

ABSTRACT

Title of Dissertation: EXAMINATION OF TROPOSPHERIC
OZONE AND ITS PRECURSORS WITHIN
AN AIR QUALITY MODEL AND
IMPLICATIONS FOR AIR QUALITY AND
CLIMATE

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Elevated levels of tropospheric ozone (O_3) caused by emissions of NO_x and VOCs negatively impact human health, crops, and ecosystems. Even if precursor emissions are reduced below current levels, predicted higher temperatures due to increased greenhouse gas emissions could impede resulting air quality benefits. Air quality models simulate the complex relationships that form O_3 and are used to guide policy decisions directed at improving O_3 . The body of this work encompasses three projects related to improvements in the representation of O_3 and precursors in air quality models. First, I examine the role of O_3 and its precursors in air quality and climate change by evaluating ozone production efficiency (OPE) and O_3 precursors within models. I modified a chemical mechanism and the emissions of NO_x to accurately represent NO_x , the reactivity of NO_x with peroxy radicals, HCHO, isoprene, as well as organic and inorganic NO_y reservoir species. Implementation of these modifications increased confidence in model simulations. Results indicate accepted inventories overestimated NO_x emissions but underestimate total VOC reactivity and OPE.

Second, I examined the dependence of surface O_3 on temperature (climate penalty factor (CPF)) throughout a period of 11 years within an air quality model and measurements. Future increases in temperature could offset benefits from future reductions in the emission of O_3 precursors. Determining and understanding the CPF is critical to formulating effective strategies to reduce future exceedances. I have demonstrated that the model can reproduce O_3 sensitivity to temperature reasonably well. By controlling emissions specifically of NO_x mankind has reduced its vulnerability.

Third, I compare satellite-observed and modeled ammonia (NH_3) under varying chemical environments over East Asia. Regulation of O_3 precursor concentrations in the atmosphere has an indirect effect on NH_3 concentrations. Air quality policy to reduce NO_x and through that also nitric acid (HNO_3) in the atmosphere can result in an increase in the concentration of NH_3 because of its neutralizing ability. Therefore, a less acidic atmosphere sequesters less NH_3 . This preliminary work exposes different areas that need to be addressed to gain greater insight into NH_3 emissions and chemistry.

EXAMINATION OF TROPOSPHERIC OZONE AND ITS PRECURSORS
WITHIN AN AIR QUALITY MODEL AND IMPLICATIONS FOR AIR
QUALITY AND CLIMATE

by

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Dedication

I dedicate this work to my mother and father; scientia est potentia.

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List of Abbreviations

ACM2	Asymmetric Convective Model 2
AERO5	Aerosol Module version 5
AERO6	Aerosol Module version 6
AIRS	Atmospheric Infrared Sounder
AK	Averaging Kernel
AQ	Air Quality
AQM	Air Quality Model
AQS	Air Quality System
ASCII	American Standard Code for Information Interchange
BC	Black Carbon
BCON	Boundary Condition
BEIS	Biogenic Emissions Inventory System
BELD	Biogenic Emissions Landuse Database
BSE	Baseline
BVOC	Biogenic Volatile Organic Compound
BW	Baltimore-Washington
BWI	Baltimore Washington International Thurgood Marshall Airport
C	Carbon
C ₂ H ₅	Ethyl
C ₂ H ₅ O ₂ ,	Ethylendioxy
C ₅ H ₈	Isoprene
CAA	Clean Air Act
CAAA	Clean Air Act Amendments
CAMx	Comprehensive Air Quality Model with Extensions
CASTNET	Clean Air Status and Trends Network
CB	Carbon Bond
CB05	Carbon Bond Mechanism version 5
CB05CL,	Carbon Bond Mechanism version 5 Chlorine Module
CB05TU	Carbon Bond Mechanism version 5 Toluene Update
CB05TUMP	Carbon Bond Mechanism version 5 Toluene Update
CB6	Carbon Bond Mechanism version 6
CCD	Charged-Coupled Device
CCTM	CMAQ Chemistry-Transport Model
netCDF	Network Common Data Format
CEMS	Continuous Emission Monitoring System
CH ₄	Methane
CL	Chlorine
CM	Chemical Mechanism
CMAQ	Community Multi-Scale Air-Quality
CMAS	Community Modeling and Analysis System
CML	Convective Mixed Layer
CO	Carbon Monoxide
CO ₂	Carbon Dioxide

CONUS	Continuous United States
CPF	Climate Penalty Factor
CREATE	Comprehensive Regional emission inventory for Atmospheric Transport Experiment
CREATE _{SO2}	Comprehensive Regional emission inventory for Atmospheric Transport Experiment with SO ₂ adjusted
CREATE _{SO2&NOx}	Comprehensive Regional emission inventory for Atmospheric Transport Experiment with SO ₂ and NO _x adjusted
CTM	Chemical Transport Model
DISCOVER-AQ	Deriving Information on Surface Conditions from Column and Vertically Resolved Observations Relevant to Air Quality
EGU	Electrical Generating Unit
EOS	Earth Observing System
EP	Edwards Plateau
EPA	Environmental Protection Agency
ERTAC	Eastern Regional Technical Advisory Committee
GEOS	Goddard Earth Observing System
GFS	Global Forecast System
GSFC	Goddard Space Flight Center
H ₂ O	Water
H ₂ O ₂ ,	Hydrogen Peroxide
H ₂ SO ₄	Sulfuric Acid
HCHO	Formaldehyde
HNO ₃	Nitric Acid
HNO ₄	Peroxynitric acid
HO	Hydroxyl
HO ₂	Hydrogen Peroxide
HONO	Nitrous acid
HPLD	Hydroperoxyenals
IASI	Infrared Atmospheric Sounding Interferometer
ICON	Initial Conditions
INTEX	Intercontinental Chemical Transport Experiment
IPCC	Intergovernmental Panel on Climate Change
ISD	Integrated Surface Data
ITM	International Technical Meeting
IUPAC	International Union of Pure and Applied Chemistry
J _{NO2}	Photolysis Rate of NO ₂
J _{NTR}	Photolysis Rate of NTR
JPL	Jet Propulsion Laboratory
JPROC	Clear-sky photolysis rate calculator
LIF	Laser Induced Fluorescence
LM	Lumped Molecule
LS	Lumped Structure
LW	Long Wave
M3DRY	Dry Deposition Module
MCIP	Meteorology-Chemistry Interface Processor

MEGAN	Model of Emissions of Gases and Aerosols from Nature
MGN	MEGAN
MISC	Model Inter-Comparison
MIX	MISC-ASIA emissions inventory for the year 2010
MODIS	Moderate Resolution Imaging Spectroradiometer
MOVES	MOtor Vehicle Emission Simulator
MOZART	Model of Ozone and Related Tracers
MPAN	Methacryloylperoxynitrate
MUR	Multi-scale Ultra-high Resolution
MW	Midwest
N ₂	Nitrogen
N ₂ O	Nitrous Oxide
N ₂ O ₅ ,	Nitrogen pentoxide
NA	Not Available
NAAQS	National Ambient Air Quality Standards
NAM	North American Model
NASA	National Aeronautics and Space Administration
NCAR	National Center for Atmospheric Research
NCDC	National Climatic Data Center
NCEP	National Centers for Environmental Protection
NE	Northeast
NEI	National Emissions Inventory
NGP	Northern Great Plains
NH ₃	Ammonia
NH ₄	Ammonium
NH ₄ NO ₃	Ammonium nitrate
NLCD	National Land Cover Database
NLDN	National Lightning and Detection Network
NMVOC	Non-Methane Volatile Organic Compound
NO	Nitric Oxide
NO ₂	Nitric Dioxide
NO ₃	Nitrate
NTR	Alkyl Nitrates
NW	Northwest
NWP	National Weather Prediction
O ₂	Oxygen
O ₃	Ozone
OC	Organic Carbon
OH	Hydroxyl Radical
OLE	Olefine
OMI	Ozone Monitoring Instrument
OPAN	Organic Peroxyacyl Nitrates
OPE	Ozone Production Efficiency
OZ	Ozarks
PAMS	Photochemical Assessment Monitoring Station
PAN	Peroxyacetyl Nitrate

PAR	Paraffin
PBL	Planetary Boundary Layer
PD	Probability Distribution
PM ₁₀	Particulate Matter $\leq 10\mu\text{m}$
PM _{2.5}	Particulate Matter $\leq 2.5\mu\text{m}$
PMBE	Percent Mean Bias Error
PN	Peroxy Nitrate
PPN	Peroxy Propionyl Nitrate
RACM2	Regional Atmospheric Chemistry Mechanism version 2
RHS	Right Hand Side
RMS	Root Mean Square Deviations
RMSE	Root Mean Square Error
RO ₂	Peroxy Radical
RRKM	Rice–Ramsperger–Kassel–Marcus
RSS	Root Sum of Squares
SAO	Smithsonian Astronomical Observatory
SAPRC	Statewide Air Pollution Research Center
SCI	Science
SCR	Selective Catalytic Reduction
SE	Southeast
SEAC ⁴ RS	Studies of Emissions, Atmospheric Composition, Clouds and Climate Coupling by Regional Surveys
SMOKE	Sparse Matrix Operator Kernel Emissions
SO ₂	Sulfur Dioxide
SOA	Secondary Organic Aerosol
SPC	South Central Plains
SST	Sea Surface Temperature
SW	Southwest
TD	Thermal Dissociation
TES	Tropospheric Emission Spectrometer
TSD	Technical Support Document
US	United States
USA	United States of America
UV	Ultraviolet
VIS	Visible
VOC	Volatile Organic Compounds
WRF	Weather, Research and Forecasting
WSM-6	WRF Single-Moment 6-class microphysics scheme

Chapter 1: Introduction

Air pollution due to high concentrations of tropospheric ozone (O_3) in the Eastern United States is a recurring problem during summer months. Between May and September in the Northern Hemisphere, high-pressure stagnation episodes are common and can persist for days causing tropospheric O_3 production to flourish and concentrations to build up over time [He *et al.*, 2013; He *et al.*, 2014; Kleinman *et al.*, 1994; Mickley *et al.*, 2004]. High levels of tropospheric O_3 have detrimental effects on human health and hinder the growth of vegetation due to its oxidizing properties [Avnery *et al.*, 2011; Bell *et al.*, 2005; Fishman *et al.*, 2010]. Tropospheric O_3 plays a key role in tropospheric chemistry as a precursor for hydroxyl radicals (OH). In turn, OH initiates photochemistry through a series of reactions with the two main precursors of O_3 , nitrogen oxides ($NO_x=NO+NO_2$) and volatile organic compounds (VOCs). In addition, O_3 is a greenhouse gas, absorbing outgoing longwave radiation and thus warming the troposphere. The total radiative forcing of tropospheric O_3 is estimated to be 0.4 ± 0.2 W/m² (AR5; [IPCC, 2013]). Therefore, a decrease of O_3 concentrations in the troposphere benefits air quality as well as climate change. In this dissertation, I investigate the role of O_3 and O_3 precursors in air quality and climate change by:

- Evaluating ozone production efficiency (OPE) and O_3 precursors within an air quality model (chapter 2);
- Examining ozone's dependence on temperature (climate penalty factor (CPF)) throughout a period of 11 years within an air quality model and measurements (chapter 3);
- Comparing satellite-observed and modeled ammonia (NH_3) under varying chemical environments over East Asia (chapter 4).

This investigation addresses the following science questions:

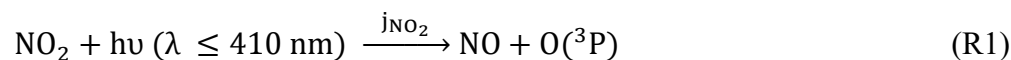
- How well does an air quality model simulate precursors of tropospheric O₃? What do we learn from simulations with corrected precursor emissions and reaction rates for key steps in the formation of O₃?
- Can an air quality model be used to assess how the concentration of O₃ responds to a changing climate? What are the implications for air quality policy?
- What are potential implications of increased ammonia in the atmosphere caused by air quality policy that reduce SO₂ and NO₂?

In the following sub-sections of Chapter 1, I discuss the chemistry of tropospheric O₃, the policies and regulations concerning O₃ as well as give more detail about O₃ precursors such as NO_x, HO_x (OH+HO₂+RO₂), peroxyacetyl nitrate (PAN), isoprene (C₅H₈), and formaldehyde (HCHO). Subsequently, I give a brief description of the regional air quality model used in my analysis.

1.1 Background

1.1.1 Tropospheric Ozone

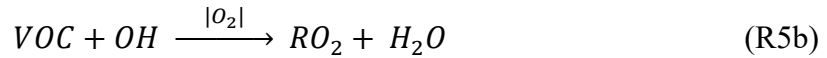
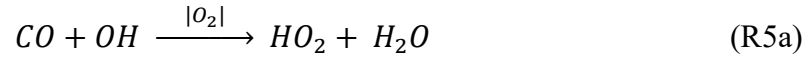
Tropospheric ozone (O₃) is often referred to as “bad ozone” due to its role as a greenhouse gas and its detrimental effects on human health [Bell *et al.*, 2005; Farhat *et al.*, 2013; Silva *et al.*, 2016] and vegetation [Avnery *et al.*, 2011; Emberson *et al.*, 2018]. Ozone is produced following the oxidation of volatile organic compounds (VOCs) in the presence of nitrogen oxides (NO_x ≡ NO + NO₂) and sunlight. The photolysis of NO₂ to NO and O(³P) is of central importance [Finlayson-Pitts and Pitts, 2000] because this process produces ground state oxygen atoms that lead to the production of O₃:



Simultaneously, NO can react with O₃ and peroxy radicals (HO₂, and/or RO₂; R = organic group):



Hence, the net production of O₃ occurs only if NO₂ had been produced with a reaction of species other than O₃ with NO. In photostationary state of reactions R1, R2, and R3, NO_x is not consumed but cycles between NO and NO₂, as such it acts like a catalyst. During the day and in urban regions NO₂ is mostly formed from reactions (R4a) and (R4b). These two reactions are the rate-limiting steps in the radical chain propagation that leads to formation of O₃. The sequence to produce O₃ is initiated by the reaction of carbon monoxide (CO) or a VOC with OH to make peroxy radicals:



The addition of OH to alkenes (to the C=C double bond) forms an intermediate that can decompose back to its reactants or be stabilized. Compared to H abstraction reaction rates, the strong molecular orbital interactions between the OH radical and the C=C double bonds afford very fast reaction rates and are pressure dependent [Finlayson-Pitts and Pitts, 2000]. Hence, at low pressures decomposition of the intermediate back to its reactants can be significant and needs to be considered when using the laboratory measured reaction rates for air quality modeling. This circumstance adds to the uncertainty in air quality model results [Ridley *et al.*, 2017].

In the United States a number of observational networks are in place to monitor surface O₃. In this work we use data from the Environmental Protection Agency (EPA) Air Quality System (AQS) and Clean Air Status and Trends Network (CASTNET) (see details Section 2.2.1 and 3.2.1). The measured O₃ is a product of primary precursor emissions from a range of global, regional, and local sources. For the U.S. that means emissions from Asia represent the global contribution [Fiore *et al.*, 2015; Jacob, 1999]. Regional contributions are associated with emissions from upwind power plants which are a significant source for O₃ precursors in the Eastern U.S. (see section 1.2.1).

Emissions from cars, trucks and small industrial processes as well as local power plants generally represent local contributions.

1.1.2 Ozone Policy

The Federal Government controls air quality through the Clean Air Act (CAA) enacted in 1963. The CAA allows for regulations on federal and state levels. The CAA from 1970 allows for regulatory programs such as the National Ambient Air Quality Standards (NAAQS) to protect public health and State Implementation Plans (SIPs) to be implemented. These and other federal government programs aimed at reducing pollution are regulated by the EPA, which was founded via executive order in 1970 by President Richard Nixon.

The CAA identifies six common air pollutants in outdoor air, called criteria pollutants. They are surface O₃, oxides of nitrogen and sulfur (NO_x and SO_x), particulate matter (PM_{2.5} and PM₁₀), CO, and lead, all of which can be harmful to human health and the environment. The NAAQS for O₃ has been revised and reevaluated multiple times (Table 1-1e). The current NAAQS for O₃, in place since October 2015, is 70 parts per billion (ppb). However, portions of this dissertation research took place prior to 2015 when the NAAQS for O₃ was 75 ppb. Hence, O₃ will be evaluated based on the 75 ppb NAAQS from this point forward.

In order to test whether a monitoring site is in compliance with the surface O₃ NAAQS, a design value (DV) has to be calculated. The DV is determined from data collected in three consecutive years from a monitor at one site. For that site the DV is then the 3-year average of the annual 4th highest daily maximum 8-hour O₃ (in ppb) with insignificant digits to the right truncated after the third decimal. The monitored location is said to be in compliance if the DV is less than or equal to 70 ppb (after 2015) or 75 ppb (after 2008 but before 2015) [EPA, 2006; 2017] areas that do not meet air quality standards are referred to as regions of nonattainment.

Each state that has a region of nonattainment is required to submit a SIP to the EPA in which abatement measures are proposed to reduce the emissions of the criteria pollutant that is in nonattainment. For example, measures to reduce NO_x and VOC from anthropogenic sources ultimately reducing O₃ formation might include: limiting the

usage of solvents in factories, using cleaner burning gasoline in addition to use vapor recovery nozzles at gasoline pumps, and tighter vehicle inspection programs.

Table 1-1: Summary of primary (to protect public health) and secondary (to protect public welfare) NAAQS for O₃ announced from 1971 to 2015 (updated from <https://nepis.epa.gov/Exe/ZyPDF.cgi?Dockey=P100KCZ5.txt>)

Final Rule	Indicator	Averaging Time	Level (ppm)	Form
1971 (36 FR 8186)	Total photochemical oxidants	1 hour	0.08	Not to be exceeded more than one hour per year
1979 (44 FR 8202)	O ₃	1 hour	0.12	Attainment is defined when the expected number of days per calendar year, with maximum hourly average concentration greater than 0.12 ppm, is equal to or less than 1
1993 (58 FR 13008)	The EPA decided that revisions to the standards were not warranted at the time.			
1997 (62 FR 38856)	O ₃	8 hours	0.08	Annual fourth-highest daily maximum 8-hour concentration, averaged over 3 years
2008 (73 FR 16483)	O ₃	8 hours	0.075	Form of the standards remained unchanged relative to the 1997 standard
2015 (80 FR 65291)	O ₃	8 hours	0.070	Form of the standards remained unchanged relative to the 1997 standard

The SIP demonstrates that, with these measures in place, a region can achieve attainment for surface O₃. However, precursors of O₃ as well as O₃ are transported across state boundaries by ambient winds; therefore one state is also affected by

pollutants from upwind states complicating compliance to the O₃ standard [Godowitch *et al.*, 2008].

1.2 Ozone Precursors

As previously described, NO_x is of central importance to O₃ production. The photolysis of NO₂ produces O(³P) radicals, and the reaction of NO with peroxy radicals (HO₂ and RO₂) regenerates NO₂, starting the cycle again. The HO₂ and RO₂ radicals are produced through the reaction of OH with CO or VOC necessary for O₃ production (section 1.2.2). Important VOC discussed in this study are isoprene and formaldehyde (section 1.2.4).

1.2.1 NO_x Chemistry and Emissions

The principal reactions governing the formation of NO from molecular nitrogen (R6, R7 and R8) occur at high temperatures during lightning discharges or combustion processes. The three equations together are called the Zeldovich mechanism.



High temperatures are necessary to break the N₂ triple bond. Therefore, R6 determines the rate at which NO is formed. Another natural NO source is soil, which emits NO and NH₃ (ammonia) though the process of microbial nitrification and denitrification [Parton *et al.*, 2001]. Once NO is emitted, NO₂ is formed by the reaction of NO with O₃, HO₂, or RO₂ (R3, R4a, or R4b). The cycling of NO and NO₂ occurs rapidly (within a minute) in the atmosphere via reactions R1, R2 and R3 (null cycle; O₃ is neither produced nor destroyed) which makes it suitable to consider the budget of NO_x (NO + NO₂) all together.

Sources of anthropogenic NO_x emissions are cars, power plants, and industrial activity. These emissions are from combustion processes. The greatest NO_x emission source in the US is the combustion of fossil fuel. Figure 1-1 shows NO_x emissions by sector as estimated in the 2014 National Emission Inventory (NEI) from the US (a) and

Maryland (b). The most dominant fossil fuel NO_x source is from mobile emissions that rely on internal combustion engines, accounting for 60% nationally and 72% in Maryland. However, studies have shown that there is a factor of 2 overestimate of mobile NO_x emissions within the NEI [Anderson *et al.*, 2014; Travis *et al.*, 2016, McDonald *et al.*, 2018]. The next largest source is stationary fuel combustion, which includes point sources such as power plants, industrial boilers, residential (e.g. wood), etc. This group produces 23% National and 20% of NO_x emissions in Maryland.

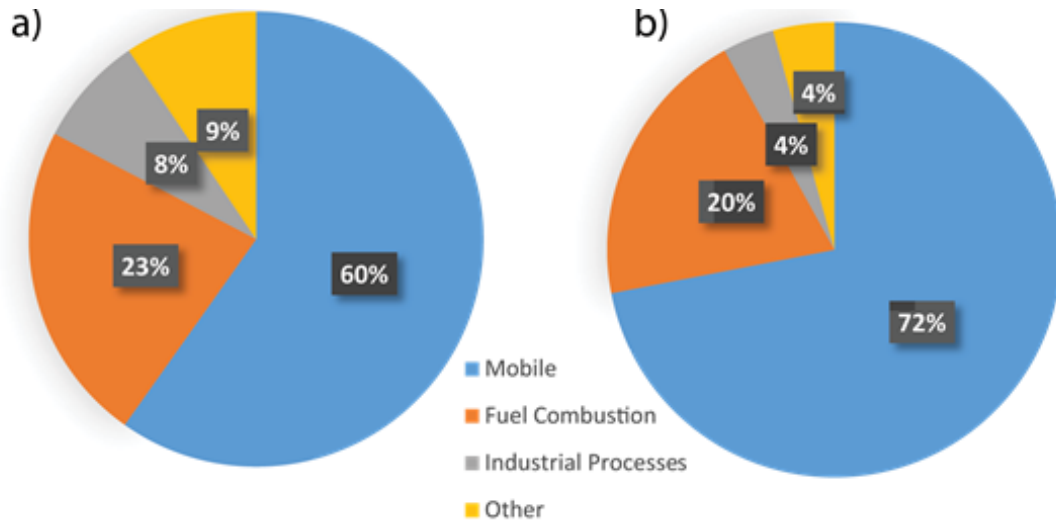


Figure 1-1: National a) and Maryland b) NO_x emissions by sector according to the 2014 NEI.

1.2.1.1 NO_x Policy

Regulations are in place to monitor and control emissions of NO_x from mobile sources and power plants. The first federal legislation concerning air pollution was the Air Pollution Control Act of 1955 that enabled funds for federal research on air pollution. The CAA of 1963 enabled federal legislation to actually put controls on air pollution. Since then, new CAAs had been released or amended. In 1975, catalytic converters in automobiles became federally mandated. This measure helps to convert the reactive species NO_x, CO, and VOCs into unreactive species such as N₂ and CO₂, but also harmful NH₃ [Fenn *et al.*, 2018]. Through the Clean Air Act Amendments of 1990 (CAAA 1990) the Photochemical Assessment Monitoring Station (PAMS) network was constructed to measure O₃, NO_x, VOC, and surface meteorology in areas that are in O₃ nonattainment (the area exceeds the ozone standard on a regular basis; see details in section 1.1.2).

In 1995, the use of reformulated gasoline and the implementation of low NO_x burners at the boilers of certain power plants became law. That same year, all fossil fuel fired power plants (with a few exceptions) in the continental US were required to have a continuous emissions monitoring system (CEMS) installed on their smokestacks. The CAA of 2003 additionally mandated the use of selective catalytic reduction (SCR) scrubbing of NO_x from exhaust at many power plants [Frost *et al.*, 2006; Goldberg *et al.*, 2015; Kim *et al.*, 2006]. Figure 1-2 shows a measurement time series from AQS sites from Maryland, Virginia and Washington D.C. of NO₂* (top panel; the * indicates that the measurement is not of true NO₂ because of interference from oxidation products of NO_x such as alkyl nitrates, peroxy nitrates, and nitric acid [Brent *et al.*, 2015; Dunlea *et al.*, 2007; Winer *et al.*, 1974]), the number of O₃ exceedances in Maryland (middle), and the number of days above 90°F (measured at Baltimore-Washington International Airport) (bottom) between 1972 and 2020. Throughout the record, summers with higher numbers of days above 90°F tend to have more O₃ exceedances than other years within approximately the same decade. There is no trend in the number of days above 90°F but there is a declining trend in NO₂* mixing ratios as well as the number of O₃ exceedances. Before 1988, the Baltimore-Washington region exceeded the 75 ppb threshold for >60 days per year. This situation equated to dangerous O₃ concentrations for nearly the entirety of a summer season. In recent years, the total number of O₃ exceedance days is less than 20 per year – approximately 1 day out of each week during summer. It is apparent from Figure 1-2 that after the implementation of the aforementioned regulations the NO₂* mixing ratio decreased. This observation suggests that air pollution improved (between 1972 to 2017) due to these regulations, which in turn contributed to the overall decrease of O₃.

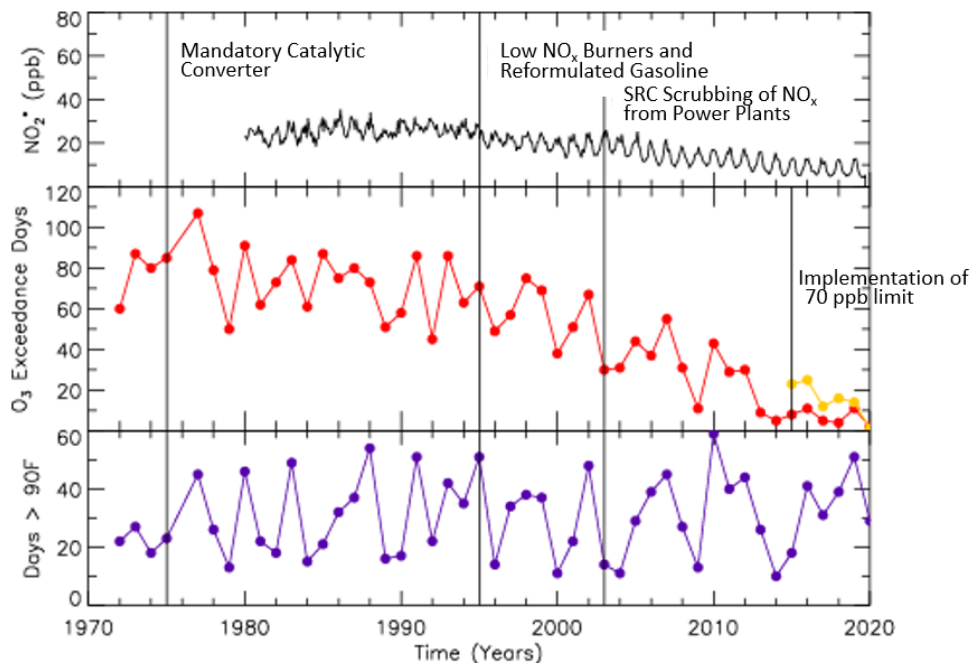
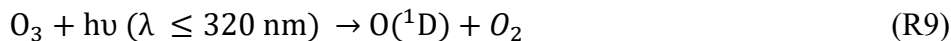


Figure 1-2: Data was compiled by Sandra Roberts from AQS sites showing (top) NO₂* mixing ratio, (middle) the number of days per year when 8-hr maximum O₃ exceeded 75 ppb (red) and 70 ppb (orange) threshold, and (bottom) the number of days per year when temperature at BWI airport is above 90°F.

1.2.2 HO_x Chemistry

Urban sources of HO_x (OH+HO₂+RO₂) radicals include VOCs (e.g. formaldehyde) and O₃. The hydroxyl radical (OH) is predominantly formed through the photolysis of O₃ followed by the reaction of O(¹D) with water:



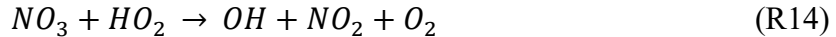
OH is well known for its oxidizing properties and often termed the detergent of the atmosphere because this highly reactive radical removes atmospheric pollutants (e.g. CO) and greenhouse gases (e.g. CH₄) via reaction R5a and R5b [Finlayson-Pitts and Pitts, 2000; Jacob, 1999; Spivakovsky *et al.*, 2000]. This removal process initiates the production of O₃. However, OH can also limit O₃ production by either reacting with NO₂ to form HNO₃ which is then removed from the atmosphere via dry or wet deposition [Hori *et al.*, 2006] or by self-reaction with HO₂ (R11) forming water and oxygen.

HO_x chemistry cannot be treated in isolation since it is closely coupled to the NO_x cycle and the chemistry of O₃. Below, HO_x chemistry in low and high NO_x environments are described. At very low NO_x and high HO₂+RO₂ mixing ratios (NO_x-limited; reductions in NO_x lead to reductions in O₃ production), the following reactions become important:



These reactions (R11 to R13) terminate the HO_x cycle (HO_x sink). Generally, ROOH is stable under atmospheric conditions. Therefore, ROOH constitutes an efficient reservoir that can eventually be photo-dissociated into RO+OH, thus regenerating radical species at a later time (downwind).

In a high NO_x environment (VOC-limited) other sinks for HO_x become more important such as the reaction of OH with NO₂ forming nitric acid (HNO₃). Minor sinks of HO_x are deposition, heterogeneous chemistry in cloud droplets and on aerosols as well as the production of pernitric acid [Martinez *et al.*, 2003]. During daytime, if enough NO is available, the self-reactions of HO₂ and RO₂ do not take place but instead HO₂ and RO₂ react with NO (R4a and R4b), which ultimately produces O₃. Under photostationary state conditions, HO₂ decreases as NO increases. During nighttime NO₃ takes the role of NO removing HO₂ from the atmosphere [Finlayson-Pitts and Pitts, 2000]:



1.2.3 Nitrogen reservoir Species

The oxidation products of reactive nitrogen species, abbreviated NO_z, such as nitric acid (HNO₃), alkyl nitrates (ANs) and peroxy nitrates (PNs) are longer lived compared to NO_x. They can be formed through reactions of VOCs with NO_x. As a result, farther downwind, ANs and PNs can dissociate to reform NO_x allowing long range transport of reactive nitrogen. Therefore, this mechanism enables formation of O₃ far

from NO_x sources [Derwent and Jenkin, 1991]. Peroxyacetyl nitrate (PAN or more accurately peroxyacetic nitric anhydride) is another reservoir for reactive nitrogen. As such, a full accounting of NO_x transport and O₃ production requires an understanding of PAN chemistry.

The majority of the following section appeared previously as Hemberck et al. [2019] in the supplements. Where appropriate, data, figures, and citations have been updated with information released after publication and the numbering has been changed to reflect incorporation into the dissertation.

PAN forms through reaction of acetaldehyde with OH and subsequent reaction with O₂ and NO₂ resulting in CH₃C(O)OONO₂. The removal of PAN occurs through reaction with OH, photolysis, thermal deposition, or deposition [Roberts and Bertman, 1992]. While in the upper troposphere photolysis is the dominant removal process of PAN, in the lower troposphere thermal deposition is dominant. The reaction of PAN with OH is not a significant removal process anywhere in the troposphere [Finlayson-Pitts and Pitts, 2000].

The following section provides detail about the PAN thermal decomposition rates. The results from this analysis have been used to modify the PAN thermal decomposition rate within an air quality model (Chapter 2). The IUPAC preferred values of the thermal decomposition rate for PAN at low and high pressure are slower in the 2006 recommendation compared to the updated rate constants in the 2014 recommendation. Figure 1-3 shows an Arrhenius plot of the thermal decomposition rate of PAN (k_{PAN}) from recommendations and laboratory results plotted as a function of inverse temperature. Recommended values from IUPAC06 (green line), JPL11 (black line) and IUPAC14 (red line) are shown for a pressure of 1 bar (750 Torr). The rate based on JPL11 is 22% faster than the IUPAC06 rate, at 298K and 1 bar. Laboratory measurements of k_{PAN} shown in Figure 1-3 were performed at different temperatures and pressures. The IUPAC expert panel recommends when evaluating k_{PAN} to use a pressure of 1 bar.

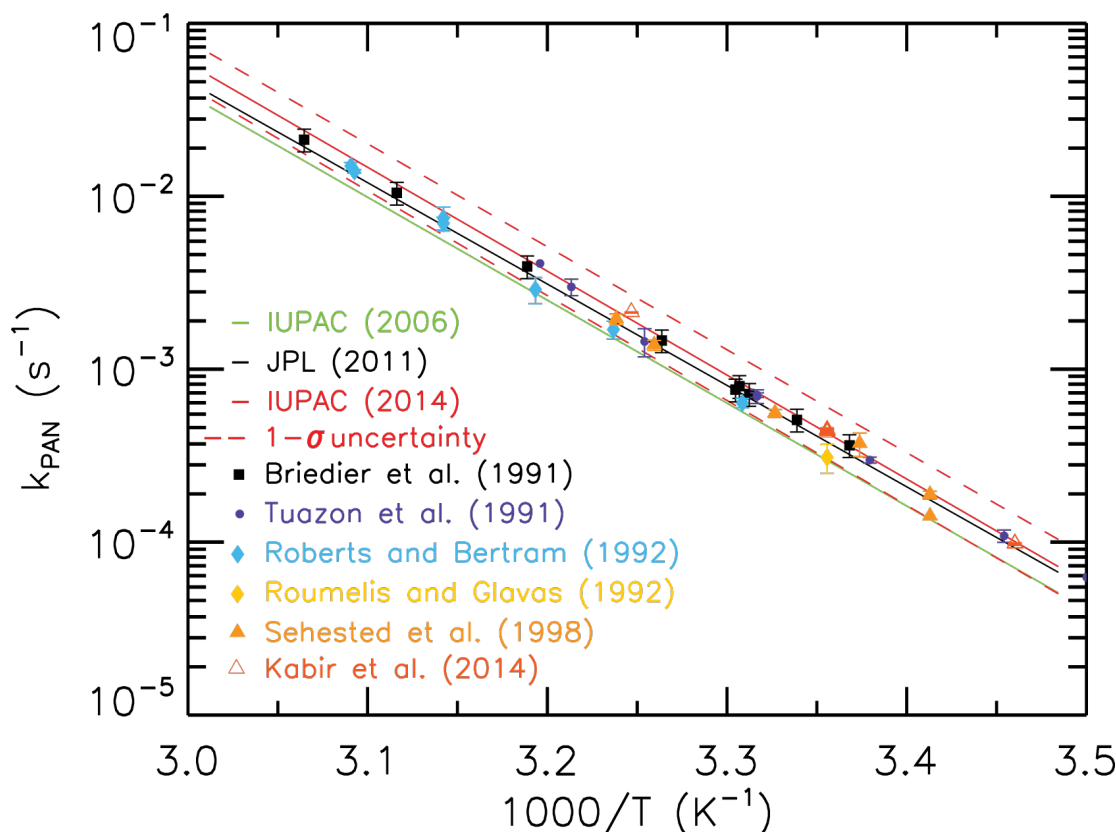


Figure 1-3: Arrhenius plot of the thermal decomposition rate of PAN (k_{PAN}) versus inverse temperature. IUPAC (2009; green), JPL (2011; black), and IUPAC (2014; red) are recommended values of PAN thermal decomposition rates shown with the IUPAC (2014) 1- σ uncertainty (dashed red line) at 1 bar. Laboratory measurements (symbols) with their respective uncertainties. The different symbols denote the pressure at which the measurement was taken (square = 600 Torr, filled triangle = 700 Torr, circle = 740 Torr, diamond = 760 Torr, open triangle = 750 Torr).

However, measurements of previous work was done at 600 Torr by Bridier et al. (1991, black squares), 700 Torr by Tuazon et al. (1991, blue circles), 760 Torr by Roberts and Bertram (1992, cyan diamonds), 760 Torr by Roumelis and Glavas (1992, yellow diamond), 700 Torr by Sehested et al. (1998, light orange filled triangles), and 750 Torr by Kabir et al. (2014, dark orange open triangles). IUPAC06 bases their preferred value on the Bridier et al. (1991, black squares) laboratory measurements at low pressure and on Bridier et al. (1991), Tuazon et al. (1991), Roberts and Bertram (1992), and Roumelis and Glavas (1992) at high pressure. The expert panel for the IUPAC06 recommendation state that their high pressure rate constant is in good agreement with Sehested et al. (1998) at 298K.

The rate constants from IUPAC are calculated using the analytical expression of Troe based of the Rice–Ramsperger–Kassel–Marcus (*RRKM*) method:

$$k_{PAN} = k_0 \cdot M / (1 + \frac{k_0 \cdot M}{k_\infty}) \cdot F_c^{1/(1 + \frac{\log_{10}(\frac{k_0 \cdot M}{k_\infty})}{N})^2} \quad (E1)$$

where, k_0 and k_∞ are the low- and high-pressure limit rate constants respectively. F_c is a coefficient that characterizes the broadening of the falloff curve and $N = 0.75$ - 1.27 $\log_{10}(F_c) \approx 1.4141$. Using Equation (E1) to calculate k_{PAN} shows that IUPAC06 underestimates the rate constant of PAN compared to most measurements (Figure 1-3; green line). The updated preferred rate constant from IUPAC14 (red solid line) agrees much better with the measurements. The result of this detailed examination of k_{PAN} is being used for analysis of an air quality model in Chapter 2.

1.2.3.1 Ammonia (NH₃)

Another major component of reactive nitrogen is ammonia (NH₃). This reduced form of nitrogen is alkaline and plays an important role in the global nitrogen cycle as a key nutrient for many ecosystems [Reis *et al.*, 2009; Zhu *et al.*, 2015]. In the atmosphere NH₃ neutralizes acidic species such as sulfuric or nitric acids (H₂SO₄ or HNO₃). Gaseous NH₃ has a lifetime in the atmosphere of ~1 day or less. However, upon reaction with H₂SO₄ or HNO₃, NH₃ forms ammonium aerosol salts ((NH₄)₂SO₄ or NH₄NO₃; fine particulate matter) with lifetimes ranging from days up to several weeks [Park *et al.*, 2004]. This condensation process allows for long range transport of reactive nitrogen [Galperin and Sofiev, 1998]. The gaseous to particle conversion occurs through direct nucleation from gaseous precursor or by accretion onto a pre-existing aerosol facilitated through water vapor.

The main source for NH₃ emission globally is agriculture (livestock, synthetic fertilizer, and crops). Natural emission sources stem from oceans, undisturbed soils, and wild animals (and their waste). Other emissions sources are biomass burning, humans, pets, industrial processes, and fossil fuels. An overabundance of reactive nitrogen reduces biodiversity, and in bodies of water with the right combination of sunlight and temperature toxic algae blooms occur [Yang *et al.*, 2008].

Nitrogen fixation is the natural process to create ammonia from molecular N₂ gas. Since most of the nitrogen on earth is in the form of molecular N₂, nitrogen fixation is the essential process to form reactive nitrogen making it the limited factor for primary production.

1.2.4 Isoprene and Formaldehyde

Isoprene (C₅H₈) is directly emitted to the atmosphere. Vegetation is the main emitter of isoprene and accounts for about a third of the global source of non-methane VOCs (NMVOCs; [Guenther *et al.*, 2012]).

Oxidation of VOCs produces formaldehyde (HCHO) in varying yields, depending on the parent hydrocarbon and ambient concentration of NO_x. Thus, biogenic VOCs drive most of the continental HCHO production in the lower troposphere [Palmer *et al.*, 2006]. Once emitted, isoprene is quickly oxidized with OH resulting in a lifetime of <1 to 3 hours. Isoprene affects air quality and climate because reactions involving decomposition products of this compound can produce O₃ [Trainer *et al.*, 1987]. In addition, isoprene can form secondary organic aerosols (SOA) [Jacob, 1999; Worton *et al.*, 2013]. As a source of RO₂, isoprene impacts HO_x and NO_x concentrations [Coates *et al.*, 2016; Mao *et al.*, 2013; Stavrakou *et al.*, 2010].

Isoprene produces organic nitrates in the presence of NO_x. In the Eastern United States, about 15-19% of emitted NO_x is consumed by isoprene and about 10% of the isoprene nitrates is transported away from the NO_x emission source [Horowitz *et al.*, 1998]. As a result, transported isoprene nitrate concentration can be higher than locally formed [Beaver *et al.*, 2012] bringing NO_x to remote locations. Eventually isoprene oxidizes to formaldehyde (HCHO).

HCHO is either produced due to VOC oxidation (high yields are generated via isoprene oxidation where biogenic emissions dominate) or is directly emitted into the atmosphere (e.g. coal combustion and animals). It is an eye irritant and carcinogen. HCHO is photochemically very active, resulting in an atmospheric lifetime of a few hours [Zhu *et al.*, 2014]. HCHO also affects the oxidative capacity of the atmosphere by two mechanisms. In the lower troposphere, HCHO is major source for HO₂

[Mahajan *et al.*, 2010; Volkamer *et al.*, 2010], while HCHO is a precursor of OH in the upper troposphere [Jaegle *et al.*, 1998].

1.3 Model Details

The Community Multiscale Air Quality (CMAQ) modeling system (Schere, 2006) is used as a regulatory tool and a platform to understand the complex interactions of atmospheric chemistry. Figure 1-4 shows a flowchart that outlines the various components of the CMAQ modelling system. In the following I give brief summaries of the components.

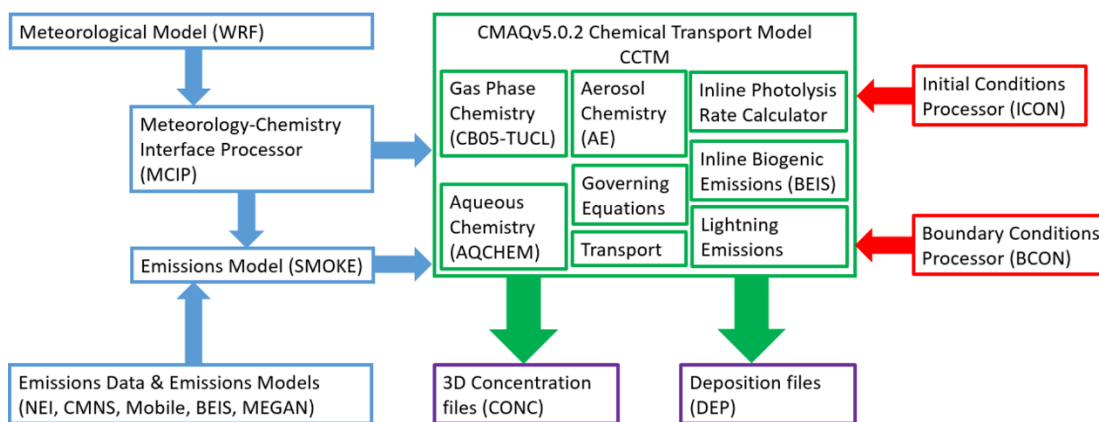


Figure 1-4 A flowchart that outlines the various components of the CMAQ modeling system.

1.3.1 Meteorological Model

The CMAQ simulations in this work use the Weather, Research and Forecasting (WRF) Model as the meteorological driver (Skamarock, 2014). The model is run at 36 km and 12 km horizontal resolution. Meteorological parameters in WRF are initialized with the North American Model (NAM) provided by the National Climatic Data Center (NCDC). Boundary conditions also use the information from NAM. Within the CMAQ model, surface fluxes of heat and moisture are found using the Pleim-Xiu surface layer scheme [J E Pleim, 2006] and Pleim-Xiu land surface model [Xiu and Pleim, 2001], respectively. The Asymmetric Convective Model 2 (ACM2; [J E Pleim, 2007]) computes convective mixing.

Table 1-2: WRF model specifications

WRF Model Options	
Time Period	May 24 through August 31, 2011
Re-initialize	Every 3 days except for soil temperature and soil moisture
Length of each run	3.5 days (first 12 hours of each run are discarded)
Initial and Boundary Conditions	NAM
SSTs	Multi-scale Ultra-high Resolution (MUR) sea surface temperature analysis
Radiation	LW: RRTM SW: Goddard
Surface Layer	Pleim-Xiu
Land Surface Model	Pleim-Xiu
Boundary Layer	ACM2
Cumulus	Kain-Fritsch
Microphysics	WSM-6
Nudging	Observational and analysis nudging
Damping	Vertical velocity and gravity waves damped at top of modeling domain

Water vapor, rain, cloud water, cloud ice, snow, and graupel [*Lim and Hong, 2005*] are calculated using the WRF Single-Moment 6-class microphysics scheme (WSM-6). Sub-grid clouds are simulated with the Kain-Fritsch convective parameterization [*Kain, 2004*]. Gravity waves and vertical velocity damping at the top of the model domain are used as described in [*Klemp et al., 2008; Loughner et al., 2011; Skamarock and Klemp, 2008*].

1.3.2 Emissions Inventories and Model

Air quality models rely upon emission inventories, which are built up from observations of sources, laboratory-based smog chamber studies as well as kinetic and mechanistic studies or from top-down inventories that observe concentrations in the atmosphere and back calculate what emissions must have been to arrive at those concentrations. Emission inventories are commonly evaluated by in-situ measurements from continuous atmospheric monitoring stations and field campaigns. Uncertainties in model inputs such as emission rates and meteorology, and because of the parameterization and simplification of the chemical mechanism, limits the ability of such models to determine O₃ sensitivities.

1.3.2.1 Sparse Matrix Operator Kernel Emissions (SMOKE)

Emission inventories are often provided at a spatial resolution that is incompatible with an air quality model (AQM). The Sparse Matrix Operator Kernel Emissions (SMOKE) modeling system is used to convert the different resolutions of the data into the resolution needed for a specific application. In addition, emission inventories typically have different temporal scales such as annual-total emissions or daily average emissions values for each emissions source. Therefore, SMOKE transforms inventory data into a gridded product by temporal allocation, chemical speciation, spatial allocation, and layer assignment. AQMs require input files in a distinct file format, therefore, SMOKE creates the Input/Output Applications Programming Interface (I/O API) Network Common Data Form (NetCDF) output format needed by CMAQ. SMOKE can process any number or types of pollutants making it a useful tool to create different sets of emissions compatible with different chemical mechanisms.

While SMOKE is used to generate anthropogenic emissions, biogenic emissions are generated using the biogenic emissions model Biogenic Emission Inventory System (BEIS) or the Model of Emissions of Gases and Aerosols from Nature (MEGAN). Lightning emissions are calculated online using lightning flash count data from the National Lightning Detection Network (NLDN) and convective precipitation information from WRF [Allen *et al.*, 2012].

1.3.2.2 Biogenic Emission Inventory System (BEIS)

BEIS version 3.6 (BEIS3) is an in-line module in CMAQ version 5.0.2. Previous versions of CMAQ had the BEIS module in SMOKE. In BEIS VOC emissions from vegetation as well as nitric oxide (NO) and carbon monoxide (CO) emissions from soil are estimated. The estimation is based on a land use database that is input to BEIS. Different land use types, such as agricultural and non-agricultural, are distinguished by the soil NO algorithm. Adjustments in areas of agriculture as specified in the Biogenic Emissions Landuse Database (BELD3) are made based on temperature, precipitation, fertilizer application, and crop canopy coverage during the growing season (April 1-October 31).

1.3.2.3 Model of Emissions of Gases and Aerosols from Nature (MEGAN)

MEGAN version 2.10 is an off-line algorithm for biogenic emissions [Guenther *et al.*, 2012] that can be input into CMAQ instead of BEIS. MEGANv2.10 also uses information on vegetation type and canopy characteristics as well as the temperature and solar radiation fields from WRF. Biogenic volatile organic compound (BVOC) emissions for BEIS and MEGAN use the same empirical algorithm, based on work of Guenther *et al.* [2006]. Differences between BEISv3.61 and MEGANv2.10 occur in the calculation of emission factors, type of canopy model, and the number of vegetation species. MEGANv2.10 uses 16 different global plant functional types as emission factors [Bash *et al.*, 2016]. In Chapter 2 CMAQ utilizes BEIS and MEGAN while in Chapter 3 only BEIS and in Chapter 4 only MEGAN is being used.

1.3.3 CMAQ Model

The CMAQ modeling system is programmed in Fortran 90 to calculate chemical compounds throughout the troposphere. The five main Fortran programs are the initial conditions processor (ICON), the boundary conditions processor (BCON), the clear-sky photolysis rate calculator (JPROC), the Meteorology-Chemistry Interface

Processor (MCIP), and the CMAQ Chemistry-Transport Model (CCTM). CMAQ is an Eulerian model that calculates a mass balance within each grid cell during a given time period by solving the transport across each cell boundary and chemical reactions within each grid cell. CMAQ has different chemical mechanisms options available, which will be discussed in the next section.

1.3.3.1 Chemical Mechanism (CM)

CMs describe the gas phase and heterogeneous chemistry in the atmosphere. In general, a CM fully describing all processes known to play a role in atmospheric chemistry would contain several thousand species and more than 20 thousand reactions [Dodge, 2000], making the CM computationally inefficient. Consequently, procedures have been developed to limit this size. Two approaches are being used to condense mechanisms:

- lumped structure (LS) approach: organics are divided into smaller reaction elements based on the types of carbon bonds in each species
- lumped molecule (LM) approach: a particular organic compound or a generalized species is used to represent similar organics.

Most mechanisms have very similar inorganic chemistry since it is fairly well understood. All use the same inorganic species: NO, NO₂, NO₃, N₂O₅, O₃, O(¹D), O(³P), OH, HO₂, HONO, HNO₃, HNO₄, H₂O₂, and CO (here, inorganic halogens have been neglected). The rate constants and corresponding reaction products are reasonably well understood. However, the few reactions that are not well understood have an impact on the ability to quantify the formation, cycling and losses of O₃ and NO_x in the lower atmosphere [Jimenez *et al.*, 2003]. All mechanisms use high parameterization of aromatic and biogenic VOCs due to their large uncertainties.

Readily available CMs for CMAQv5.02 are CB05CL, CB05-TUCL, CB05TUMP SAPRC-99, SAPRC07TB, and SAPRC07TC (SAPRC; Statewide Air Pollution Research Center). Newer versions of some of these mechanisms are available, but implementation for these models does not exist for the version of CMAQ used in this dissertation.

The CB mechanism is a lumped structure mechanism and can be used for urban- and regional-scale modeling. Organics are grouped together by their bond type which means, for example, most single bond carbon atoms, regardless of the molecule in which they occur, are represented by a one carbon atom alkane surrogate called PAR (after paraffin). Most carbon double bonds (alkene) are represented by a two-carbon atom surrogate called OLE (after olefin). This means Propene will be represented as 1 PAR and 1 OLE since it contains one alkyl group and one carbon-carbon double bond group [Dodge, 2000]. In chapter 2 and 3 a version of the CB mechanism is used.

In chapter 4 the SAPRC mechanism is used, which relies on the lumped molecule scheme for condensing organic chemistry. As a result, SAPRC has a more detailed organic chemistry than the carbon bond mechanisms, though the inorganic chemistry is almost the same (updated based on the results of the most recent evaluations). The SAPRC-99 mechanism includes representations of chemical reactions of almost 780 types of VOCs for reactivity assessment. Since SAPRC-99 are represented by a generalized reaction, look-up tables are included with the mechanism that list product yield parameters and reaction rate constants for many different alkanes. Therefore, the user can specify what species are to be lumped together and the parameters for the generalized reaction are then derived from the look-up table, depending on the system being modeled [Dodge, 2000]. The SAPRC mechanism is supposed to be more suitable for prediction of secondary particulate matter (PM) [Carter, 2010] compared to CB mechanisms.

1.3.3.2 Initial Conditions Processor (ICON)

ICON generates the first hour of a simulation from an ASCII file of vertically resolved concentration profiles. These concentrations are commonly taken from an existing CCTM output file. When performing nested simulations, a CCTM output file from a coarser grid simulation can be used. Within ICON one can select any of the readily available CMs (in CMAQv5.0.2) and define the horizontal and vertical grids. The format of the output is a binary netCDF file.

1.3.3.3 Boundary Conditions Processor (BCON)

The purpose of BCON is to create initial boundary conditions to be used by CMAQ. BCON can generate a netCDF file similar to the ICON output file and must be set to the same options (e.g., spatial resolution and CM) as were specified in ICON. In addition to these selections BCON can also have time-varying boundary conditions. ICON and BCON interpolate the data from an ASCII restart file to vertical resolutions that are consistent with the CCTM configuration.

1.3.3.4 Clear-Sky Photolysis Rate Calculator (JPROC)

CMAQv5.0.2 includes an in-line photolysis module that can be used to calculate photolysis rates as an alternative to JPROC. However, in my research I used JPROC to generate look-up tables of clear-sky photodissociation reaction rates. JPROC requires temperature profiles, profiles of aerosol extinction coefficient, data on cross sections and quantum yields of each species, top of the atmosphere solar radiance as well as standard seasonal profiles of ozone. Optionally, JPROC uses ozone total columns from the NASA Ozone Monitoring Instrument (OMI). A radiative transfer model calculates the actinic flux from these inputs. The look-up tables are clear-sky only. Hence, adjustment of photolysis rates to account for attenuation due to clouds is performed in-line within the CCTM.

1.3.3.5 Meteorology-Chemistry Interface Processor (MCIP)

The WRF meteorological fields are read in by MCIP [Otte and Pleim, 2010], which then generates netCDF output files that are ingested by SMOKE and CCTM. MCIP calculates the time-varying, species-dependent dry deposition velocities for the CCTM. This processor can uniformly trim cells off as well as create a subset of a domain. Vertically, layers can be collapsed, though this feature produces results that are highly sensitive to the settings used within MCIP. Similarly to JPROC, MCIP has the capability to constrain to satellite observations of clouds. Thus far MCIP can only read WRF output though theoretically it could be modified to process other meteorological models.

1.3.3.6 CMAQ Chemistry-Transport Model (CCTM)

The output files from the preprocessors (ICON, BCON, JPROC, MCIP) are ingested in the CCTM as well as the SMOKE output. Configuration options used in my research are listed in Table 1-3 below for the base case scenario. Within my preliminary work modification to the base case scenario are described (Section 2.4).

Table 1-3: CMAQ Settings for 2011 Simulation in Chapter 2

CMAQ Model Options	
Time Period	June 24 through July 31, 2011
Chemical mechanism	CB05-TUCL
Aerosols	AERO5
Dry deposition	M3DRY
Vertical diffusion	ACM2
Chemical initial and boundary conditions	GEOS-CHEM v8-03-02
Anthropogenic emissions	2011: NEI, CEMS, MOVES
Biogenic emissions	Calculated within CMAQ with BEISv3.61
Biomass burning emissions	FINNv1
Lightning emissions	Calculated within CMAQ

Chapter 2: Measured and Modelled Ozone Photochemical Production in the Baltimore-Washington Airshed

This chapter was previously published under the same title, as an article in the scientific journal *Atmospheric Environment X* [Hembeck *et al.*, 2019]. I am the lead author of this work, and I acknowledge collaboration with 8 co-authors. The article was published online on 19 February 2019. Here, the numbering of sections, figures, and tables reflects incorporation into the greater dissertation. The supplemental material from the article is distributed throughout this dissertation.

2.1 Introduction

High levels of tropospheric ozone (O_3) have detrimental effects on human health [Bell *et al.*, 2005; EPA, 2014a; West *et al.*, 2006] and vegetation [Avnery *et al.*, 2011]. Poor air quality episodes due to high surface O_3 typically occur in the Eastern United States during summer months when high-pressure stagnation events are common, allowing surface O_3 to accumulate in the region [He *et al.*, 2013; He *et al.*, 2014; Kleinman *et al.*, 1994; Mickley *et al.*, 2004]. Surface O_3 exceeded the prior National Ambient Air Quality Standard (2008 NAAQS) of 75 ppb (8 hour O_3 average) [EPA, 2013] in the state of Maryland for 29 days during summer 2011, the time period of this study. Maryland achieved attainment of the 75 ppb standard for the ozone season (1 May through 30 September) in 2015. On 1 October 2015, the Environmental Protection Agency (EPA) finalized a new standard for surface O_3 of 70 ppb. Currently, Maryland is in the process of formulating a “good neighbor” State Implementation Plan (SIP) to show how the 2015 NAAQS for surface O_3 will be attained in future years.

Tropospheric O_3 is a secondary pollutant, produced by chemical reactions involving carbon monoxide (CO), volatile organic compounds (VOCs) and nitrogen oxides ($NO_x \equiv NO + NO_2$) [Crutzen, 1973; Jacob, 1999; Lin *et al.*, 1988]. In addition, surface O_3 is influenced by a variety of meteorological conditions. Stagnation events that cause local emissions to accumulate are one phenomenon associated with bad air quality. Another meteorological condition conducive for bad air quality in the mid-Atlantic region of the United States is when O_3 precursors (CO, VOCs, and NO_x) are

advected from upwind municipalities in the Ohio River Valley by the Bermuda high pressure system, a persistent weather pattern during summer [Vukovich and Sherwell, 2003]. On a smaller spatial scale, vertical mixing in the morning upon break-up of the nocturnal boundary layer transports O₃ and precursors from the residual layer down to the surface, such that local air quality depends on both nearby and distant emissions [Hu *et al.*, 2013; Mazzuca *et al.*, 2017; Mazzuca *et al.*, 2016; Zhang and Rao, 1999].

Our study is focused on evaluating the chemical mechanism within the Community Multi-scale Air Quality (CMAQ) model, using aircraft data collected in Maryland during the summer 2011 phase of the NASA Deriving Information on Surface Conditions from Column and Vertically Resolved Observations Relevant to Air Quality (DISCOVER-AQ, hereafter D-AQ) campaign [Flynn *et al.*, 2014; Schroeder *et al.*, 2016]. Evaluation of CMAQ is a priority because this model is used as regulatory tool to design strategies to achieve surface O₃ standards by the U.S. EPA as well as various States; CMAQ is also used to quantify surface O₃ in other countries [San Jose *et al.*, 2006; Wang *et al.*, 2015; Xing *et al.*, 2015]. To develop effective policy strategies such as the SIPs that states in violation of the federal standards are required to submit to the U.S. EPA, it is important that CMAQ accurately reflect the relation between photochemical production of O₃ and ambient levels of CO, NO_x, and VOCs. The photochemical production of O₃ with respect to these precursors follows a complex, non-linear relation [Chameides and Walker, 1974; Lin *et al.*, 1988; Mazzuca *et al.*, 2016; Schroeder *et al.*, 2016; Schroeder *et al.*, 2017; Sillman, 2000].

Air quality models (AQMs) such as CMAQ rely on proper parameterization of tropospheric photochemistry, within a segment of code called the “chemical mechanism”. The chemical mechanism uses inputs of reaction rate constants and absorption cross sections provided by expert panels such as the NASA Jet Propulsion Laboratory [JPL; Burkholder *et al.*, 2015] and the International Union of Pure and Applied Chemistry [IUPAC; Atkinson *et al.*, 2006], which are based on their analysis of many published laboratory studies. Most importantly, the chemical mechanism within any air quality model reflects a gross simplification of a complex set of reactions known to govern processes such as the decomposition of isoprene [e.g., Marvin *et al.*, 2017], due to the computational burden of running AQMs at high spatial and temporal

resolution. The JPL and IUPAC panels also provide uncertainty estimates for the reaction rate constants and absorption cross sections. The chemical mechanism within CMAQ does not explicitly account for uncertainties in kinetic parameters. Ridley et al. [2017] used a Lagrangian chemical transport model in conjunction with the Monte Carlo method to show that kinetic uncertainties can account for up to 10-12 ppb variation in the mixing ratio of O₃.

It has been shown that CMAQ tends to over-estimate surface O₃ at urban locations in the Mid-Atlantic [Nolte et al., 2008; Ring et al., 2018; Trail et al., 2014, Travis et al. 2016]. Accurate simulation of measured O₃ is a necessary but not sufficient condition for establishing the proper behavior of the chemical mechanism within an air quality model, due to the aforementioned non-linear relation of O₃ production as a function of NO_x and VOCs. In the 1980s and early 1990s, much of the focus on achieving the surface O₃ standards had been on reducing the emission of VOCs, which led to considerable declines of surface O₃ in Los Angeles and New York City as well as more modest improvement in other regions of the U.S., including the state of Maryland [Jacob, 1999]. Significant reductions in the emission of NO_x also occurred due to federal regulations starting in various years (as indicated in parentheses) that required mandatory catalytic converters in automobiles (1976), the use of reformulated gasoline (1995), the implementation of low NO_x burners at the boilers of certain power plants (1995), and selective catalytic reduction scrubbing of NO_x from exhaust at many power plants (2003) [Frost et al., 2006; Goldberg et al., 2015; Kim et al., 2006].

Liu et al. [1987] introduced the term ozone production efficiency (OPE), which they defined as a dimensionless quantity that tracks the number of molecules of O₃ produced per molecule of NO_x, before NO_x is converted to HNO₃ or some other reservoir species. Their analysis, which focused on surface data collected at Niwot Ridge, Colorado and a number of other rural stations, demonstrated the importance of non-methane carbons (i.e., VOCs) for the photochemical production of O₃ as well as generally good agreement between modeled and measured OPE. Trainer et al. [1993] devised a method to deduce OPE from the slope of observed O₃ versus NO_x oxidation products, which they defined as NO_y (total reactive nitrogen) minus NO_x. They reiterated the importance of biogenic hydrocarbons based on their analysis of OPE

inferred from data acquired at four surface sites in the rural, Eastern U.S.

Kleinman et al. [2002] revised the definition of OPE by considering the slope of O_x (defined as the sum of O_3 plus NO_2) versus NO_y minus NO_x , which they termed NO_z . They used O_x rather than O_3 in the definition of OPE because O_3 is affected by the reaction of NO with O_3 , whereas O_x is conserved by this reaction. Kleinman et al. [2002] showed, based on the analysis of aircraft data acquired over Phoenix, Arizona, that OPE displays a classic non-linear dependence as a function of the maximum value of NO_x in various plumes. Their observations revealed large values of OPE (between 5 to 7) for the low range of NO_x (near 5 ppb) and smaller values of OPE (about 2) at the high range of NO_x (40 to 50 ppb). The decline in OPE at elevated NO_x is likely due to two factors: radical termination via reaction $OH+NO_2+M$ forming HNO_3 (which is a sink for NO_x as well as HO_x ($OH+HO_2$)) and a decline in the HO_2/OH ratio driven by higher NO [Sillman, 2000]. In other words, NO_x is recycled without loss more efficiently at low ambient mixing ratios. For the low range of NO_x shown in Figure 8 of Kleinman et al. [2002], production efficiency of tropospheric O_3 is controlled by NO_x (i.e., reductions in the emissions of NO_x lead to less O_3), whereas for the high range of NO_x , O_3 is controlled by VOCs. A recent paper by Henneman et al. [2017] showed that OPE has been increasing over time in the Eastern U.S. due to the decline in ambient NO_x .

Here, we briefly review numerical values of OPE reported by many papers. The studies conducted prior to 2002 tended to use O_3 for the quantification of OPE, whereas latter studies used O_x . The OPE value and its interpretation does change, depending on whether O_3 or O_x is used to determine OPE [Sillman, 2000]. Prior observations of OPE show a wide range of values, extending from 1 to 65 molecules of O_3 produced per molecule of NO_x oxidized, depending on location as well as ambient levels of VOCs. Highest values of OPE have been found in clean oceanic air masses, such as over the Atlantic close to the United Kingdom, where OPE was reported to be as high as 65 [Rickard et al., 2002]. Moderate values of OPE are found at rural sites, such as: Scotia, Pennsylvania, which exhibited OPE of 8.5 [Trainer et al., 1993]; Metter, Georgia with OPE of 11.4 [Kleinman et al., 1994]; and, Giles County, Tennessee with OPE of 12.3 [Olszyna et al., 1994]. Low values of OPE are commonly found in urban regions, such

as Birmingham, Alabama with OPE of 7 [Trainer *et al.*, 1995], Nashville, Tennessee with OPE of 2.5 to 4.7 [Nunnermacker *et al.*, 1998], and the Baltimore-Washington metropolitan region with OPE of 8.3 [He *et al.*, 2013]. Ge *et al.* [2013] reported an OPE of 1.0 to 6.8 for Beijing, China. Very low values of OPE are found close to Electric Generating Units (EGUs) that rely on the combustion of coal, such as near the Paradise power plant in Nashville, Tennessee, for which an OPE of 2 has been reported [Nunnermacker *et al.*, 2000]. In general, the closer a sampled air mass lies to large sources of NO_x , the lower the OPE becomes, due to the reasons outlined at the end of the prior paragraph. It is likely that low mixing ratios of ambient VOC over oceanic regions, such as that sampled by Rickard *et al.* [2002], contribute to the high value of OPE reported in their study.

Next, we review a few studies that have calculated OPE within the CMAQ model and compared to observed OPE. Godowitch *et al.* [2011] used model output from CMAQ version 4.7, which utilized the Carbon Bond version 2005 (CB05) chemical mechanism [Yarwood *et al.*, 2005]. Their empirical determination of OPE was based on analysis of airborne measurements of O_3 , NO , NO_2 , and NO_y obtained within the planetary boundary layer by instruments on board the U.S. Department of Energy's Gulfstream BNL-G1 research aircraft. Their flights were conducted during afternoons in July 2002 in southern New England and the northern part of the Mid-Atlantic States. They found that OPE within CMAQ was slightly lower (OPE = 6.7) than that inferred from data (OPE = 7.6) (uncertainties for OPE were not provided in their study). Observations and model simulations both demonstrated highest values of OPE for the lowest levels of NO_x , and a decline in OPE with rising levels of NO_x .

Sarwar *et al.* [2013] used CMAQ version 5.0 with two chemical mechanisms: CB05 updated with toluene reactions (CB05-TUCL) [Whitten *et al.*, 2010] and RACM2 [Goliff *et al.*, 2013]. They compared results from CMAQ to OPE inferred from ground-based measurements of O_3 , NO_x , and NO_y at three locations in the Southeast U.S.: Yorkville, Georgia; Centerville, Alabama; and Oak Grove, Mississippi. The average observed OPE for all three sites was 13.7, larger than they reported for their CMAQ simulations using either mechanism. Values of OPE from CMAQ were 6.5 using CB05-TUCL and 9.0 using RACM2. The two chemical mechanisms differ in

how they lump organic species and the number of chemical reactions [Goliff *et al.*, 2013; Whitten *et al.*, 2010]. Their value of OPE found using CB05-TUCL (which is the same mechanism used in our study) was about 34% lower than inferred from observations. The RACM2 mechanism resulted in a higher value of OPE, bridging about half of the gap between measured and modeled OPE found using CB05-TUCL. The RACM2 mechanism includes a more explicit representation of alkyl nitrates (ANs) and peroxy alkyl nitrates (PNs) than CB05-TUCL, resulting in lower calculated values of ANs as well as PNs and consequently higher values of NO_x/NO_y . The NO_x/NO_y ratio is directly related to OPE. A mechanism with a higher ratio will simulate more recycling of NO_x prior to conversion to reservoir species compared to a mechanism with a lower ratio, provided the same values for NO_2 photodissociation frequency and the rate constant for NO and O_3 are used in both mechanisms.

Our paper is focused on evaluation of OPE within CMAQ utilizing data collected during the D-AQ flights in July 2011 [Flynn *et al.*, 2014; Schroeder *et al.*, 2016] as well as satellite measurements of tropospheric column formaldehyde (HCHO) and nitrogen dioxide (NO_2) obtained by the Ozone Monitoring Instrument (OMI) aboard the NASA Aura satellite [Duncan *et al.*, 2010; Schroeder *et al.*, 2016]. In addition to examination of modeled and measured OPE, we also compare CMAQ values of radicals and reservoir profiles to aircraft measurements within the convectively mixed layer, acquired during a series of profiles over six air quality monitoring stations. The CMAQ representation of surface O_3 is also compared to ground-based measurements acquired at these six sites. Our baseline simulations make use of the CB05-TUCL mechanism within CMAQ version 5.0.2 [Whitten *et al.*, 2010]. We use various representations of biogenic emissions, as described below, and also show results for a change to the CB05-TUCL mechanism [Canty *et al.*, 2015] designed to approximate the improvement in the treatment of alkyl nitrates and peroxy alkyl nitrates that has been implemented in RACM2 [Sarwar *et al.*, 2013].

2.2 Measurements and Methods

During the NASA DISCOVER-AQ (D-AQ) campaign in 2011, many measurements from ground, aircraft, and satellite-based instruments were collected

[Flynn *et al.*, 2014; Schroeder *et al.*, 2016]. A complete description of DISCOVER-AQ is available at <http://www-air.larc.nasa.gov/cgi-bin/ArcView/discover-aq.dc-2011>. A brief description of the observations used in our study is given below.

2.2.1 Ground Based Measurements

The U.S. EPA Air Quality System (AQS) ground-based sites typically provide *in-situ* measurements of O₃, NO₂, and PM_{2.5}. Here, we use data collected from six AQS sites located in Maryland (Beltsville, Padonia, Aldino, Fairhill, Edgewood, and Essex) that were an integral part of the 2011 D-AQ campaign. Figure 2-1 displays the location of these sites (black ×) relative to two major, nearby cities as well as the nearest CMAQ grid box (red rectangles) and central grid point (red circles). In this study, we use ground-based measurements of O₃ to compare to output from various CMAQ simulations of surface O₃. The mixing ratio of O₃ at all six sites is measured via ultraviolet absorption photometry, with a precision of 0.1 ppb and uncertainty of 5% [EPA, 2006].

2.2.2 P-3B Aircraft Measurements

The NASA P-3B aircraft used during D-AQ provides *in-situ* measurements of many trace gases. Table 2-3 shows a subset of species measured with instruments onboard of the P-3B aircraft used in this study, along with the precision and accuracy of the various measurements. The P-3B aircraft flew on 14 days in July 2011. The flight paths were coordinated such that the P-3B spiraled over the six EPA AQS sites shown in Figure 2-1, either down from cruise altitude (3 to 5 km altitude) to within the convectively mixed layer (about 300 m altitude) or up from the mixed layer back to cruise altitude.

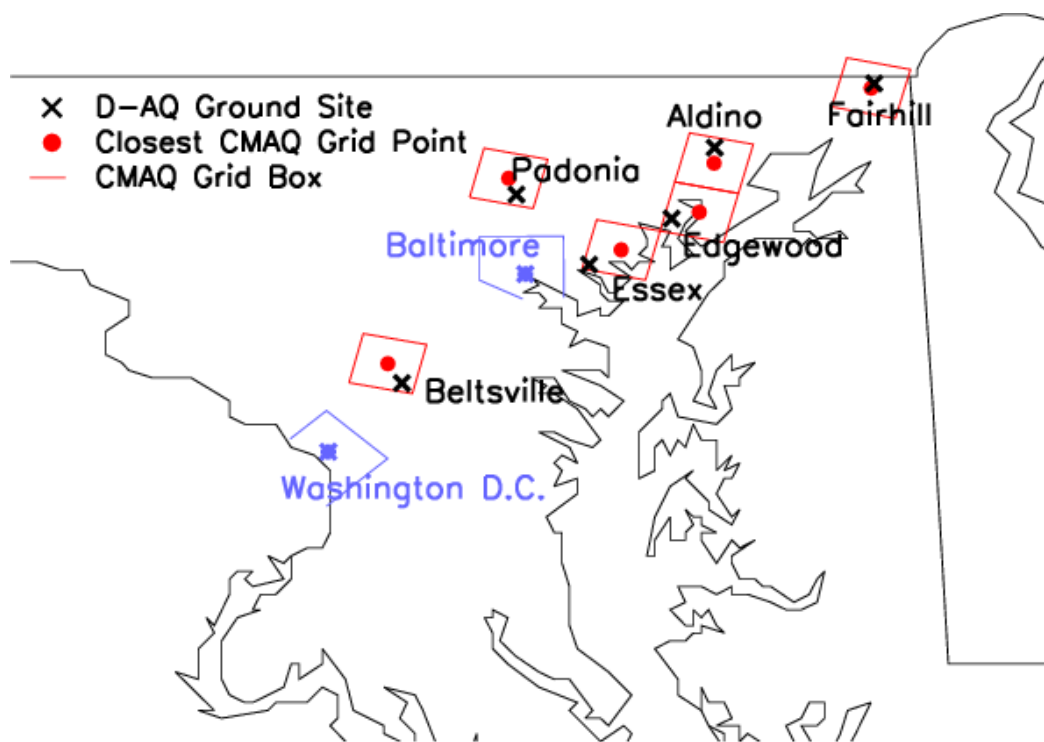


Figure 2-1 Map of the Baltimore-Washington region showing six ground sites (black x) and closest CMAQ grid point (red circle) as well as the CMAQ grid box surrounding the ground site (red box).

Flight legs between the various sites were flown either at cruise altitude or else at about 300 m altitude, within the mixed layer. In this study we only use data collected for spirals within the convectively mixed layer (CML, defined as pressure > 820 hPa), because O_x and NO_z tend to exhibit a compact, near linear relationship in the lower troposphere. The top of the CML, ~ 820 hPa, is based on visual inspection of profiles of potential temperature, CO, and H_2O . Since each spiral occurs within a small geographic footprint, it is reasonable to assume that the biogenic release of isoprene, which controls the level of HCHO during summer in the Mid-Atlantic, is homogenous over the extent of an individual spiral (i.e., horizontal distance of ~ 5 km). Throughout, we use 1 minute averaged data provided in merge files distributed by the D-AQ project <https://www-air.larc.nasa.gov/cgi-bin/ArcView/discover-aq.dc-2011?Merge=1>.

The abundance of NO_2 was measured by two instruments on the NASA P-3B aircraft. The thermal dissociation-laser induced fluorescence instrument (TD-LIF) operated by the University of California at Berkeley [Day *et al.*, 2002; Farmer *et al.*, 2006] acquires

alternating measurements of NO₂, HNO₃, ANs and PNs (each quantity is measured for a ~12 sec duration). The TD-LIF measurement of NO₂ has a 1 σ accuracy of 5% and a precision of 10 ppt at sampling frequency of 10 sec. The 4-channel chemiluminescence instrument (P-CL) from the National Center for Atmospheric Research (NCAR)

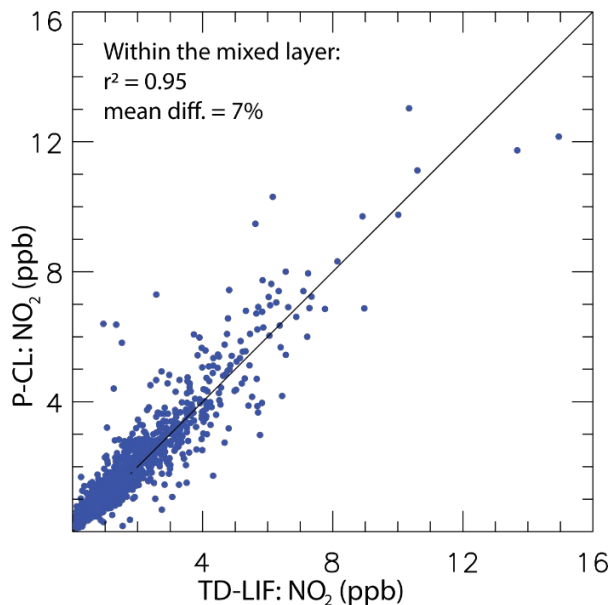


Figure 2-2. Scatterplot of NO₂ aircraft measurements from the TD-LIF instrument versus the P-CL instrument within the mixed layer. The 1:1-line is also shown.

[Ridley and Grahek, 1990] simultaneously measures NO, NO₂, NO_y and O₃ with a sampling frequency of 1 sec, with a 1 σ accuracy of 15% and a precision of 20 ppt for NO₂. A scatter plot of TD-LIF NO₂ versus P-CL NO₂ for 1 minute averaged data in the mixed layer reveals a mean difference of 7% (Figure 2-2), with NO₂ from the P-CL instrument generally being higher than from TD-LIF.

2.3 Satellite

Measurements

We use retrievals of total column HCHO [Abad *et al.*, 2015] and tropospheric column NO₂ [Krotkov *et al.*, 2017] from the Ozone Monitoring Instrument (OMI) on the NASA Aura satellite. The OMI instrument is a UV/VIS solar backscatter spectrometer in a polar sun-synchronous orbit, with a ~1:40 pm local overpass time during daylight [Abad *et al.*, 2015]. Spectra are recorded using a two-dimensional charged-coupled device (CCD). The spatial resolution of each OMI pixel is 13 km × 24 km for the center of each swath and 26 km × 135 km at swath edge, both at nadir.

Here we use total vertical columns of HCHO from the Version 3.0 (Collection 3) Smithsonian Astronomical Observatory (SAO) retrievals based on the use of measured radiances in the 325 to 357 nm spectral region. The reference sector correction described by Gonzalez *et al.* [2015] is applied to this data product. The HCHO data were obtained from <https://urs.earthdata.nasa.gov/>, last accessed late

August 2017. The satellite observations provided by OMI do not occur on a regular grid [Bucsela *et al.*, 2013]. For comparison to CMAQ, we have averaged the OMI HCHO product onto a $0.25^\circ \times 0.25^\circ$ (latitude, longitude) grid. For this averaging process, column HCHO is weighted based on satellite viewing angle and screened for an effective cloud fraction less than 0.3, as described by Acarreta *et al.* [2004] and Stammes *et al.* [2008]. Retrievals are only considered valid if the flag “MainDataQualityFlag” equals zero (which provides assurance that at least 50% of the tropospheric column captures observed information) and if the flag “XTrackQualityFlag” equals zero (which indicates the influence of the row anomaly on the measurements is minimized). Since the stratosphere makes a negligible contribution to total column HCHO, we treat the OMI column HCHO product as being representative of the tropospheric column [Millet *et al.*, 2006]. The precision of column HCHO for one pixel is 10^{16} molecules cm^{-2} and improves with multi-pixel averaging [Boeke *et al.*, 2011; Zhu *et al.*, 2017]. The accuracy of column HCHO varies between 25% and 31% with a cloud fraction of less than 0.2 [Millet *et al.*, 2006].

We use Version 3.0 retrievals of tropospheric vertical column NO_2 from OMI [Krotkov *et al.*, 2017]. These data are also available at <https://urs.earthdata.nasa.gov/>, last accessed late August 2017. The retrieval of vertical column NO_2 is based on the use of measured radiances in 405 to 465 nm spectral region. A similar screening and averaging process as for column HCHO was used, with the appropriate quality flags, to grid the vertical NO_2 columns. In detail, the “XTrackQualityFlag” to account for the row anomaly equals zero and the “VcdQualityFlags” which is a summary flag to account for errors during processing equals zero. The precision of tropospheric column NO_2 is $\sim 0.5 \times 10^{16}$ molecules cm^{-2} and the accuracy is about 30% for clear sky to 60% for partly cloudy conditions [Krotkov *et al.*, 2017].

2.3.1 Method to Infer Peroxy Radical Concentrations

Though the D-AQ campaign provided an extensive data set, hydroperoxyl radical (HO_2) and organic peroxy radicals (RO_2) were not measured. These compounds are essential to our understanding of the chemical mechanism within CMAQ because the production of surface O_3 is limited by the speed of the reaction of NO with radicals

such as HO₂ and RO₂ (e.g., CH₃O₂, C₂H₅O₂, and CH₂C(CH₃)C(O)O₂, the isoprene oxidation product peroxy methacrolein). The resulting products can form NO₂ either directly (e.g., HO₂ + NO → OH + NO₂) or after thermal decomposition (e.g., of PAN (CH₃C(O)OONO₂; peroxyacetyl nitrate), PPN (CH₃CH₂C(O)OONO₂; peroxy propionyl nitrate), and MPAN (CH₂C(CH₃)C(O)OONO₂; methacryloylperoxynitrate)). Therefore, the production rate of O₃ is limited by:

$$\text{Prod O}_3 = k_{\text{HO}_2+\text{NO}} \cdot [\text{HO}_2][\text{NO}] + \sum_i [k_{\text{RO}_2+\text{NO}}]_i \cdot [\text{RO}_2]_i \cdot [\text{NO}] \quad (1)$$

where i represents various RO₂ radicals. Assuming NO₂ is in local photochemical steady state, the sum of hydroperoxyl and organic peroxy radicals (multiplied by the appropriate rate constants) can be inferred from the measured NO₂/NO ratio. Measurements of NO, NO₂, O₃, J_{NO₂}, and a value for k_{O₃+NO} of 3.0×10⁻¹² exp(-1500/T) cm³ s⁻¹ [JPL03; Sander et al. 2003] are used to infer the sum of peroxy radicals multiplied by the respective rate constants for reaction with NO:

$$k_{\text{HO}_2+\text{NO}} \cdot \text{HO}_2 + \sum_i [k_{\text{RO}_2+\text{NO}}]_i \cdot [\text{RO}_2]_i = \frac{[\text{NO}_2]}{[\text{NO}]} \cdot J_{\text{NO}_2} - k_{\text{O}_3+\text{NO}} \cdot \text{O}_3. \quad (2)$$

This expression assumes production and loss of NO₂ are equal; both sides of the equation have units of s⁻¹. Equation (2) is valid in CMAQ during daytime hours (10 am to 4 pm local solar time; note, the sun is highest in the sky at ~1 pm in the region sampled by D-AQ during summer), as shown in Figure 2-3. The figure shows a comparison of simulated ΣRO₂ (left hand side of Equation (2)) versus inRO_x (right hand side of Equation (2)) from the SCI-PAN simulation during day time hours (10 am to 4 pm local solar time). Day time hours were chosen, since NO₂ is nearly in instantaneous photochemical steady state, i.e. Equation (2) is valid.

In the following, we will refer to the right hand side of equation (2) as the inferred value (inRO_x) and the left hand side as the real value (ΣRO₂) of the rate at which HO₂

and RO₂ radicals react with NO. Our analysis assumes that the chemistry described

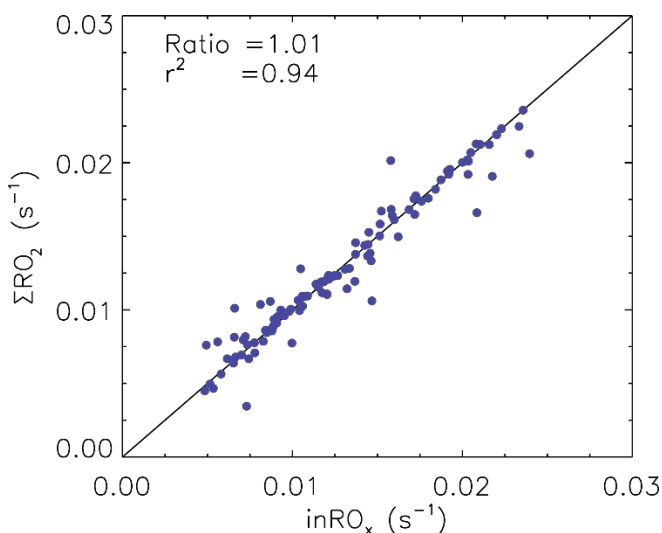


Figure 2-3 Scatterplot of simulated ΣRO_2 versus inRO_x from the SCI-PAN simulation. The inRO_x values shown here are used to compare mean inRO_x from the model to mean inRO_x values from measurements (see Figure 2.13). The 1:1-line is also shown.

above is complete. This calculation cannot distinguish HO₂ from RO₂, but provides a good estimate of the frequency at which all peroxy radicals react with NO. Finally, the value for $k_{\text{O}_3+\text{NO}}$ used in Equation (2) is the same as used in the CB05-TUCL chemical mechanism, which is from JPL03 [Sander *et al.*, 2003]; the same value for this rate constant is given in the latest JPL compendium [Burkholder *et al.*, 2015], hereafter JPL15). The computed value of inRO_x

depends on the accuracy of $k_{\text{O}_3+\text{NO}}$ and J_{NO_2} , as discussed below.

The accuracy of inRO_x depends on the numerous factors that appear on the right hand side (RHS) of Equation (2). For the first term on the RHS, the accuracy of NO and NO₂ are 5% and 15%, respectively. The accuracy of the photolysis frequency of J_{NO_2} , given by $\int F(\lambda)\sigma_{\text{NO}_2}(\lambda)\Phi_{\text{NO}_2}(\lambda) d\lambda$, is 20% based on the JPL03 uncertainties for σ_{NO_2} and Φ_{NO_2} (these estimates are independent of temperature). Even though J_{NO_2} is reported with a precision of 8%, we used the accuracy uncertainty below. Combining these three accuracy uncertainties in a root sum of squares (RSS) fashion leads to a 26% uncertainty for the first term of the RHS of Equation (2). The 1σ uncertainty of the $k_{\text{NO}+\text{O}_3}$ rate constant given by JPL03 is 14% and the 1σ accuracy of O₃ is 5%. Combining these two values in an RSS fashion leads to a 15% uncertainty for the second term. Therefore, the overall 1σ uncertainty of the RHS of Equation (2) is estimated to be 30%.

2.4 Model Description

This study uses the U.S. Environmental Protection Agency (EPA) Community Multiscale Air Quality (CMAQ) model, version 5.0.2 [CMAS-Center, 2013] with Carbon Bond version 2005 [Yarwood *et al.*, 2005] updated with toluene reactions [Whitten *et al.*, 2010] including the chlorine chemistry extension (CB05-TUCL; https://www.airqualitymodeling.org/index.php/CMAQv5.0_Chemistry_Notes, accessed September 2017). The Weather Research and Forecasting (WRF) Model, version 3.4 [Skamarock and Klemp, 2008] was run offline by the EPA to generate meteorological fields [EPA, 2014b] (temperature, boundary layer height, humidity, three dimensional winds, etc.) processed with the Meteorological Chemistry Interface Processor (MCIP) version 4.2 [Otte and Pleim, 2010] before being ingested into CMAQ. WRF is initialized with the North American Model (12NAM) provided by the National Climatic Data Center (NCDC), also taken as meteorological boundary conditions. The generated meteorological fields are also used as input to the Sparse Matrix Operator Kernel Emissions (SMOKE) model, version 3.5.1, which generates gridded anthropogenic emission fields (Section 1.3.2.1). Both WRF and CMAQ were run at 12 km $\times$ 12 km horizontal resolution, for a model domain covering the eastern United States (Figure 2-4). The figure depicts average maximum 8-hr ozone at the surface for July 2011, from the baseline CMAQ simulation (BSE). This figure shows the extent of the CMAQ domain in the Eastern United States. Both WRF and CMAQ have 34 vertical layers (σ coordinate) from the surface to about 20 km, with $\sim$ 20 layers in the lowest 2 km. Convective conditions are simulated with the asymmetric convective model (ACM2) [Pleim, 2007] in WRF, allowing for rapid upward transport in buoyant air parcels and turbulent diffusion induced by vertical shear.

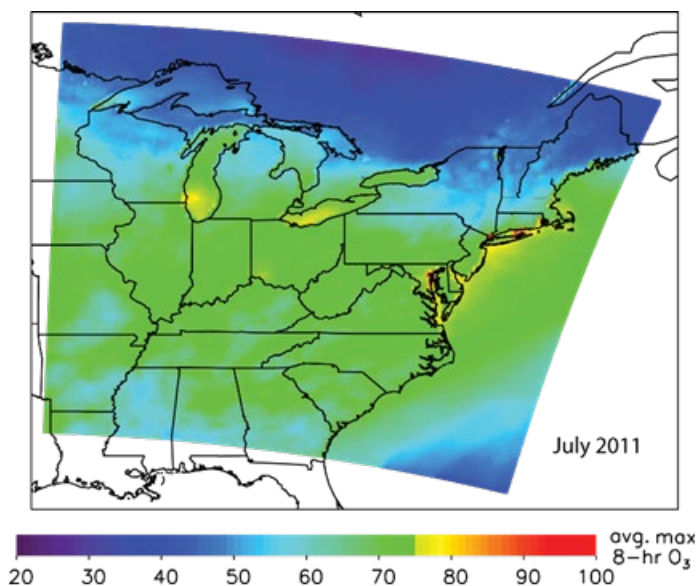


Figure 2-4 Spatial distribution of average maximum 8-hr ozone for July 2011 at the surface from the BSE simulation. Colored areas depict the CMAQ domain for simulations used in this study.

electricity-generating) software for temporalization. The Motor Vehicle Emission Simulator 2014 (MOVES2014) was used to provide estimates of emissions from cars, trucks, and motorcycles [EPA, 2014], for the summer of 2011. Initial and boundary conditions for CMAQ are obtained from the GEOS-CHEM v8-03-02 global chemistry model, run at a horizontal resolution of $2.0^{\circ} \times 2.5^{\circ}$ (latitude, longitude) [Bey *et al.*, 2001].

Isoprene (C_5H_8), present in large amounts in the Eastern United States, and other biogenic emissions were simulated using either the Biogenic Emissions Inventory System, version 3.6.1 (BEISv3.61) [Bash *et al.*, 2016] or Model of Emissions of Gases and Aerosols from Nature, version 2.10 (MEGANv2.10) [Guenther *et al.*, 2012]. Most of the simulations shown below are based on BEISv3.61, which leads to better agreement between measured and modeled HCHO and C_5H_8 than found upon our use of MEGANv2.10 [see also Kaiser *et al.*, 2018]. A detailed comparison of BEISv3.61 and MEGANv2.10 is given by Bash *et al.* [2016]. The following section provides more detail about MEGANv2.10 and BEISv3.61 and was published as supplements to this paper.

Emissions from electrical generation units (EGUs) are created from the Continuous Emission Monitoring System (CEMS) database, using the Eastern Regional Technical Advisory Committee (ERTAC;

[https://www.epa.gov/air-emissions-inventories/eastern-regional-technical-advisory-committee-ertac-](https://www.epa.gov/air-emissions-inventories/eastern-regional-technical-advisory-committee-ertac-electricity-generating)

In this body of work either BEISv3.61 or MEGANv2.10 are utilized for biogenic emissions. Both algorithms use information on vegetation type and canopy characteristics as well as the temperature and solar radiation fields from WRF. Biogenic volatile organic compound (BVOC) emissions for BEIS and MEGAN use the same empirical algorithm, based on work of Guenther et al. [2006]. Differences between BEISv3.61 and MEGANv2.10 occur in the calculation of emission factors, type of canopy model, and the number of vegetation species. For example, BEISv3.61 uses species- or species-group-specific emission factors from the Biogenic Emission Landuse Database (BELD 4). The new version of BELD 4 integrates Moderate Resolution Imaging Spectroradiometer (MODIS) plant function types and the 2006 National Land Cover Database (NLCD), whereas MEGANv2.10 uses 16 different global plant functional types as emission factors [Bash et al., 2016].

Table 2-1 Configuration of different CMAQ simulations

	BSE	SCI	SCI-PAN	SCI-MGN
CMAQ version	5.0.2	5.0.2	5.0.2	5.0.2
Chemical Mechanism	CB05-TUCL	CB05-TUCL	CB05-TUCL	CB05-TUCL
Biogenic Emissions	BEIS v3.61	BEIS v3.61	BEIS v3.61	MEGAN v2.10
50% mobile NO _x	No	Yes	Yes	Yes
Photolysis rate(NTR)×10	No	Yes	Yes	Yes
Changes in PAN chemistry	No	No	Yes	No

We present results of four CMAQ simulations, detailed below as well as in Table 2-1. The first simulation was conducted using the CB05-TUCL mechanism, anthropogenic emissions based on the 2011 NEI, and biogenic emissions from BEISv3.61. This model run is our baseline simulation (BSE) and reflects the CMAQ modeling system

distributed by the U.S EPA at time of paper submission. Next, we describe three other configurations of CMAQ as well as the motivation for these runs.

It has been shown that simulations of NO_y using the 2011 NEI overestimate observed NO_y by 33% or more in the Baltimore-Washington airshed, which has been attributed to a factor of 2 overestimate of mobile NO_x emissions within the NEI [Anderson *et al.*, 2014; Travis *et al.*, 2016, McDonald *et al.*, 2018]. Prior analysis of the urban to rural ratio of NO_x simulated by CMAQ in baseline configuration reveals that NO_x is either converted too quickly to a reservoir species or the meteorology within CMAQ causes NO_x to remain too close to urban source regions, possibly due to inefficient venting of the boundary layer [Castellanos *et al.*, 2011; Canty *et al.*, 2015]. Our second configuration of CMAQ assumes two changes relative to baseline: a 50% reduction in the mobile emission of NO_x [Anderson *et al.*, 2014] and a factor of 10 increase in the photolysis rate of alkyl nitrates (J_{NTR} ; ANs are lumped to one species in CB05-TUCL called NTR) [Canty *et al.*, 2015]. We term this simulation the Science Framework (SCI) because these specific modifications to the model are motivated by analysis of observations to determine the appropriate changes to the CB05-TUCL mechanism and emissions needed to achieve good agreement between modeled and measured NO_x , NO_2 , NO_y , and ANs [Anderson *et al.*, 2014; Canty *et al.*, 2015; Goldberg *et al.*, 2016]. In the baseline simulation the lifetime of NTR due to photolysis during summer is ~ 10 days, with J_{NTR} being calculated using the cross section of isopropyl nitrate that produces NO_2 and HO_2 . However, the most abundant species in the family of alkyl nitrates are hydroxynitrates of biogenic origin, with lifetimes on order of ~ 1 day [Horowitz *et al.*, 2007; Perring *et al.*, 2009; Beaver *et al.*, 2012]. To account for the more abundant shorter-lived alkyl nitrate species, a factor of 10 increase has been applied to J_{NTR} . These changes bring CB05-TUCL into better agreement with the representation of alkyl nitrates within mechanisms such as RACM2.

We now turn to oxidized VOCs, specifically peroxyacetyl nitrate (PAN) and its homologues. Within CB05-TUCL, the peroxy nitrate family is represented by three terms: PAN, PANX, and OPAN. Here, PAN refers to $\text{CH}_3\text{C}(\text{O})\text{OONO}_2$, PANX represents higher order oxidized peroxyacyl nitrates such as MPAN and PPN, OPAN considers organic peroxyacyl nitrates such as p-methylbenzyl nitrate

(CH₃C₆H₄CH₂ONO₂) [Bethel *et al.*, 2000], produced by decomposition of unsaturated dicarbonyl compounds. During D-AQ, total peroxy nitrates were measured via laser induced fluorescence (Table 2-3). Below, we show that the sum of PAN+PANX+OPAN (termed PANs) from the baseline (BSE) and science (SCI) simulations are more than a factor of 2 larger than observed PANs. Consequently, we consider a third run of CMAQ, termed Science-PAN (SCI-PAN) designed to improve the model representation of oxidized peroxyacyl nitrates.

Here we describe the chemical kinetics of the SCI-PAN run. Peroxyacetyl nitrate is the most studied and usually most abundant of all peroxy nitrate compounds (e.g., Singh *et al.* [1992], LaFranchi *et al.* [2010], Phillips *et al.* [2013]). The thermal decomposition rate of PAN has been determined by several laboratory studies, over a wide temperature range (e.g., Bridier *et al.* [1991]; Kabir *et al.* [2014]), but not at temperatures below 280 K. The decomposition rates of other peroxy nitrate compounds are less well quantified. Within CB05-TUCL, the same numerical values are used for the thermal decomposition of PAN and PANX: i.e., low and high pressure limits of $4.9 \times 10^{-3} \exp(-12100/T) \text{ s}^{-1}$ and $5.4 \times 10^{16} \exp(-13830/T) \text{ s}^{-1}$, respectively. These numerical values originate from Atkinson *et al.* [2006] (here after IUPAC06), which also recommends the use of N=1.4141 (broadening factor) for the pressure dependence in the fall-off region for this rate constant. However, the CB05-TUCL mechanism within the CMAQ code distributed by EPA uses a value of N=1 for the thermal decomposition of PAN and PANX, which appears to be an inadvertent mistake in the RXDT.f file distributed by the EPA. To be consistent with the code distributed by EPA, we also use N=1 for our BSE and SCI simulations. The use of N=1 (CB05-TUCL code) rather than the correct value of N=1.4141 (IUPAC06 table) results in a 12% increase in the thermal decomposition of PAN at 298 K and 1 bar (Table 2-2).

The IUPAC recommendation for the thermal decomposition of PAN was updated in February 2014 ([http://iupac.pole-ether.fr/htdocs/datasheets/pdf/ROO_15_CH3C\(O\)O2NO2_M.pdf](http://iupac.pole-ether.fr/htdocs/datasheets/pdf/ROO_15_CH3C(O)O2NO2_M.pdf)). This update, which we refer to as IUPAC14, was based on reanalysis of older laboratory studies. Specifically, IUPAC14 recommends low and high pressure limits of $1.1 \times 10^{-5} \exp(-10100/T) \text{ s}^{-1}$ and $1.9 \times 10^{17} \exp(-14100/T) \text{ s}^{-1}$, respectively, as well as N=1.4141.

The new recommendation for k_{PAN} (thermal decomposition rate of PAN, units s^{-1}) is in good agreement with the recent laboratory study by Kabir et al. [2014] (Figure 1-3). The IUPAC14 value of k_{PAN} is 44% larger than the IUPAC06 recommendation at 298 K and 1 bar (Table 2-2). We use IUPAC14 for the SCI-PAN simulation for PAN and PANX. The value of k_{PAN} for the IUPAC14 simulation is 29% higher than the value used in our BSE, SCI, and SCI-MGN runs of CMAQ (Table 2-3 and Figure 2-5). More recent versions of the chemical mechanism, such as CB05e51 and CB6r3, have implemented a broadening factor of $N=1.41$ in the distributed code at the time of paper submission. However, both of these two new mechanisms use the IUPAC06 recommendation for the low and high pressure limits of the k_{PAN} . As a result, k_{PAN} in the CB05e51 and CB6r3 chemical mechanisms is underestimated (Figure 1-3; green line) compared to most laboratory measurements. This has also been noted by Appel et al. [2017] who used CMAQv5.1 and implemented IUPAC14 and $N=1.41$ into CB5e51. Finally, the JPL15 recommendation for k_{PAN} (not used in any recent CMAQ mechanism) results in a value that is 11% slower than IUPAC14.

Within CMAQ, higher order oxidized peroxyacyl nitrates (PANX) are assumed to be lost by reaction with OH. The CB05-TUCL mechanism uses a value of $3.0 \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ for the temperature independent rate constant for the reaction of OH with PANX. The origin of this particular constant is, according to Yarwood et al. [2005], the “average based on NASA/JPL [2003] $\text{CH}_3/\text{C}_2\text{H}_5$ nitrate ratio and IUPAC [2005] PAN+OH” (here IUPAC [2005] refers to the Atkinson et al. [2006] publication). Orlando et al. [2002] reported a value of $3.2 \pm 0.8 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ for the reaction of OH with MPAN, a factor of 100 faster than used within CB05-TUCL (note: MPAN is a main component of PANX when isoprene emissions are high). Since the CB05e51 update to CB05 released November 2015 at https://www.airqualitymodeling.org/index.php/Cb05e51_ae6_v5.1_mech.def specifies a rate constant of $2.9 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ for OH+MPAN, we make use of this value in the SCI-PAN simulation. This rate constant lies well within the experimental uncertainty of the laboratory determination [Orlando et al., 2002]. In summary, our third simulation termed SCI-PAN assumes a significant increase in loss rate of PAN and PANX via both thermal decomposition and reaction with OH.

Specifically, SCI-PAN uses: a) the IUPAC14 recommendation of the low and high pressure limit for the thermal decomposition of PAN, for both PAN and PANX including $N=1.4141$ for the pressure dependence; b) $2.9 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ (same as in CB05e51) for the temperature independent rate constant of the reaction of PANX with OH. Most of the modeled differences of PAN and PANX between SCI and SCI-PAN shown in section 3 are due to changes in the thermal decomposition rather than the increase in the rate constant for PANX+OH. The comparison of observed and simulated PANs shown in the next section suggests that in the actual atmosphere, the loss rate (i.e., thermal decomposition and/or reaction with OH) of PAN and PANX occurs about a factor of 2 more quickly than represented in the CB05-TUCL mechanism. The faster thermal decomposition rate of IUPAC14 improves the agreement between modelled and measured PAN species.

In this section I am detailing the calculation of k_{PAN} . This section has been added from the supplements of this published work. The following analysis represents the basis on how k_{PAN} was changed within CMAQ. Three different recommended values of k_{PAN} are considered: IUPAC06, IUPAC14, and JPL15. Thus far, the carbon bond chemical mechanisms in CMAQ use the preferred values from IUPAC06 to calculate k_{PAN} within the model (i.e. CB05-TUCL, CB05e1, CB6r3, etc.). Figure 2-5 shows the Arrhenius plot of (k_{PAN}) from recommendations (IUPAC06 in green; JPL15 in black; IUPAC14 in red) and CMAQ (based on how this reaction is coded in the subroutine); in light blue (using IUPAC06) and dark blue (using IUPAC14) versus inverse temperature. CMAQ values of k_{PAN} tend to be higher than the respective recommended values (i.e., IUPAC06 compared to CMAQ (IUPAC06) and IUPAC14 compared the CMAQ (IUPAC14)) because, as explained in the main paper, the CMAQ mechanism was distributed with N set to 1 rather than the recommended value of 1.4141.

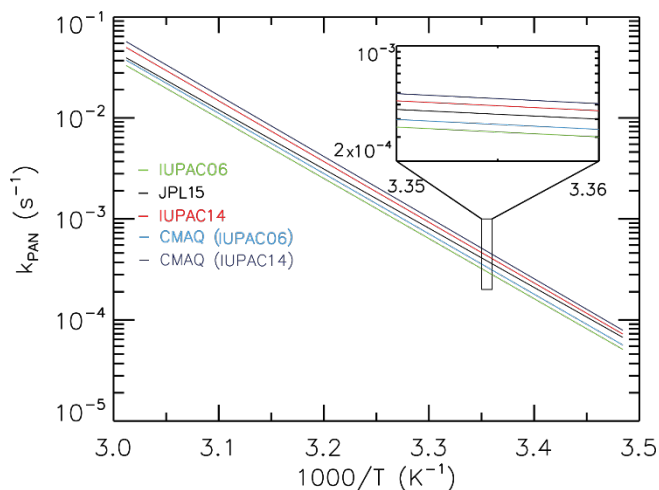


Figure 2-5 Arrhenius plot of the thermal decomposition rate of PAN (k_{PAN}) versus inverse temperature. IUPAC (2006; green), JPL (2015; black), and IUPAC (2014; red) are recommended values of PAN thermal decomposition rates. CMAQ (IUPAC06; light blue) and CMAQ (IUPAC14; dark blue) represent k_{PAN} with the recommended values of IUPAC (2006) and IUPAC (2014) respectively using the calculation as implemented in CMAQ. Insert shows zoomed plot at 298K.

for JPL15 but instead make use of the forward reaction rate and equilibrium rate constant to calculate k_{PAN} .

Table 2-2 Rate constants for k_{PAN} evaluated at 298K and 1 bar for various recommendations and values of N that enter into the IUPAC expression.

Source	N	Rate s^{-1}	CMAQ Run
IUPAC06	1.4141	2.98×10^{-4}	
CMAQ CB05-TUCL based on IUPAC06	1.0	3.33×10^{-4}	BSE, SCI, SCI-MGN
IUPAC14	1.4141	4.30×10^{-4}	SCI-PAN
IUPAC14 altered to examine sensitivity of k_{PAN} to N	1.0	4.75×10^{-4}	
JPL15	n.a.	3.81×10^{-4}	

As shown in Figure 2-3, the IUPAC14 recommendation for k_{PAN} is in very good agreement with numerous laboratory measurements. Therefore, rate constant for the thermal decomposition in chemical mechanisms used in air quality models should be updated to the IUPAC14 recommendation. Presently, the latest CMAQ mechanism,

Table 2-2 provides the rate constants from the various sources, all 298 K and 1 bar, as found using E1 (see Chapter 1) and the value of N given in the table. The consequence of using $N = 1$ in the CB05-TUCL mechanism, rather than the recommended value, is a ~10% increase in the thermal decomposition rate relative to the reaction rate compared to the IUPAC recommendation. The JPL15 rate evaluated at 298 K and 1 bar is also given, for completeness. We are not using Equation (1) to determine k_{PAN}

CB6r3, still uses the IUPAC06 recommendation, with the correct value of 1.41 for N. As shown in Table 2-2, this results in a value of k_{PAN} that is nearly 40% slower than the IUPAC14 value. Fortuitously, the incorrect designation of $N = 1$ in CMAQ code caused k_{PAN} to lie closer to IUPAC14, and hence laboratory data, than is found upon correcting the error in N. CMAQ simulations will likely continue to overestimate PAN until the IUPAC14 value of k_{PAN} is correctly implemented.

The fourth simulation uses biogenic emissions of VOCs from MEGANv2.10 [Guenther *et al.*, 2012]. For the Baltimore-Washington airshed (at the six surface sites) and during meteorological conditions on D-AQ flight days, the emission of isoprene found using MEGANv2.10 is about a factor of 1.5 larger (a factor of 2 for the whole CMAQ domain) than found using BEISv3.61. A major focus of our paper is the comparison of $k[\text{HO}_2] + \sum k[\text{RO}_2]$ from CMAQ to the value of this quantity (in RO_x) calculated from D-AQ data. We have coupled the use of MEGANv2.10 with the assumptions for chemical kinetics of the SCI run (i.e., default kinetics for PAN and PANX in CB05-TUCL) of CMAQ because this combination yields the largest reasonable value of $k[\text{HO}_2] + \sum k_i[\text{RO}_2]_i$ given the available choices. We term this final simulation SCI-MGN (Table 2-1).

2.5 Results and Discussion

A map of the Baltimore-Washington airshed is depicted in Figure 2-1. The six ground sites: Beltsville, Padonia, Aldino, Fairhill, Edgewood, and Essex are labeled black and the closest CMAQ grid points and boxes are depicted in red. We have aligned CMAQ output for the four simulations to surface and aircraft measurements both in space (vertically as well as horizontally for aircraft data) and time, by using CMAQ output at the nearest grid point for the closest time.

2.5.1 Ozone and Its Precursors

Here, we compare three of the four CMAQ simulations of surface O_3 to observations obtained at six D-AQ ground stations (Figure 2-6). Figure 2-6a to Figure 2-6c show 8-

hr averaged surface O₃ for July 2011 between 10 am and 7 pm versus CMAQ output (also 8-hr average, i.e. 8-hr O₃ for 10 am, 8-hr O₃ for 11 am, etc.).

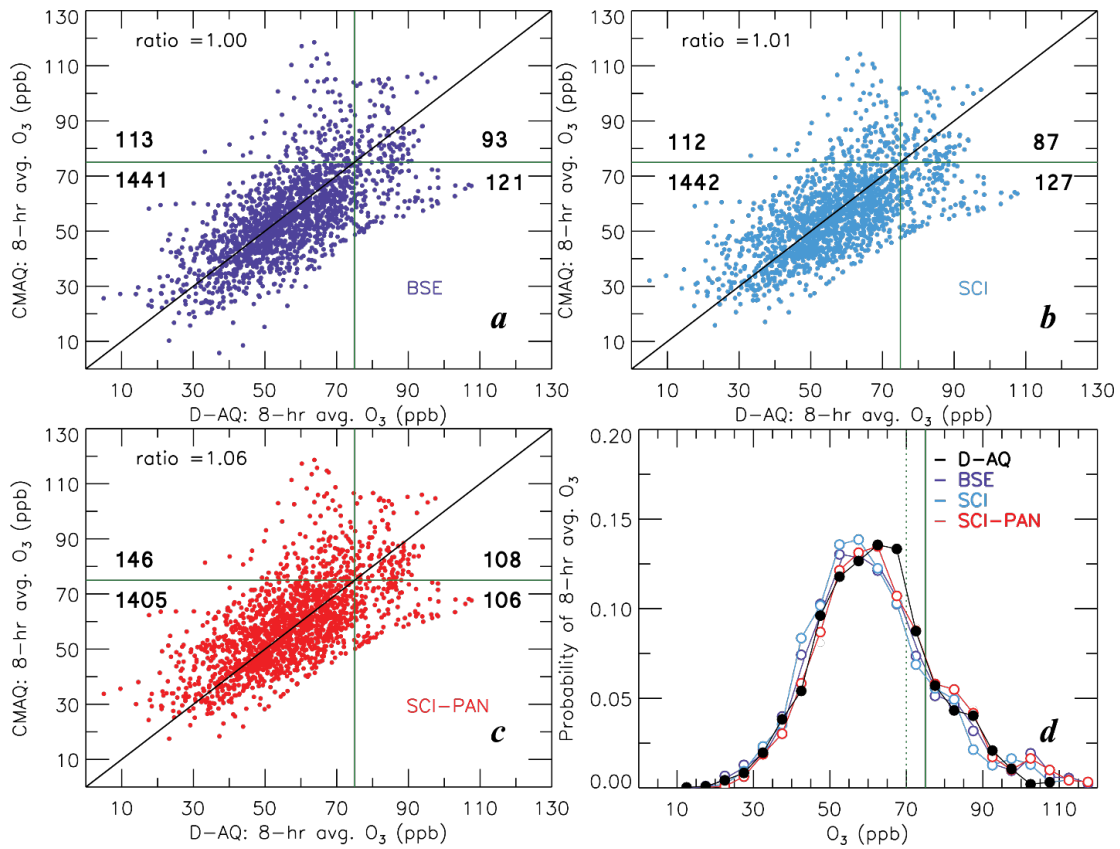


Figure 2-6 Panels a)-c) show 8-hr averaged O₃ from D-AQ surface data vs. CMAQ output for the BSE (a), SCI (b), and SCI-PAN (c) simulations. The black line depicts the 1:1-line and the green lines depict the old O₃ standard of 75 ppb. Average ratio is the ratio of CMAQ output over D-AQ data. The four numbers in each quadrant reflect the number of points in each section. Panel d) shows probability of 8-hr averaged O₃ from six Maryland ground sites (Beltsville, Padonia, Aldino, Fairhill, Edgewood, and Essex) in 5 ppb O₃ bins for measurements (black) and three CMAQ simulations (colored) for the month of July 2011. The dashed green line depicts the new O₃ standard of 70 ppb (since 2015) and the solid line the old O₃ standard of 75 ppb.

The green lines depict the 75 ppb NAAQS O₃ standard, in effect at the time of measurements, dividing each panel into four sections.

Figure 2-6a to Figure 2-6c show that the baseline model simulation and the modified simulations all capture measured 8-hr averaged surface O₃ quite well, as reflected by the mean ratio of CMAQ output over D-AQ data (given in each panel) being close to 1. The number of data points in each quadrant is about the same in Figure 2-6a and Figure 2-6b, which show measurements versus the BSE and SCI CMAQ simulations,

respectively. The lower left and upper right quadrants of Figure 2-6a and 2-6b constitute 1534 (=1441+93; BSE) and 1529 (=1442+87; SCI) data points. Therefore, ~1534 (~87%) of the BSE model results correctly predict the times when O₃ was above (93) or below (1441) the federal standard. However, 234 (~13%) of the simulations lie either in the upper left (CMAQ predicts O₃ to exceed the standard, but this did not occur) or lower right (observed O₃ exceeded the standard but was not captured by CMAQ) for BSE. For the SCI simulation, 239 points lie either in the upper left or lower right quadrants, which is very similar to the BSE simulation. The total number of data points in these two quadrants in Figure 2-6c, the SCI-PAN CMAQ simulation, is slightly larger compared to the other simulations. The number of SCI-PAN points giving an incorrect prediction of 8-hr averaged O₃ has grown by 18 points compared to BSE, a ~1% increase relative to the total number of data points shown on any of the three panels. It is important to note that we are analyzing 8-hr averaged O₃ in measurements and simulations, over the course of an entire month. Therefore, the over-estimation of surface O₃ by the CMAQ simulations as shown in previously publications using a different metric, averaged daily maximum 8-hr O₃ [Nolte *et al.*, 2008; Ring *et al.*, 2018; Trail *et al.*, 2014, Travis *et al.* 2016], is not apparent Figure 2-6.

Figure 2-6d shows the probability distribution (PD) of 8-hr averaged O₃ for the month of July 2011. The data points (black) and the three CMAQ simulations (colored) using BEISv3.61 are grouped into 5 ppb O₃ bins. Best agreement between measurements and simulation of the PD of 8-hr averaged O₃ is achieved by the SCI-PAN simulation, where the mean of the absolute difference between the black PD curve (observation) and red curve (model) is 0.005. The mean of the absolute differences for the BSE and SCI simulations relative to observation are 0.008 and 0.009, respectively. While the analysis of the PD of 8-hr averaged O₃ identifies the SCI-PAN simulation to be closest to observations, such is not the case when comparing scatter plots of 8-hr averaged O₃ (Figure 2-6a to Figure 2-6c). Modifications to the baseline run reflected in the SCI and SCI-PAN simulations increase 8-hr O₃ (i.e., ratio relative to all observations is larger than for BSE), resulting in slightly worse agreement with observed O₃ for much of the domain but better agreement (particularly for SCI-PAN) with the PD of the data for

values of O₃ between 45 and 55 ppb as well as between 70 to 80 ppb. The SCI and SCI-PAN simulations also provide better representation of O₃ precursors, as shown below. Next, we compare D-AQ aircraft measurements to the three CMAQ simulations of five dominant NO_y species (NO, NO₂, HNO₃, PANs, NTR). Figure 2-7 shows the NO_y species averaged throughout the convectively mixed layer (CML) from simulations and measurements of all 248 P-3B aircraft spirals collected at the six locations during the 14 flight days. Numerical values along with measurement uncertainties of the quantities shown in Figure 2-7 are given in Table 2-3. The table provides numerical values of the five major nitrogen species (NO, NO₂, HNO₃, NTR, and PANs) measured during D-AQ. These values represent the average over all spirals within the mixed layer, and are depicted in Figure 2-7.

Table 2-3 Measured (D-AQ) and 3 modeled (CMAQ) NO_y species mixing ratios averaged over all P3-B spirals within the mixed layer. NTR and PANs are acronyms used in CMAQ encompassing all alkyl nitrates and peroxy nitrates, respectively

	NO (ppb)	NO ₂ (ppb)	NO _x (ppb)	HNO ₃ (ppb)	NTR (ppb)	PANs (ppb)	NO _y (ppb)
D-AQ	0.269 ±0.013	1.194 ±0.239	1.463 ±0.239	1.456±0.218	0.434±0.065	0.925±0.093	4.278±0.343
BSE	0.192	1.217	1.409	1.586	1.175	1.821	5.991
SCI	0.140	0.927	1.067	1.295	0.701	1.698	4.761
SCI-PAN	0.162	1.060	1.222	1.432	0.722	1.306	4.682
SCI-MGN	0.125	0.899	1.024	1.146	0.913	2.107	5.190

The single species NTR in CB05-TUCL represents alkyl nitrates such as isopropyl nitrate, n-propyl nitrate, isobutyl nitrate, and isoprene nitrates. Simulations overestimate, on average, NTR by 171% (BSE), 62% (SCI), and 66% (SCI-PAN). All of these discrepancies are much larger than the 15% 1σ accuracy uncertainty for the measurement of NTR (Table 2-3), which suggests further improvement to the representation of NTR in CB05-TUCL may be needed.

We now turn our attention to the peroxy nitrates, which serve as important reservoirs within the NO_y family. Observed ‘PANs’ is actually the sum of total peroxy nitrates, including peroxyacetyl nitrate (actual PAN), peroxy propionyl nitrate (PPN), methacryloylperoxynitrate (MPAN) and related species. The chemical mechanism CB05-TUCL lumps these species into PAN, PANX, OPAN; the sum is shown as PANs in Figure 2-8. The breakdown of PANs within CMAQ (i.e., PAN, PANX, and OPAN)

is shown in Figure 2-6, along with the D-AQ measurement of peroxy nitrates. Our CMAQ simulations overestimate, on average, PANs by 97% (BSE), 84% (SCI), and 30% (SCI-PAN) (Figure 2-8, Table 2-3, and Figure 2-6). These discrepancies are also much larger than the 10% 1σ measurement accuracy of PAN (Table 2-3), indicating that CMAQ overestimates the peroxy nitrate component of NO_y through the PBL. This accumulation of peroxy nitrates within the PBL in CMAQ could be related to a tendency of anthropogenic NO_x to be located more closely to large urban areas than is apparent from satellite observations of column NO_2 [Canty *et al.*, 2015].

This section is added from the supplements and discusses the 1σ uncertainty of the IUPAC14 preferred values for k_{PAN} . As mentioned before, in 2014 the preferred values from IUPAC for low and high pressure rate coefficients were revised. Rate coefficients from Bridier *et al.* [1991], Tuazon *et al.* [1991], Roberts and Bertram [1992], and Sehested *et al.* [1998] were fit, using a falloff a curvature parameter (F_c) of 0.3. Figure also 2-5 shows the 1σ value of IUPAC14 ($\text{IUPAC14} \pm 1\sigma$; red dashed lines) representing an increased/decreased thermal decomposition rate. The 1σ -uncertainty was calculated using the following equation:

$$\Delta \log k(T) = (\Delta \log k(298K) + 0.4343 \left\{ \frac{\Delta E}{R} \left(\frac{1}{T} - \frac{1}{298} \right) \right\}) / 2 \quad (\text{E2})$$

where $\Delta \log k(298K)$ and $\frac{\Delta E}{R}$ are provided on the IUPAC14 data sheet for the low and high pressure limit. There is no overlap between the measurements and the $\text{IUPAC14} + 1\sigma$ line (Figure 1-3; upper red dashed line), even when considering the uncertainties from the laboratory measurements.

Though the $\text{IUPAC14} + 1\sigma$ value of k_{PAN} is an overestimation compared to the laboratory data, we have implemented it into CMAQ as a sensitivity study. This new simulation, denoted $\text{SCI-PAN} + 1\sigma$, is identical to the SCI-PAN simulation described in main except for the use of a faster rate for the thermal decomposition of PAN (and PANX). There are no laboratory studies of PANX since PANX represents many different peroxy nitrates such as MPAN and PPN. Newer versions of the chemical mechanism such as CB05e51 have a more explicit handling of peroxy nitrates i.e. MPAN is its own species. As mentioned before, in our simulations which uses CB05-TUCL we use the thermal decomposition rate of PAN for PANX. Values of PANs from

the SCI-PAN+1 σ simulation are in better agreement with measured PANs (Figure 2-7). Also, the SCI-PAN+1 σ simulation results in an OPE of 7.31 ± 3.33 , which is larger than OPE of 6.18 ± 2.99 from the SCI-PAN simulation. The OPE value from the SCI-PAN+1 σ simulation is in better agreement with measurements (OPE = 8.44 ± 4.11). Therefore, the kinetics of major members of the PAN family may be an appropriate target for future laboratory study. Conversely, the change of thermal decomposition rate from IUPAC06 to IUPAC14 or IUPAC14+1 σ does not affect calculated values for inRO_x; all three simulations yield values of $0.0012 \pm 0.0005 \text{ s}^{-1}$. The shortfall of CMAQ values of inRO_x compared to inRO_x inferred from D-AQ data, for all of these simulations, suggests one or more VOC compounds degrades more efficiently into HO₂ and/or RO₂ in the actual atmosphere than represented by CMAQ.

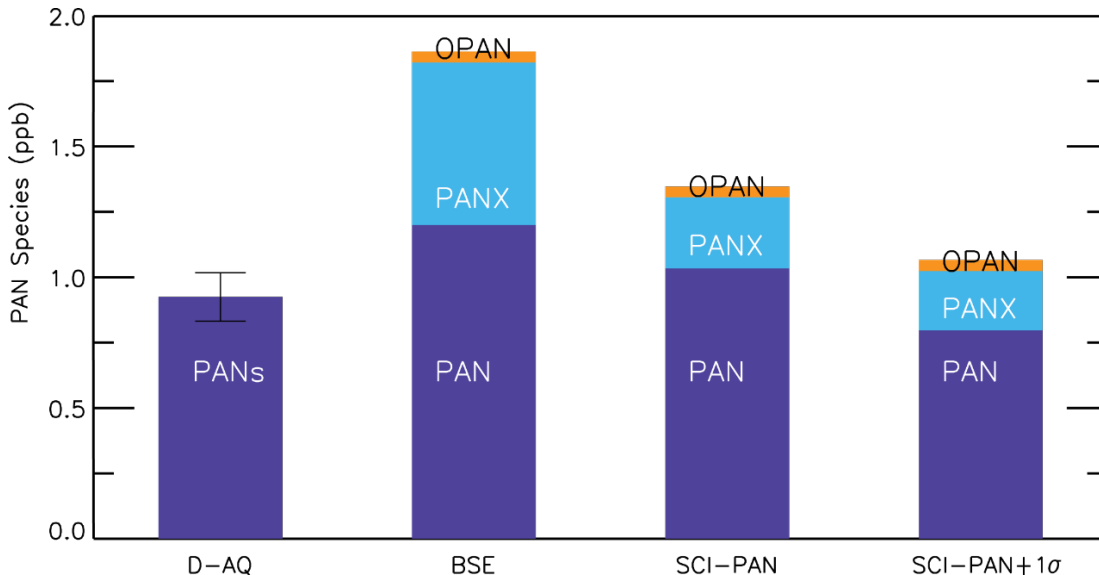


Figure 2-7 Comparison of measured (D-AQ) and 3 modeled (CMAQ) averaged PAN species from all P3-B spirals within the mixed layer.

Very good agreement of measured and modelled peroxy nitrates can be achieved upon using a value of k_{PAN} increased by the 1 σ uncertainty for the low and high pressure limits given by IUPAC14 (Figure 2-7). However, this 1 σ increase in the rate of PAN thermal decomposition results in a value of k_{PAN} that is noticeably larger than six laboratory determinations (Figure 1-3). While it is tempting to adjust k_{PAN} by the 1 σ uncertainty that leads to good agreement with the D-AQ observations of PANs, we have chosen to use the actual IUPAC14 recommendation for k_{PAN} in our CMAQ

simulations shown in the main body of this paper, because this value of k_{PAN} is consistent with the suite of laboratory measurements.

We now describe measured and modelled HNO_3 , NO , NO_2 , and total NO_y . Nitric acid is an important reservoir within the NO_y family, as the formation of HNO_3 represents the termination of radical chemistry. All three CMAQ simulations shown in Figure 2-8 capture the observed concentration of HNO_3 rather well (see also Table 2-3). The SCI-PAN simulation lies closest to observed HNO_3 , with a percent difference of 1.6%. All of the simulations lie within the 1σ measurement accuracy uncertainty of 15%. Here we will focus on NO_x , rather than NO and NO_2 , since the proper simulation of the measured NO to NO_2 ratio depends on accurate representation of the photolysis frequency of NO_2 . The BSE simulation of NO_x is only 4% lower than observed. However, this simulation leads to a 40% overestimate of NO_y .

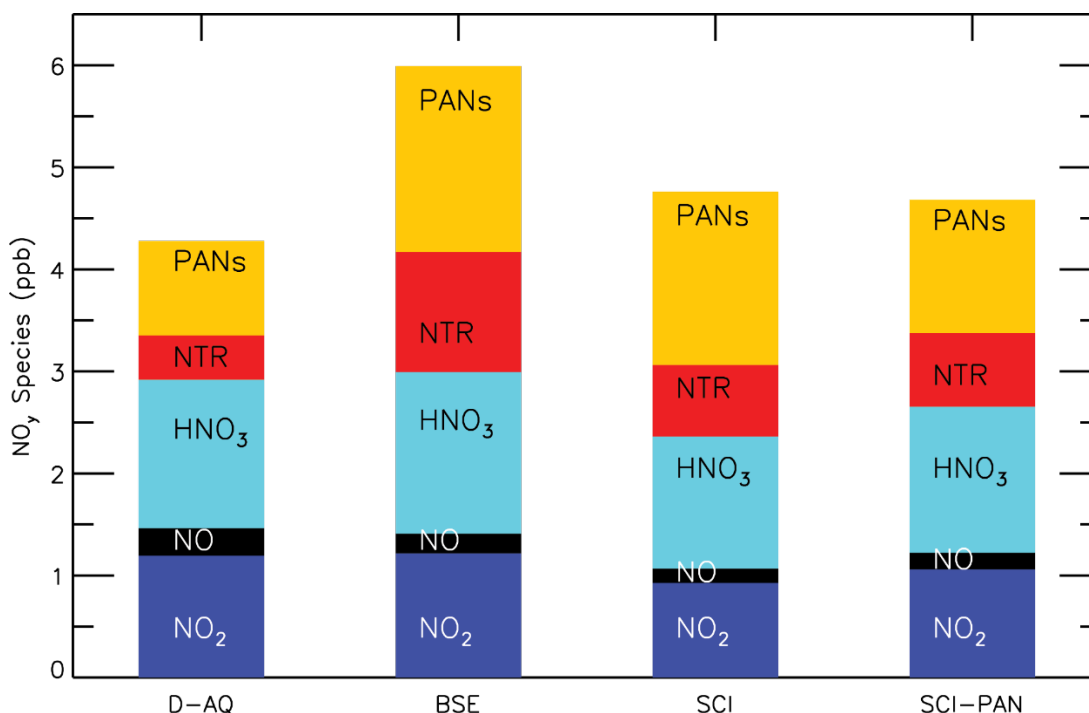


Figure 2-8 Comparison of measured (D-AQ) and modeled (BSE, SCI, and SCI-PAN) mixing ratio of various NO_y compounds (NO , NO_2 , and HNO_3) or groups (NTR and PANs), averaged over all P3-B spirals within the mixed layer. Only the five main components of the NO_y family are shown. NTR and PANs are acronyms used in CMAQ encompassing all alkyl nitrates and peroxy nitrates, respectively.

Analysis of the slope of CO anomalies versus NO_y anomalies within the CML for the D-AQ dataset resulted in the determination that mobile emissions of NO_x had

been overestimated within the NEI, by a factor of 2 for the Baltimore-Washington region during summer 2011 [Anderson *et al.*, 2014]. The SCI (and SCI-PAN) simulations both include a 50% reduction in mobile NO_x emissions as well as a few other adjustments (Table 2-1), resulting in a 27% (and 16%) underestimate of observed NO_x and an 11% (and a 9%) overestimate of total NO_y, respectively (Figure 2-8 and Table 2-3). For NO_y, both science simulations lie within the 1 σ measurement accuracy uncertainty (12%).

Reducing mobile NO_x emissions within the model framework leads to a decrease in the concentration of NO_x for the SCI and SCI-PAN simulations, resulting in slightly worse agreement with observed NO_x. However, both simulations exhibit better agreement with observed NO_y: much of this improvement is due to the changes to the thermal decomposition and OH reactivity of PAN assumed for these model runs. The simulation of NO_x is better in the SCI-PAN framework compared to the SCI simulation due to the introduction of a more realistic treatment of peroxy nitrates. The SCI-PAN run also provides good agreement with observed NTR and PAN, although both quantities are still overestimated within the model (Table 2-3). These comparisons highlight the highly coupled nature of the species that constitute the NO_y family.

Next, we compare the sum of measured alkyl nitrates (ANs; denoted as NTR to be consistent with the CMAQ specification) to simulated alkyl nitrates as well as modelled and measured PANs for the flight on 29 July 2011. Figure 2-9a and Figure 2-9c show measured NTR (colored circles) and simulated NTR (colored contours) for the BSE (Figure 2-9a) and SCI-PAN (Figure 2-9c) simulations. Figure 2-9b and Figure 2-9d show scatter plots of measured and simulated NTR for the BSE and SCI-PAN simulations. The BSE run of CMAQ overestimates NTR by a factor of 3.8 (Figure 2-9b). A large overestimate of alkyl nitrates by CMAQ has been shown for 29 July 2011 previously by Canty *et al.* [2015] using CB05 and v4.7.1 of the model.

Although the factor of 10 increase in photolysis rate of NTR suggested by Canty *et al.* improves the representation of NTR in the model, the observed values are still overestimated by a factor of 2.2 (Figure 2-9d). As noted above, further improvement in the CB05 representation of alkyl nitrates is needed. A reduction of the NTR lifetime is achieved in the CB6r2 chemical mechanism [Goldberg *et al.*, 2016] and newer

versions of the carbon bond mechanism, such as CB05e51 for CMAQv5.1 and CB6r3 included in CMAQv5.2, due to a more detailed representation of various alkyl nitrates as well as the implementation of an aerosol uptake pathway of alkyl nitrates through hydrolysis. Aerosol uptake accounts for about 60% of the loss of alkyl nitrates in the boundary layer of the southeast U.S. [Fisher *et al.*, 2016].

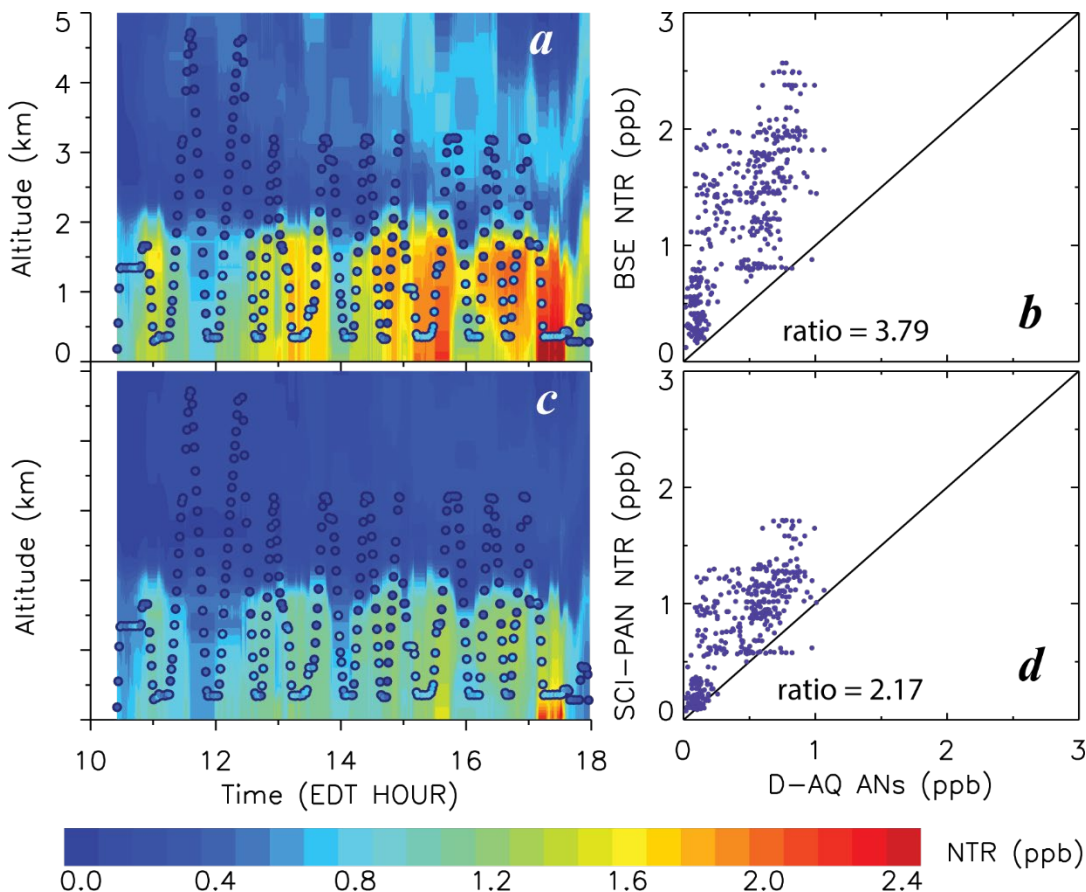


Figure 2-9 Comparison of measured and simulated alkyl nitrates (NTR) for 29 July 2011: (a) the background colored contours show baseline CMAQ (BSE) output calculated for time and location of the P-3B aircraft. Colored points show the alkyl nitrate data from the P-3B aircraft. (b) Scatterplot of aircraft measurements of NTR versus CMAQ output for the BSE simulation, where the model has been sampled at the time and place of the aircraft observations. (c) Same as (a) for the SCI-PAN simulation: i.e., CB05-TU chemical mechanism modified such that the lifetime of NTR is reduced by a factor of 10, increased rates for the thermal dissociation rate of PAN and PANX and the reaction of PANX+OH, as well as a 50% reduction in the mobile emissions of NO_x emissions. (d) Same as (b) but for the SCI-PAN simulation. The scatter plots show a 1:1-line in black; each panel also provides the mean value of modeled divided by measured NTR.

Aerosol uptake of alkyl nitrates is not included within the CB05-TUCL mechanism used here. The inclusion of aerosol uptake of alkyl nitrates in CB6r3 represents a

significant step forward in the simulation of this chemical family. These newest versions of CMAQ became available midway through our study, and our use of CMAQ v5.0.2 follows many other papers in the past few years. The D-AQ dataset provides an important future opportunity to assess the representation of alkyl nitrates within the latest versions of CMAQ, especially as chemical mechanisms are improved to provide more realistic speciation within this family.

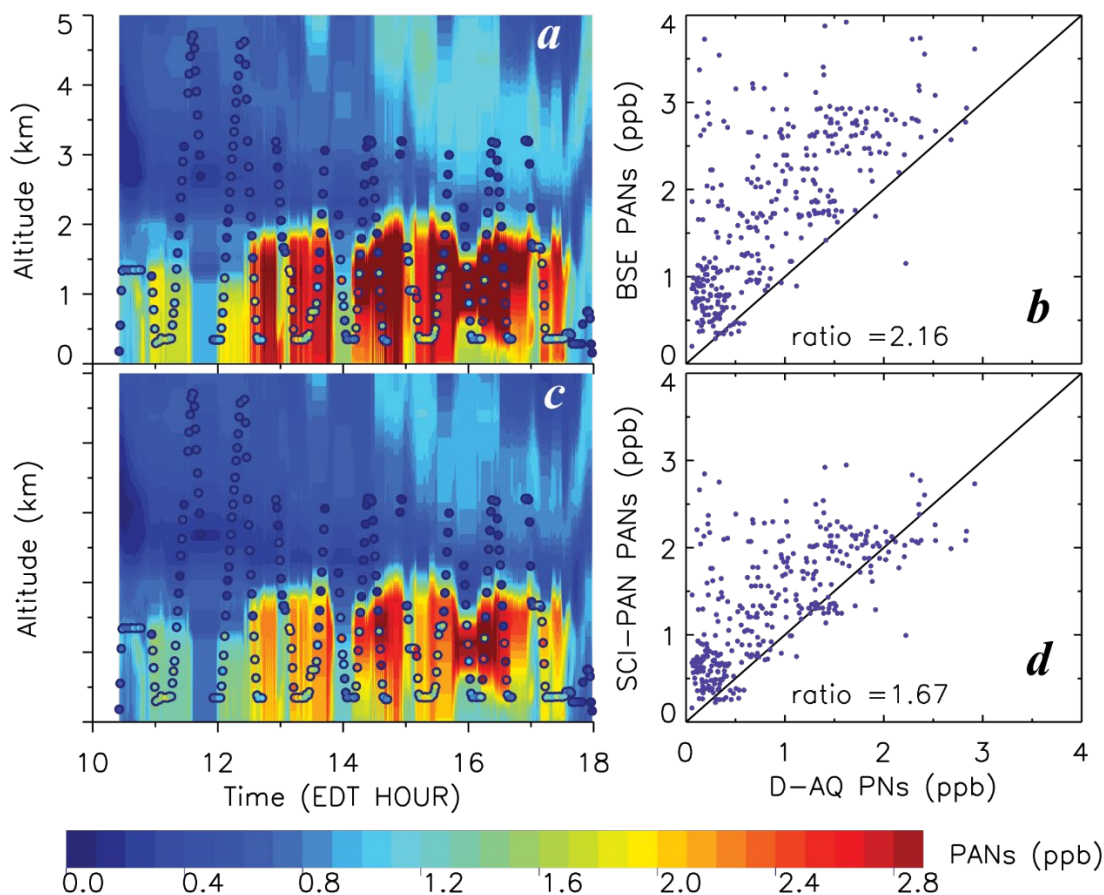


Figure 2-10 Comparison of measured and simulate peroxy nitrates (PANs) for 29 July 2011: (a) the background colored contours show baseline CMAQ (BSE) output calculated for time and location of the P-3B aircraft. Colored points show the total peroxy nitrate data (PNs) from the P-3B aircraft. Panel (b) shows a scatterplot of measurements PANs from the aircraft versus BSE output. (c) and (d) Same as (a) and (b), but for the SCI-PAN simulation. The scatter plots show a 1:1-line in black; each panel also provides the mean value of modeled divided by measured PANs.

Next we compare measured and simulated peroxy nitrates. Figure 2-10a and Figure 2-10c show measurements (colored circles) and simulations (colored contours) of peroxy nitrates (PANs) for the BSE (Figure 2-10a) and SCI-PAN (Figure 2-10c) simulations for the flight on 29 July 2011. When the color of the data points is the same

as the background (i.e., when the colors merge) the model output and measurements are in good agreement. The BSE run of CMAQ overestimates measured PANs on this day by about a factor of 2.2. The representation of PANs is improved in the SCI-PAN simulation for this flight; however, PANs are still overestimated by a factor of 1.7. These comparisons show that increasing the thermal decomposition rate of PAN and PANX improves the representation of PANs in CMAQ (Figure 2-8 and Figure 2-10). Nonetheless, on some days (i.e., 29 July 2011) modelled PANs are much larger than measured, even for the SCI-PAN simulations. When this situation occurs the model is sequestering NO_x in a form that is unavailable for photochemical production of O_3 in the Baltimore-Washington airshed. This reactive nitrogen could be released downwind of the region, but only if air parcels experience significant warming.

2.5.2 Ozone Production Efficiency

Here, we compare OPE from CMAQ to values of OPE inferred from aircraft spirals in the mixed layer conducted during D-AQ. For each spiral, OPE is derived from the slope of O_x ($\equiv \text{O}_3 + \text{NO}_2$) versus NO_z ($\equiv \text{NO}_y - \text{NO}_x$) for data collected within the convectively mixed layer (pressure > 820 hPa; solid circles in Figure 2-11), as explained in Section 1. A value for OPE is only computed if the relation between O_x and NO_z for a specific spiral exhibits a value of r^2 (squared correlation coefficient of O_x versus NO_z) greater than 0.65. This criteria is applied independently to both the D-AQ data and the CMAQ output. A recently published paper by Ninneman et al. [2017] suggests using r^2 greater than either 0.4 or 0.5 to assure the sampling of homogeneous conditions characterized by high temperatures and low or no cloud cover. We use a conservative threshold of $r^2 \geq 0.65$, resulting in a subset of 86 spirals out of the 158 for which data are available for all relevant species needed to compute O_x and NO_z (and hence OPE). Allowing a smaller threshold of $r^2 \geq 0.4$ or restricting the analysis to the same spirals for both the measurements and CMAQ output does not change any of our scientific conclusions (Figure 2-13). However, the use of $r^2 \geq 0.4$ results in larger uncertainty in OPE inferred from D-AQ data because the presence of scatter in the relation of O_x versus NO_z suggests the sampled air masses may not be chemically coherent. Influences other than production of O_3 by the cycling of NO_x combined with

conversion of NO_x to reservoirs can cause scatter in the relation. Such complicating factors include air masses with various initial abundances of O_3 and NO_x that are combined by mixing, the influence of fresh emissions on only a segment of the sampled spiral, or removal of HNO_3 by deposition [Trainer *et al.*, 1993].

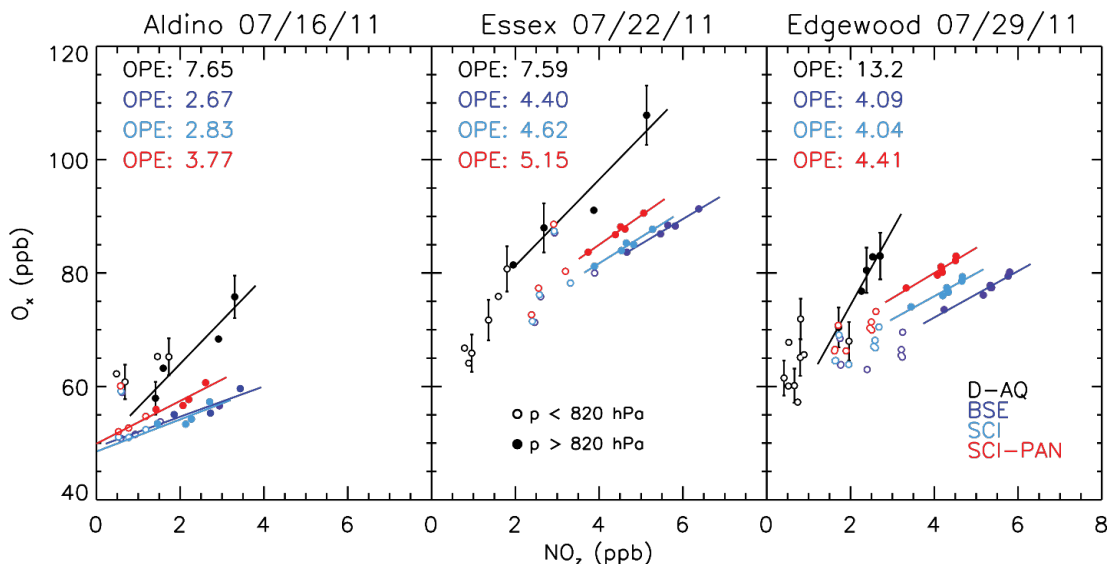


Figure 2-11 Determinations of the OPE from the relation between O_x and NO_z on three days (left panel: low O_3 ; middle panel: high O_3 ; right panel: medium O_3) and locations (Aldino, Essex, and Edgewood) in July 2011. Observations from the D-AQ aircraft with error bars (1σ total measurement uncertainty) for every second data point are in black, output from a baseline CMAQ model run (BSE) is in dark blue, output from a CMAQ model run for biogenic emissions from BEISv3.61, increased photolysis rate of NTR, and reduced mobile emissions of NO_x (SCI) is in light blue, and output using the CMAQ SCI framework along with increases to the thermal dissociation rate of PANX and reaction rate of PANX+OH (SCI-PAN) is in red. Solid circles depict values within the mixed layer and open circles depict values above mixed layer. The various lines show linear least squares fits to O_x versus NO_z data collected in the mixed layer (solid circles); OPE is the slope of the linear least squares fit lines.

Figure 2-11 shows representative O_x versus NO_z on three days and locations for measurements (black) and simulations (colored). Closed circles depict samples collected at pressures greater than 820 hPa, in the CML. Open circles depict samples collected at pressures less than 820 hPa, above the CML. The leftmost panel is representative of a low O_3 day (surface max. 8-hr O_3 : 56 ppb), the middle panel is representative of a high O_3 day (surface max. 8-hr O_3 : 92 ppb), and the right panel is representative of a medium O_3 day (surface max. 8-hr O_3 : 78 ppb); panels are arranged chronologically. Other days with low, medium, or high maximum O_3 show results for OPE similar to that presented in Figure 2-11. Within the CML (solid circles), O_x shows

a linear dependence on NO_z in both the measurements and the model. OPE is determined from the slope of a linear fit of O_x versus NO_z of data acquired in the CML; numerical values are given on each panel of Figure 2-11. The values of OPE inferred from the D-AQ observations on these three days tends to be more than a factor of two larger than OPE computed using CMAQ output. While OPE on days with low and high O_3 in CMAQ are about a factor of 2 underestimated, the medium O_3 day shows the greatest discrepancy for OPE between measurements (D-AQ: 13.2) and simulations (BSE: 4.1, SCI: 4.0, SCI-PAN: 4.4). For these selected days and locations the SCI-PAN simulation shows best agreement with the actual atmosphere. In the following sections we will further explore the strength and weakness of the various CMAQ simulations with respect to OPE.

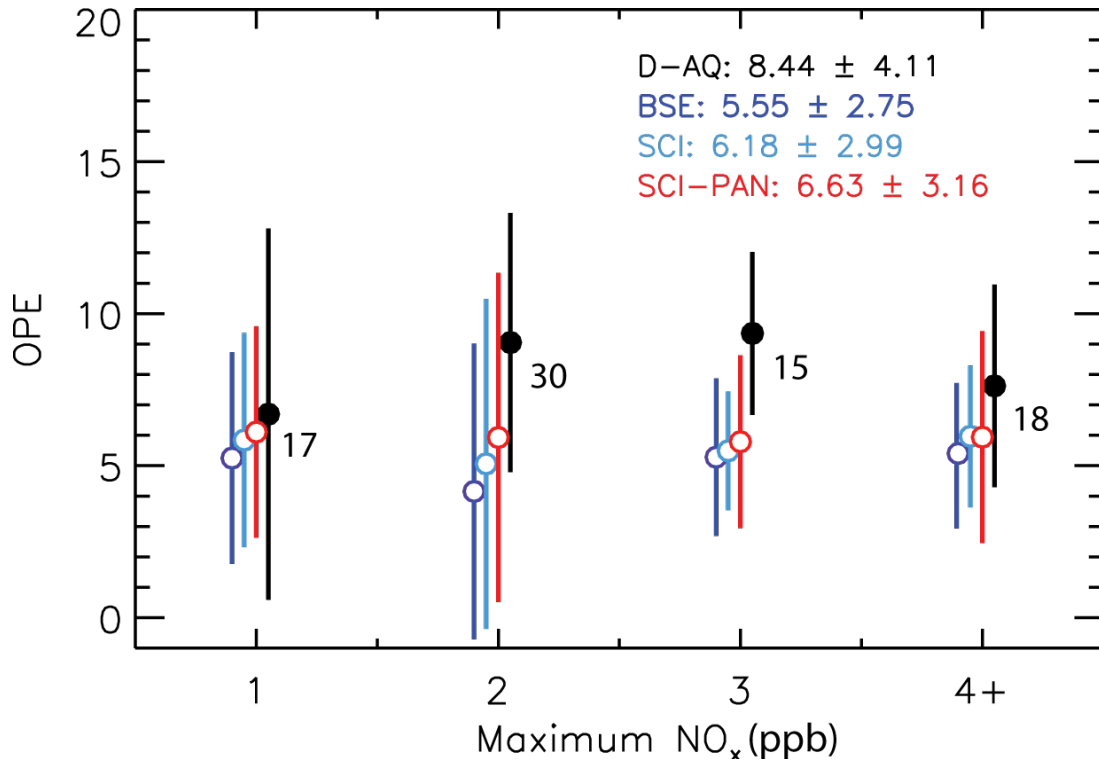


Figure 2-12. Comparison of OPE versus maximum NO_x . Circles depict mean OPE values and error bars are the 1σ standard deviation. The D-AQ aircraft data are black (solid circles), output from a baseline CMAQ model run (BSE) is dark blue, output from a CMAQ model run with increased photolysis rate of NTR and reduced mobile emissions of NO_x (SCI) is shown using light blue, and output from the CMAQ SCI framework along with increases to the thermal dissociation rate of PANX and reaction rate of PANX+OH (SCI-PAN) is in red. The mean and standard deviation denotes the average of all spirals in each data set for which r^2 between O_x and NO_z is greater than 0.65, with the spirals grouped according to the maximum value of NO_x encountered in either the modeled or measured spirals. The first bin includes all data for which the maximum mixing ratio $\text{NO}_x \leq 1.0$ ppb; the second bin includes data for which maximum

NO_x lies between 1 and 2.0 ppb; the third bin is for maximum NO_x between 2 and 3 ppb; and the last bin contains all spirals with maximum NO_x > 3 ppb. The highest maximum NO_x during D-AQ spirals was 6.98 ppb. Numbers next to the D-AQ data represent the number of spirals included in each NO_x bin. The numerical notation on the figure shows the mean and standard deviation of all spirals with $r^2 \geq 0.65$, for the D-AQ data as well as the CMAQ output.

To further investigate photochemical smog production, we sort the OPE values into 1 ppb maximum NO_x bins. Maximum NO_x is determined individually for each linear regression (i.e., the maximum value of NO_x in each spiral). Furthermore, we exclude OPE values that do not fall within two standard deviations (2σ) of the mean of other values in each bin. The total number of measured spirals using the 2σ -criterion is reduced to 80 (previously 86; 6 OPE values lie more than 2σ from the mean). We apply the same sampling criteria used to select the spirals from the measurements ($r^2 \geq 0.65$ and 2σ -criterion) to output from the CMAQ simulations resulting in a sample size of 100+ spirals (Table 2-4). Figure 2-12 shows the comparison of measured (black) and simulated (BSE: dark blue, SCI: light blue, and SCI-PAN: red) OPE as a function of maximum NO_x. The last bin includes OPE values that have a maximum NO_x of 4 ppb and larger in order to have a roughly similar number of spirals in each bin. On average the OPE from the various models simulations is lower than observation by $34 \pm 20\%$ (BSE), $27 \pm 16\%$ (SCI), and $21 \pm 13\%$ (SCI-PAN) (i.e., for BSE the model resulted in OPE of 5.55; the data yielded 8.44; therefore we report the model was $(8.44 - 5.55) / (8.44) \times 100\% = 34\%$ low relative to observation). The CMAQ simulation with reduced mobile NO_x emissions and increased dissociation rates of NTR and PANX in the chemical mechanism shows best agreement with measured OPE. We have compared OPE from a fourth simulation (SCI-MGN) that uses biogenic emissions from MEGANv2.10 instead of BEISv3.61 (Table 1) but exclude showing results in Figure 2-12, since the OPE from this simulation did not show a significant improvement in OPE values compared to the SCI simulation.

Table 2-4 summarizes the statistics for OPE values for 80 spirals in the measurements and 100+ spirals for each of the model simulations. The first numerical column in Table 2-4 shows the mean of all 80 spirals (mean all), whereas the second column represents the mean of the five OPE values computed from sorting the data into 1 ppb NO_x bins (mean binned). The measurements show a greater range of OPE values (Std. dev: 4.11)

compared to model simulations (Std. dev.: ~3). The value of OPE based on the BSE simulation is lower than OPE inferred from D-AQ data across all of the statistical measures (i.e., mean, median, 5th and 95th percentiles) by 36% (range of 32 to 39%). The percentage underestimate of OPE is 29% (range 24 to 32% across statistical measures) for the SCI simulation. The best simulation of OPE is attained for the SCI-PAN run, which results in an estimate that is 22% (range 17 to 27%) below observed OPE, due to a better representation of nitrogen precursor species that are involved in the formation of surface O₃. The OPE results for the SCI-MGN simulation lie between the values from the SCI and SCI-PAN simulation. Across nearly all the statistical categories in Table 2-4, the SCI-PAN simulations yield values of OPE that are closest to the observations.

Table 2-4: Values of mean, median, 5th-percentile, and 95th-percentile of OPE from 80 spirals in the measurements and >100 for all model simulations.

	Mean (all) / Std. dev.	Mean (binned) / Std. dev.	Median	5 th percentile	95 th percentile	# of Spirals
D-AQ	8.44 / 4.11	8.17 / 1.24	8.20	2.73	16.35	80
BSE	5.55 / 2.75	5.02 / 0.58	5.04	1.85	10.66	111
SCI	6.18 / 2.99	5.58 / 0.40	5.55	2.03	12.45	102
SCI-PAN	6.63 / 3.16	5.94 / 0.13	6.08	2.25	13.58	101
SCI-MGN	6.49 / 2.93	6.50 / 1.59	5.94	2.62	12.36	105

Finally, we comment on the magnitude and shape of the OPE versus maximum NO_x relation. The domain sampled during D-AQ contained modest mixing ratios of NO_x, resulting in relatively high values of OPE. High mixing ratios of NO_x were sampled infrequently during the spirals. Therefore, we cannot determine with confidence whether OPE decreases with increasing NO_x, which is the expected behavior, even though the last two D-AQ points in Figure 2-7 (as well as Figure 2-13) display this tendency.

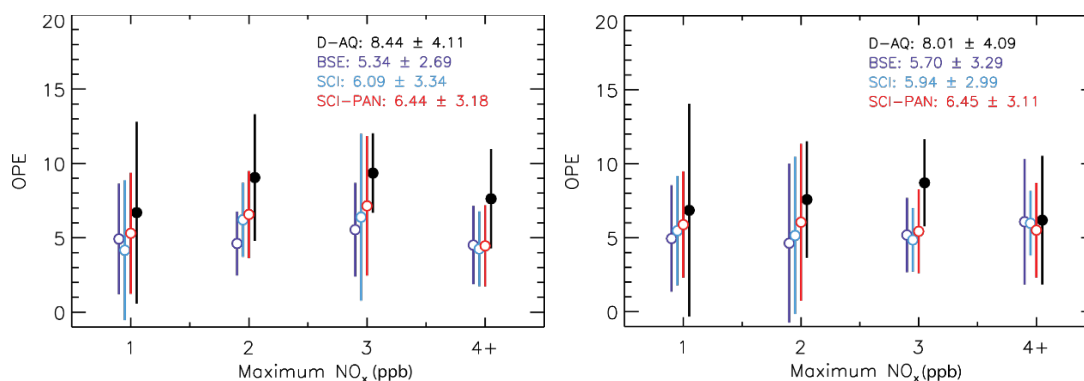


Figure 2-13 Left: Same as Figure 2-12, except that the simulations were sampled with the same 80 spirals selected for the aircraft measurements. Right: Same as Figure 2-12, except that an $r_2 \geq 0.4$ between O_x versus NO_z had been used to filter the data, prior to the determination of OPE.

Kleinman et al. [2002] shows OPE for a much larger range of maximum NO_x (0 to 43 ppb) than sampled during D-AQ; when NO_x is greater than 4 ppb in their study, OPE decreases with increasing NO_x . The OPE is a measure of how effectively NO_2 can be recycled and form O_3 before it is converted to a photochemically inactive species such as HNO_3 . However, O_3 production or destruction is also dependent on peroxy radical concentrations that control the removal of NO_x and VOCs. Therefore, we next examine the peroxy radical concentrations within measurements and model simulations.

2.5.3 Inferred Peroxy Radicals

Figure 2-14 shows $inRO_x$ versus maximum NO_x , for the same 80 spirals (measurements) and 100+ spirals (model simulations) used in Figure 2-12. Again, measurements are depicted in black and simulations are color-coded (BSE: dark blue, SCI: light blue, and SCI-PAN: red, SCI-MGN: green). Error bars in Figure 2-13 depict the standard deviation of values within each bin, where again the measurements and model output are binned with respect to maximum NO_x within each profile. Generally, the size of the error bars is larger than the calculated uncertainty of 30% for $inRO_x$. The observations display a decreasing trend with increasing maximum NO_x that is also evident in the simulations. The decrease of peroxy radical abundance as a function of increasing NO_x is consistent with near-surface O_3 being in the NO_x -limited regime during this phase of D-AQ, as shown by Schroeder et al. [2017]. Under this condition, radical termination occurs mainly by reactions that involve NO_x .

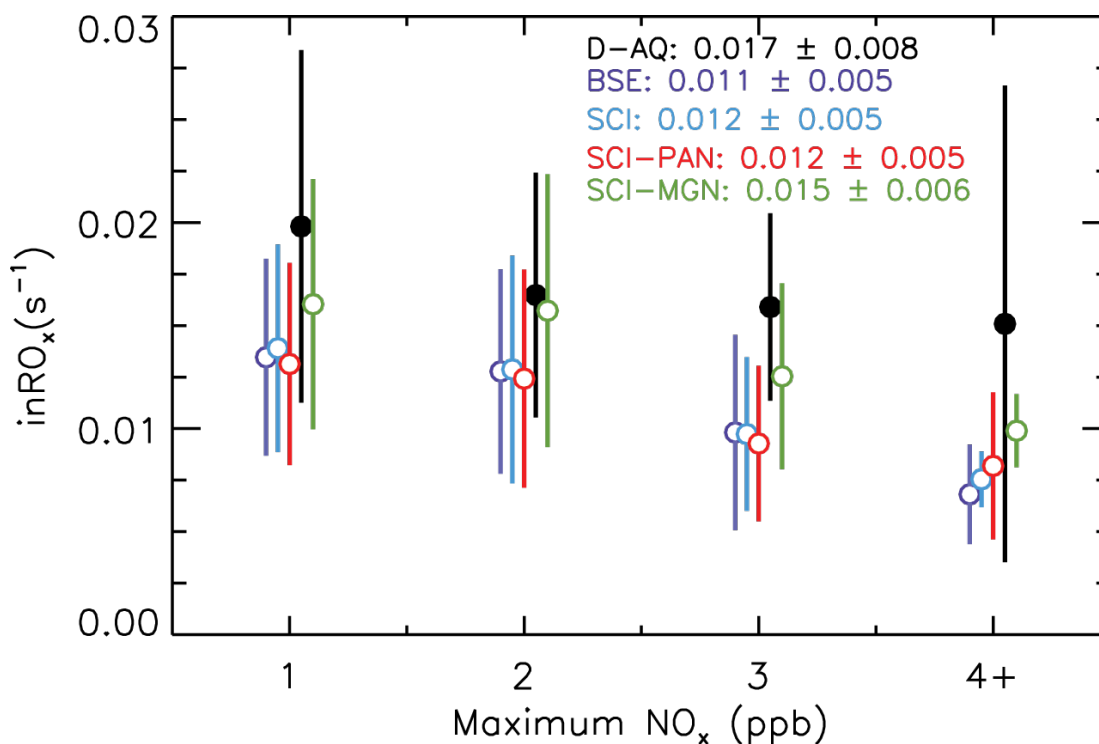


Figure 2-14. Comparison of inRO_x versus binned maximum NO_x. Results are shown for the same CMAQ simulations (i.e., BSE, SCI, and SCI-PAN) used in Figs. 6 and 7, plus one additional simulation. The SCI-MGN (green) simulation uses the science framework, with biogenic emissions from MEGANv2.10 rather than BEISv3.61. The symbols with error bars show the mean and standard deviation for all spirals in each data set for which r^2 between O_x and NO_z is greater than 0.65, where the measurements and CMAQ output are again binned using maximum NO_x. The numerical notation on the figure shows the mean and standard deviation of all spirals with $r^2 \geq 0.65$, for the D-AQ data as well as the CMAQ output.

The average observed inRO_x from all the individual spirals (0.017 s⁻¹) is higher than the average of any model simulation (ranging from 0.011 to 0.015 s⁻¹) by 35±19% (BSE), 30±19% (SCI and SCI-PAN), and 12±7% (SCI-MGN). Thus, the changes implemented to anthropogenic emissions and the chemical mechanism in CMAQ increase inRO_x, but not enough to match observations. Using a different spiral sampling method, such as restricting the simulations to the same 80 spirals identified in the measurements or using spirals where O_x versus NO_z has a correlation coefficient threshold of $r^2 \geq 0.4$, does not change any of our conclusions about inRO_x (Figure 2-15).

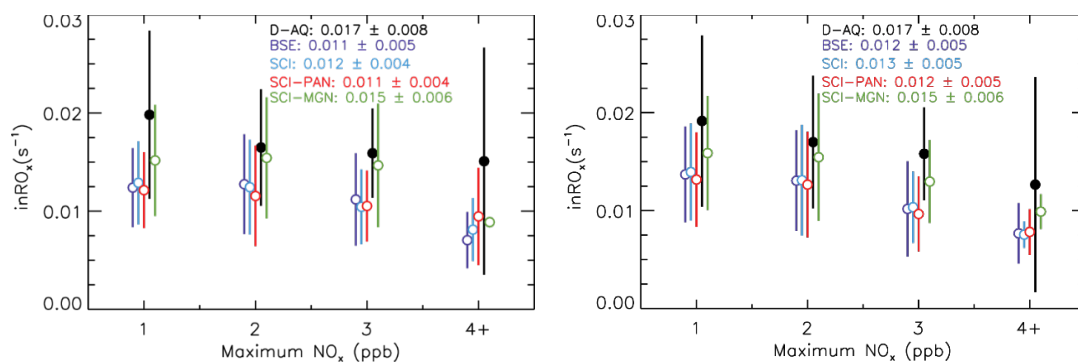


Figure 2-15 Left: Same as Figure 2-14, except that the simulations were sampled with the same 80 spirals selected for the aircraft measurements. Right: Same as Figure 2-14, except that an $r^2 \geq 0.4$ between O_x versus NO_z had been used to filter the data, prior to the determination of OPE.

We now examine whether the underestimate of inRO_x in the simulations results from shortcomings in the simulated abundance of certain VOCs and oxidation products. Results are shown for baseline simulation, the SCI-PAN simulation that used BEISv3.61 (hereafter BEIS) emissions, and the SCI-MGN simulation that relied on MEGANv2.10 (hereafter MEGAN) emissions. Simulations using MEGAN produce higher values of inRO_x (0.015 s^{-1}) than simulations using BEIS ($\sim 0.012 \text{ s}^{-1}$, Figure 2-13). However, as shown in Figure 2-15, SCI-MGN generates about a factor of 3.7 more isoprene and a factor of 1.5 more HCHO than was measured in the CML during D-AQ. Therefore, the mixing ratios of these organic compounds in SCI-MGN are substantially higher than observed. In contrast, output from the SCI-PAN simulation compares rather well with observed mixing ratios of isoprene and HCHO in the CML. The SCI-PAN simulation overestimates isoprene by a factor of 1.23 and underestimates HCHO by a factor of 0.86.

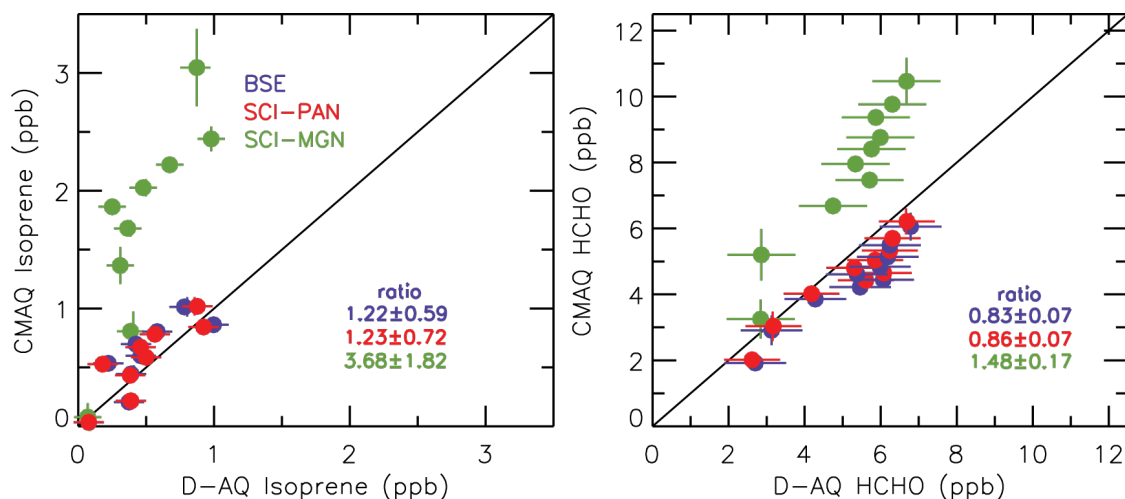


Figure 2-16. Comparison of isoprene (left) and HCHO (right) from CMAQ simulations to binned D-AQ aircraft observations. Each bin contains 30 data points; the mean is depicted by a circle, and the 1σ standard deviation by error bars. Results for the baseline simulation are shown in blue; the SCI-PAN simulation using biogenic emissions from BEISv3.61 is in red and the SCI-MGN simulation using biogenic emissions from MEGANv2.10 is shown using green. The notation on the two panels shows the mean and 1σ standard deviation of modeled divided by measured isoprene (left) and HCHO (right), for all data.

Even though the SCI-MGN simulation increases the value of inRO_x in the model, the increase in isoprene emissions driven by MEGAN is not supported by measurements of isoprene and HCHO. This suggests either an underestimate of some VOC species other than isoprene within our model framework, or greater net production of HO_2 and RO_2 than in the chemical mechanism. The CB05-TUCL mechanism does not include explicit recycling pathways for HO_x radicals upon loss of isoprene and other VOCs, other than production of HO_2 at the end of the VOC chain. Wolfe et al. [2012] showed that the photolysis isoprene decomposition products can increase the concentration of OH by 5-16%, with the high range occurring over the rainforest regions of South America and Africa. The computed enhancement was on the low end of the range in the Mid-Atlantic of the United States. The photolysis of isoprene hydroperoxyenals has been implemented in CB6r2, via the new quantity HPLD. If the box model results of Wolfe et al. [2012] are representative of the magnitude of the increase in HO_x radicals upon implementation of this recycling pathway, the implementation of this process will account for a portion of the discrepancy shown in Figure 2-14.

2.5.4 Comparisons to Satellite Data

Here, we compare CMAQ output to retrievals of total column HCHO [Abad *et al.*, 2015] and tropospheric column NO₂ [Krotkov *et al.*, 2017] from the Ozone Monitoring Instrument (OMI) on the NASA Aura satellite (see Section 2.3) obtained over the Eastern U.S. The use of satellite data allows us to evaluate the performance of CMAQ over various metropolitan areas, including the Baltimore-Washington region (BW) sampled by the NASA aircraft and a few other similar urban regions (Chicago and Detroit) that have not been subject to intense aircraft measurements utilizing a payload comparable to that deployed during DISCOVER-AQ. The urban areas of Chicago and Detroit are expected to be less affected by biogenic emissions of isoprene than the BW region. The satellite data record allows us to extend the evaluation of the representation of urban chemistry within CMAQ to these other highly populated urban regions.

Figure 2-17 shows column HCHO for the month of July 2011 from observations (2-18a: OMI) and CMAQ simulations (2-18b: SCI-PAN; 2-18c: SCI-MGN). Profiles of HCHO output from CMAQ are convolved with the averaging kernel used in the satellite retrieval specific to the time and place of each observation [Bucsela *et al.*, 2008]. The resulting columns are retained for comparison only if the effective cloud fraction reported by OMI, for the same time and location, was less than 0.3 (see Section 2.3). The retained columns are then weighted based on satellite viewing angle in the same manner as the OMI product and averaged onto the same 0.25°×0.25° (latitude, longitude) grid used for the aggregation of OMI data. Generally, the CMAQ simulation using MEGANv2.10 has higher column HCHO throughout the domain, particularly in heavily vegetated regions (southeastern US) compared to CMAQ simulations using BEIS. Kaiser *et al.* [2018] recently showed that MEGANv2.10 overestimates HCHO in the southeastern US based on comparison of output from the GEOS-CHEM model to *in-situ* observations obtained during the 2013 NASA SEAC⁴RS campaign. They describe (their section 4) various reasons why the emission of isoprene in MEGANv2.10 should be decreased by 46%, 48%, and more than a factor of 3 in the Ozarks (OZ), South Central Plains (SPC), and Edwards Plateau (EP) ecoregions,

respectively. Our comparisons of the SCI-MGN simulation to version 3.0 OMI HCHO over the yields similar results (Figure 2-17).

Next, we focus on three urban areas: Chicago, Detroit, and BW (white boxes in Figure 2-17). We evaluate OMI data and CMAQ output for these three regions due to their high values of column NO₂ (Figure 2-18) and especially the BW region, since we can compare to the conclusions drawn from our analysis of *in-situ* observations of HCHO from D-AQ described above. Figure 2-17d to 2-17f show column HCHO from CMAQ versus OMI for these three geographical regions. For column HCHO, the CMAQ run using BEIS (SCI-PAN) leads to column HCHO that is 16%, 21%, and 12% lower than observed from OMI over Chicago, Detroit, and BW, respectively. The CMAQ run using MEGAN results in column HCHO that is only ~5% lower than observed over Chicago and Detroit, and 23% larger than observed in the BW region. Chicago and Detroit's proximity to biogenically active regions is very different than BW, which is close to forests that release large amounts of isoprene emission during summer. Table 2-4 summarizes the square of the correlation coefficient (r^2) and root mean square deviations (RMS) for isoprene (aircraft data) and HCHO (aircraft and satellite data) relative to CMAQ output for the BW region. These numerical values show that the SCI-PAN simulation using BEIS compares better, overall, to observations of isoprene and HCHO than the SCI-MGN simulation using MEGAN. However, the fact that column HCHO as measured by OMI during July 2011 is simulated better using BEIS over the BW region, whereas column HCHO over Chicago and Detroit is more closely matched by the CMAQ simulation using MEGAN (Figure 2-18d and 2-18e), complicates choosing one biogenic VOC emission algorithm over the other.

The accuracy of the retrieval of column HCHO is an area of active research. Zhu et al. [2016] suggested, based upon comparison of OMI column HCHO to output from the GEOS-CHEM model, that the OMI retrievals of column HCHO might be "biased low in the mean by 20 to 51%". This conclusion was based on prior extensive comparison of HCHO from GEOS-CHEM to in situ observations of HCHO. If OMI column HCHO is indeed biased low by 20 to 50%, and all else is equal (i.e., same averaging kernels), then values of the ratios shown in Figure 2-17 would decline by

between 0.66 (1/1.50) to 0.83 (1/1.2). In this case, nearly all the simulations conducted would exhibit poorer agreement with observed column HCHO than shown in Figure 2-17. The exception is the SCI-MGN simulation for the BW region, which would have a ratio of either 1.03 (20% bias) or 0.82 (50% bias). One of the factors that affects the retrieval of column HCHO is the background correction (Ω_0), defined as the “HCHO vertical column simulated by CTM for the remote Pacific at corresponding latitude and observing time” [Zhu *et al.*, 2106]. Anderson *et al.* [2017] showed that column HCHO in the remote Pacific during winter 2014 was about $5.1 \pm 0.76 \times 10^{15} \text{ cm}^{-2}$, considerably larger than found using global models.

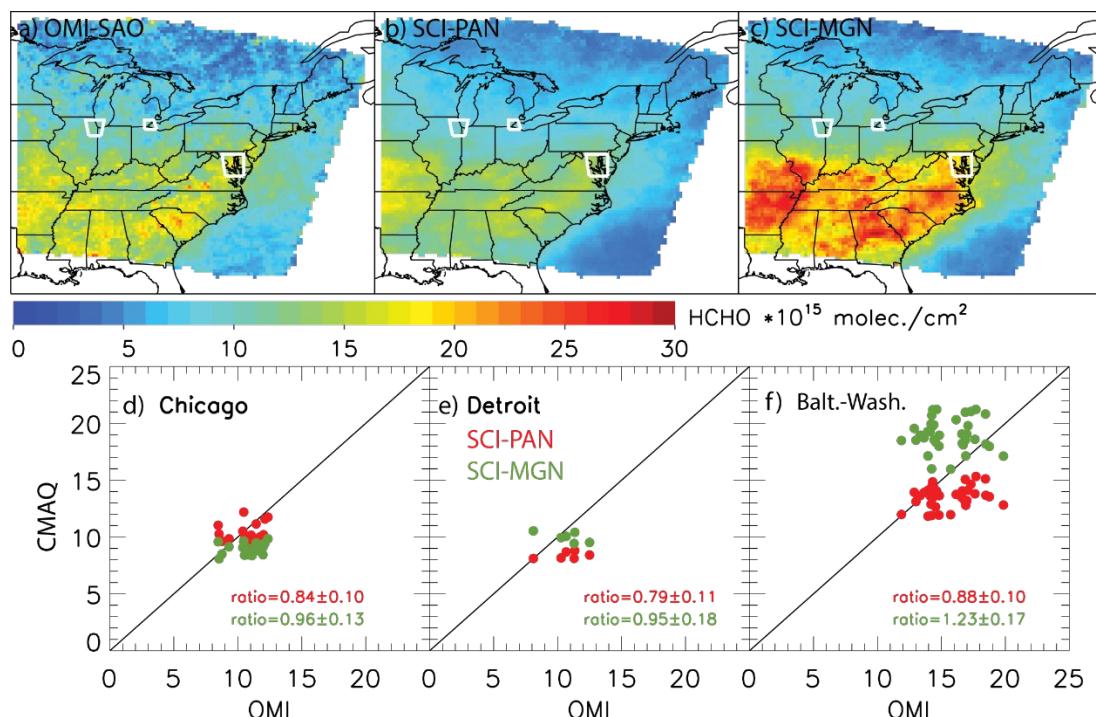


Figure 2-17. Spatial distribution of column HCHO during July 2011 from (a) OMI-SAO. The level 2 swath data for the OMI retrieval has been screened for quality flags (see text), weighted based on viewing angle, and gridded onto a $0.25^\circ \times 0.25^\circ$ lat/lon grid. Only observations where the cloud fraction is less than 30% are used (b) Column HCHO from a CMAQ model run (SCI-PAN) using biogenic emissions from BEISv3.61, near Aura overpass time. Model output has been convolved with the satellite averaging kernel and screened, weighted, and gridded in the same manner as the satellite data. (c) Output from a CMAQ model run using biogenic emissions from MEGANv2.10 (SCI-MGN), processed in the same manner as sued for panel (b). The white boxes on the top three panels highlight the geographical regions of Chicago, Detroit, and BW. Panels (d), (e), and (f) show CMAQ modeled column HCHO (SCI-PAN; red and SCI-MGN; green) versus OMI column HCHO for the three geographical regions. The mean and standard deviation of the ratio of CMAQ column HCHO divided by OMI column HCHO are indicated for both CMAQ simulations.

They attributed the model deficiency to neglect of an oceanic source acetaldehyde. Zhu et al. [2016] used values of 3.0 to $3.8 \times 10^{15} \text{ cm}^{-2}$ for Ω_0 based on results from GEOS-CHEM. The use of a larger value of Ω_0 (based on actual observations in the remote Pacific) in the retrieval of HCHO would result in a decline of the reported column abundance of HCHO. Given the present uncertainties regarding the accuracy of satellite retrievals of column HCHO, we rely on the Version 3.0 (Collection 3) retrievals as provided by the SAO group.

Table 2-5. RMS and r^2 for isoprene and HCHO from the CMAQ model versus observations.

	Isoprene (D-AQ) RMS (ppb) / r^2	HCHO (D-AQ) RMS (ppb) / r^2	HCHO (OMI-SAO; whole domain) RMS ($10^{15} \text{ molec./cm}^2$) / r^2
SCI-PAN	0.26 / 0.77	1.06 / 0.94	1.22 / 0.97
SCI-MGN	1.38 / 0.67	2.61 / 0.92	5.19 / 0.97

Next, we compare column NO_2 from OMI to CMAQ over the same geographical region. The CMAQ profiles of NO_2 have been processed in the same manner (i.e., convolution, screening, weighting, and gridding) as described above for HCHO. Figure 2-18 shows column NO_2 from OMI [Krotkov et al., 2017] (Figure 2-18a) and CMAQ output from the SCI-PAN (Figure 2-18b) and SCI-MGN (Figure 2-18c) simulations. Both CMAQ simulations use the science framework (SCI), i.e. a 50% reduction in mobile emissions of NO_x as well as reduction of the photolytic lifetime of NTR by a factor of 10. The CMAQ simulations using these modifications overestimate column NO_2 by more than a factor of 2 for Chicago and Detroit, and by 50% (using BEIS) or 15% (using MEGAN) for the BW region. The assumption of faster thermal decomposition rate of PAN and PANX in the SCI-PAN simulation results in more column NO_2 compared to the SCI-MGN and SCI simulations (not shown). The larger abundance of NO_2 due to faster dissociation of PAN and PANX in the SCI-PAN simulation is apparent in Figure 2-3. However, the baseline simulation of CMAQ results in even poorer agreement with measured NO_2 for these three urban areas (bottom panel of Figure 2-11) compared to the SCI-PAN simulation. The baseline CMAQ simulation overestimates column NO_2 by a factor of 3 for Chicago and Detroit and by 50% for the BW region. The CMAQ model has a tendency to keep anthropogenic emission of NO_x too close to urban source regions, based on a literal

interpretation of the satellite data, as first shown by Canty et al. [2015]. This model tendency can perhaps be improved by a better representation of boundary layer venting (here, we have used the ACM2 scheme of Pleim [2007], as described in Section 2.5). Our comparisons of measured and modeled column NO_2 show that further improvements in the simulation of NO_x by CMAQ are needed.

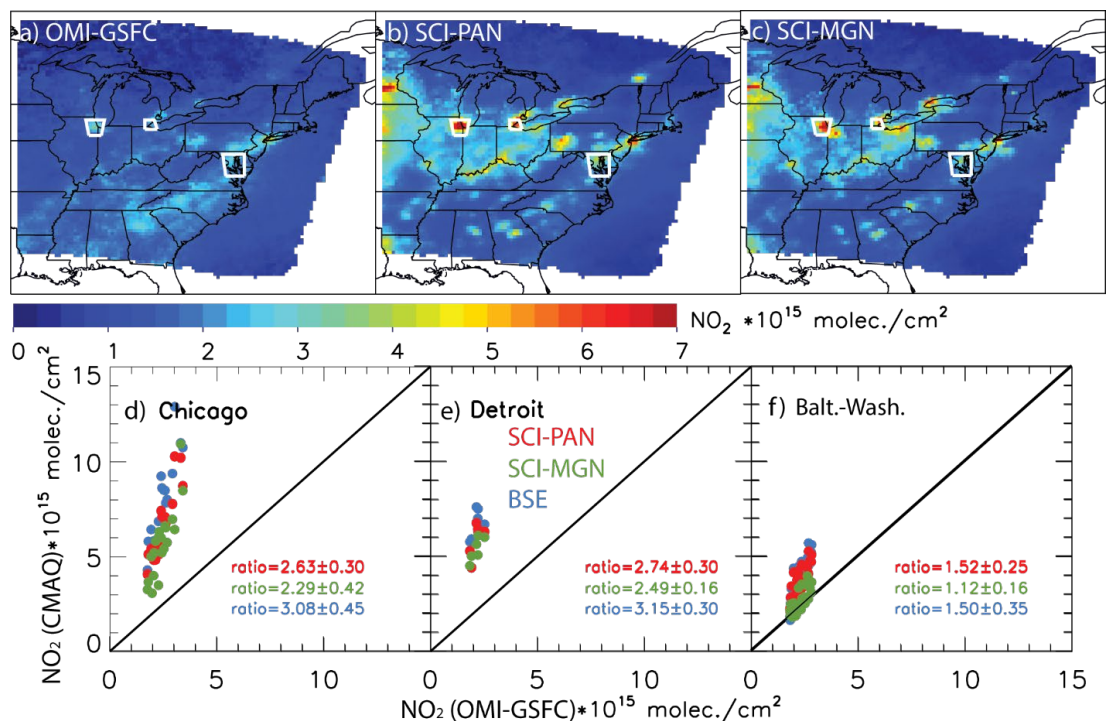


Figure 2-18 Same as Figure 2-18 except that the figures depict column NO_2 from (a) OMI-GSFC (b) output from a CMAQ model run (SCI-PAN) using biogenic emissions from BEISv3.61, and (c) output from a CMAQ model run using biogenic emissions from MEGANv2.10 (SCI-MGN). Depict blue in figures (d), (e), and (f) is the baseline (BSE) simulation from CMAQ versus OMI-GSFC data.

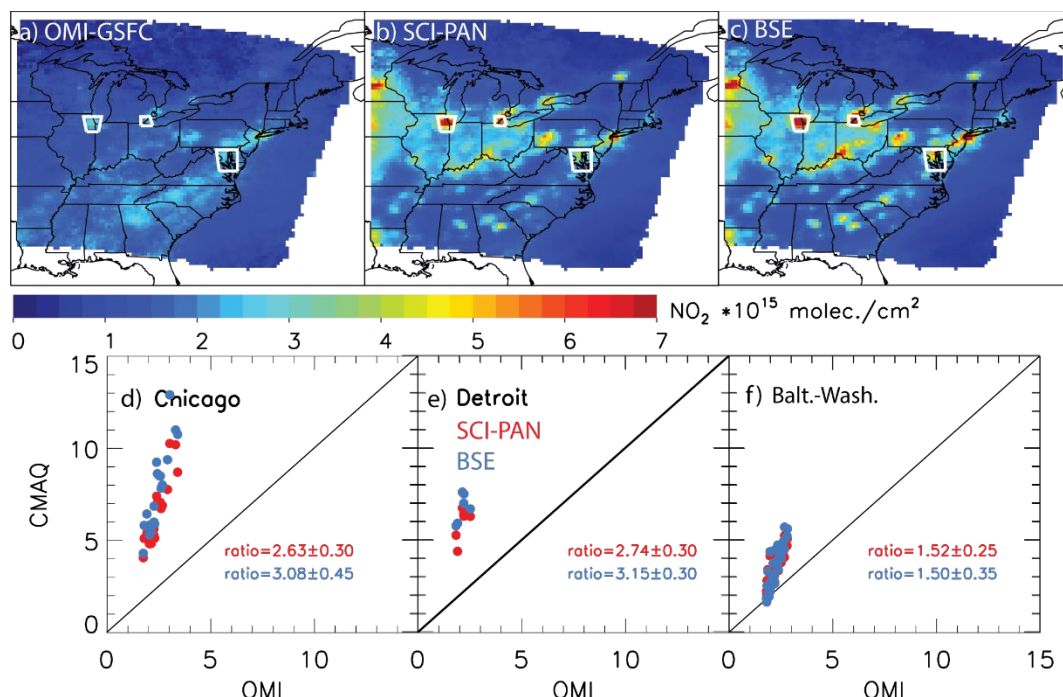


Figure 2-19 Same as figure 2-18 except that OMI NO₂ column is compared to the baseline (BSE) CMAQ simulation instead of the SCI-MGN simulation.

In the context of effective air quality implementation strategies, the ratio of HCHO to NO₂ can indicate whether the rate of O₃ production is more sensitive to policy-driven reductions in either VOCs or NO_x. Duncan et al. [2010] defines the transitional regime as locations where HCHO/NO₂ ratios are between 1 and 2. Values of the HCHO/NO₂ ratio greater than 2 indicate that a region is in a NO_x-limited regime, whereas values of this ratio less than 1 indicate the region is in the VOC-limited regime. Schroeder et al. [2017] showed that the BW region lies within the NO_x-limited regime, based on their analysis of column HCHO/NO₂ computed from July 2011 D-AQ data. This property of the BW region is also reflected in Figure 2-20, which shows the ratio of column HCHO/NO₂ from OMI. Using the Duncan et al. [2010] classification, the entire BW region lies in the NO_x-limited regime during July 2011.

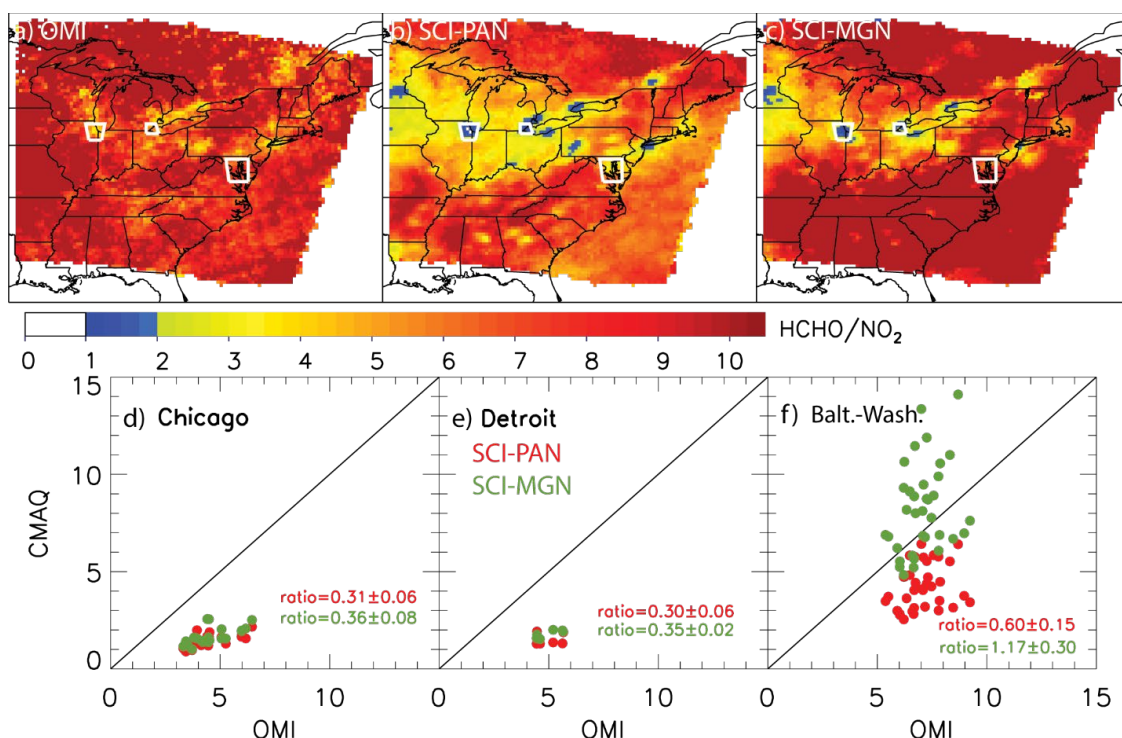


Figure 2-20 Same as Figure 2-18, except the ratio of column HCHO divided by column NO₂ is shown.

Next, we examine the photochemical regime for other areas. The HCHO/NO₂ column ratio from OMI over Chicago and Detroit, and indeed most of the domain shown in Figure 2-20a, indicates these areas lie within the NO_x-limited regime. However, the HCHO/NO₂ column ratio from the SCI-PAN (Figure 2-20b) and SCI-MGN (Figure 2-20c) runs of CMAQ are quite lower than values measured by OMI. Both model runs suggest Chicago and Detroit are in the VOC-to-NO_x transitional regime, as shown in blue on Figure 2-20b and 2-20c. In general, HCHO/NO₂ column ratios for the SCI-MGN simulation are greater than those for the SCI-PAN simulation, leading to a smaller geographic area within the transitional regime. The very large difference between modeled and satellite HCHO/NO₂ column ratios (Figure 2-20d and e) for Chicago and Detroit suggests surface O₃ may respond more effectively to future reductions in NO_x than would be indicated by CMAQ simulations. The ratio of column HCHO divided by column NO₂ from a baseline run of CMAQ yields values that are slightly lower than the SCI-PAN simulation shown in Figure 2-20. Therefore, surface O₃ may exhibit stronger declines to further reductions of NO_x than is indicated by baseline runs of CMAQ.

One possible cause for the underestimation of the HCHO/NO₂ column ratio in CMAQ relative to OMI could be the assumption that marine emissions near shorelines only occur at the surface within the 2011 EPA emissions inventory that is used in this study. Ring et al. [2018] showed that when marine emissions near a shoreline are vertically distributed to account for stack-height and plume rise, then areas denoted as VOC-limited (e.g., Detroit and Chicago) become smaller compared to a baseline simulation, bringing observations and model in better agreement. Another possible reason CMAQ might underestimate the HCHO/NO₂ ratio is the tendency of the model to have excess NO_x in urban areas, due to inadequacies in the boundary layer venting and recycling of NO_x from reservoir species. Even though the CMAQ simulations shown in Figure 2-19 have included a 50% reduction in mobile NO_x emissions, urban regions still show high column NO₂ (red) relative to OMI satellite observations. Finally, if the Version 3.0 OMI satellite retrieval of HCHO is indeed biased low as suggested by Zhu et al. [2016], then the discrepancy between the measured and modeled HCHO/NO₂ ratio shown in Figure 2-20 would rise for all cases, except for SCI-MGN over the BW region (Figure 2-20f).

2.6 Conclusions

The extensive observational dataset from the July 2011 NASA DISCOVER-AQ campaign provides an opportunity to investigate the ability of CMAQ to simulate O₃ and its precursors in the Baltimore-Washington airshed. The CMAQ baseline simulation using 2011 NEI estimates shows the mixing ratio of surface O₃ is in reasonably good agreement with observations: i.e., for the month of July 2011 87% of 8-hr averaged O₃ simulations correctly identify whether or not surface O₃ exceeded the 75 ppb standard. However, the BSE simulation of CMAQ consistently overestimates mixing ratios of NO_y, NTR, and PANs compared to D-AQ observations. As a result, the BSE simulation underestimates both the ozone production efficiency by 34±20% and reactivity of HO₂ and RO₂ radicals (and thus their effective abundances) by 35±19%, respectively.

Based on observations, we modified the BSE simulation (CB05-TUCL in CMAQ) as follows: a 50% reduction of NO_x emissions from all mobile sources, a factor

of 10 reduction in the photolytic lifetime of NTR, and the use of the IUPAC (2014) rate for the thermal dissociation of PAN for both PAN and PANX. A simulation using all these changes, SCI-PAN, results in significantly better agreement between modelled and measured NO_y , NTR, and PANs. Runs with the thermal dissociation of PANs set at $+1\sigma$ of the recommended IUPAC value result in even better agreement with observations. The computed value of OPE for SCI-PAN lies closer to observed OPE than found for the BSE simulation, but nonetheless is about $21\pm13\%$ lower than observed. The simulated reactivity of $\text{HO}_2 + \text{RO}_2$ radicals for SCI-PAN is slightly larger than found for BSE, lying $30\pm19\%$ below the observed value.

The SCI-PAN simulation used biogenic emissions of VOCs from BEISv3.61. Although, the use of MEGANv2.10 improves OPE relative to the use of BEIS, computed abundances of isoprene and formaldehyde are substantially overestimated compared to D-AQ data. Our study suggests either the formation of HCHO upon the decomposition of isoprene requires improvement within the CB05-TUCL mechanism or some VOC species other than isoprene is responsible for the underestimation of $\text{HO}_2 + \text{RO}_2$ reactivity within CMAQ. In the future, we will analyze the modifications to isoprene oxidation within air quality model mechanisms that Marvin et al. [2017] demonstrated lead to more accurate representation of the HCHO to isoprene ratio. Also, the availability of measurements of a suite of VOCs from Photochemical Assessment Monitoring Stations (PAMS) at sites such as Essex, Maryland [EPA, 2018; e.g., Vinciguerra et al., 2015] will provide a means to assess whether VOCs other than isoprene are responsible for the shortfall in modelled $\text{HO}_2 + \text{RO}_2$ reactivity.

We also compared modelled tropospheric column HCHO and NO_2 (convolved with the averaging kernels) to measurements (and their ratio) obtained by the OMI instrument onboard the NASA Aura satellite. We focused on three urban areas, Chicago, Detroit, and the Baltimore-Washington (BW) region. The CMAQ run using BEIS results in reasonable agreement with column HCHO measured by OMI, with modeled values being 16%, 21%, and 9% lower than observed over Chicago, Detroit, and BW. The CMAQ run using MEGAN results in column HCHO that is $\sim 5\%$ lower than observed over Chicago and Detroit, but 28% larger than observed in the BW region. These comparisons reflect the complexity of choosing the appropriate biogenic

VOC emission algorithm for a given ecoregion. Finally, the reduction in mobile NO_x emissions and the modifications to the chemical mechanism (i.e., our SCI-PAN and SCI-MGN simulations) also reduce model overestimates of column NO₂ for the Chicago and Detroit urban regions.

To evaluate any air quality model that simulates O₃, it is useful to examine model representation of the factors that govern the photochemical production term: i.e., the rates of NO+HO₂ and NO+RO₂ [Frost *et al.*, 2016; Lewis *et al.*, 2000; Monks *et al.*, 2015; Ren *et al.*, 2003]. The modifications to the CB05-TUCL mechanism and the emission of NO_x were designed to provide more accurate representation of NO_x, the reactivity of NO_x with peroxy radicals, HCHO, isoprene, as well as organic and inorganic NO_y reservoir species. Improvement in simulating the underlying processes controlling the formation of O₃ will lead to higher confidence in the prediction of surface O₃ events and as well as more effective mitigation strategies. The regulatory model CMAQ with CB05-TUCL and the NEI emissions overestimates reactive nitrogen species, and underestimates OPE and the reactivity of HO₂+RO₂ with NO. We have shown that the CMAQ model performs better, compared to a wide variety of observations, with a 50% reduction in mobile source NO_x emissions and faster loss of peroxy nitrate and alkyl nitrate species. However, significant differences persist, indicating further improvements are needed. Our comparisons suggest future work should examine the possibilities of underestimated emissions of VOCs, greater production of HO₂ and RO₂ from VOCs, and even faster thermal dissociation of peroxy nitrates than assumed in our SCI-PAN simulation.

Chapter 3: Investigation of the Community Multiscale Air Quality (CMAQ) model using the Climate Penalty Factor (CPF)

This chapter was previously submitted for publication under the same title, as an article in the scientific journal *Atmospheric Environment*. I am the lead author of this work, and I acknowledge collaboration with 4 co-authors. The article was submitted on 13 October 2021. Here, the numbering of sections, figures, and tables reflects incorporation into the greater dissertation.

3.1 Introduction

The globally averaged land and ocean surface temperature has increased by $1\pm0.2^{\circ}\text{C}$ since pre-industrial time, and the global mean temperature will likely increase by 0.2°C every decade in the near future [IPCC, 2018]. If emission reductions do not occur, modeling studies forecast ozone (O_3) near the Earth's surface to rise by 1-10 ppb by the end of this century due to climate change [Fiore *et al.*, 2012; Jacob and Winner, 2009; Liao *et al.*, 2006; Murazaki and Hess, 2006]. In highly polluted regions, O_3 is expected to increase as much as 14 ppb during summer due to global warming [Doherty *et al.*, 2013]. Further studies suggest that the worsening of air pollution due to projected rising temperature leads to subsequent increases in mortality, morbidity [Bell *et al.*, 2005; Jacob and Winner, 2009; Lelieveld *et al.*, 2015; Peng *et al.*, 2013], and damage to crops [Avnery *et al.*, 2011; Mauzerall and Wang, 2001], even as emissions of O_3 precursors decline. Future reductions in the emission of these O_3 precursors will need to be stricter to attain prescribed air quality standards for surface ozone.

Formation of surface O_3 depends on emissions of volatile organic compounds (VOCs), reactive nitrogen oxides NO_x ($\text{NO}_x=\text{NO}+\text{NO}_2$), and carbon monoxide (CO) [Crutzen, 1973; Finlayson-Pitts and Pitts, 2000]. Production of O_3 exhibits a complex, non-linear dependence on the concentrations of these gases [Sillman, 1999; Sillman *et al.*, 1997]. Surface ozone is also highly sensitive to various weather systems, such as frontal passages [Mickley *et al.*, 2004] and persistent high pressure weather systems such as the Bermuda high frequently located over the western North Atlantic in the summer [Zhu and Liang, 2013]. Exceedances of the U.S. Environmental Protection

Agency (EPA) National Ambient Air Quality Standard (NAAQS) for surface O₃ typically occur on hot summer days [Brent *et al.*, 2015; Lin *et al.*, 2001].

There are many reasons elevated levels of surface O₃ tend to be associated with hot conditions. High ambient temperatures are often concurrent with stagnation and increased incident solar radiation. With rising temperatures, water vapor increases, resulting in greater production of O₃ in high NO_x regions due to increased abundances of odd hydrogen (HO_x=OH+HO₂) radicals, formed by the reaction of O(¹D) with H₂O [Steiner *et al.*, 2006]. Rate constants of many reactions critical to the formation of O₃ increase with temperature [Stockwell *et al.*, 2012]. An increase in temperature enhances the thermal decomposition of compounds such as peroxyacetyl nitrate (PAN), a reservoir species for NO_x; this frees up odd hydrogen (HO_x=OH+HO₂), ultimately forming O₃ [Sillman *et al.*, 1990; Sillman and Samson, 1995]. Biogenic emissions of VOCs, particularly isoprene (C₅H₈), increase with rising temperature [Liao *et al.*, 2006; Wiedinmyer *et al.*, 2011]. Also, anthropogenic emissions of NO_x increase with rising temperature, particularly during summer due to greater demand for electricity [He *et al.*, 2013]. Conversely, NO_x emissions from diesel vehicles decrease with increasing temperature [Hall *et al.*, 2020a].

The climate penalty factor (CPF) quantifies the dependence of surface ozone on temperature [Bloomer *et al.*, 2009; Jacob and Winner, 2009; Wu *et al.*, 2008]. Combining the CPF with forecasts of the future rise in temperature can be used to provide an estimate of the possible impact of warming on surface ozone. Several definitions for the calculation of the ozone climate penalty exist [Rasmussen *et al.*, 2013]. Here, we use the Bloomer *et al.* (2009) definition: i.e., the CPF is based on the slope of various components of the probability distribution function of long-term measurements of O₃ as a function of temperature, following the aggregation of ozone data into various temperature bins. For the eastern U.S., Bloomer *et al.* quantified the CPF as ~3.2 ppbv/°C (range: 3.0 to 3.6 ppbv/°C) prior to 2002 and ~2.2 ppbv/°C (range: 2.0 to 2.5 ppbv/°C) after 2002, based on analysis of surface O₃ and temperature measurements at predominantly rural sites. They showed that the lower CPF after 2002 was due to reductions in the emission of NO_x from power plants following the EPA NO_x State Implementation Plan (SIP) in 2002 under the Clean Air Act (CAA). As a

result of the reduction in power plant emissions of NO_x as well as reduced vehicular emissions of NO_x, surface O₃ levels in the Midwest and Eastern U.S. have steadily declined after 2002 [Cooper *et al.*, 2020; Jing *et al.*, 2017]. Nonetheless, surface O₃ exceedances in the Eastern U.S. and Midwest still occur, particularly on hot summer days [He *et al.*, 2014].

Between 2000 and 2010, surface O₃ decreased nationwide by 10%, based on the long-term trend measurements (750 AQS sites) (<https://www.epa.gov/air-trends/ozone-trends>). The eastern U.S. shows a greater decrease in surface O₃ than the western U.S. Similar results were found for summertime O₃ trends by Cooper *et al.* [2012]. They investigated O₃ trends from measurements at rural U.S. locations between 1990 and 2010 and found a trend of surface O₃ of −0.45 ppb/yr in the eastern U.S. and an increasing trend of 0.10 ppb/yr in the western U.S. This difference in the sign of surface O₃ trends is attributed to the stronger impact of domestic emission controls in the eastern U.S., while the western U.S. trend is less clear due to variations in transport from Asia, wildfires, temperature, and domestic emissions [Lin *et al.*, 2017].

As noted above, future increases in temperature could offset benefits from future reductions in the emission of O₃ precursors. Determining and understanding the CPF is critical to formulating effective strategies to minimize the occurrence of future exceedances. The focus of this paper is the use of measurements to evaluate the representation of the temperature dependence of surface O₃ within the Community Multi-scale Air Quality (CMAQ) model, for the contiguous U.S (CONUS). CMAQ is an active open-source air quality model developed by the EPA Atmospheric Modeling and Analysis Division and distributed by the Community Modeling and Analysis System (CMAS) center [CMAS-Center, 2013]. For our evaluation of CMAQ, we compare surface O₃ measurements from the EPA Air Quality System (AQS) and Clean Air Status and Trends Network (CASTNET) measurement locations to values of ozone output by CMAQ. Observations from CASTNET tend to be in rural locations, whereas AQS measurements are acquired predominantly in urban sites, although occasionally also in rural locations. Here, we use multiyear model output from May 1 – September 30 for 11 years (2002 – 2012). The CPF from both observations and CMAQ output are calculated as described in Bloomer *et al.* [2009]. Davis *et al.* [2011] suggested CMAQ

underestimates the sensitivity of O₃ to daily maximum temperature, based on an analysis of the four year period 2002 to 2005 for 74 cities of the Eastern U.S. during the O₃ season (1 May to 30 September for each year). This finding suggests CMAQ might underestimate increases in surface ozone caused by a warmer climate.

In our study, we provide a longer and more spatially-resolved view of CPF between various climate regions within the CONUS. We use output from CMAQ found with the chemical mechanism CB05TU-CL for the O₃ season, spanning May 1 to September 30, for years 2002 to 2012. These years span the availability of CMAQ output. We investigate the sensitivity of O₃ production in CMAQ to temperature and compare it to observations.

3.2 Methodology

3.2.1 Surface Ozone and Temperature Observations

We use surface O₃ and temperature data from the Clean Air Status and Trends Network (CASTNET; <http://www.epa.gov/castnet>). These measurement sites are located predominantly in rural areas. Ultraviolet absorbance is used to measure O₃ using the verification procedure described in Table 3 of https://www3.epa.gov/castnet/docs/QA_Quarterly_2019_Q4.pdf. Temperature is measured at 2 m with $\pm 0.5^{\circ}\text{C}$ accuracy and $\pm 1^{\circ}\text{C}$ precision using platinum resistance temperature devices. We also use O₃ data from the Air Quality System (AQS; <http://www.epa.gov/aqs>) with a precision of 0.1 ppb for hourly averages and uncertainty of 5% [EPA, 2006] and temperature data from either the co-located temperature sensors or from a nearby (within 12 km of the O₃ measurement location) meteorological station (Integrated Surface Data (ISD) archived at the National Climatic Data Center (NCDC); <https://gis.ncdc.noaa.gov>). We use AQS measurement sites that are predominantly located in urban or semi-urban regions.

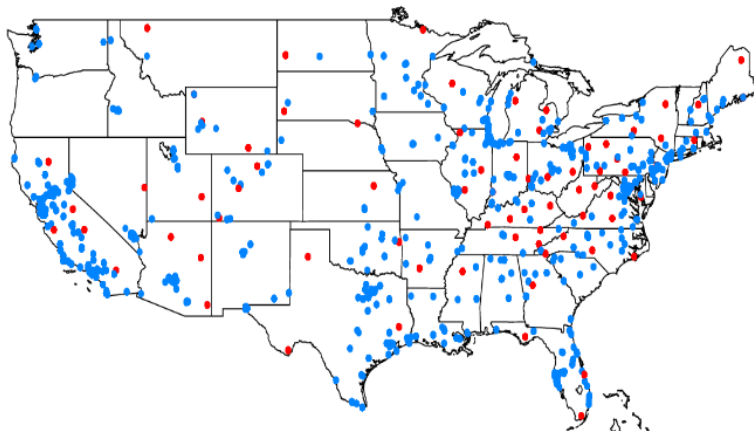


Figure 3-1: Locations of CASTNET (red) and AQS (blue) sites during 2002-2012 used for comparison to CMAQ output.

Figure 3-1 shows a map denoting the locations of CASTNET (red) and AQS (blue) sites used for comparison to CMAQ output. Spatial and temporal (some sites discontinued while others do not have data in the earlier years)

differences occur throughout the CONUS. A greater concentration of AQS sites is visible on the east coast as well as on the coast of California.

We aggregate measurement stations into 7 regions (Figure 3-2). The grouping of sites into different regions is motivated by geography and past statistical analyses [Chan, 2009; Eder *et al.*, 1993; Lehman *et al.*, 2004]. Here we use the same climatic regions as in the 4th U.S. National Assessment Climate Report (Northeast, NE; Midwest, MW; Northern Great Plains, NGP; Northwest, NW; Southwest, SW; Southern Great Plains, SGP; and Southeast, SE), for which various climate metrics were discussed [USGCRP, 2018]. Table 1 lists the number of CASTNET and AQS stations within each of these regions. All ozone measurements have been checked using EPA guidance on quality flags (<https://www.epa.gov/aqs/aqs-code-list>), and admitted into the analysis only if the O₃ and temperature flags were not B, C, D, F, I, M, or P. Between 2002 and 2012, the location of some of the AQS sites has changed and the overall number of AQS sites has increased. These variations in AQS locations are due to a desire to improve the coverage of regions undergoing poor air quality as well as logistical considerations [Pope and Wu, 2014]. The use of AQS sites over the temporal range of our study, even if the data are not continuous at specific locations, allows for better statistical representation of each region [Yan *et al.*, 2018]. Here the analyzed hourly data span from May 1 to September 30 for the years 2002 to 2012.

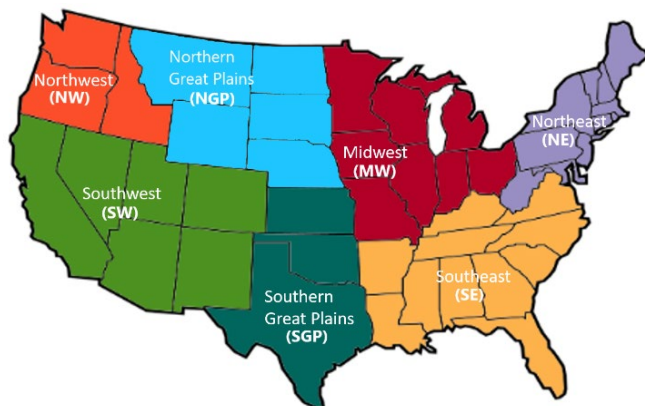


Figure 3-2: Map of the 7 regions used in this analysis (modified from <https://nca2018.globalchange.gov/chapter/front-matter-guide/>)

Table 3-1: The table lists the number of stations used within each region.

Region	CASTNET	AQS (2002)	AQS (2012)
NE	22	52	59
MW	14	77	59
NGP	13	3	12
NW	0	5	6
SW	15	100	108
SGP	6	38	44
SE	23	80	85
CONUS	93	355	373

3.2.2 Modeling Details and Inputs

All simulations were conducted using CMAQ version 5.0.2 and provided to us from the EPA. Simulations are described in Zhan et al. [2019] and are briefly summarized here. The modeling domain covers the entire CONUS using a 12 km grid size with 35 vertical layers (the top of the lowest layer is at ~19 m). Options used for the CMAQ simulations include the carbon bond chemical mechanism with updated toluene chemistry CB05-TU [Sarwar et al., 2011; Whitten et al., 2010] and the AERO6 aerosol module. Meteorological fields are simulated for each year using the Weather Research Forecast model, version 3.4 (WRF v3.4) with 4-dimensional data assimilation and no nudging in the planetary boundary layer. WRF input is driven by reanalysis data obtained by blended 3-hourly reanalysis fields (combination of 6-hour data from the Meteorological Assimilation Data Ingest System and 3-hour forecast of the intermediate North American Mesoscale (NAM) Model) that are organized into 12 km NAM Data Assimilation System fields. WRF output is post-processed to create CMAQ ready input files using the Meteorology-Chemistry Input Processor (MCIP) v.4.1.3.

Anthropogenic emissions input is based on the 2002, 2005, 2008, and 2011 National Emissions Inventories (NEI) using the Sparse Matrix Operator Kernel

Emissions processing system version 3.1 [Houyoux *et al.*, 2000], with year-specific mobile emissions derived from the U.S. Environmental Protection Agency (EPA) Motor Vehicle Emission Simulator (MOVES). Biogenic emissions are from the Biogenic Inventory System (BEISv3.14) [Bash *et al.*, 2016; Kinnee *et al.*, 1997]. Year-specific lightning strike data from the National Lightning Detection Network are used, in order to include the production of NO_x from lightning [Allen *et al.*, 2012]. Hourly boundary conditions for CMAQ were created for each year using output from GEOS-Chem v 8-03-02 (v9-01-02 (2002-2004)) (GEOS: Goddard Earth Observing System) driven by meteorological fields from GEOS-5 [Bey *et al.*, 2001]. In our analysis, we select CMAQ output for the grid points closest in time and space to the surface observations.

3.3 Calculating the Climate Penalty Factor (CPF)

We use the Bloomer *et al.* (2009) method for calculation of the climate penalty factor (CPF) of O₃ in our analysis. Previous research has shown that the relationship between O₃ and temperature over a temperature range of 16°C to 37°C is roughly linear [Bloomer *et al.*, 2009; Camalier *et al.*, 2007; Mahmud *et al.*, 2008; Sillman and Samson, 1995]. We calculate the CPF for each O₃ season, for every year from 2002 to 2012. We use the same temperature range of 19°C-37°C as Bloomer *et al.* for the southern climate regions (SE, SGP, and SW) and a lower temperature range of 16°C-34°C for the northern climate regions (NE, MW, NGP, and NW). The shift to a lower temperature range for northern climate regions ensures a statistically significant number of data points in each temperature bin.

Figure 3-3 provides a graphical explanation of our calculation of CPF. This figure shows 24hr hourly O₃ vs hourly temperature for various portions of the probability distribution of O₃, for the SE region for CMAQ and data (CASTNET) in 2002 (May-September). Observations are shown in black and CMAQ output in gray.

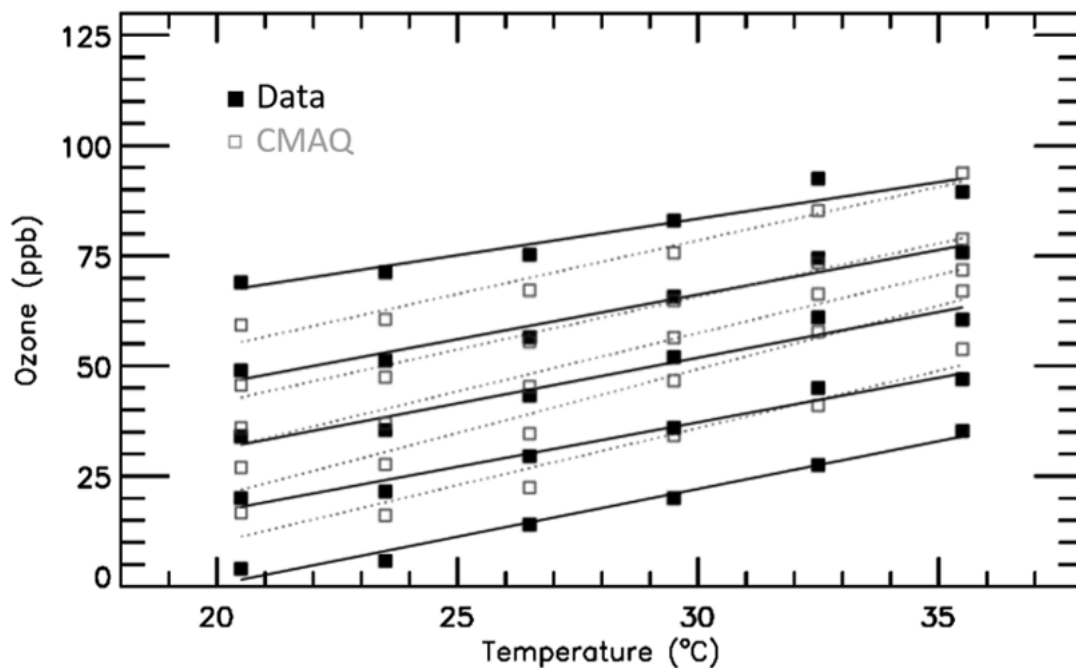


Figure 3-3: Ozone vs. temperature plotted in 3°C temperature bins across the range 19 to 37°C for the 5th, 25th, 50th, 75th, and 95th percentiles (black and gray regression lines) of the ozone distributions (from bottom to top) for the Southeastern climate region in 2002. Points and lines shown in black represent measurements obtained from surface sites (CASTNET); gray indicates CMAQ model results. The dashed lines are the results from CMAQ using the grid points nearest to the measurement sites. Values are plotted at the mid-point of the 3°C temperature bin.

First, hourly observations and model results are placed into 3°C wide temperature bins. Next, the 5th, 25th, 50th, 75th, and 95th percentiles of the distribution of O₃ are found for all the ozone values within each temperature bin, either for all observations (black squares) or modelled points (gray squares). The slope for each regression line through the five resulting percentiles is then calculated, and the mean of all five slopes represents the CPF (Table 3-2). Hence for the SE region, the mean CPF values are 1.99 ppb/°C from CASTNET and 2.59 ppb/°C from CMAQ.

Table 3-2: Southeastern climate region regression slope values and mean of slopes (CPF) for 2002 for CASTNET data and CMAQ output.

	5 th	25 th	50 th	75 th	95 th	Mean CPF
	slope (ppb/°C)	slope (ppb/°C)	slope (ppb/°C)	slope (ppb/°C)	slope (ppb/°C)	(ppb/°C)
Observation	2.17	2.02	2.07	2.03	1.66	1.99
CMAQ	2.59	2.88	2.64	2.41	2.42	2.59

3.4 Results and Discussion

3.4.1 Ozone and temperature

In our analysis we use mean seasonal (May-September) temperature data averaged for each climate region. This averaging results in 66 temperature data points for CASTNET sites and 77 temperature data points for AQS sites. In CMAQ, the temperature of one grid point is representative for a whole 12x12 km grid cell. Hence, the simulated temperature of one grid point to one measurement within a grid cell can be biased. Figure 3-4a shows a scatterplot of measured and simulated seasonal mean temperature for each region and year. The asterisks depict data collected at CASTNET locations while the squares depict data collected at AQS locations. The colors used in Figure 3-4 refer to the seven different climatic regions. The legend within Figure 3-4a shows the root mean square error (RMSE) of the seasonal mean temperature of each region for CASTNET on the left and AQS on the right. The black line depicts the 1:1-line.

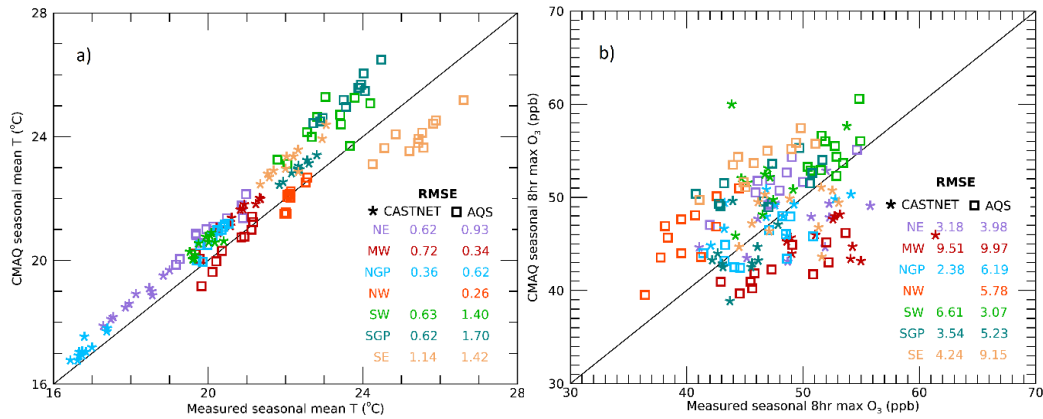


Figure 3-4: Comparison of measured and modelled seasonal (May-September) mean T (a) and seasonal daily 8-hr max O₃ (b) for CASTNET (asterisks) and AQS (squares) locations between 2002-2012 (generally 11 points for each region). Different regions are color coded (see Figure 3-2) and the 1:1-line is denoted in black. Table 3-3 summarizes the statistics for seasonal mean temperature of each region and data set. The statistics used here are mean, standard deviation, mean difference, percent mean bias error (PMBE), and RMSE:

$$\text{mean: } \bar{x} = \frac{1}{N} \sum_i x_i ; \quad \bar{y} = \frac{1}{N} \sum_i y_i$$

$$\text{standard deviation: } \sigma_x = \sqrt{\frac{1}{N} \sum_i (\bar{x} - x_i)^2}; \quad \sigma_y = \sqrt{\frac{1}{N} \sum_i (\bar{y} - y_i)^2}$$

$$\text{mean difference: } \bar{x}_{diff} = \bar{x}(\text{Urban}) - \bar{x}(\text{Rural}); \quad \bar{y}_{diff} = \bar{y}(\text{Urban}) - \bar{y}(\text{Rural})$$

$$PMBE = \sum_i (y_i - x_i) * \frac{100}{\sum_i x_i}$$

$$RMSE = \sqrt{\frac{\sum_i (x_i - y_i)^2}{N}}$$

where x_i represents the i^{th} data point from the measurements, y_i the i^{th} output from the simulations, and N is the sample size. Generally, throughout the CONUS temperatures are higher by about 2.12°C in urban regions (AQS sites; squares) than rural regions (CASTNET sites; asterisk).

Table 3-3: Comparison of observed ($\bar{x}$) and simulated ($\bar{y}$) seasonal mean temperature with (in parentheses) σ for various regions of the U.S. The observed ($\bar{x}_{diff}$) and simulated ($\bar{y}_{diff}$) differences in temperature between mostly rural CASTNET sites and mostly urban AQS sites and the RMSE are also shown

Region	Dataset	$\bar{x}(\sigma_x)$ ($^{\circ}\text{C}$)	$\bar{x}_{diff}$ ($^{\circ}\text{C}$)	$\bar{y}(\sigma_y)$ ($^{\circ}\text{C}$)	$\bar{y}_{diff}$ ($^{\circ}\text{C}$)	RMSE ($^{\circ}\text{C}$)
NE	CASTNET	18.15(0.57)	1.93	18.76(0.57)	2.23	0.62
	AQS	20.08(0.64)		20.99(0.68)		0.93
MW	CASTNET	20.78(0.42)	-0.31	21.49(0.41)	-1.08	0.72
	AQS	20.47(0.59)		20.41(0.69)		0.34
NGP	CASTNET	16.84(0.30)	3.31	17.16(0.36)	3.57	0.36
	AQS	20.15(0.28)		20.73(0.44)		0.62
NW	CASTNET	22.15(0.20)	3.15	22.04(0.39)	3.83	0.26
	AQS	19.89(0.28)		20.49(0.30)		0.63
SW	CASTNET	23.04(0.74)	1.3	24.32(0.76)	2.37	1.40
	AQS	22.33(0.28)		22.95(0.28)		0.62
SGP	CASTNET	23.62(0.56)	3.28	25.32(0.66)	0.79	1.70
	AQS	22.10(0.55)		23.21(0.58)		1.14
SE	CASTNET	25.38(0.65)	2.12	24.00(0.57)	1.87	1.42
	AQS	20.01(0.40)		20.68(0.42)		0.56
CONUS	CASTNET	22.13(0.52)		22.55(0.60)		0.95
	AQS					

The higher surface temperature in urban compared to rural regions averaged over the CONUS is also apparent in the output from the simulations, with a mean temperature

difference of 2.00°C (Table 3-3). We attribute this temperature difference to the urban heat island effect [Pleim *et al.*, 2013; Santamouris *et al.*, 2015; Zhang *et al.*, 2009]. The only region that does not show a significant difference of seasonal mean temperature between urban and rural locations is the MW region. Overall, CMAQ captures the CONUS seasonal mean temperature well, with a small positive RMSE of 0.56°C (rural) and 0.95°C (urban). In the SE region, CMAQ exhibits the highest positive seasonal mean temperature difference of 1.38°C with respect to AQS data whereas the SW region displays the highest negative seasonal mean temperature of difference of – 1.28°C. For the results that follow, we assume that the small differences between simulated and measured temperature do not bias the CPF.

We calculate the mean of seasonal daily maximum 8-hr averaged O₃ from the hourly O₃ observations and compare to output from simulations. Figure 3-4b shows a scatterplot of measurements versus simulations of seasonal 8-hr max O₃ (see also Table 4). The seasonal 8-hr max O₃ is biased high in CMAQ, with a positive PMBE of 5.47% in urban locations (average of all the PMBE values for AQS sites given in Table 4). Conversely, rural locations exhibit a small negative PMBE of –0.83% (average of all PMBE values for CASTNET) for O₃. The urban/rural PMBE discrepancy is present for all regions except the MW, which displays a strong negative PMBE for urban and rural regions. We attribute the urban/rural discrepancy within CMAQ to its tendency to keep anthropogenic emission of NO_x too close to urban source regions, a model deficiency first described by Canty *et al.* [2015]. A portion of this discrepancy could be due to the dependency of CMAQ to use too long of a lifetime for alkyl nitrates [Canty *et al.*, 2015; Goldberg *et al.*, 2016; Hembeck *et al.*, 2019]. In addition, the biogenic emission model (BEIS) within CMAQ has the tendency to under predict soil NO_x emission [Li *et al.*, 2019]. As a result, less soil NO_x is available to form surface O₃ in upwind regions within the simulation.

Simulations using CMAQ capture seasonal 8-hr max O₃ from all measurement sites within the CONUS well, although the RMSE is sometimes greater than the observed standard deviation; see also Figure 3-4. The CONUS RMSE of the seasonal 8-hr max O₃ is 5.38 ppb (average of all sites). However, the model tends to overestimate observed

surface O₃ in urban regions (PMBE = 5.47%) and underestimate surface O₃ in rural regions (PMBE = -0.83%), despite the good overall statistical agreement.

The agreement between modeled and observed of O₃ varies greatly by climate region. CMAQ overestimates observed seasonal 8-hr max O₃ for most climatic regions. The highest PMBE of 16% (~9 ppb) is found for urban regions of the SE. We attribute the model's high PMBE for O₃ (see Figure 3-4b) to the overestimation of NO_x emissions [Anderson *et al.*, 2014; McDonald *et al.*, 2013; Toro *et al.*, 2021; Travis *et al.*, 2016]. Travis *et al.* and Anderson *et al.* show in their papers that in the time of this study (2002-2012), the NEI overestimated surface NO_x emissions from mobile and possibly other sources.

Table 3-4: Comparison of observed ($\bar{x}$) and simulated ($\bar{y}$) seasonal mean surface O₃ with (in parentheses) σ for various regions of the U.S. The table also gives the observed ($\bar{x}_{\text{diff}}$) and simulated ($\bar{y}_{\text{diff}}$) differences in O₃ between mostly rural CASTNET sites and mostly urban AQS sites, the PMBE, and the RMSE.

Region	Dataset	$\bar{x}(\sigma_x)$ (ppb)	$\bar{x}_{\text{diff}}$ (ppb)	$\bar{y}(\sigma_y)$ (ppb)	$\bar{y}_{\text{diff}}$ (ppb)	PMBE (%)	RMSE (ppb)
NE	CASTNET	49.41(4.17)	-1.62	47.28(2.99)	4.00	-4.32	3.18
	AQS	47.79(3.08)		51.28(2.32)		7.31	3.98
MW	CASTNET	52.81(3.63)	-4.67	45.62(1.76)	-3.18	-13.61	9.51
	AQS	48.14(3.60)		42.44(2.14)		-11.85	9.97
NGP	CASTNET	47.53(3.78)	-1.26	48.37(1.91)	-3.40	1.77	2.38
	AQS	46.27(3.03)		44.97(2.03)		-2.80	6.19
NW	CASTNET	NA	NA	NA	NA	NA	NA
	AQS	40.12(2.44)		46.08(3.29)		14.86	5.78
SW	CASTNET	46.89(2.77)	5.64	52.15(3.95)	2.77	11.22	6.61
	AQS	52.53(1.50)		54.92(2.39)		4.57	3.07
SGP	CASTNET	44.55(1.80)	2.12	43.77(2.75)	7.66	-1.74	3.54
	AQS	46.67(3.79)		51.43(2.21)		10.19	5.23
SE	CASTNET	49.01(3.11)	-2.52	48.15(2.55)	5.78	-1.75	4.24
	AQS	46.49(3.03)		53.93(2.32)		16.00	9.15
CONUS	CASTNET	48.25(3.39)	-1.39	47.67(2.59)	1.62	-0.83	4.55
	AQS	46.86(2.14)		49.29(4.44)		5.47	6.20

Both papers suggest a reduction of surface NO_x emissions, ranging between 30-70%, is needed to agree with their empirical determinations of NO_x emissions. Toro *et al.* evaluate oxidized nitrogen compounds using the same multi-year CMAQ simulations as in our study, and also find that CMAQ5.0.2 has a high NO_x mean bias for NO_x compared to AQS data, particularly during summer in the SE region, although they attribute the bias to errors in mixing. Additional studies comparing modeled and

measured column NO₂ [Canty *et al.*, 2015; Goldberg *et al.*, 2016; Hembeck *et al.*, 2019] support the contention that high NO_x is a likely driver of model high bias in seasonal 8-hr max O₃ in the SE. Other factors such as improper representation of biogenic emissions of VOCs [Hembeck *et al.*, 2019] as well as marine emissions of NO_x [Ring *et al.*, 2018] may also play a role in the high O₃ bias within CMAQ. The MW region however displays a different relationship, with CMAQ underestimating seasonal 8-hr max O₃ on average by up to 10 ppb (Figure 3-4).

A scatter plot of the CPF from measurements and simulations (Figure 3-5) shows an overall good representation of the empirical CPF inferred from the many thousands of surface O₃ and temperature measurements.

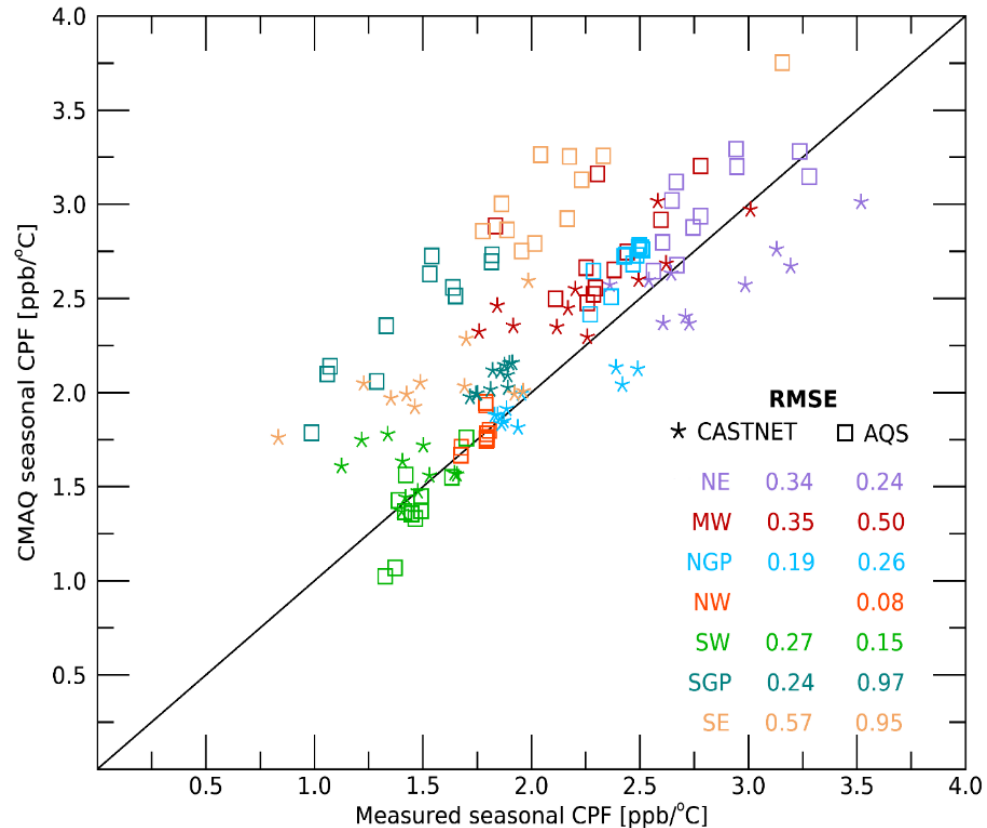


Figure 3-5: Comparison of seasonal (May-September) CPF between measurements and simulations from CASTNET (asterisks) and AQS (squares) locations. Different regions are color coded and the 1:1-line is denoted in black. The table within the figure shows the root mean square error (RMSE) of the CPF of each region for CASTNET on the left and AQS on the right. Symbols as in Figure 3-4.

For the entirety of all of the ground-based sites the average observed CPF value is 1.97 ± 0.48 ppb/°C and the averaged simulated value is 2.23 ± 0.58 ppb/°C. The CMAQ simulations of the CPF within the CONUS are generally higher than the value of CPF computed from the observations by $6.55\% \pm 31\%$ for rural regions (CASTNET locations) and by $20\% \pm 41\%$ for urban regions (AQS locations). Particularly good agreement between measurements and the CMAQ simulation is found for the SW region, with a small RMSE of 0.27 ppb/°C in rural locations and 0.15 ppb/°C in urban locations. A large discrepancy between measurements and simulations exists in the SE region, with an RMSE of 0.57 ppb/°C in rural locations and 0.95 ppb/°C in urban locations. The SE region shows the greatest overestimate in modelled O₃ concentrations with a PMBE of +16%, but this high bias does not appear to result from overestimated temperatures. In this region modelled temperatures on average are 1°C lower than measurements.

Table 3-5: Comparison of observed ($\bar{x}$) and simulated ($\bar{y}$) seasonal CPF with (in parentheses) σ for various regions of the U.S. The observed ($\bar{x}_{\text{diff}}$) and simulated ($\bar{y}_{\text{diff}}$) differences in CPF between mostly rural CASTNET sites and mostly urban AQS sites, the PMBE, and the RMSE are also given.

Region	Dataset	$\bar{x}(\sigma_x)$ (ppb/°C)	$\bar{x}_{\text{diff}}$ (ppb/°C)	$\bar{y}(\sigma_y)$ (ppb/°C)	$\bar{y}_{\text{diff}}$ (ppb/°C)	PMBE (%)	RMSE (ppb/°C)
NE	CASTNET	2.84(0.35)	-0.01	2.60(0.20)	0.4	-7.88	0.34
	AQS	2.83(0.25)		3.00(0.23)		6.16	0.24
MW	CASTNET	2.27(0.38)	0.05	2.55(0.25)	0.2	12.35	0.35
	AQS	2.32(0.24)		2.75(0.26)		18.59	0.5
NGP	CASTNET	2.05(0.27)	0.38	1.95(0.12)	0.73	-4.53	0.19
	AQS	2.43(0.09)		2.68(0.12)		10.35	0.26
NW	CASTNET		0.04		-0.2		
	AQS	1.77(0.05)		1.80(0.10)		1.57	0.08
SW	CASTNET	1.43(0.16)	0.04	1.59(0.13)	-0.2	11.12	0.27
	AQS	1.47(0.11)		1.39(0.21)		-5.46	0.15
SGP	CASTNET	1.83(0.07)	-0.4	2.07(0.07)	0.32	12.94	0.24
	AQS	1.43(0.30)		2.39(0.32)		67.14	0.97
SE	CASTNET	1.55(0.35)	0.6	2.06(0.22)	1.02	32.90	0.57
	AQS	2.15(0.38)		3.08(0.29)		43.46	0.95
CONUS	CASTNET	1.94 (0.47)	0.06	2.11 (0.35)	0.33	6.55	0.31
	AQS	2.00 (0.48)		2.36 (0.58)		20.26	0.45

Hence, the overestimate of NO_x emissions [Anderson *et al.*, 2014; Travis *et al.*, 2016]

is likely the driving factor for the large discrepancy between measurements and simulations.

Hall et al. [2020b] showed that vehicular NO_x emissions (especially diesel) increase with decreasing ambient temperature at a rate of $\sim 2\%/^{\circ}\text{C}$ and may account for a substantial fraction of the NO_x emissions high bias in the SE. This dependency is not presently implemented in the emissions drivers of CMAQ, and this effect will be examined in future studies.

Figure 3-6 depicts the average CPF for each region for the two datasets (black, gray) and simulations (blue, light blue). The black and blue bars correspond to CASTNET locations, and the grey and light blue columns correspond to AQS locations. The high bias of the CPF in CMAQ in the SE region is particularly evident in Figure 3-6.

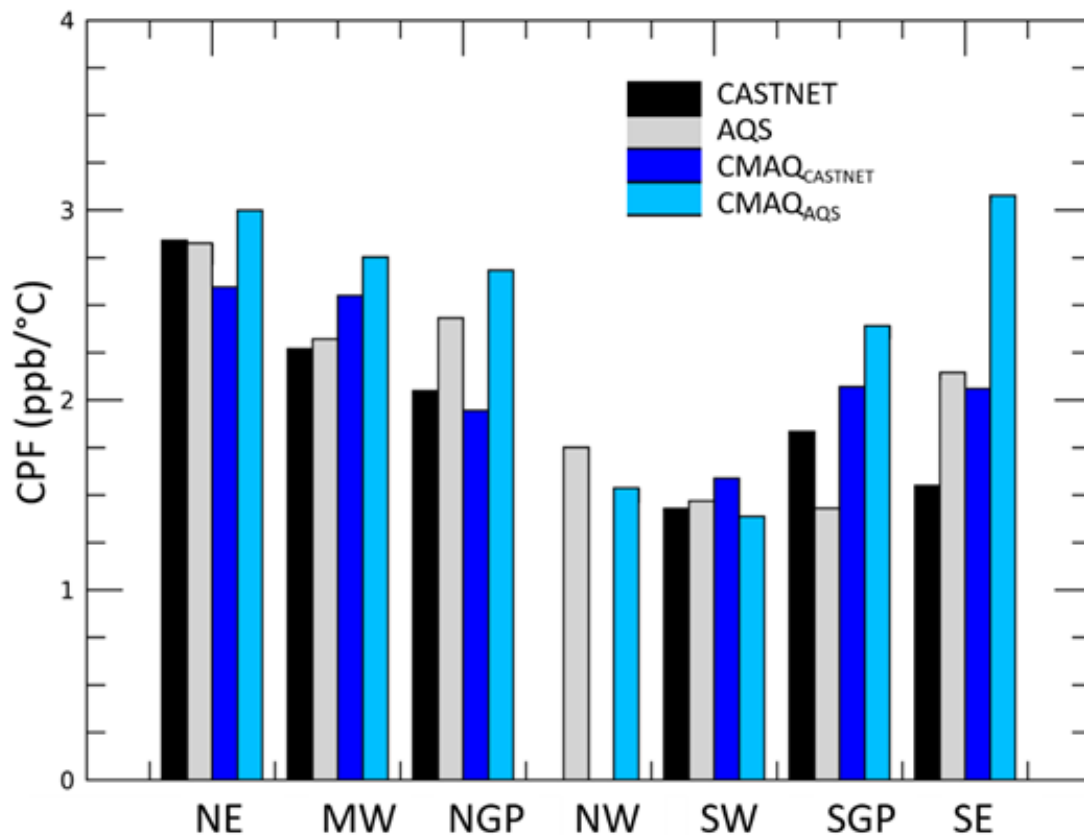


Figure 3-6: Bar plots showing mean CPF (2002-2012) for six different regions from CASTNET (black bars) and 7 different regions from AQS (gray bars). Simulations for comparable times and locations to observations are shown as blue bars.

Figure 3-7 depicts the timeseries of the CPF for each climatic region over the 11-year period for rural regions (except the NW where no rural stations existed).

The black points represent CASTNET data and the red points CMAQ output (evaluated at the CASTNET locations).

Slope (m) and p -value (p indicates the probability that an observed difference could have occurred by random chance) are also indicated. There is an overall decreasing trend of the CPF during the 11-year period of -0.02 ± 0.03 ppb/ $^{\circ}$ C/yr from CASTNET measurements and of -0.03 ± 0.02 ppb/ $^{\circ}$ C/yr from CMAQ; the NE region displays the most significant decreasing trend (smallest p -value) in the data ($m = -0.08$ ppb/ $^{\circ}$ C/yr) as well as in simulation ($m = -0.05$ ppb/ $^{\circ}$ C/yr).

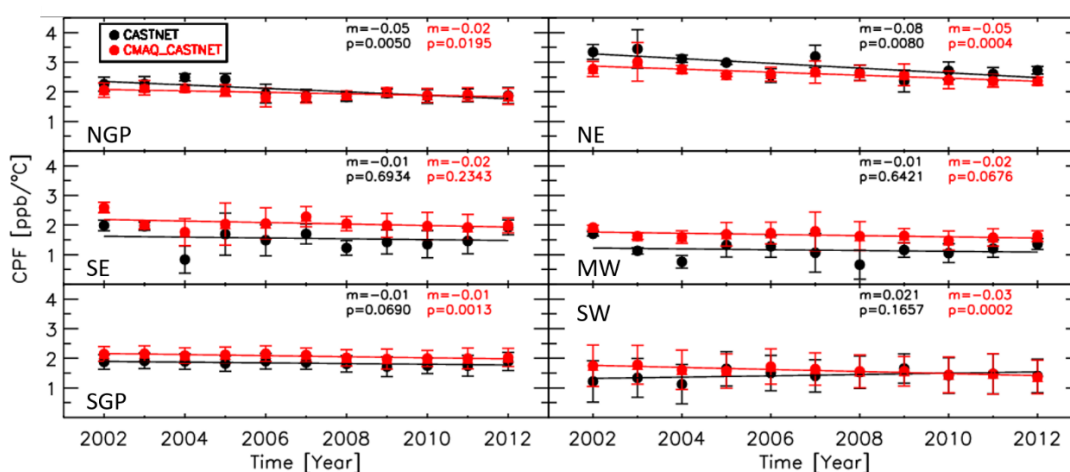


Figure 3-7: Timeseries of the CPF from 2002 to 2012 for 6 climatic regions within the CONUS. CASTNET data are in black and the results of CMAQ simulations are in red. The slope (m ; ppb/ $^{\circ}$ C/yr) and p -values are denoted for each region. Error bars represent the standard deviation for each year.

Figure 3-8 depicts the timeseries of the CPF for each climatic region over the 11-year period for urban regions. On an annual basis there is good agreement of the CPF between measurements and simulations in the NGP, NE, NW, and SW regions. In the SE, MW, and SGP, the simulations overestimate the CPF although slopes based on measurements and simulations are similar. The overall decreasing trend (average of all seven regions) of the CPF during the 11-year period is -0.04 ± 0.03 ppb/ $^{\circ}$ C/yr from AQS measurements and -0.04 ± 0.02 ppb/ $^{\circ}$ C/yr from simulations; the greatest decrease in CPF can be found in the SGP region. The slopes of the timeseries are more statistically significant (smaller p -values) in urban regions and greater in magnitude (Figure 3-8) compared to those in rural regions (Figure 3-7). We attribute the urban/rural difference in the slope of CPF to higher concentrations of surface NO_x and

O₃ in urban regions than in rural regions. The urban/rural difference is evident in measurements as well as in simulations, but a greater urban/rural variation exists in the simulations (see Figure 3-6) due to NO_x being high and/or kept too close to the source [Canty *et al.*, 2015; Hembeck *et al.*, 2019]. Simulations generally capture the trend of the CPF during the 11-year period i.e., the model roughly matches the sign and magnitude of the trends seen in the observations.

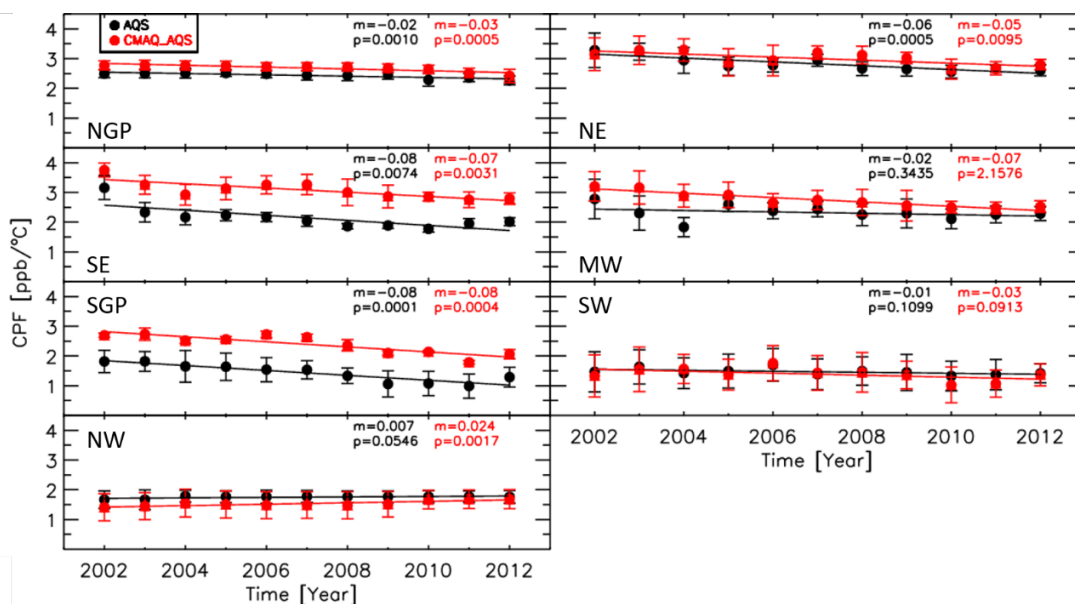


Figure 3-8: Timeseries of the CPF from 2002 to 2012 for 7 climate regions within the CONUS. AQS data are in black and CMAQ output is in red.

3.5 Conclusions

Using hourly surface observations of O₃ and T from CASTNET, AQS, and NCDC from March to September 2002 to 2012 for each year and the whole 11-year period for seven individual climate regions within the CONUS we find that on average seasonal temperature and daily maximum O₃ measurements are represented well within CMAQ. For the CONUS, temperature is slightly overestimated by $\sim 0.6^{\circ}\text{C}$ and O₃ on average by ~ 5 ppb (the bias is greater for urban regions compared to rural regions). We calculated CPF values for data and simulations similarly and find that CMAQ produces CPF values close to measured data. The average observed value of CPF for the CONUS over 2002 to 2012 is 1.97 ± 0.48 ppb/ $^{\circ}\text{C}$ and the average simulated value of all sites is 2.23 ± 0.58 ppb/ $^{\circ}\text{C}$; the RMSE for all years and locations is 0.38 ppb/ $^{\circ}\text{C}$ or about 13%. The modelled CPF has a 14% (0.33 ppb/ $^{\circ}\text{C}$) higher bias in urban (AQS) than in

rural (CASTNET) regions compared to CPF inferred from surface observations, possibly because of overestimated total (especially vehicular) NO_x emissions and underestimated soil NO_x emissions (less transport of NO_x to upwind regions) for the modelled period. In addition, CMAQ using the chemical mechanism CB05TU-CL keeps some O₃ precursors too close to urban sources [*Canty et al.*, 2015; *Hembeck et al.*, 2019], resulting in higher O₃ bias in urban regions compared to rural regions.

The SE region exhibits the greatest overestimate in the modelled concentration of O₃ in urban regions (16%) as well as CPF (~43%) compared to empirical values. Temperature within the CMAQ simulation was underestimated, suggestive that temperature is not causing the CPF values to be high. Ozone, however, was significantly overestimated, likely because of overestimated precursor emissions in CMAQ, which is consistent with many studies of NO_x inventories for the period 2002-2012. Since the value of CPF declines with falling concentrations of NO_x, the SE may experience slightly lower sensitivity of ozone to climate change than suggested by the CMAQ runs considered here. Most other regions within the CONUS have a decreasing trend in CPF over the 11-year period in both measurements and simulations. For the CONUS, values of CPF decreased in rural regions by -0.02 ± 0.03 ppb/°C/yr in observations and -0.03 ± 0.02 ppb/°C/yr in simulations and in urban regions by -0.04 ± 0.04 ppb/°C/yr in observations and simulations. These decreasing values of CPF indicate that emissions controls have reduced the impact of climate change (warming) on surface ozone. Our study indicates that the CPF within CMAQ is captured well in most climate regions and (all other factors being held constant) a 2°C increase in temperature could increase ozone by ~4 ppb. This finding suggests that CMAQ is capturing the impact of changing meteorology on ozone and could a useful tool to assess the climate penalty of surface O₃ due to global warming. Next steps might include studies with CMAQ driven by meteorology in a warmer future climate based on output of climate model simulations – this type of simulation should give a reasonable indication of the additional pollution controls needed to overcome the impact of higher temperatures.

Chapter 4: Comparison of satellite-observed and modeled ammonia (NH₃) under varying chemical environments across East Asia

This chapter describes preliminary work utilizing CMAQ output of ammonia (NH₃) and comparing it to satellite data. The simulations were conducted by Hyun Cheol Kim at the NOAA Air Resources Laboratory for the purposes of investigating NH₃ abundances within CMAQ under varying chemical environments.

4.1 Introduction

Ammonia (NH₃) plays an important role in the global nitrogen cycle as a key nutrient for every ecosystem [Fowler *et al.*, 2013a; Fowler *et al.*, 2013b; Reis *et al.*, 2009; Zhu *et al.*, 2015]. Globally NH₃ emissions are rising due to an increase in agricultural livestock in conjunction with growing use of nitrogen fertilization [Paulot *et al.*, 2014; Warner *et al.*, 2017]. While agricultural processes are the major source of NH₃ emissions globally, several other sources contribute to local or regional enhancements in atmospheric NH₃. Motor vehicles equipped with catalytic converters can reduce NO to NH₃, contributing significantly to local emission of NH₃. In urban areas that lack agricultural practices, vehicles can be the dominant source of NH₃ [Farren *et al.*, 2021; Fenn *et al.*, 2018; Perrino *et al.*, 2002; Sun *et al.*, 2017]. Therefore, the rapid industrialization and energy consumption in recent years in China causes serious concern to air quality in East Asia due to the increase in emissions of anthropogenic pollutants (indirectly from increase in livestock and directly from an increase in vehicle emissions of NH₃). NH₃ degrades air quality because of its role in the formation and composition of particulate matter, which also affects the radiative forcing of climate [Reiss *et al.*, 2007]. Light reflecting white aerosols (organic carbon) can turn brown (brown carbon) in the presence of NH₃ that then absorb light causing a warming of the atmosphere [Updyke *et al.*, 2012; Wang *et al.*, 2020a]. Water quality is affected due to high NH₃ deposition making surface water toxic; in addition, a change in pH can cause fish to die from pH shock [Yang *et al.*, 2008].

Even though NH₃ is important in the global nitrogen cycle it has not been measured with high accuracy as well as good spatial and/or temporal coverage [Nair

and Yu, 2020]. There is a lack of in-situ measured NH_3 due to the difficult process of measuring it because of its chemical properties [Li *et al.*, 2006]. Great care must be taken to sample NH_3 due to its high reactivity and stickiness [Schilt *et al.*, 2004]. It is absorbent and desorbent on most surfaces and could react with the sensor. In addition, NH_3 rapidly changes phases (gas/liquid/particulate) [Alexa and Mikuska, 2020; Yamada *et al.*, 2012].

Measuring NH_3 through remote sensing has its own challenges. NH_3 has a short lifetime (~ 1 day in the boundary layer), resulting in high spatiotemporal differences within individual pixels. In addition, most of the NH_3 is located in the boundary layer and total NH_3 mixing ratios are low (parts per trillion by volume to parts per billion by volume). Thus, satellite measurements require high sensitivity to the lowermost troposphere [Wang *et al.*, 2020b; Warner *et al.*, 2016]. Satellites retrieving NH_3 emissions use infrared radiance differences (Beer's Law). The first satellite used to retrieve NH_3 was the Tropospheric Emission Spectrometer (TES) onboard the EOS Aura satellite [Alvarado *et al.*, 2011; Sun *et al.*, 2015]. However, TES provides limited global coverage on a daily basis. In this study we use remote sensed NH_3 from the Atmospheric Infrared Sounder (AIRS) aboard the NASA Aqua satellite. AIRS provides global coverage and daily NH_3 retrievals. We compare NH_3 concentrations from the AIRS satellite to simulations from the Community Multiscale Air Quality (CMAQ).

CMAQ is a chemical transport model that requires accurate emissions inventories to assess air quality policies (see section 1.3.2). The main issue in developing an accurate emissions inventory for NH_3 is the sheer breadth of emission sources including all the uncertainties in measuring and validating them (historically few measurements). In this study we use three emissions inventories for the East Asia region to investigate CMAQ under various chemical environments and compare them to satellite measurements.

4.2 Satellite Measurements

The Atmospheric Infrared Sounder (AIRS) instrument on board NASA's Earth Observing System (EOS) Aqua satellite measures NH_3 from space. The satellite was launched 4 May 2002 and covers nearly the whole globe twice daily with local overpass

time of 1.30pm (ascending node). The AIRS instrument's spectral region is between 650 and 2670 cm^{-1} containing 2387 discrete channels. For the retrieval of NH_3 , 12 channels are being used from the following spectral windows: 860–875, 928–932, and 965–967 cm^{-1} . AIRS clear sky coverage is only 10–15% at 13.5 km^2 single-view pixel size (Warner et al., 2013). However, Susskind et al. (2003) described a method that increases data coverage to 50–70 %. AIRS has good sensitivity to lower tropospheric NH_3 due to its averaging kernel (AK) peaking at about 918 hPa and the planetary boundary layer generally extending above this altitude in the early afternoon. In this study we use monthly NH_3 level 3 data with $1^\circ \times 1^\circ$ grid resolution [Warner et al., 2017] obtained from https://disc.gsfc.nasa.gov/datacollection/AIRSAC3MNH3_3.html, last accessed late August 2021. AIRS reports ammonia concentrations in units of ppb.

4.3 CMAQ

This study uses the U.S. Environmental Protection Agency (EPA) Community Multiscale Air Quality (CMAQ) model, version 4.7.1 with the chemical mechanism Statewide Air Pollution Research Center version 99 (SAPRC99) and aerosol module AERO5. The Weather Research and Forecasting (WRF) Model, version 3.3 [Skamarock and Klemp, 2008] was run offline to generate meteorological fields [EPA, 2014b] (temperature, boundary layer height, humidity, three dimensional winds, etc.) processed with the Meteorological Chemistry Interface Processor (MCIP) version 3.6 [Otte and Pleim, 2010] before being ingested into CMAQ. WRF is initialized with the National Centers for Environmental Protection (NCEP) Global Forecast System (GFS) $0.5^\circ \times 0.5^\circ$ global product which are also taken as meteorological boundary conditions. The generated meteorological fields are also used as input to the Sparse Matrix Operator Kernel Emissions (SMOKE v3.1) model, which generates gridded anthropogenic emission fields. Both WRF and CMAQ were run at $27 \text{ km} \times 27 \text{ km}$ horizontal resolution, for a model domain covering East Asia (Figure 4-1) for 2011 and 2016. Both WRF and CMAQ have 22 vertical layers (σ coordinate) with the top of the first layer being at 32 m.

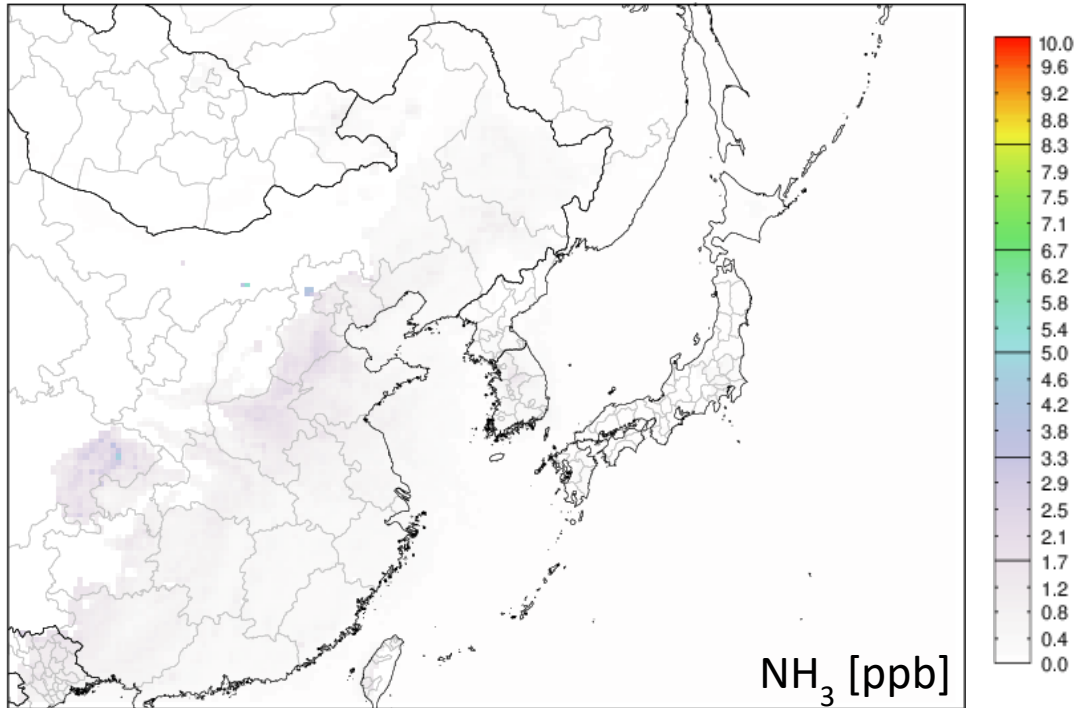


Figure 4-1: Map of CMAQ modelling domain covering East Asia

4.4 Emissions Inventories

We process three different anthropogenic emissions inventories in SMOKE to obtain a compatible spatial resolution product for CMAQ, i.e. the Intercontinental Chemical Transport Experiment-Phase B (INTEX-B) 2006 emissions inventory, the Model Inter-Comparison Study for Asia (MISC-ASIA) emissions inventory (MIX inventory for the year 2010; in the following called MIXED-ASIA), and the Comprehensive Regional emission inventory for Atmospheric Transport Experiment (CREATE version 2.3) for the year 2015 [*Jang et al.*, 2020]. The CREATE inventory is used as baseline input for a 2016 CMAQ simulation. We produced two additional simulations other than the baseline, one with adjusted SO₂ and one with SO₂ and NO₂ adjusted. The adjustments were made in part because the CREATE emissions inventory reflects emissions during 2015 but the CMAQ simulation is for 2016.

Table 4-1 Species included in the included in the emissions inventory

Emissions Inventory	Species	Emissions
INTEX-B	SO ₂ , NO _x , CO, NMVOCs, PM10, PM2.5, black carbon, organic carbon	8 species in 2006 as follows: 47.1 Tg SO ₂ , 36.7 Tg NO _x , 298.2 Tg CO, 54.6 Tg NMVOC, 29.2 Tg PM10, 22.2 Tg PM2.5, 2.97 Tg BC, and 6.57 Tg OC

MIXED-ASIA	SO ₂ , NO _x , CO, NMVOCs, NH ₃ , PM10, PM2.5, black carbon, organic carbon, CO ₂	10 species in 2010 as follows: 51.3 Tg SO ₂ , 52.1 Tg NO _x , 336.6 Tg CO, 67.0 Tg NMVOC (non-methane volatile organic compounds), 28.8 Tg NH ₃ , 31.7 Tg PM10, 22.7 Tg PM2.5, 3.5 Tg BC, 8.3 Tg OC, and 17.3 Pg CO ₂
CREATE	SO ₂ , NO _x , CO, non-methane volatile organic compounds (NMVOC), NH ₃ , OC, BC, PM10, PM2.5, CO ₂ , CH ₄ , N ₂ O, and Hg	Information only available for SO ₂ with 3.5 Tg

The emissions adjustment procedure for SO₂ and NO₂ emissions is a top-down adjustment and described in detail in [Bae *et al.*, 2020]. In brief, the adjustment to the modelled emissions is calculated as follows:

$$\frac{E_{adj}}{E_{mod}} = \frac{C_{obs}}{C_{mod}} \quad (E3)$$

where E_{adj} are the adjusted emissions, E_{mod} are the modelled emissions (baseline), C_{obs} and C_{mod} are the observed and modelled concentrations, respectively. For this study surface observations of SO₂ and NO₂ are used to adjust emission inventories.

We use biogenic emissions from Model of Emissions of Gases and Aerosols from Nature (MEGAN vs. 2.04) [Guenther *et al.*, 2006]. Emissions from MEGAN are widely used outside the U.S. [Carlton and Baker, 2011; Jiang *et al.*, 2019; Wang *et al.*, 2020b]. Biogenic emissions greatly depend on meteorology. We use year specific meteorology; therefore, the simulations using the INTEX-B and MIXED-ASIA emissions inventory have the same 2011 meteorology while the simulations using the CREATE emissions inventory has the 2016 meteorology. Hence, comparisons of 2011 simulations with 2016 simulations need to be done with a lot of care.

4.5 Preliminary Findings

We look at 2011 satellite data and compare to CMAQ output using either the INTEX-B or the MIXED-ASIA emissions inventory. Figure 4-2 shows a timeseries of mean (solid lines) and maximum (dotted lines) NH_3 concentrations from the satellite (black) with 1σ uncertainty and simulations (red and purple) for 2011. Overall, using the MIXED-ASIA inventory in CMAQ provides better representation of observed NH_3 . The poorer performance of the absolute NH_3 concentrations in CMAQ found using the INTEX-B emissions is likely due to the creation year of 2006 for this inventory. The INTEX-B inventory did not capture the emissions peak in the summer but rather placed it in the spring. This result indicates that this inventory might feature more fertilizer application during spring, or the source strength is overestimated. Using AIRS satellite data Warner et al. [2017] showed that over a 13-year period that NH_3

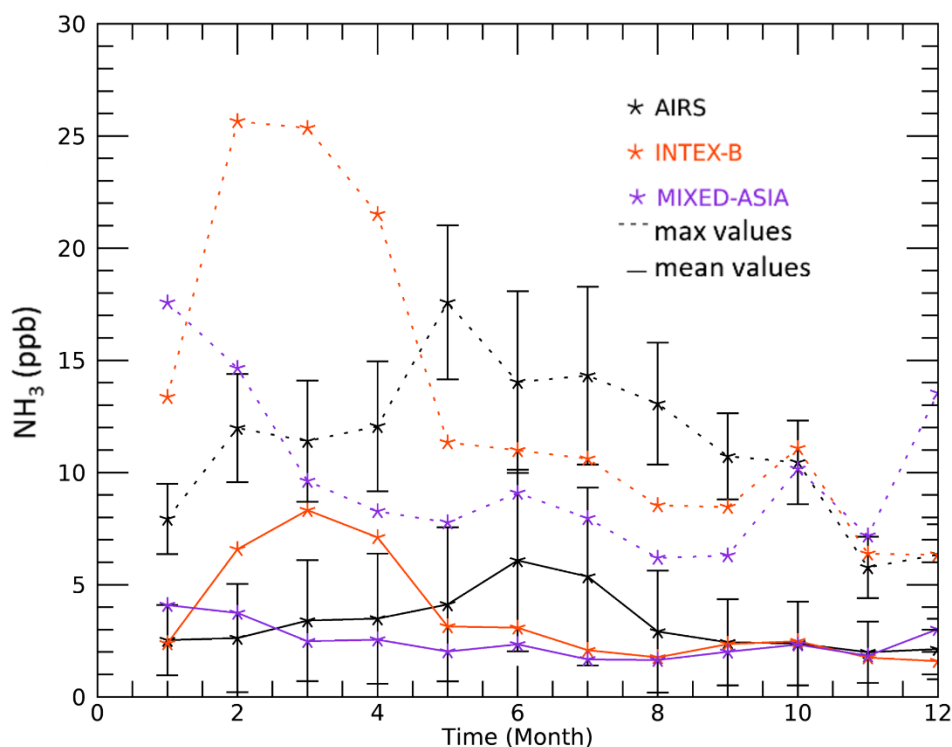


Figure 4-2 Timeseries plot of mean (solid lines) and maximum (dotted lines) NH_3 concentrations from the satellite (black) with 1σ uncertainty and simulations (red and purple) for 2011 for the domain shown in Figure 4.1.

concentrations over China are greatest in June and July, with a secondary spring maximum. The summer maximum of NH_3 in 2011 from measurements is clearly visible

while a secondary maximum in the spring is not evident in 2011. Our analysis shows that CMAQ underestimates NH_3 concentrations in the summer, a result also found by Shepard et al. 2015 analyzing NH_3 column density over the US from the Infrared Atmospheric Sounding Interferometer IASI instrument (Metop-A satellite) compared to CMAQ.

In addition, a likely reason for NH_3 in the simulation using the MIXED-ASIA emissions inventory to be generally lower than the simulation using the INTEX-B emissions inventory could be because SO_2 and NO_2 emissions are both lower in the INTEX-B emissions inventory (see table 4-1). Less SO_2 and NO_2 in the atmosphere result in less H_2SO_4 or HNO_3 acids and in turn less NH_3 is needed to neutralize such acids. Hence, higher NH_3 concentrations are expected in simulations using the INTEX-B emissions inventory compared to using the MIXED-ASIA emissions inventory.

Figure 4-3 shows a timeseries of mean (solid lines) and maximum (dotted lines) NH_3 concentrations from the satellite (black) and simulations (red, purple, and pink) for 2016.

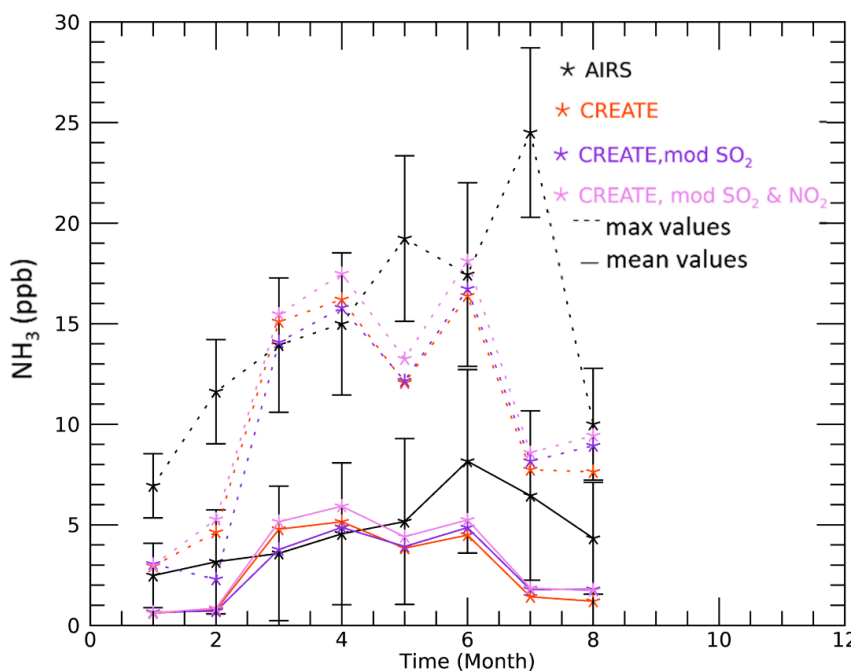


Figure 4-3: Timeseries of mean (solid lines) and maximum (dotted lines) NH_3 concentrations from the satellite (black) with 1σ uncertainty and simulations (red, purple, and pink) for 2016.

Here, the CMAQ simulations use the CREATE emissions inventory. Overall, the satellite data and CMAQ output for NH₃ compare better than using the INTEx-B or MIXED-ASIA emissions inventory. The mean concentrations of NH₃ in the spring from measurements compares best to the simulation that uses the CREATE_{SO2} emissions inventory. However, in the summer the measurements show a greater increase during June and July compared to all simulations.

SO₂ is adjusted using equation E3 in CREATE_{SO2}. That means depending on the ratio of measured to baseline SO₂ concentrations the SO₂ emissions are either increased or reduced. Figure 3 in Bea et al. [2020] shows this ratio with values of less than 1 in most regions. Therefore, throughout the domain SO₂ emissions are reduced using the CREATE_{SO2} which results in an increase in NH₃ in the domain. NH₃ is a neutralizing agent in the atmosphere; therefore, we expected more NH₃ in the atmosphere since less NH₃ is needed to neutralize acids such as H₂SO₄ or HNO₃. The simulation using the CREATE_{SO2&NO2} emissions inventory shows overall higher NH₃ concentrations compared to the baseline simulation and the simulation using CREATE_{SO2} emission inventory.

Comparing AIRS data from 2011 and 2016, an increase in NH₃ concentrations can be observed in China. The measured mean increase of NH₃ concentrations between June (2011-2016) is 2.08 ppb. This increasing trend was also found by Warner et al. [2017] who showed that multiple factors favored the increase in NH₃ concentrations between September 2002 to August 2016. One factor is the increase in application of fertilizer during this period and another the decrease of sulfur emissions which scavenges NH₃ from the atmosphere. SO₂ and NH₃ emissions are roughly anti-correlated [Warner et al., 2017].

Spatial figures for each month of 2011 and January – August of 2016 are shown below (Figures 4-4, 4-5, and 4-6). Results show that absolute values of NH₃ concentrations vary greatly between month in measurements and simulations. During spring (March, April, May), the poorest agreement between AIRS measurements and the simulation using the INTEx-B emissions inventory is found, with average concentrations of 3.67 ± 0.39 ppb and 6.19 ± 2.71 ppb, respectively. This difference is most likely due to the previous stated reason that this emissions inventory is outdated.

However, CMAQ simulations do locate the NH_3 concentrations in the same proximity as the satellite product for most months. The comparison of AIRS measurements to simulations using the MIXED-ASIA and CREATE emissions inventories have NH_3 concentrations in the right location but seem to have emissions sources differ in strength and/or in timing of the release of NH_3 compared to the real world.

For example, mean NH_3 concentrations in the measurements have a maximum in the summer (Figure 4-3). The maximum NH_3 value (~ 17 ppb) is captured in June by all simulations but not for July. Now when investigating the spatial figures for June and July of 2016 (Figure 4-6) the spatial extend of NH_3 concentrations compares well to measurements however there are more red pixels (high NH_3 concentrations) in the measurements for June compared to simulations. In July the simulations do not display any red pixels hence the maximum and mean NH_3 concentrations are much lower compared to measurements. To investigate these differences between measurements and simulations further analysis is needed. Such as analyzing the emissions inventories used in this study directly in order to pinpoint if the underestimate of NH_3 in CMAQ is related to the source strength/type. This analysis would benefit from a comparison to ground based measurements of NH_3 , SO_2 , and NO_2 .

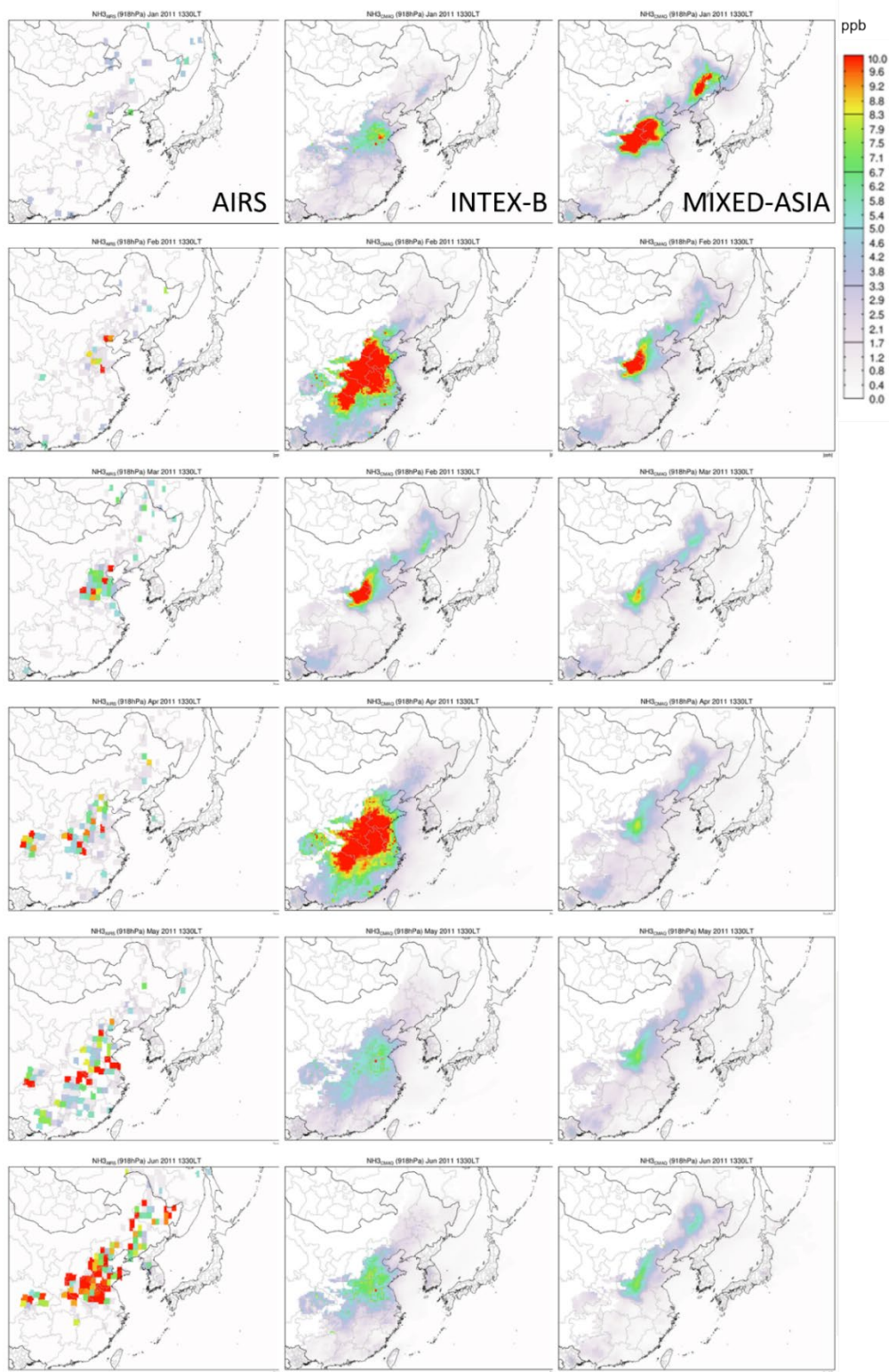


Figure 4-4 Map showing NH_3 concentrations in Northeast Asia from measurements (AIRS) and simulations using INTEX-B and MIXED-ASIA emissions inventories from January – June 2011.

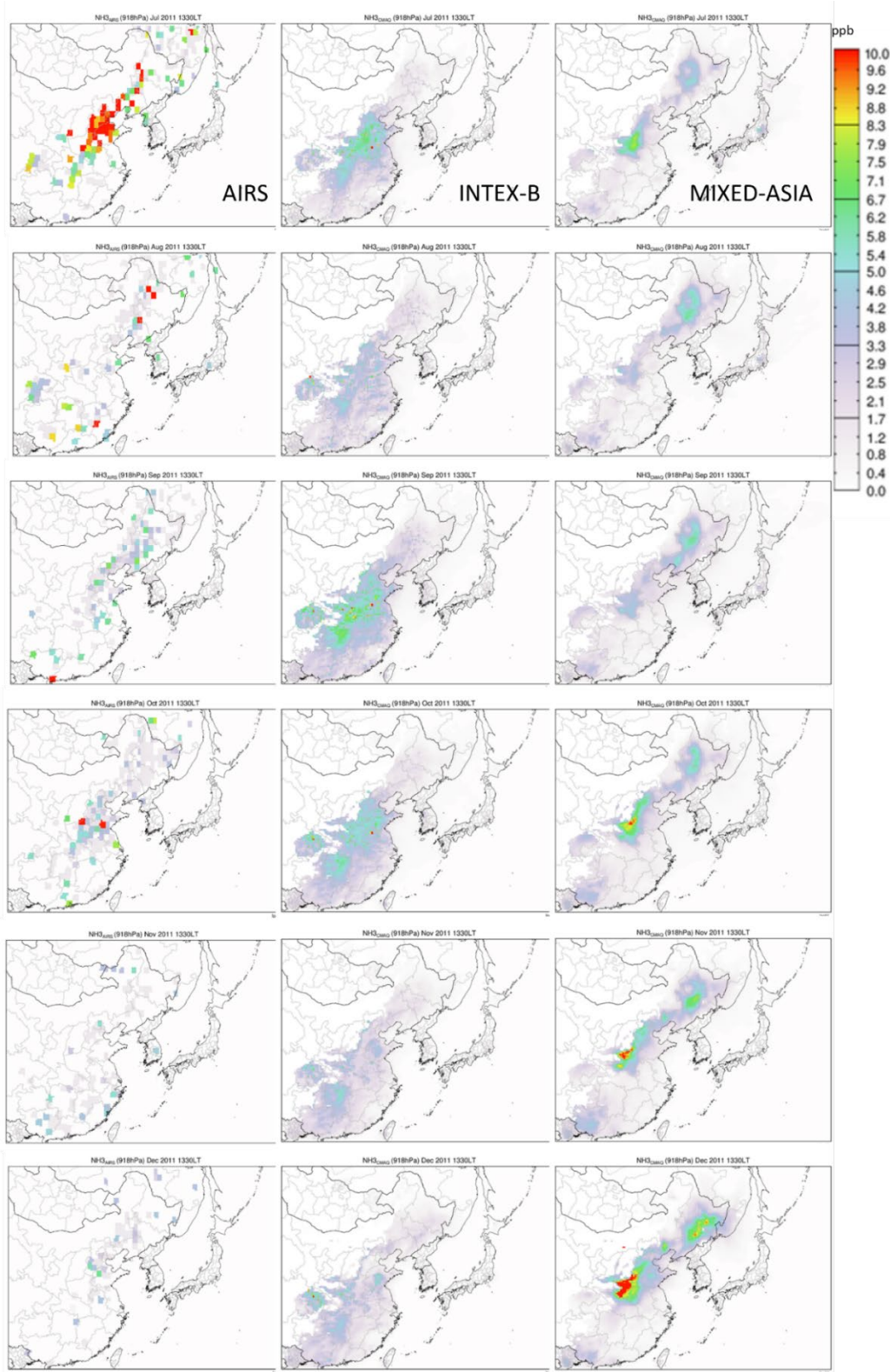


Figure 4-5 Map showing NH_3 concentrations in Northeast Asia from measurements and simulations using INTEX-B and MIXED-ASIA emissions from July – December 2011.

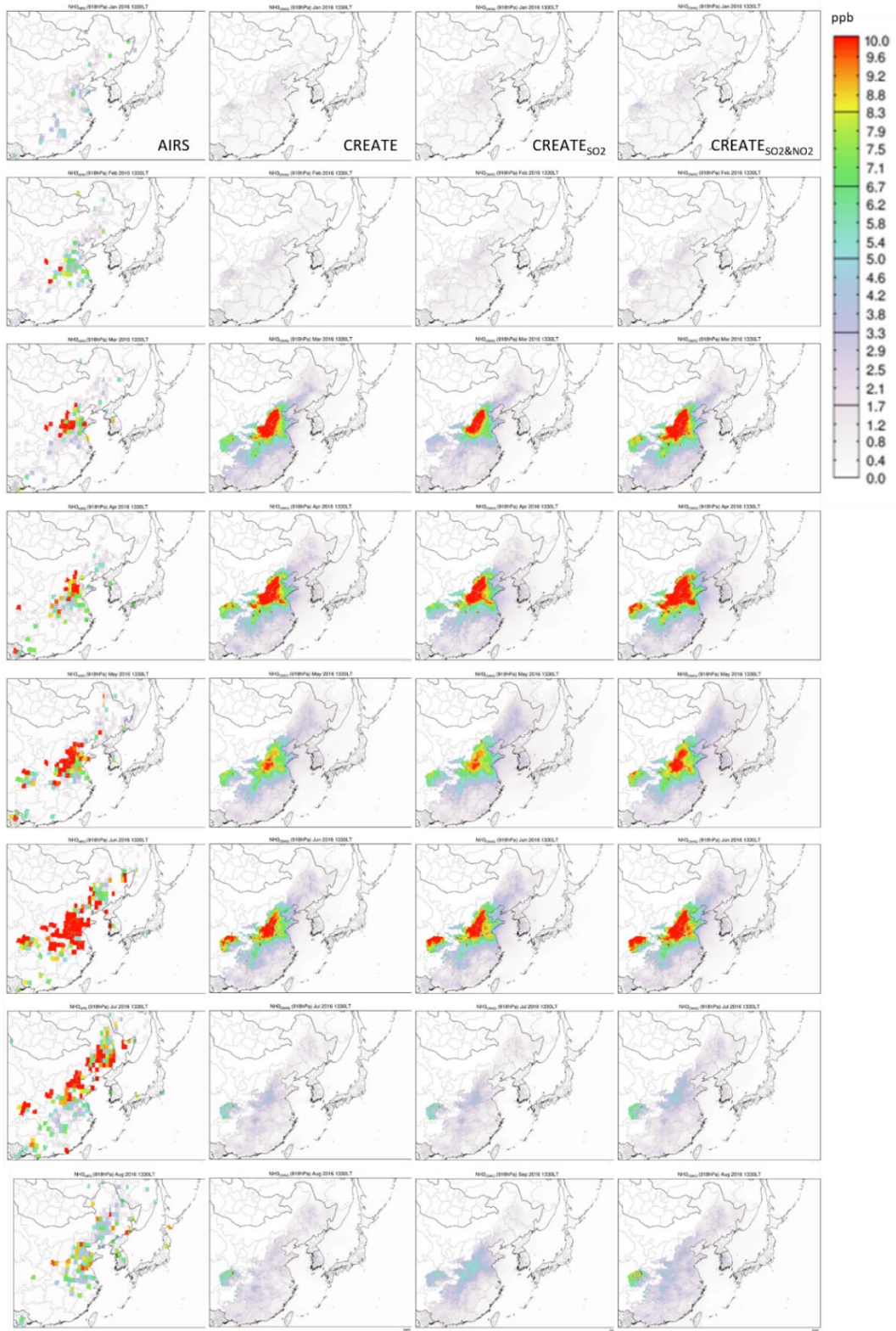


Figure 4-6 Map showing NH₃ concentrations in Northeast Asia from measurements and simulations using INTEX-B and MIXED-ASIA emissions from January – August 2016.

Chapter 5: Conclusions and Implications

The body of this work comprises the utilization, modification, and analysis of the air quality model CMAQ by comparing simulations to measurements at the surface, from aircraft campaigns and tropospheric observations from satellite retrievals. Science questions addressed in this work focus on the desire to improve CMAQ and makes future predictions of O_3 , precursors to O_3 , and ammonia concentrations more accurate such that policy decisions can be made with greater certainty.

In Chapter 2, data collected during the July 2011 NASA DISCOVER-AQ campaign in the Baltimore-Washington region were used to quantify ozone production efficiency (OPE) from measurements and were compared to output from the Community Multiscale Air Quality (CMAQ) model. The baseline model run of CMAQ underestimates observed OPE by $34 \pm 20\%$. The payload of D-AQ lacked direct observations of HO_2 and RO_2 , so we infer the rate at which these peroxy radicals react with NO (termed $inRO_x$) from observations of NO, NO_2 , O_3 , and $j(NO_2)$. The baseline run of CMAQ underestimates $inRO_x$ by $35 \pm 19\%$. A modified run of CMAQ with;

- a factor of 10 reduction in the lifetime of organic nitrates,
- a factor of 2 reduction in mobile NO_x emissions,
- an updated thermal dissociation rate of PAN and PANX (IUPAC 2014),
- a correction for the rate constant for $OH + PANX$

results in better overall model performance based on data that include column NO_2 measured by the Ozone Monitoring Instrument, a value of

- OPE that is improved from 34 to 21% less than observed, and
- $inRO_x$ that is improved from 35 to 30% low.

Sensitivity analysis indicates that the peroxy radical discrepancy involves either emission of VOCs other than isoprene or HCHO, or a problem with the model production of HO_2 and RO_2 . Our analysis suggests surface O_3 may exhibit stronger declines to further reductions of NO_x than is indicated by baseline runs of CMAQ. I was the lead author on this chapter, published on 19 February 2019 in *Atmospheric Environment X*.

In Chapter 3, the Climate Penalty Factor (CPF) was investigated to quantify the adverse impact of increasing temperatures on surface O_3 because elevated levels of tropospheric ozone caused by anthropogenic emissions of NO_x and VOCs have a negative impact on human health, crops, and ecosystems. Even if precursor emissions are reduced from current levels, predicted higher temperatures due to increased greenhouse gas emissions could impede air quality benefits. We computed the CPF from surface observations at CASTNET (mostly rural) and AQS (mostly urban) sites and compare these values to CMAQ output for the contiguous U.S. and seven sub-regions for the ozone season (May 1 through September 30) for each year from 2002 through 2012. CMAQ can in general reproduce with reasonable accuracy the CPF for the CONUS. This finding suggests that CMAQ is capturing the impact of changing meteorology on ozone and is a useful tool to assess the climate penalty of surface O_3 due to global warming. In predominantly rural regions (CASTNET) observed CPFs average 2.00 ppb/ $^{\circ}C$ while simulated CPFs average 2.11 ppb/ $^{\circ}C$. Higher CPFs are found in predominantly urban regions (AQS) where observed CPFs are 2.06 ppb/ $^{\circ}C$ and simulated CPFs are 2.39 ppb/ $^{\circ}C$. CMAQ reproduces CPFs at rural sites reasonably well but tends to overestimate CPFs at urban sites. Upon examination of each sub-region, the CMAQ simulation for the Southeast shows a substantial overestimate (43%) of CPF for urban (AQS) sites. Conversely, the CMAQ simulations for the Northeast show a slight underestimate (8%) of the CPF at rural (CASTNET) sites. Both results for CPF (overestimated for urban sites and either underestimated or close to observed for rural sites) could be related to the tendency of this version of CMAQ (with a long lifetime for alkyl nitrates) to overestimate NO_x or keep it too close to the urban source locations. Our analysis suggests that CMAQ may attribute a somewhat greater fraction of O_3 production to an increase in temperature than observed. Finally, there is a $\sim 2\%$ decrease in CPF throughout the CONUS during the 11-year period in both measurements and the CMAQ simulations, suggesting that reductions in NO_x emissions can mitigate the impact of climate change on surface ozone. I am the lead author on this chapter, which was submitted for publication on 13 October 2021 to *Atmospheric Environment*.

In Chapter 4, preliminary work utilizing CMAQ output of ammonia (NH_3) and comparing it to satellite data is described. The simulations were conducted by Hyun Cheol Kim for the purposes of investigating NH_3 abundances within CMAQ under varying chemical environments. Three different emissions inventories (INTEX-B, MIXED-ASIA, CREATE) were utilized plus 2 sensitivity simulations ($\text{CREATE}_{\text{SO}_2}$ and $\text{CREATE}_{\text{SO}_2\&\text{NO}_2}$). While Chapter 4 highlights preliminary results it lacks a comprehensive investigation of the chemistry of NH_3 . However, a few conclusions can be drawn from this analysis:

- The INTEX-B emissions inventory is outdated and should not be used to simulate present day NH_3 emissions over East Asia.
- Concentrations of NH_3 within CMAQ are underestimated using the MIXED-ASIA or CREATE emissions inventory.
- More realistic representation of SO_2 and NO_2 emissions in the emissions inventory bring NH_3 concentration in simulations closer to measured values from AIRS.

5.1 Recommendations for Future Work

Chapters 2 and 3 heavily focus on the representation of nitrogen species within CMAQ. Nitrogen species are important precursors to O_3 ; however, VOCs are also quite important. Errors in the model representation of VOCs can potentially impact organic N reservoirs. In Chapter 2, I utilized a calculation to estimate the total production rate of HO_2 and RO_2 within CMAQ. This calculation could not distinguish HO_2 from RO_2 , but provided a good estimate of the frequency at which all peroxy radicals react with NO . These results suggest that future work should examine the possibility of underestimated VOC emissions in the EPA emissions inventory. In addition, a greater HO_2 and/or RO_2 production, and faster thermal dissociation of organic peroxy nitrates within CMAQ could improve simulations of O_3 concentrations. *In situ* observations of HO_x radicals, although rare due to the difficulty of measuring such species, would provide the necessary information. Field campaigns conducted to examine air quality need to integrate HO_x measurements into their field campaigns.

Further investigation is also recommended to quantify contributions to uncertainties in kinetic parameters within the chemical mechanism in CMAQ to improve simulations for O₃. Simulations do not explicitly account for these uncertainties. Ridley et al. [2017] used a Lagrangian chemical transport model in conjunction with the Monte Carlo method to show that kinetic uncertainties can account for up to 10-12 ppb variation in the mixing ratio of O₃. I have shown in Chapter 2 that updating the thermal dissociation rate of PAN to rates reflecting the state of the science not only improves model performance, showing the importance of updated reaction rates within a chemical mechanism but also showed that investigating the uncertainties is very insightful.

In Chapter 2, OPE was determined within the CML defined as pressure > 820 hPa. Future work could benefit from a detailed comparison of CML depth for the Baltimore/Washington region. The CML can be determined based on temperature and humidity (thermodynamic approach), a chemical that changes significantly across the lower troposphere such as CO₂ and O₃ (chemical approach), and/or from aerosols (aerosol backscatter approach). Depending on which of these approaches are used the CML depths can deviate from each other and would need to be assessed [Hennemuth and Lammert, 2006]. During DISCOVER-AQ lidar measurements are available that use aerosol backscatter to determine the CML. Hegarty et al. [2018] discuss, in conjunction of high resolution WRF modelling, two lidar instruments and a satellite retrieval to find the best estimate for the CML.

In Chapters 2 and 3, OPE, inRO_x, and the CPF were all evaluated using version 5.0.2 of CMAQ. Also, the CMAQ simulations in Chapter 3 span years 2002 to 2012. Our understanding of tropospheric O₃ photochemistry would benefit from re-examination of OPE, inRO_x, and CPF using newer versions of CMAQ, as well as runs of CMAQ that cover the gap between 2012 and present time.

Chapter 4 exposes caveats that require further investigation of NH₃. In turn, that includes measurements with better temporal and spatial coverage. The investigation should include determining all NH₃ emission sources as well as their strength. The analysis in Chapter 4 can be expanded to include comparison of other gaseous species such as SO₂, NO_x, and PM. New findings from Kong et al. [2021] make matters even

more complex. They found that after aerosol formation, due the reaction of SO_2 with NH_3 , the ammonium sulfate salts entertain surface reactions that form elemental sulfur and nitrogen gas depending on the amount of water vapor in the air. Hence, investigation of ammonium sulfate salt as a major source of nitrogen species downwind of NH_3 sources is instrumental for our understanding of NH_3 emissions/chemistry. Another recent paper by Kickman et al. [2021] using NH_3 retrieval from IASI shows the great benefit of using satellite data to discern the complex dependencies of NH_3 emissions in selected African regions. However, their results still suggest that the evaluation of retrieval products would benefit from high-quality surface observations. I suggest, due to the inter dependencies of surface measurements, remote sensed retrievals, and simulations of NH_3 a comprehensive investigation is needed considering these interdependences. This future effort will contribute towards a better understanding of ammonia in the atmosphere.

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