 24.2%) over the EMEP sites, respectively, which is mainly due to the overpredictions of coarse particles (e.g., Cl\(^{-}\)) over these sites and uncertainties in the sea-salt and dust emissions. Both MOZART-4x and CB05_GE underpredict PM\(_{10}\) by 33.61 μg m\(^{-3}\) (or by 33.4%) and 26.71 μg m\(^{-3}\) (or by 26.6%) over the MEPC sites in mainland China, respectively, which is mainly due to the uncertainties in the emissions in primary gases (e.g., SO\(_{2}\), NO\(_x\), NH\(_3\), and VOCs) and particulate species (e.g., SO\(_4^{2-}\), BC, and POA). Granier et al. (2011) compared the regional emissions among different inventories and indicated large uncertainties in the emissions over China. For example, the differences of BC biomass
burning emissions over China among different inventories can be as large as a factor of 2.1, and the differences of SO₂ anthropogenic emissions can be as large as a factor of 1.8.

4.1.2 VOCs and Organic Aerosols

VOCs species such as HCHO, ISOP, and TOL are underpredicted over CONUS, likely due to the uncertainties in the biogenic emissions from MEGAN2.1, anthropogenic emissions (e.g., HCHO and TOL) and the chemical reactions as well as a coarse horizontal resolution used in this work. Both MOZART-4x and CB05_GE underpredict BC with NMBs of -29.3% and -29.3%, respectively. The underpredictions of BC are likely due to the underestimations of BC emissions, as well as uncertainties in the transport and wet removal by convection (Ma et al., 2013; Wang et al., 2013; Tilmes et al., 2015).

OC is slightly overpredicted with an NMB of 2.1% by MOZART-4x over CONUS, whereas it is moderately underpredicted with an NMB of -20.7% by CB05_GE. OC is evaluated against observations at the IMPROVE sites, and SOA dominates OC at these sites for both simulations with MOZART4-x and CB05_GE, with SOA/OC ratios of 83.0% and 59.6%, respectively. Although no SOA measurements are available from IMPROVE for evaluation, the differences in OC predictions can be attributed to the differences in SOA predictions because of dominances of SOA in total OC. Compared to the SOA observations at the four sites in the U.S. from Lewandowski et al. (2013), MOZART-4x underpredicts SOA by 0.03 μg m⁻³ (or by 1.9%), whereas CB05_GE
underpredicts SOA by 0.4 μg m$^{-3}$ (or by 23.1%). Note that the SOA statistics are calculated using only four pairs of seasonal mean values at four sites in the U.S. where the observed SOA data are available during 2008-2010; they therefore may not be representative because of limited data used for calculation. Figure 2 compares simulated and observed SOA concentrations at the four sites. MOZART-4x predicts higher SOA than CB05_GE at all four sites, which reduces underpredictions at Cleveland and Medina, OH but increases overpredictions at Bakersfield and Pasadena, CA. This indicates a better capability of MOZART-4x to simulate SOA at sites with relatively high SOA concentrations (≥ 1 μg m$^{-3}$) compared to CB05_GE despite its tendency of overpredictions at sites with lower SOA levels. The higher SOA concentrations predicted by MOZART-4x can be attributed to the higher OH levels and higher biogenic emissions in MOZART-4x. However, the concentration of OC is largely underpredicted by both MOZART-4x and CB05_GE over Europe, with NMBs of -74.2% and -75.1%, respectively, indicating the uncertainties in the emissions of SOA precursors and SOA formation treatment. For example, the aqueous-phase oxidation of VOCs in clouds is not taken into account in this work, which, however, can contribute several percentages of SOA in some areas and seasons over Europe (Couvidat et al., 2013). The hydrocarbon-like organic aerosol (HOA) predicted by MOZART-4x and CB05_GE correlated well with the observations at 33 sites in the Northern Hemisphere (e.g., with correlation coefficients of 0.93 for both simulations) but the amount is largely underpredicted by
both MOZART-4x and CB05_GE, with NMBs of -77.2% and -76.7%, respectively, indicating that the POA may be too volatile with the implementation currently in the model. Oxygenated organic aerosol (OOA), which is roughly equivalent to the sum of SOA and SVOA, is also largely underpredicted at the 33 sites by both MOZART-4x and CB05_GE, with NMBs of -56.5% and -62.3%, respectively. This is mainly due to the uncertainties in the oxidation rate and fragmentation rates as well as SOA formation treatment. The underpredictions of HOA and OOA result in an underprediction of total organic aerosol (TOA) by both MOZART-4x and CB05_GE, with NMBs of -67.8% and -71.2%, respectively.

4.2 Chemical Column Evaluation

Figure 3 shows the zonal mean of column concentrations of CO, HCHO, glyoxal, NO$_2$, and TOR for June, July, and August during 2008-2010. In general, MOZART-4x and CB05_GE predict similar zonal mean profiles of these species. Both MOZART-4x and CB05_GE underpredict column CO, due to a significant underestimation of CO emissions (Tilmes et al., 2015) and uncertainties in OH predictions. During summer, column HCHO is overpredicted over middle latitudes (30-60° N) in the Northern Hemisphere and tropical regions (0-10° S) in the Southern Hemisphere, while it is largely underpredicted over the rest of regions. The underprediction of column HCHO is likely due to the uncertainties in the emissions of HCHO and its precursors as well as pathways for secondary HCHO formation. Both MOZART-4x and CB05_GE underpredict column
glyoxal, with more underpredictions in CB05_GE. The underpredictions of glyoxal are mainly due to the uncertainties in the glyoxal chemical production and removal (Knote et al., 2014b). Several studies indicate that aromatics, isoprene, and ethyne are the major contributors to glyoxal formation (Washenfelder et al., 2011; Knote et al., 2014b). In MOZART-4x, glyoxal can be produced from photolysis of the oxidation products of toluene, and oxidation products of aromatics (e.g., benzene, toluene, and xylenes), isoprene, and ethyne. CB05_GE does not include pathways for glyoxal production through photolysis, but includes glyoxal production from oxidation of alkenes (e.g., OLE, IOLE, ethene, and ISOP) and aromatics (e.g., toluene and xylenes). Uncertainties in the emissions of these precursors and the production pathways can propagate into the predicted glyoxal concentrations. MOZART-4x includes additional pathways for glyoxal production through photolysis and improved treatments for glyoxal production from additional oxidized VOCs (e.g., benzene) products (Knote et al., 2014b), which can result in higher glyoxal than in CB05_GE. The major chemical loss of glyoxal includes photochemical loss and oxidation by OH. The uncertainties in OH levels can propagate into glyoxal predictions as well. In addition, CB05_GE includes an additional pathway for glyoxal loss through its uptake by aerosols, which is not included in MOZART-4x. This can explain in part the lower glyoxal concentrations predicted by CB05_GE than by MOZART-4x. An advanced treatment for glyoxal formation should be therefore developed in the future. Both MOZART-4x and CB05_GE overpredict column NO₂,
likely due to the uncertainties in the NO\textsubscript{2} aircraft emissions and overpredictions of 
lightning NO\textsubscript{x}, as well as the satellite retrievals. The lightning NO\textsubscript{x} emissions are 
calculated online (i.e., 6.2 and 6.4 TgN yr\textsuperscript{-1} in CB05\_GE and MOZART-4x, respectively), 
which is about 1.2-2.2 TgN yr\textsuperscript{-1} higher than that in Lamarque et al. (2012) and Tilmes et 
al. (2015). Tilmes et al. (2015) have shown that increased lightning NO\textsubscript{x} emissions in 
CAM-chem can lead to an increase in OH levels and therefore a decrease in the lifetime 
of methane and an underestimation of CO in the model. As discussed in Yarwood et al. 
(2012), the errors in satellite NO\textsubscript{2} retrievals are dominated by atmospheric mass factor, 
which has a large uncertainty due to errors in the specification of clouds, surface albedo, 
a priori NO\textsubscript{2} profile shape, and aerosols. Boersma et al. (2004) also reported that the error 
in the tropospheric NO\textsubscript{2} retrievals is 35-60\%, especially over polluted areas. These can 
partly explain the overpredictions of column NO\textsubscript{2}. The higher zonal-mean concentrations 
of NO\textsubscript{2} in CB05\_GE than those in MOZART-4x are likely due to additional NO\textsubscript{2} 
production from the reactions of VOCs with NO\textsubscript{3} radical in CB05\_GE (e.g., reactions of 
NO\textsubscript{3} with OLE, IOLE, and ethene). The zonal-mean distribution of summer TOR from 
CB05\_GE is similar to that from MOZART-4x. TOR is overpredicted over 40\(^o\) S-50\(^o\) N, 
and underpredicted over 40\(^o\) S-60\(^o\) S. The higher TOR from CB05\_GE is mainly due to 
higher O\textsubscript{3} production from higher NO\textsubscript{2} and lower O\textsubscript{3} loss from lower OH in CB05\_GE 
than in MOZART-4x.

4.3 **Vertical Profile Evaluation**
Figure 4 compares the vertical profile of major gases against the aircraft observations (i.e., ARCPAC, ARCTAS, START08, and CalNex). Compared with aircraft measurements, MOZART-4x and CB05_GE predict similar \( \text{O}_3 \) and CO profiles, whereas there are large differences in \( \text{NO}_x \) (above 9 km) and \( \text{NO}_y \) profiles (below 12 km). \( \text{O}_3 \) profiles from MOZART-4x and CB05_GE overall agree well with aircraft measurements, although \( \text{O}_3 \) is slightly overpredicted near the surface. As discussed previously, the significant underpredictions of CO profiles in both MOZART-4x and CB05_GE are mainly due to the underestimations of CO biomass burning emissions and uncertainties in OH predictions. Both MOZART-4x and CB05_GE underpredict the vertical concentrations of \( \text{NO}_x \) at higher altitudes (e.g., above 9 km in ARCTAS and STRAT08), with a slightly better agreement in CB05_GE than in MOZART-4x. The concentrations of \( \text{NO}_x \) near the surface are slightly overpredicted by both simulations. The underpredictions of the concentrations of \( \text{NO}_x \) at higher altitudes are likely due in part to the uncertainties in the \( \text{NO}_x \) emissions, the chemical reactions of nitrogen cycles (e.g., heterogeneous reactions of \( \text{NO}_2, \text{NO}_3, \) and \( \text{N}_2\text{O}_5 \) over the surface of aerosol particles), the convection scheme, as well as the aircraft campaign data. Some field campaigns (e.g., ARCPAC) focus on the polluted regions with a significant contribution from biomass burning and local sources (Tilmes et al., 2015). The underestimations of emissions from these sources and uncertainties in the vertical mixing scheme can result in the underpredictions of their profiles. \( \text{NO}_y \) includes all the reactive nitrogen species. The simulated \( \text{NO}_y \) profiles from
CB05_GE agree better with those observed during APCPAC, ARCTAS, and CalNex than those from MOZART-4x, whereas MOZART-4x predicts slightly better NO$_y$ profile against START08 in the lower troposphere than CB05_GE. OH concentrations are underpredicted by both MOZART-4x and CB05_GE against ARCTAS observations, whereas H$_2$O$_2$ mixing ratios are well predicted above 4 km but underpredicted below 4 km. Compared to CB05_GE, MOZART-4x predicts slightly higher H$_2$O$_2$ within 4-km above the surface. However, the performance here only represents the local conditions, instead of global conditions. Figure 5 compares the vertical profile of simulated CCN against the aircraft observations from CCN_China. Both MOZART-4x and CB05_GE slightly overpredict CCN (at supersaturation of 0.2%) profile over Beijing area, with less overpredictions in MOZART-4x.

### 4.4 Cloud/Radiative Evaluation

Table 4 shows the statistical performance for major cloud/radiative variables for MOZART-4x and CB05_GE simulations. Radiative variables such as OLR, FSDS, and FLDS show excellent agreement with observations, with NMBs within $\pm$8% for both simulations. However, SWCF is overpredicted by both MOZART-4x and CB05_GE, with NMBs of 26.4% and 27.7%, respectively, and LWCF is underpredicted by both MOZART-4x and CB05_GE, with NMBs of -21.6% and -16.7%, respectively. All predicted radiative variables show high correlation with observations, with correlation coefficients of 0.9 to 0.99. CF is well predicted by MOZART-4x, with an NMB of 6.3%,
whereas CCN5, CDNC, COT, and LWP are moderately overpredicted or underpredicted, with NMBs of -32.1%, 19.7%, -26.0%, and 2.8%, respectively. The performance of cloud variables is similar in CB05_GE, with NMBs of 6.0%, -29.0%, 20.8%, -26.0%, and 1.7% for CF, CCN5, CDNC, COT, and LWP, respectively. AOD is also underpredicted by both MOZART-4x and CB05_GE, with NMBs of -23.9% and -24.6%, respectively.

Figure 6 shows the Taylor diagram (Taylor, 2001) comparing the model performance of MOZART-4x with that of the CB05_GE for cloud and radiative predictions. The similarity between the two patterns is quantified in terms of their correlations (i.e., angle), their standard deviations (i.e., y axis), and the ratio of their variances (i.e., x axis). In general, the performance of major cloud/radiative variables between MOZART-4x and CB05_GE are similar. The major differences in the performance of cloud/radiative variables between MOZART-4x and CB05_GE are the variances of CCN5, CDNC, and SWCF, which is mainly due to the predicted aerosol distributions. The larger deviation of COT and LWP from observations (i.e., the two points located outside the diagram in Figure 6) suggests the uncertainties both in the model treatments for cloud dynamics and thermodynamics as well as in the satellite retrievals.

Due to the underpredictions of cloud variables (e.g., COT and CCN5), OLR is slightly overpredicted by 7.8 W m\(^{-2}\) (or by 3.6%), and LWCF is underpredicted by 4.8 W m\(^{-2}\) (or by 21.6%) in MOZART-4x. Similarly, OLR is slightly overpredicted by 6.7 W m\(^{-2}\)
Figure 7 shows the comparisons of satellite observations with model predictions for AOD, CCN5, CDNC, COT, and SWCF averaged during 2008-2010. The underpredictions of AOD over oceanic areas can be attributed to the uncertainties in the sea-salt emissions and inaccurate predictions of other PM components (e.g., marine organic aerosols) over the ocean and overestimation of oceanic AOD in the MODIS collection 5.1 (Levy et al., 2013). The underprediction of AOD over land (e.g., tropical islands) is mainly due to the significant underestimation of biomass burning emissions in the model (Tilmes et al., 2015). AOD is higher in MOZART-4x over most land areas (except East Asia and Europe) than in CB05 GE. The higher AOD in MOZART-4x is mainly due to higher SOA (e.g., over most land areas) and higher NO$_3^-$ (e.g., over CONUS) in MOZART-4x. The lower AOD over East Asia and Europe in MOZART-4x is mainly due to the lower SO$_4^{2-}$ as there is an additional pathway of SO$_2$ (oxidized by O$_3$) included in CB05 GE but it is not included in MOZART-4x and lower NH$_4^+$ to neutralize lower SO$_4^{2-}$ through thermodynamic equilibrium. This additional pathway also results in higher H$_2$SO$_4$ predictions in CB05 GE and higher aerosol number concentration through homogeneous nucleation. Therefore, CCN5 is higher in CB05 GE than in MOZART-4x (see Figure 7). CDNC is moderately overpredicted for both cases. Cloud droplet formation is sensitive to both particle number concentrations and updraft velocity (Reutter et al., 2009). The overprediction of CDNC is due partly to high activation
fractions (e.g., inclusion of adsorption activation from insoluble CCN and effective
uptake coefficient of 0.06 used in this work) (Gantt et al., 2014) as well as the
uncertainties in the model treatments for cloud microphysics (e.g., resolved clouds and
subgrid-scale cumulus clouds) and satellite retrievals (e.g., error propagation of the input
variables to derive CDNC) (Bennartz, 2007). COT is largely overpredicted over
Southeast Asia and South America and underpredicted over polar regions for both
simulations. Overpredictions in CDNC and COT can increase cloud albedo and therefore,
increase SWCF over the low and middle latitudes. The large underpredictions of COT
over polar regions can be attributed to the uncertainties in plane-parallel visible-near-
infrared retrievals with low solar zenith angle (Seethala and Horváth, 2010) and the
influence of radiatively active snow on overlying cloud fraction (Kay et al., 2012). Due to
the different gas-phase mechanisms, the predicted SWCF (Figure 7) and LWCF (Figure
not shown) are different, with a global average difference of 0.5 W m$^{-2}$ and 1.1 W m$^{-2}$,
respectively. However, the absolute differences in simulated SWCF can be as large as
13.6 W m$^{-2}$ as shown in Figure 7. The large differences of SWCF and LWCF between
MOZART-4x and CB05_GE are mainly over subtropical regions (e.g., 20 °S - 20 °N),
which is mainly due to lower COT in MOZART-4x than in CB05_GE.

5. Model-to-Model Comparisons

5.1 Column Comparisons
5.1.1 Column Gases

Figures 8a and b compare the column mass abundance of major gaseous and aerosol species simulated by MOZART-4x and CB05_GE. As shown in Figure 8a, column CO predicted by MOZART-4x is about $2.4 \times 10^{20} \text{ m}^{-2}$ (or by 2.3%) lower than that by CB05_GE in the global mean. The different column CO concentrations are due to different pathways for chemical production and loss of CO between MOZART-4x and CB05_GE, and different OH levels in MOZART-4x and CB05_GE. The chemical production of CO is mainly from photolysis and oxidation of VOCs species, and the chemical loss of CO is mainly from the oxidation by OH. Different concentrations of VOCs species can result in different chemical production of CO. Meanwhile, the only chemical loss of CO in CB05_GE is the oxidation of CO by OH, which produces HO$_2$ and CO$_2$. Higher OH levels in MOZART-4x can result in more CO loss. MOZART-4x includes an additional loss pathway of CO oxidized by OH to produce CO$_2$ and H. As a result, the combined rate constant for both pathways of CO oxidation by OH in MOZART-4x is about 4% higher than in CB05_GE. All these differences result in 2301 and 2265 Tg yr$^{-1}$ chemical loss of CO in MOZART-4x and CB05_GE, respectively.

The global mean differences in the simulated column concentrations of SO$_2$ and NH$_3$ between MOZART-4x and CB05_GE are $2.0 \times 10^{18} \text{ m}^{-2}$ (or by 12.5%) and $1.9 \times 10^{17} \text{ m}^{-2}$ (or by 3.1%), respectively. The lower column abundance of SO$_2$ in CB05_GE is mainly due the additional pathway for SO$_2$ loss through oxidation by O$_3$ over the surface.
of dust particles, which is not included in MOZART-4x. This pathway can produce more
$SO_4^{2-}$ and therefore, more NH$_3$ is partitioned into the particulate phase to form NH$_4^+$
which can neutralize additional $SO_4^{2-}$, resulting in lower column abundance of NH$_3$ in
CB05_GE. Both column concentrations of NO$_x$ and NO$_y$ from MOZART-4x are about
9.4 $\times 10^{17}$ m$^{-2}$ (or by 9.5%) and 3.6 $\times 10^{19}$ m$^{-2}$ (or by 46.3%) lower than that from
CB05_GE. The higher NO$_x$ in CB05_GE is mainly due to the lower OH available for the
chemical loss through the reaction of NO$_2$ with OH. NO$_y$ in MOZART-4x includes NO$_x$,
nitrate radical (NO$_3$), nitrogen pentoxide (N$_2$O$_5$), HNO$_3$, peroxynitric acid (HO$_2$NO$_2$),
chlorine nitrate (ClONO$_2$), bromine nitrate (BrONO$_2$), peroxyacetyl nitrate (PAN),
organic nitrate (ONIT), methacryloyl peroxynitrate (MPAN), peroxy radical from the
reaction of NO$_3$ with ISOP (ISOPNO3), and lumped isoprene nitrate (ONITR), whereas
NO$_y$ in CB05_GE includes NO$_x$, NO$_3$, N$_2$O$_5$, HNO$_3$, HO$_2$NO$_2$, ClONO$_2$, BrONO$_2$, nitrous
acid (HONO), PAN, higher peroxyacetyl nitrates (PANX), and organic nitrate (NTR). The
reactions for reactive nitrogen species are different in MOZART-4x and CB05_GE,
resulting in different NO$_y$ predictions. Figure S1 in the supplementary material shows the
dominant species in NO$_y$ predicted by the simulations using both MOZART-4x and
CB05_GE. As shown in Figure S1, NO$_x$, HNO$_3$, and TPAN (PAN+MPAN for MOZART-
4x and PAN+PANX for CB05_GE) are the major components for NO$_y$ concentrations,
with the ratios of 90.5% and 91.7%, respectively, for the sum of the mixing ratios of top
three species to that of NO$_y$. NO$_x$ dominates over East Asia, eastern U.S., and western
Europe, whereas TPAN dominates over most oceanic area. Figure S2 in the supplementary material shows the absolute and relative differences for major NO\textsubscript{y} species between MOZART-4x and CB05_GE. As shown in Figure S2, MOZART-4x predicts lower column TPAN by 2.9×10\textsuperscript{19} molecules m\textsuperscript{-2} (or by 63.4%), which dominates the differences in NO\textsubscript{y} predictions between the two simulations. The differences in TPAN predictions can be attributed to the differences in the kinetic reactions. Table S2 in the supplementary material lists the reactions involving TPAN. As shown in Table S2, besides the differences in the reaction rate calculation, MOZART-4x includes one additional reaction, i.e., PAN destruction by OH, which is not included in CB05_GE. In addition, simulated OH levels are higher in MOZART-4x than those in CB05_GE, which could result in more TPAN loss through oxidation by OH. These differences can explain the lower TPAN mixing ratios in MOZART-4x than those in CB05_GE and thus lower column NO\textsubscript{y} mass abundances in MOZART-4x than those in CB05_GE. Table S3 in the supplementary material lists the NO\textsubscript{y} species used in the calculation for Figure 4 and other NO\textsubscript{y} related comparisons. Figure S3 in the supplementary material shows the absolute differences in NO\textsubscript{y} (with and without inclusion of aerosol nitrate) between MOZART-4x and CB05_GE. If aerosol nitrate is accounted for in the NO\textsubscript{y} definition, the differences in NO\textsubscript{y} between the two mechanisms decrease over East Asia, eastern U.S., Europe, and middle Africa as aerosol nitrate is higher in MOZART-4x over these regions (see Figure 6b). For the rest of areas, the differences in NO\textsubscript{y} between the two mechanisms
increase if aerosol nitrate is accounted for in the NO\textsubscript{y} definition. The tropospheric column O\textsubscript{3} from MOZART-4x is about 1.5 DU (or by 4.7%) lower than that from CB05_GE.

Table 5 shows the tropospheric O\textsubscript{3} budget from MOZART-4x and CB05_GE. The burdens of tropospheric O\textsubscript{3} from MOZART-4x and CB05_GE are 325 Tg and 333 Tg, respectively, which is comparable to the previous studies using CAM (Lamarque et al., 2012; Young et al., 2013). The O\textsubscript{3} burden from MOZART-4x in this work is about 12 Tg (or 3.8%) higher than that in Tilmes et al. (2015), which is mainly due to the additional kinetic reactions included in this version of MOZART-4x. The dry deposition flux of O\textsubscript{3} from MOZART-4x is 679 Tg yr\textsuperscript{-1}, which is about 3.7% lower than that from CB05_GE (i.e., 705 Tg yr\textsuperscript{-1}). The lower O\textsubscript{3} dry deposition flux is mainly due to the lower O\textsubscript{3} concentration simulated by MOZART-4x. The O\textsubscript{3} chemical production and loss from CB05_GE and MOZART-4x are roughly within the range of Young et al. (2013). The O\textsubscript{3} chemical production from MOZART-4x is comparable to that of Lamarque et al. (2012), but the O\textsubscript{3} chemical production from CB05_GE is about 12.8% higher than Lamarque et al. (2012). In this table, chemical production is calculated mainly from reactions of NO with peroxy radicals and chemical loss is calculated mainly from the oxygen radical in the reaction of excited oxygen atom (O\textsuperscript{1}D) with water vapor (H\textsubscript{2}O) and from the reactions of O\textsubscript{3} with the HO\textsubscript{2}, OH, and alkenes. Different peroxy radicals and alkenes treated and different reaction rates used in the two mechanisms can contribute to the different chemical production and chemical loss of O\textsubscript{3}. The O\textsubscript{3} lifetime is calculated based on the
ratio of O$_3$ burden to the total O$_3$ loss (dry deposition + chemical loss). The O$_3$ lifetime from CB05_GE is comparable to those reported by Young et al. (2013), and the O$_3$ lifetime from MOZART-4x is comparable to those reported by Lamarque et al. (2012) and Tilmes et al. (2015).

Column concentrations of OH, HCHO, and ISOP from MOZART-4x are higher than CB05_GE, with global mean values of $9.7 \times 10^{13}$ m$^{-2}$ (or by 0.8%), $3.5 \times 10^{17}$ m$^{-2}$ (or by 1.3%), and $1.1 \times 10^{18}$ m$^{-2}$ (or by 25.6%), respectively. The higher column concentrations of OH and HCHO are likely due to the photolysis of more peroxide species, better HO$_x$ recycling, and higher precursors for secondary HCHO (e.g., ISOP) in MOZART-4x. MOZART-4x includes detailed organic peroxide species, whereas in CB05_GE, all the organic peroxide species are lumped into one species (i.e., ROOH).

The uncertainties in HO$_x$ recycling in CB05_GE can also result in uncertainties in OH predictions. The higher ISOP is mainly due to higher biogenic emissions and less chemical loss in MOZART-4x than that in CB05_GE. In MOZART-4x, the chemical loss of ISOP is mainly from the oxidation of ISOP by OH, O$_3$, and NO$_3$. However, in CB05_GE, the chemical loss of ISOP includes not only the oxidation of ISOP by OH, O$_3$, and NO$_3$, but also the consumption of ISOP by atomic oxygen (i.e., O), NO$_2$, and Cl.

### 5.1.2 Column Aerosols

As shown in Figure 8b, the differences in the domain average column mass abundances of most aerosol species (e.g., NH$_4^+$, BC, Cl$^-$, and POA) between MOZART-
4x and CB05_GE are within ± 0.02 mg m$^{-2}$. The differences in the column SO$_4^{2-}$ vary from -25.2 to 0.4 mg m$^{-2}$, with the global mean of -0.2 mg m$^{-2}$. The simulated column concentrations of SO$_4^{2-}$ from MOZART-4x are much lower than those from CB05_GE over East Asia, west Europe, and Middle Africa. SO$_2$ can be oxidized by O$_3$ to form SO$_4^{2-}$ on the surface of dust particles in CB05_GE, which explains additional formation of SO$_4^{2-}$ by CB05_GE over these regions. The differences of the spatial distributions and magnitudes in the column concentrations of NH$_4^+$ are similar to those of SO$_4^{2-}$ over land areas, which is associated with thermodynamic equilibrium. The column concentrations of NO$_3^-$ simulated by MOZART-4x are higher over East Asia, India, and Europe than those by CB05_GE, which is mainly due to its competition with SO$_4^{2-}$ in forming ammonium salts in the particulate phase in those regions where the column NH$_3$ concentrations are high (Figure 8a). Dust emissions are very sensitive to the wind speed. Slightly changes in wind speeds can result in significant change in dust emissions, thus, dust concentrations.

The column concentrations of SOA predicted by MOZART-4x are about 0.18 mg m$^{-2}$ (or by 8.4%) higher than those predicted by CB05_GE. The higher SOA column concentrations are mainly over most continental areas in the middle and low latitudes. The SOA mainly includes biogenic SOA, anthropogenic SOA, and semi-volatile SOA. The differences of SOA are mainly due to the higher BVOCs emissions and higher OH levels in MOZART-4x than in CB05_GE. Different branching ratios used in MOZART-
4x and CB05_GE can also contribute to the different SOA predictions. MOZART-4x includes explicit species and more types of precursors for alkylperoxy radicals (RO$_2$), and different reaction rate constants for different reactions, whereas in CB05_GE, all oxidized VOCs are lumped as one species (i.e., RO$_2$) and branching ratios are estimated based on the only three reactions (i.e., reactions of RO$_2$ with NO, HO$_2$, and RO$_2$). These differences can contribute to the differences in the estimation of branching ratios, and therefore, affect the partitioning between organic gas and aerosols through the 1.5 D VBS treatment implemented in CAM5-NCSU.

5.2 SOA Comparisons

Figure 9 shows the contributions to total SOA (TSOA) concentrations from anthropogenic sources (ASOA), biogenic sources (BSOA), glyoxal (GLSOA), and semi-volatile organic aerosol (SVSOA) over Australia, Europe, North America, South Africa, South America, and East Asia over 2008-2010. The contributions of ASOA to TSOA predicted by MOZART-4x and CB05_GE are about 17-44%, and 10-47%, respectively, with South America the least and East Asia the most. The contributions of BSOA to TSOA predicted by MOZART-4x and CB05_GE are about 31-75%, and 26-76%, respectively, with East Asia the least and South America the most. The contribution of GLSOA to TSOA predicted by CB05_GE is about 2-6%. CB05_GE used in this work includes a simple conversion of glyoxal to condensable VOCs, which can be uptaken by
preexisting particles to form SOA. However, this conversion is not included in

MOZART-4x. Therefore, there is no GLSOA predicted by MOZART-4x despite it predicts higher glyoxal as shown in Figure 3. The contributions of SVSOA to TSOA predicted by MOZART-4x and CB05_GE are about 8-37%, and 8-41%, respectively, with South America the least and South Africa the most. Among four types of SOA, both MOZART-4x and CB05_GE predict BSOA as the main contributor over most regions (e.g., Australia, North America, South Africa, and South America) and ASOA as the main contributor over East Asia, which is mainly due to the much higher anthropogenic emissions over East Asia. Europe is a different example. MOZART-4x predicts BSOA as the top contributor (44%) and ASOA as the second largest contributor (40%), whereas CB05_GE predicts ASOA as the top contributor (45%) and BSOA as the second largest contributor (36%). Both MOZART-4x and CB05_GE predict ASOA as the top contributor (46-59%) for spring, fall, and winter, and BSOA as the top contributor (57% and 47%, respectively) for summer over Europe. Since MOZART-4x predicts higher BSOA than CB05_GE, BSOA is dominant in MOZART-4x on the annual average. The higher BSOA from MOZART-4x than CB05_GE is mainly due to the higher BVOCs emissions in MOZART-4x and higher OH levels in MOZART-4x. The total BVOCs emission in MOZART-4x is about $2.5 \times 10^{-3}$ kg m$^{-2}$ yr$^{-1}$, which is about $7.2 \times 10^{-5}$ kg m$^{-2}$ yr$^{-1}$ (or 2.9%) higher than CB05_GE. The higher BVOCs emissions in MOZART-4x are mainly due to the different species mapping for MEGAN emission calculations. The
differences of SOA from biogenic alkenes between MOZART-4x and CB05_GE are MYRC and BCARY in MOZART-4x, and OCI, HUM, and TER in CB05_GE (as shown in Table 1). In CAM-chem that uses MOZART, MEGAN calculates all of the individual species and CAM-chem sums them up to map with the MOZART mechanism species. For example, MYRC emissions consist of myrcene and ocimene, BCARY emissions consist of beta-caryophyllene, alpha-bergamotene, beta-bisabolene, beta-farnesene, and alpha-humulene, and LIMON emissions consist of limonene, phellandrene, and terpinene. Therefore, the biogenic emissions for more types of VOCs in MOZART-4x are higher than those in CB05_GE, resulting in higher BSOA in MOZART-4x. The differences in SOA from aromatics between MOZART-4x and CB05_GE are BENZENE in MOZART-4x and PAH in CB05_GE (as shown in Table 1). The emissions of PAH are higher over Europe, East Asia, eastern U.S., and South Africa. The benzene emissions are about 1 order of magnitude higher than the emissions of PAH, and the rate constant of the oxidation of benzene by OH is temperature dependent whereas it is constant for oxidation of PAH by OH. In addition, OH levels are higher in MOZART-4x than those in CB05_GE. These differences could result in different ASOA between two simulations. Both MOZART-4x and CB05_GE predict higher SVSOA contributions over South Africa than other regions, which is mainly due to the higher POA emissions (e.g., biomass burning) over this region. Although the percentage contributions of different types of SOA predicted by
MOZART-4x and CB05_GE are similar over most regions, the absolute mass concentrations of different types of SOA are different. For example, TSOA predicted by MOZART-4x is about 0.02-2.0 mg m\(^{-2}\) higher than by CB05_GE over these regions. ASOA predicted by MOZART-4x is about 0.068-1.017 mg m\(^{-2}\) higher than predicted by CB05_GE over most regions except Europe (0.054 mg m\(^{-2}\) lower) and East Asia (0.062 mg m\(^{-2}\) lower). BSOA predicted by MOZART-4x is about 0.162-1.365 mg m\(^{-2}\) higher than predicted by CB05_GE over most regions except Australia (0.003 mg m\(^{-2}\) lower).

MOZART-4x includes SOA formation from benzene, which can predict higher ASOA formation. In addition, OH predicted by MOZART-4x is higher than CB05_GE (See Figure 8a), which can produce more condensable SOA gaseous precursors through oxidations of VOCs. The higher BVOCs emissions in MOZART-4x due to different mapping for MEGAN species can also contribute to the higher BSOA formation in MOZART-4x.

Both MOZART-4x and CB05_GE predict POA burdens of 0.36 Tg, which is about 0.1 Tg lower than those by Shrivastava et al. (2015), indicating that POA may be too volatile with the current implementation of VBS SOA in CESM/CAM5 and possible lower POA emissions used in this work. MOZART-4x predicts SOA burden of 1.82 Tg, which is slightly higher (by 0.05 Tg) than that predicted by Shrivastava et al. (2015). This can be attributed to different emissions used in CESM/CAM5 and Shrivastava et al. (2015), as well as differences in the model treatment for SOA formation in both work.
For example, nine volatility bins are used in this work to represent the aging and gas-particle partitioning of POA, instead of five volatility bins used in Shrivastava et al. (2015). In addition, compared to the reaction (3) in Shrivastava et al. (2015), the remaining mass is assumed to be lost to a species with a volatility higher than the volatility values in the VBS structure, instead of being oxidized to form CO/CO₂.

6. Conclusions

In this work, MOZART-4x and CB05_GE are coupled with CAM5-NCSU. MOZART-4x uses lumped species approach to represent organic chemistry whereas CB05_GE uses lumped structure approach. MOZART-4x and CB05_GE include different surrogates for SOA precursors, which can result in different SOA predictions. MOZART-4x includes HOₓ recycling associated with improved isoprene chemistry whereas CB05_GE contains simpler isoprene chemistry, which can result in different OH and isoprene predictions and thus, SOA predictions. CB05_GE includes additional oxidation of SO₂ by O₃ over the surface of dust particles to produce additional SO₄²⁻, which is not included in MOZART-4x. These differences can result in different secondary gas and aerosols predictions.

The comparisons between the two gas-phase mechanisms are conducted in terms of chemical and cloud/radiative predictions. Predictions of major gases and inorganic aerosols predicted by MOZART-4x and CB05_GE are overall similar. Significant
differences in some species (e.g., NOy, glyoxal, and SOA) predictions are mainly due to the different reaction pathways treated in the two mechanisms. Large biases exist for surface SO2, CO, NH3, PM2.5 and PM10 predictions against available observations, which is likely due to the uncertainties in the emissions or emission injection heights. Several studies indicate that the uncertainties in regional emissions (e.g., BC and SO2) can be expected to be as large as a factor of 2 or larger (Bond et al., 2007; Smith et al., 2011). Large discrepancies still remain for major species such as SO2, NOx, BC, and CO among different inventories (Granier et al., 2011). Both surface CO mixing ratios and column CO mass abundances are underpredicted, which is mainly due to underestimations in the CO emissions from biomass burning and possible uncertainties in the OH production. Surface SO2 mixing ratio is overpredicted whereas column SO2 abundance is underpredicted, indicating the uncertainties in the vertical mixing scheme or emission injection heights as reported in East Asia (Zhang et al., 2015a, b), as well as satellite retrievals. For example, Lee et al. (2009) found that there is an overall error in the annual SO2 retrievals of 45-80% over polluted regions, especially over eastern China. Uncertainties in online dust and sea-salt emissions can also result in inaccurate predictions in PM2.5 and PM10. Both MOZART-4x and CB05_GE overpredict surface O3 over CONUS, Europe, and East Asia, which is due in part to less O3 titration resulted from underpredictions of NOx, the dilution of NOx emissions resulted from the use of a coarse grid resolution, as well as uncertainties in the O3 dry deposition simulated in the
The concentration of OC over CONUS is well predicted by MOZART-4x, with an NMB of 2.1%, whereas it is moderately underpredicted by CB05_GE, with an NMB of -20.7%. Compared to the observations at the four sites in the U.S. from Lewandowski et al. (2013), SOA is well predicted by MOZART-4x, with an NMB of -1.9%, whereas it is moderately underpredicted by CB05_GE, with an NMB of -23.1%, indicating a better capability to predict SOA over these sites by MOZART-4x despite its tendency to overpredict SOA concentrations at sites with low SOA levels such as Bakersfield and Pasadena, CA. However, the concentrations of OC over Europe are largely underpredicted by both MOZART-4x and CB05_GE, with NMBs of -74.2% and -75.1%, respectively, indicating the uncertainties in the emissions, chemical reactions, as well as SOA formation treatment. The different AOD predictions between CB05_GE and MOZART-4x are mainly due to different predictions in SOA, \( \text{SO}_4^{2-} \), \( \text{NH}_4^+ \), \( \text{NO}_3^- \), and dust concentrations.

The cloud/radiative predictions from the two simulations are also similar, with slightly better domain average performance of CCN5, LWP, and LWCF in CB05_GE. But MOZART-4x predicts slightly better CCN profile over Beijing than CB05_GE compared to aircraft measurements. The different gas-phase mechanisms result in different predictions in aerosols and clouds, and therefore, a domain average difference of 0.5 W m\(^{-2}\) in simulated SWCF, which can be as large as 13.6 W m\(^{-2}\) over subtropical
In summary, MOZART-4x and CB05_GE differ in their approaches to represent VOCs and surrogates for SOA precursors. MOZART-4x includes a more detailed representation of isoprene chemistry compared to CB05_GE. Based on the above comparisons of simulations using both mechanisms and evaluation against available measurements in this study, MOZART-4x with the 1.5 D VBS SOA module in CESM-NCSU generally gives a better agreement with observations for surface concentrations of O$_3$ over Europe, HNO$_3$, HCHO, ISOP over CONUS, SOA, SO$_4^{2-}$, NO$_3^-$, and NH$_4^+$ over CONUS and Europe, and column mass abundances of HCHO, C$_2$H$_5$O$_2$, SO$_2$, and O$_3$, whereas CB05_GE generally gives a better agreement for surface concentrations of SO$_2$, NH$_3$, O$_3$ over CONUS and East Asia, HNO$_3$ over Europe, PM$_{2.5}$ and PM$_{10}$ over Europe, PM$_{10}$ over East Asia, vertical profiles of NO$_3$-, and column mass abundances of CO. Both simulations give predictions of cloud/radiative variables with slightly better domain average performance of CCN5, LWP, and LWCF in CB05_GE.

7. Code and Data Availability

The results in this paper are based on output from simulations performed with the NCAR Community Earth System Model (CESM) version 1.2.2 (https://www2.cesm.ucar.edu/models/current) with additional model development and modifications by the Air Quality Forecasting Laboratory, North Carolina State University, Raleigh, NC, U.S.A. The added codes have been provided to NCAR for potential future
release to NCAR for community use. Upon request, we can provide the inputs, the namelist file, a brief instruction, and sample output for a 1-day test case.

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References


R., Cubison, M. J., Dunlea, E., Huffman, J. A., Onaasch, T. B., Alfarra, M. R.,
Williams, P. I., Bower, K., Kondo, Y., Schneider, J., Drewnick, F., Borrmann, S.,
Weimer, S., Demerjian, K., Salcedo, D., Cottrell, L., Griffin, R., Takami, A.,
Miyoshi, T., Hatakeyama, S., Shimoto, A., Sun, J. Y., Zhang, Y. M., Dzepina, K.,
Kimmel, J. R., Sufer, D., Jayne, J. T., Herndon, S. C., Trimborn, A. M., Williams, L.
R.: Evolution of organic aerosols in the atmosphere, Science, 326, 1525-1529,

Karamchandani, P., Zhang, Y., Chen, S.-Y., and Balmori-Bronson, R.: Development of an
extended chemical mechanism for global-through-urban applications, Atmospheric

Kay, J. E., Hillman, B. R., Klein, S. A., Zhang, Y., Medeiros, B., Pincus, R., Gettelman,
A., Eaton, B., Boyle, J., Marchand, R., and Ackerman, T. P.: Exposing global cloud
biases in the Community Atmosphere Model (CAM) using satellite observations and
their corresponding instrument simulators, J. Climate, 25, 5190-5207,

Kim Y., Sartelet, K., and Seigneur C.: Comparison of two gas-phase chemical kinetic
mechanisms of ozone formation over Europe, J. Atmo. Chem., 62, 89-119,

gas-phase chemical mechanism, Atmos. Chem. Phys. 11, 583-598, doi:10.5194/acp-

Kim, Y., Couvidat, F., Sartelet, K., and Seigneur, C.: Comparison of Different Gas-Phase
Mechanisms and Aerosol Modules for Simulating Particulate Matter Formation, J. of
Air & Waste Management Association, 61, 1218-1226,

Boville, B. A., Harvey, L., Randall, C., Emmons, L., Lamarque, J.-F., Hess, P.,
Orlando, J., Tyndall, G., Tie, X. X., Randel, W., Pan, L., Gettelman, A., Granier, C.,
Diehl, T., Niemeier, U., and Simmons, A. J.: Sensitivity of chemical tracers to
meteorological parameters in the MOZART-3 chemical transport model, J. Geophys.

Knote, C., Tuccella, P., Curci, G., Emmons, L., Orlando, J. J., Madronich, S., Baró, R.,
Jiménez-Guerrero, P., Lueckeen, D., Hogrefe, C., Forkel, R., Werhahn, J., Hirtl, M.,
Pérez, J. L., San José, R., Giordano, L., Brunner, D., Khairunnisa, Y., and Zhang, Y.:


Lamarque, J. F., Shinedell, D. T., Josse, B., Young, P. J., Cionni, I., Eyring, V.,
Bergmann, D., Cameron-Smith, P., Collins, W. J., Doherty, R., Dalsoren, S.,
A., Nagashima, T., Naik, V., Plummer, D., Righi, M., Rumbold, S. T., Schulz, M.,
Skeie, R. B., Stevenson, D. S., Strode, S., Sudo, K., Szopa, S., Voulgarakis, A., and
Zeng, G.: The atmospheric chemistry and climate model intercomparison project:
overview and description of models, simulations and climate diagnostics, Geosci.

Lamarque, J.-F. and Solomon, S.: Impact of Changes in Climate and Halocarbons on
Recent Lower Stratosphere Ozone and Temperature Trends, J. Climate, 23, 2599-
2611, 2010.

Lee, C., Martin, R. V., Donkelaar, A. van, O’Byrne, G., Krotkov, N., Richter, A., Huey, L.
G., and Holloway, J. S.: Retrieval of vertical columns of sulfur dioxide from
SCIAMACHY and OMI: Air mass factor algorithm development, validation, and
error analysis, J. Geophys. Res., 114, D22303, doi:10.1029/2009JD012123,
2009.

Lewandowski, M., Piletic, I. R., Kleindienst, T. E., Offenberg, J. H., Beaver, M. R., Jaoui,
M., Docherty, K. S., and Edney, E. O.: Secondary organic aerosol characterization at
field sites across the United States during the spring-summer period, Int. J. Environ.

Gettleman, A., Morrison, H., Vitt, F., Conley, A., Park, S., Neale, R., Hannay, C.,
S., Flanner, M. G., and Mitchell, D.L.: Toward a minimal representation of aerosols
in climate models: description and evaluation in the Community Atmosphere Model

partI: performance evaluation and seasonal variation, Atmos. Environ., 44 (2010),

SAPRC99 vs. CB4 chemical mechanism on model predictions: Ozone and gas-phase


tropospheric hydroxyl radical and methane lifetime from the Atmospheric Chemistry
and Climate Model Intercomparison Project (ACCMIP), Atmos. Chem. Phys., 13,

stratosphere-troposphere analyses of regional transport 2008 (START08)

Price, C. and Rind, D.: A simple lightning parameterization for calculating global
lightning distributions, J. Geophys. Res., 97, 9919-9933, doi:10.1029/92JD00719,

Price, C., Penner, J., and Prather, M.: NOx from lightning 1, Global distribution based on

Reutter, P., Su, H., Trentmann, J., Simmel, M., Rose, D., Gunthe, S. S., Wernli, H.,
Andreae, M. O., and Pöschl, U.: Aerosol- and updraft-limited regimes of cloud
droplet formation: influence of particle number, size and hygroscopicity on the
activation of cloud condensation nuclei (CCN), Atmos. Chem. Phys., 9, 7067-7080,

Grieshop, A. P., Lane, T. E., Pierce, J. R., and Pandis, S. N.: Rethinking organic
aerosols: Semivolatile emissions and photochemical aging, Science, 315, 1259-1262,

Ryerson, T. B., Andrews, A. E., Angevine, W. M., Bates, T. S., Brock, C. A., Cairns, B.,
Cohen, R. C., Cooper, O. R., de Gouw, J. A., Fehsenfeld, F. C., Ferrare, R. A.,
Fischer, M. L., Flagan, R. C., Goldstein, A. H., Hair, J. W., Hardesty, R. M.,
Hostetler, C. A., Jimenez, J. L., Langford, A. O., McCauley, E., McKeen, S. A.,
Prather, K., Quinn, P. K., Seinfeld, J. H., Senff, C. J., Sorooshian, A., Stutz, J.,
California Research at the Nexus of Air Quality and Climate Change (CalNex) field

updated carbon bond mechanism on predictions from the Community Multiscale Air
Quality Model, J. Appl. Meteorol. Climatol., 47, 3-14,


Vehkamaki, H., Kulmala, M., Napari, I., Lehtinen, K. E. J., Timmreck, C., Noppel, M.,
and Laaksonen, A.: an improved parameterization for sulfuric acid-water nucleation
rates for tropospheric and stratospheric conditions, Journal of Geophysical Research-

Wang, M. and Penner, J. E.: Aerosol indirect forcing in a global model with particle

Wang, K., Yahya, K., Zhang, Y., Wu, S.-Y., and Grell G.: Implementation and initial
application of a new chemistry-aerosol option in WRF/Chem for simulation of
secondary organic aerosols and aerosol indirect effects, Atmos. Environ, 115,

Ma, P.-L., and Vinoj, V.: Sensitivity of remote aerosol distributions to representation
of cloud–aerosol interactions in a global climate model, Geosci. Model Dev., 6, 765-

Washenfelder, R., Young, C., Brown, S., Angevine, W., Atlas, E., Blake, D., Bon, D.,
Cubison, M., De Gouw, J., Dusanter, S., Flynn, J., Gilman, J. B., Graus, M., Griffith,
S., Grossberg, N., Hayes, P. L., Jimenez, J., Kuster, W., Lefer, B. L., Pollack, I.,
contribution to organic aerosol for Los Angeles, California, during CalNex 2010, J.

Young, P. J., Archibald, A. T., Bowman, K. W., Lamarque, J.-F., Naik, V., Stevenson, D.
S., Tilmes, S., Voulgarakis, A., Wild, O., Bergmann, D., Cameron-Smith, P., Cionni,
I., Collins, W. J., Dalsoren, S. B., Doherty, R. M., Eyring, V., Faluvegi, G., Horowitz,
L. W., Josse, B., Lee, Y. H., MacKenzie, I. A., Nagashima, T., Plummer, D. A., Righi,
M., Rumbold, S. T., Skeie, R. B., Shindell, D. T., Strode, S. A., Sudo, K., Szopa, S.,
Yarwood, G., Kemball-Cook, S., Johnson, J, Wilson, G, Dornblaser, B, and Estes, M:
Evaluating NOx Emission Inventories for Air Quality Modeling Using Satellite,
Model and SEARCH NO2 Data, 11th Annual CMAS Conference, Chapel Hill, NC,
October 16, 2012.

Yarwood, G., Rao, S., Yocke, M., and Whitten, G. Z.: Updates to the carbon bond
mechanism: CB05, Report to the U.S. Environmental Protection Agency, RT-04-


Table 1. Gas-phase organic aerosol precursors in the two mechanisms

<table>
<thead>
<tr>
<th>Precursors</th>
<th>MOZART-4x(^1)</th>
<th>CB05_GE(^2)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Aromatics</td>
<td>TOLUENE, BENZENE, XYLENES, CRESOL</td>
<td>TOL, XYL, CRES, PAH</td>
</tr>
<tr>
<td>Alkanes</td>
<td>BIGALK</td>
<td>ALKH</td>
</tr>
<tr>
<td>Anthropogenic alkenes</td>
<td>C3H6, BIGENE</td>
<td>OLE, IOLE</td>
</tr>
<tr>
<td>Biogenic alkenes</td>
<td>APIN, BPIN, LIMON, MYRC, BCARY, ISOP</td>
<td>APIN, BPIN, LIM, OCI, HUM, TER, ISOP</td>
</tr>
</tbody>
</table>

\(^1\) BIGALK: lumped alkanes C > 3; C\(_3\)H\(_6\): propene; BIGENE: lumped alkanes C > 3; APIN: α-pinene + others; BPIN: β-pinene+others; LIMON: limonene + others; MYRC: myrcene + others; BCARY: beta-caryophyllene + other sesquiterpenes; ISOP: isoprene.

\(^2\) TOL: toluene and other monoalkyl aromatics; XYL: xylene and other polyalkyl aromatics; CRES: cresol and higher molecular weight phenols; PAH: polycyclic aromatic hydrocarbons; ALKH: long-chain alkanes, C >6; OLE: terminal olefin carbon bond (R-C=C); IOLE: internal olefin carbon bond (R-C=C-R); APIN: α-pinene; BPIN: β-pinene; LIM: limonene; OCI: ocimene; HUM: humulene; TER: terpinene; ISOP: isoprene.
### Table 2. Datasets for model evaluation

<table>
<thead>
<tr>
<th>Species/Variables</th>
<th>Dataset (Number of sites)</th>
</tr>
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<tbody>
<tr>
<td>Cloud fraction (CF)</td>
<td>MODIS</td>
</tr>
<tr>
<td>Cloud optical thickness (COT)</td>
<td></td>
</tr>
<tr>
<td>Cloud liquid water path (LWP)</td>
<td></td>
</tr>
<tr>
<td>Precipitating water vapor (PWV)</td>
<td></td>
</tr>
<tr>
<td>Aerosol optical depth (AOD)</td>
<td></td>
</tr>
<tr>
<td>Column cloud condensation nuclei (ocean) at S = 0.5% (CCN5)</td>
<td></td>
</tr>
<tr>
<td>Cloud droplet number concentration (CDNC), LWP</td>
<td>Bennartz (2007)</td>
</tr>
<tr>
<td>Shortwave cloud radiative forcing (SWCF)</td>
<td>CERES-EBAF</td>
</tr>
<tr>
<td>Longwave cloud radiative forcing (LWCF)</td>
<td></td>
</tr>
<tr>
<td>Downwelling longwave radiation at surface (FLDS)</td>
<td></td>
</tr>
<tr>
<td>Downwelling shortwave radiation at surface (FSDS)</td>
<td></td>
</tr>
<tr>
<td>Outgoing longwave radiation (OLR)</td>
<td>NOAA/CDC</td>
</tr>
<tr>
<td>Carbon monoxide (CO)</td>
<td>East Asia: NIESJ (2133), TAQMN (70), KMOE (258)</td>
</tr>
<tr>
<td>Ozone (O$_3$)</td>
<td>CONUS: CASTNET (141), Europe: Airbase (3846), BDQA (490), EMEP (317), East Asia: TAQMN (70), KMOE (258)</td>
</tr>
<tr>
<td>Sulfur dioxide (SO$_2$)</td>
<td>CONUS: CASTNET (141), Europe: Airbase (3846), BDQA (490), EMEP (317), East Asia: MEPC (84), NIESJ (2133), KMOE (258), TAQMN (70)</td>
</tr>
<tr>
<td>Nitric acid (HNO$_3$)</td>
<td>CONUS: CASTNET (141), Europe: EMEP (317)</td>
</tr>
<tr>
<td>Ammonia (NH$_3$)</td>
<td>Europe: Airbase (3846), EMEP (317)</td>
</tr>
<tr>
<td>Nitrogen dioxide (NO$_2$)</td>
<td>CONUS: ARS (25877), Europe: Airbase (3846), BDQA (490), EMEP (317), East Asia: NIESJ, TAQMN, KMOE</td>
</tr>
<tr>
<td>Sulfate (SO$_4^{2-}$), Ammonium (NH$_4^+$), Nitrate (NO$_3^-$)</td>
<td>CONUS: CASTNET (141), IMPROVE (199), STN (18129), Europe: Airbase (3846), EMEP (317)</td>
</tr>
<tr>
<td>Chloride (Cl$^-$)</td>
<td>CONUS: IMPROVE (199), Europe: Airbase (3846), EMEP (317)</td>
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<tr>
<td>Organic carbon (OC)</td>
<td>CONUS: IMPROVE (199), Europe: EMEP (317)</td>
</tr>
<tr>
<td>Black carbon (BC), Total carbon (TC)</td>
<td>CONUS: IMPROVE (199), STN (18129)</td>
</tr>
<tr>
<td>Formaldehyde (HCHO), Isoprene (ISOP), and Toluene (TOL)</td>
<td>CONUS: AQS (25877)</td>
</tr>
<tr>
<td>Hydrocarbon-like organic aerosol (HOA), Oxygenated organic aerosol (OOA), Total organic aerosol (TOA)</td>
<td>Northern Hemisphere: Zhang et al. (2007) and Jimenez et al. (2009) (Z07 &amp; J09) (33)</td>
</tr>
<tr>
<td>Secondary organic aerosol (SOA)</td>
<td>CONUS: Ohio (2) and California (2) (Lewandowski et al., 2013)</td>
</tr>
<tr>
<td>Particulate matter with diameter less than and equal to 2.5 μm (PM$_{2.5}$)</td>
<td>CONUS: IMPROVE (199), STN (18129), Europe: BDQA (490), EMEP (317)</td>
</tr>
<tr>
<td>Particulate matter with diameter less than and equal to 10 μm (PM$_{10}$)</td>
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</tr>
<tr>
<td>Column CO</td>
<td>Guide: MOPITT</td>
</tr>
<tr>
<td>Column NO$_2$, Column SO$_2$, Column HCHO, Column glyoxal (C$_2$H$_4$O$_2$)</td>
<td>Guide: SCIAMACHY</td>
</tr>
<tr>
<td>Tropospheric ozone residual (TOR)</td>
<td>Guide: OMI/MLS</td>
</tr>
<tr>
<td>O$_3$, CO, NO$_x$, and NO$_y$ profiles</td>
<td>ARCPAC (Mar.-Apr., 2008), ARCTAS (Apr.-Jun., 2008), START08 (Apr.-Jun., 2008), and CalNex (May-Jun., 2010)</td>
</tr>
<tr>
<td>CCN_China</td>
<td>Beijing: Zhang et al. (2011) (Jul.-Sep., 2008)</td>
</tr>
</tbody>
</table>

NOAA/CDC: National Oceanic and Atmospheric Administration Climate Diagnostics Center; MODIS: Moderate Resolution Imaging Spectroradiometer; CERES-EBAF: Clouds and Earth’s Radiant Energy System-Energy Balanced and Filled product; MOPITT: the Measurements Of Pollution In The Troposphere; OMI/MLS: the Aura Ozone Monitoring Instrument in combination with Aura Microwave Limb Sounder; SCIAMACHY: the SCanning Imaging Absorption spectroMeter for Atmospheric CHartographY; CASTNET: Clean Air Status and Trends Network; IMPROVE: Interagency Monitoring of Protected Visual Environments; STN: Speciation Trends Network; AQs: Air Quality System; EMEP: European Monitoring and Evaluation Program; BDQA: Base de Données sur la Qualité de l’Air; AirBase: European air quality database; MEPC: Ministry of Environmental Protection of China; TAQMN: Taiwan Air Quality Monitoring Network; NIESJ: National Institute for Environmental Studies of Japan; KMOE: Korean Ministry of Environment; ARCPAC: Aerosol, Radiation, and Cloud Processes affecting Arctic Climate in 2008 (Brock et al., 2011); ARCTAS: Arctic Research of the Composition of the Troposphere from Aircraft and Satellites (Jacob et al., 2010); START08: Stratosphere-Troposphere Analyses of Regional Transport in 2008 (Pan et al., 2010); CalNex: California Nexus 2010 (Ryerson et al., 2013).
<table>
<thead>
<tr>
<th>Species</th>
<th>Domain</th>
<th>Obs</th>
<th>MOZART-4x</th>
<th>CB05_GE</th>
</tr>
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<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Sim</td>
<td>NMB (%)</td>
</tr>
<tr>
<td>CO (ppb)</td>
<td>East Asia</td>
<td>438.7</td>
<td>150.9</td>
<td>-65.6</td>
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<tr>
<td></td>
<td>Europe</td>
<td>4.7</td>
<td>9.5</td>
<td>100.9</td>
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<td>Toluene (ppb)</td>
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<td>2.9</td>
<td>4.3</td>
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<td>112.4</td>
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<td></td>
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<td>34.7</td>
<td>44.7</td>
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<td>78.6</td>
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<td></td>
<td>East Asia</td>
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<td>48.3</td>
<td>62.4</td>
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<td>ISOP (ppb)</td>
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<td>0.2</td>
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<td>0.2</td>
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<td>Col. CO</td>
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<td>1.2×10¹⁸</td>
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<td>(molec.cm⁻²)</td>
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<td>5.5×10¹⁴</td>
<td>8.5×10¹⁴</td>
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<td>Col. NO₂</td>
<td>Globe</td>
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<td>(molec.cm⁻²)</td>
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<td>62.1</td>
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<tr>
<td>(μg m⁻³)</td>
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<td>-6.0</td>
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<td>1.2</td>
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<td>Cl⁻ (μg m⁻³)</td>
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<td></td>
<td>Europe</td>
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<td>273.4</td>
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<td>BC (μg m⁻³)</td>
<td>CONUS</td>
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<td>0.2</td>
<td>-29.3</td>
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<td>OC (μg m⁻³)</td>
<td>CONUS</td>
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<td>1.0</td>
<td>2.1</td>
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<td></td>
<td>Europe</td>
<td>2.9</td>
<td>0.7</td>
<td>-74.2</td>
</tr>
<tr>
<td>TC (μg m⁻³)</td>
<td>CONUS</td>
<td>1.8</td>
<td>1.3</td>
<td>-29.6</td>
</tr>
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<td>SOA⁴</td>
<td>CONUS</td>
<td>1.8</td>
<td>1.8</td>
<td>-1.9</td>
</tr>
<tr>
<td>HOA⁴</td>
<td>N.H.⁵</td>
<td>2.1</td>
<td>0.5</td>
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<td>OOA⁴</td>
<td>N.H.⁵</td>
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<td>2.1</td>
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<td>TOA⁴</td>
<td>N.H.⁵</td>
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<td>2.5</td>
<td>-67.8</td>
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<tr>
<td>PM₂·⁵ (μg m⁻³)</td>
<td>CONUS</td>
<td>7.4</td>
<td>10.3</td>
<td>38.9</td>
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<tr>
<td></td>
<td>Europe</td>
<td>14.4</td>
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<td>-20.4</td>
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<tr>
<td>PM₁₀ (μg m⁻³)</td>
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<td>20.6</td>
<td>12.6</td>
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<tr>
<td></td>
<td>Europe</td>
<td>22.1</td>
<td>18.8</td>
<td>-14.9</td>
</tr>
<tr>
<td></td>
<td>East Asia</td>
<td>88.0</td>
<td>59.0</td>
<td>-32.9</td>
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</tbody>
</table>

¹ The unit is μg m⁻³ for CONUS and ppb for East Asia. ² The unit is μg m⁻³ for Europe and ppb for CONUS and East Asia. ³ The unit is ppb for CONUS and East Asia, and μg m⁻³ for Europe. ⁴ SOA: secondary organic aerosol; HOA: hydrocarbon-like organic aerosol; OOA: oxygenated organic aerosol; TOA: total organic aerosol; ⁵ N.H.: northern hemisphere; ⁶ MB: mean bias; NMB: normalized mean bias (%); NME: normalized mean error (%); RMSE: root mean squared error; Corr.: correlation coefficient.
Table 4. Performance statistics of cloud/radiative variables

<table>
<thead>
<tr>
<th>Variables</th>
<th>Networks</th>
<th>Obs</th>
<th>MOZART-4x</th>
<th>CB05_GE</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>Sim</td>
<td>NMB ( % )^2</td>
</tr>
<tr>
<td>OLR (W m^-2)</td>
<td>NOAA/ CDC</td>
<td>217.0</td>
<td>224.8</td>
<td>3.6</td>
</tr>
<tr>
<td>FLDS (W m^-2)</td>
<td>CERES</td>
<td>306.7</td>
<td>307.3</td>
<td>0.2</td>
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<tr>
<td>FSDS (W m^-2)</td>
<td>CERES</td>
<td>163.4</td>
<td>150.9</td>
<td>-7.6</td>
</tr>
<tr>
<td>SWCF (W m^-2)</td>
<td>CERES</td>
<td>-40.7</td>
<td>-51.5</td>
<td>26.4</td>
</tr>
<tr>
<td>LWCF (W m^-2)</td>
<td>CERES</td>
<td>22.4</td>
<td>17.6</td>
<td>-21.6</td>
</tr>
<tr>
<td>CCN5 (# cm^-3)</td>
<td>MODIS</td>
<td>2.2x10^8</td>
<td>1.5x10^8</td>
<td>-32.1</td>
</tr>
<tr>
<td>CF (%)</td>
<td>MODIS</td>
<td>67.3</td>
<td>71.5</td>
<td>6.3</td>
</tr>
<tr>
<td>COT</td>
<td>MODIS</td>
<td>16.5</td>
<td>12.2</td>
<td>-26.0</td>
</tr>
<tr>
<td>AOD</td>
<td>MODIS</td>
<td>0.15</td>
<td>0.11</td>
<td>-23.9</td>
</tr>
<tr>
<td>PWV (cm)</td>
<td>MODIS</td>
<td>1.9</td>
<td>2.0</td>
<td>5.6</td>
</tr>
<tr>
<td>CDNC (# cm^-3)</td>
<td>Bennartz (2007)</td>
<td>105.8</td>
<td>126.6</td>
<td>19.7</td>
</tr>
<tr>
<td>LWP (g m^-2)</td>
<td>MODIS</td>
<td>142.0</td>
<td>65.2</td>
<td>-54.1</td>
</tr>
<tr>
<td></td>
<td>Bennartz (2007)</td>
<td>84.6</td>
<td>87.0</td>
<td>2.8</td>
</tr>
</tbody>
</table>

1 OLR: outgoing long wave radiation; FLDS: downwelling longwave radiation at the surface; FSDS: downwelling shortwave radiation at the surface; SWCF: shortwave cloud radiative forcing; LWCF: longwave cloud radiative forcing; CCN5: column CCN (ocean) at supersaturation of 0.5%; CF: cloud fraction; COT: cloud optical thickness; AOD: aerosol optical depth; PWV: precipitable water vapor; CDNC: cloud droplet number concentration; LWP: liquid water path.

2 NMB: normalized mean bias (%); NME: normalized mean error (%); RMSE: root mean squared error; Corr.: correlation coefficient.
### Table 5. Tropospheric Ozone Budget

<table>
<thead>
<tr>
<th>Ozone</th>
<th>MOZART-4x</th>
<th>CB05_GE</th>
<th>Lamarque et al. (2012)</th>
<th>Young et al. (2013)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Burden (Tg)</td>
<td>325</td>
<td>333</td>
<td>328</td>
<td>337 ± 23</td>
</tr>
<tr>
<td>Dry Deposition (Tg yr⁻¹)</td>
<td>679</td>
<td>705</td>
<td>705</td>
<td>1003 ± 200</td>
</tr>
<tr>
<td>a Chemical Production</td>
<td>4974</td>
<td>5743</td>
<td>4897</td>
<td>5110 ± 606</td>
</tr>
<tr>
<td>(Tg yr⁻¹)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>b Chemical Loss</td>
<td>4259</td>
<td>5194</td>
<td>4604</td>
<td>4668 ± 727</td>
</tr>
<tr>
<td>(Tg yr⁻¹)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Lifetime (days)</td>
<td>24</td>
<td>21</td>
<td>26</td>
<td>22.3 ± 2.0</td>
</tr>
</tbody>
</table>

a Chemical production is mainly contributed by reactions of NO with peroxy radicals.

b Chemical loss is mainly contributed by the oxygen radical in the O(¹D) + water (H₂O) reaction and by the reactions of ozone with the hydroperoxyl radical (HO₂), OH, and alkenes.
Figure captions

Figure 1. Scatter plots of O₃, PM, organic carbon (OC), secondary organic aerosol (SOA), hydrocarbon-like organic aerosol (HOA), oxygenated organic aerosol (OOA), total organic aerosol (TOA) over various sites during 2008-2010.

Figure 2. Comparisons of simulated and observed SOA concentrations at the four field study sites during 2009-2010. The observations are based on Lewandowski et al. (2013).

Figure 3. Zonal-mean profiles of HCHO, glyoxal, CO, NO₂, and TOR from CB05_GE and MOZART-4x simulations for June, July, and August during 2008-2010.

Figure 4. Simulated vertical profiles of O₃, CO, NOₓ, and NO₃, against aircraft measurements. The black solid line represents observations from aircraft measurements (Pan et al., 2010; Brock et al., 2011; Ryerson et al., 2011; Jacob et al., 2010). The red solid and blue solid lines represent model output from MOZART-4x and CB05_GE, respectively.

Figure 5. Simulated vertical profiles of CCN against aircraft measurements. The black solid line represents observations from aircraft measurements of Zhang et al. (2011). The red solid and blue solid lines represent model output from MOZART-4x and CB05_GE, respectively.

Figure 6. Taylor diagram of comparison of cloud and radiative predictions between MOZART-4x and CB05_GE.

Figure 7. Comparison of satellite observations with predictions of AOD, CCN5, CDNC, COT, and SWCF by MOZART-4x and CB05_GE.

Figure 8a. Absolute differences averaged during 2008-2010 in tropospheric column concentrations of major gaseous species between MOZART-4x and CB05_GE.

Figure 8b. Absolute differences averaged during 2008-2010 in tropospheric column concentrations of major aerosol species between MOZART-4x and CB05_GE.

Figure 9. Column abundances (mg m⁻²) averaged during 2008-2010 of secondary organic aerosols (SOA) from anthropogenic sources (ASOA), biogenic sources (BSOA), and glyoxal (GLSOA), and semi-volatile organic aerosol (SVSOA) over Australia, Europe, North America, South Africa, South America, and East Asia.
Figure 1. Scatter plots of O₃, PM, organic carbon (OC), secondary organic aerosol (SOA), hydrocarbon-like organic aerosol (HOA), oxygenated organic aerosol (OOA), total organic aerosol (TOA) from various sites during 2008-2010. The X (observations) and Y (simulations) axes are in log scale. Red dots represent MOZART-4x and blue dots represent CB05_GE. R is the correlation coefficient between simulated results and observational data. Z07: Zhang et al. (2007); J09: Jimenez et al. (2009); L13: Lewondowski et al. (2013).
Figure 1. Continued.
Figure 2. Comparisons of simulated and observed SOA concentrations at the four field study sites during 2009-2010. The observations are based on Lewandowski et al. (2013).
Figure 3. Zonal-mean profiles of HCHO, glyoxal, CO, NO$_2$, and TOR from CB05 GE and MOZART-4x simulations for June, July, and August during 2008-2010.
Figure 4. Simulated vertical profiles of O$_3$, CO, NO$_x$, NO$_y$ (including aerosol nitrate), OH and H$_2$O$_2$, against aircraft measurements. The black solid line represents observations from aircraft measurements (Pan et al., 2010; Brock et al., 2011; Ryerson et al., 2011; Jacob et al., 2010; Zhang et al., 2011). The red solid and blue solid lines represent model output from MOZART-4x and CB05 GE, respectively.
Figure 4. Continued.
Figure 5. Simulated vertical profiles of CCN against aircraft measurements. The black solid line represents observations from aircraft measurements of Zhang et al. (2011). The red solid and blue solid lines represent model output from MOZART-4x and CB05_GE, respectively.
Figure 6. Taylor diagram of comparison of cloud and radiative predictions between MOZART-4x and CB05_GE. The results are based on 3-year average. This diagram represents the similarity between MOZART-4x and CB05_GE. X-axis represents the ratio of variances between observations and simulations (proportional to the reference point identified as “REF”), and Y-axis represents the normalized standard deviation between the two patterns (proportional to the radial distance from the origin). Two variables, COT and LWP, are located outside the diagram because the ratios of variance between simulated results and observations (the values of 1.81 from MOZART-4x and 1.79 from CB05_GE in the top) are larger than 1.75 for LWP and the correlation coefficients (the values of -0.32 from MOZART-4x and -0.31 from CB05_GE in the bottom) for COT are negative.
Figure 7. Comparison of satellite observations with predictions of AOD, CCN5, CDNC, COT, and SWCF by MOZART-4x and CB05_GE.
Figure 7. continued.
Figure 8a. Absolute differences averaged during 2008-2010 in tropospheric column concentrations of major gaseous species between MOZART-4x and CB05_GE.
Figure 8b. Absolute differences averaged during 2008-2010 in tropospheric column concentrations of major aerosol species between MOZART-4x and CB05_GE.
<table>
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![Figure 9](image13) Column abundances (mg m$^{-2}$) averaged during 2008-2010 of secondary organic aerosols (SOA) from anthropogenic sources (ASOA), biogenic sources (BSOA), and glyoxal (GLSOA), and semi-volatile organic aerosol (SVSOA) over Australia, Europe, North America, South Africa, South America, and East Asia.