Improved representation of volatile organic compounds (VOCs) chemistry for urban air quality simulation

Wenlu Wu

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Declaration of Authorship

The candidate confirms that the work submitted is his own, except where work which has formed part of jointly authored publications has been included. The contribution of the candidate and the other authors to this work has been explicitly indicated below. The candidate confirms that appropriate credit has been given within the thesis where reference has been made to the work of others.

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The candidate carried out the WRF-GC experiments, analysed the results, and wrote the text. The candidate, T. Fu, S. Arnold and D. Spracklen designed the study. A. Zhang, W. Tao, X. Wang, Y. Hou, J. Mo, J. Chen, X. Feng, and H. Lin developed the WRF-GC model. All authors contributed to the manuscript.

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Abstract

Near surface ozone (O₃), produced via the oxidation of volatile organic compounds (VOCs) in the presence of NO_x (\equiv NO + NO₂) and sunlight, is a critical environmental concern in China. Current air quality models do not represent the temperature dependence of anthropogenic VOC (AVOC) emissions and oversimplify the representation of VOC photochemistry, leading to inaccurate O₃ predictions. This thesis aims to addresses these challenges, enhancing O₃ modelling accuracy and providing insights for regional air quality management. First, this study developed a parameterization describing the temperature-dependence of AVOC emissions. The parameterization was then applied to a regional air quality model (WRF-GC) to quantify the impacts of temperature-sensitive AVOC emissions on ozone formation in the Beijing-Tianjing-Hebei (BTH) region of China. Over a typical warm-season temperature range of 291 K to 304 K, the temperature sensitivity of total AVOC emissions in the BTH region was 6.25% K⁻¹, while biogenic VOC (BVOC) emissions exhibited higher temperature sensitivity of 11.2% K⁻¹. Temperature-enhanced AVOC and BVOC emissions increased the simulated day-to-day surface ozone variability in the BTH by 1.3 µg m⁻³ K⁻¹ and 2 µg m⁻³ K⁻¹, respectively, exacerbating ozone exceedances during warm periods. The inclusion of temperature-sensitive AVOC emissions enhances the model's accuracy in simulated ozone, particularly in VOC-limited urban areas, and aligns simulated ozone-temperature sensitivities more closely with observed values. This study subsequently compares the impacts of varying degrees of VOC photochemical complexity on simulated ozone formation, focusing on aromatic in a box model framework. The research reveals that two simplified mechanisms, namely the chemical mechanism of the GEOS-Chem model and the Common Representative Intermediates (CRI) mechanism, underestimate the RO_x (\equiv OH + HO₂ + RO₂) production from aromatics by 23% and 29%, respectively, relative to that simulated with the near-explicit Master Chemical Mechanism (MCM). This discrepancy was traced to insufficient productions of a key intermediate, methylglyoxal, in the two simplified mechanisms. Optimizing the aromatic yields of methylglyoxal in the GEOS-Chem mechanism reduced its RO_x underestimation from 23% to 6% and its underestimation of ozone net production from 22% to 10%, relative to those simulated with the MCM simulations. This thesis further examined whether tuning methylglyoxal yields is a viable way to improve the ozone simulation in the WRF-GC regional air quality model, which uses the GEOS-Chem mechanism. It was found that, by scaling up the aromatic yield of methylglyoxal by a factor 1.5, WRF-GC's simulated methylglyoxal

concentration was brought closer to that simulated with the MCM mechanism (mean underestimation reduced from 0.57 ppb to 0.42 ppb). This improved methylglyoxal representation then propagated to bring the simulated levels of RO_x , CH_2O , and ozone (mean underestimation reduced from 0.6 ppb to 0.3 ppb) closer to that simulated with the MCM. The adjustments also enhanced PAN formation and reduced NO overestimations. These findings highlight the critical roles of VOCs' temperature-sensitive emissions and photochemical complexity in surface ozone simulations. By refining the representation of VOCs' emission and photochemistry, particularly emphasizing methylglyoxal as a tuneable intermediate in the aromatic scheme, this study provides actionable guidance to improve air quality models as a useful tool for air quality management.

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Abbreviations

ACI	Aerosol-Cloud Interactions			
ARI	Aerosol-Radiation Interactions			
AFCID	Anthropogenic Fugitive, Combustion, and Industrial Dust			
AVOC	Anthropogenic Volatile Organic Compounds			
AOSS	Atmospheric Observation Supersite of Shenzhen			
AR4	IPCC Fourth Assessment Report			
AR5	IPCC Fifth Assessment Report			
AR6	IPCC Sixth Assessment Report			
BC	Boundary Conditions			
BTH	Beijing-Tianjin-Hebei			
BVOC	Biogenic Volatile Organic Compounds			
CEDS	Community Emissions Data System			
CNEMC	China National Environmental Monitoring Center			
CRI	Common Representative Intermediates Mechanism			
DSMACC	Dynamically Simple Model of Atmospheric Chemical Complexity			
EKMA	Empirical Kinetic Modeling Approach			
ERF	Effective Radiative Forcing			
FNR	Formaldehyde to NO_2 Column Concentration Ratios			
FP	Fenwei Plain			
GBD	Global Burden of Disease Study			
GC	GEOS-Chem			
GEOS	Goddard Earth Observing System			
GDAS	Global Data Assimilation System			
GFED4	Global Fire Emissions Database Version 4			
GTS	Global Telecommunications System			
НЕМСО	Harmonized Emissions Component			
IC	Initial Conditions			
KPP	Kinetic Preprocessor			
LDAR	Leak Detection and Repair			
MCM	Master Chemical Mechanism			

MDA8	Maximum Daily 8-Hour Average					
MEE	Ministry of Ecology and Environment of People's Republic of China					
MEGAN	Model of Emissions of Gases and Aerosols from Nature					
MEIC	Multi-resolution Emission Inventory for China					
MIR	Maximum Increment Reactivity					
MIX	Mosaic Asian Anthropogenic Emission Inventory					
MM5	F ifth-Generation Pennsylvania State University-National Center for					
	Atmospheric Research Mesoscale Model					
NASA	National Aeronautics and Space Administration					
NCAR	National Center for Atmospheric Research					
NCEI	National Centers for Environmental Information					
NCEP FNL	National Centers for Environmental Prediction Final					
NCP	North China Plain					
NMVOCs	Non-Methane Volatile Organic Compounds					
NSI	Non-Solvent-use Industrial activities					
PRD	Pearl River Delta					
RRTMG	Rapid Radiative Transfer Model					
ODEs	Ordinary Differential Equations					
OMI	Ozone Monitoring Instrument					
OFP	Ozone Formation Potential					
OVOC	Organic Volatile Organic Compounds					
PMF	Positive Matrix Factorization					
SCB	Sichuan Basin					
S/IVOCs	Semi- and Intermediate Volatility Compounds					
SOA	Secondary Organic Aerosols					
STE	Stratosphere-Troposphere Exchange					
VOCs	Volatile Organic Compounds					
WHO	World Health Organization					
WMGHGs	Well-Mixed Greenhouse Gases					
WPS	WRF Preprocessing System					
WRF	Weather Research and Forecasting					
YRD	Yangtze River Delta					

1. Introduction and motivation

1.1 Motivation

Air pollution is a critical environmental issue that adversely impacts human health, ecosystems, and the Earth's climate. Air pollution is mainly caused by the emission of pollutants and their precursors from various anthropogenic sources, including power generation, industrial activities, transportation, agriculture, waste management, and residential activities (Popescu and Ioana, 2010; Holman, 1999). These pollutants and precursors may be released directly into the atmosphere in the form of gases or particulates, or they may be formed secondarily in the atmosphere through physical or chemical processes. Human exposure to air pollutants can lead to both accute or chronic health effects (Lakey et al., 2016; Brunekreef et al., 2002), such as respiratory and cardiovascular diseases, neurological disorders, prenatal complications, and even premature deaths (Murray et al., 2020; GBD 2019). These health consequences impose significant economic costs on society, including healthcare expenses and loss of productivity (Khoshnevis and Khanalizadeh, 2017; Avnery et al., 2011). Additionally, air pollution degrades ecosystems, affecting biodiversity and ecosystem services, such as clean water, fertile soil, and climate regulation (Zepp et al., 2003; Ramanathan et al., 2001).

Surface ozone (O₃) is a major air pollutant in many parts of the World. Ozone in the troposphere and at the surface is predominantly produced via complex, non-linear photochemical reactions involving volatile organic compounds (VOCs) and nitrogen oxides (NO_x \equiv NO + NO₂) in the presence of sunlight (Jacob, 1999). Surface ozone causes respiratory problems, aggravates asthma, reduces lung function (Zhang et al., 2019; Jerrett et al., 2009), and it is estimated to results in 210,000 deaths globally in 1990, increasing to 370,000 by 2019 according to Global Burden of Disease Study 2019 (GBD 2019) (Hu et al., 2024; Murray et al., 2020). Ozone pollution also damages crops, forests, and other vegetation, endangering food security and biodiversity (Feng et al., 2015; Gheorghe and Barbu, 2011; Chameides et al., 1994).

As one of the world's most populous and rapidly developing countries, China faces significant challenges with air pollution, including high concentrations of surface ozone (MEE, 2024; Wang et al., 2017). Over the past decade, surface ozone pollution concentrations have escalated in many Chinese cities, becoming the predominant cause for air quality standard exceedances during the warm season (MEE, 2024; Lu et al., 2018). Therefore, it is crucial to better understand the causes

of ozone pollution in China and develop robust and accurate air quality models that can accurately simulate ozone pollution, particularly with regard to the contributions of VOCs.

Atmospheric VOCs play a crucial role in the formation of surface ozone (Jacob, 1999). VOCs are emitted from a wide range of anthropogenic sources, including power generation, transportation, industrial processes, agriculture, residential activities, waste management (Kansal et al., 2009). Atmospheric VOCs are also emitted from natural sources, such as vegetation, soil, and the ocean (Sindelarova et al., 2014). In the presence of sunlight and NO_x, VOCs undergo complex photochemical reactions to form organic peroxy radicals that lead to the formation of ozone (Jacob, 1999). VOCs also consume or regenerate atmospheric oxidants, thereby modulating the lifetime of other pollutants and greenhouse gases in the atmosphere and thus affect climate. Therefore, accurately representing VOCs chemistry in atmospheric models is essential for the management of ozone pollution and climate change (She et al., 2024; Balamurugan et al., 2022). To achieve this accurate representation, a comprehensive understanding is required, encompassing the characteristics of VOC emissions, their interactions with atmospheric physical conditions, and the intricate photochemical cascades they undergo (Liu et al., 2021; Maji et al., 2020; Qu et al., 2015). Atmospheric VOCs are also involved in the formation of secondary organic aerosols (SOA), which have implications for air quality, climate, and human health. As such, managing atmosphere VOCs could potentially mitigate ozone and fine particulate pollution simultaneously.

The representation of atmospheric VOC emissions in current models requires further development, particularly due to the temperature sensitivity of these volatile compounds (Huang et al., 2022; Song et al., 2019). While most models account for the temperature dependence of VOC emissions from biogenic sources, they often lack a mechanistic representation for anthropogenic sources. As temperatures rise, emissions from activities such as fuel and solvent evaporation and leakage increase, leading to a higher potential for ozone formation (Niu et al., 2021; Na et al., 2005; Song et al., 2019). This issue is especially pertinent in the context of climate change, as rising temperatures may exacerbate ozone pollution (Gu et al., 2020). Additionally, current emissions inventories frequently lack the spatial and temporal resolution necessary to capture this variability, particularly in urban areas. Therefore, it is crucial to better understand and incorporate the temperature dependence of anthropogenic VOC emissions into models to enhance their accuracy.

The current simplifications of VOCs photochemistry pose challenges for the accurate predictions of models (Bottorff et al., 2023). Approximately 500 VOC species have been detected in the atmosphere (Park et al., 2013; Xu et al., 2003; Lewis et al., 2000), and the actual order is estimated ranges from 10^4 to 10^5 species (Goldstein and Galbally, 2007). The photochemical processes involving these VOCs include numerous intermediate species and reactions, many of which are still poorly understood. As the demand for more precise and accurate air quality simulations grows, models are being developed with higher spatial resolutions. This increased spatial resolution enables the capture of complex atmospheric processes at smaller scales. However, many models still rely on highly lumped chemical mechanisms due to computational resource limitations. At these finer spatial resolutions, some lumped species may not react locally but are instead transported, resulting in discrepancies between the objectives of accurate air quality simulations and the chemical representations employed.

In summary, the inadequacies in the representation of VOCs in these models lead to inaccurate simulations of ozone and SOA, addressing these shortcomings is crucial for improving the reliability of air quality forecasts

1.2 Aims of this thesis

This doctoral thesis is committed to addressing the aforementioned challenges associated with understanding the impact of VOCs on ozone formation. The ultimate objective is to enhance our modeling capabilities of VOC contributions to ozone formation, thereby offering valuable insights for air quality management strategies. The specific objectives of this thesis are as follows:

 Develop a parameterization to represent the temperature-dependent AVOC emissions for use in atmospheric chemistry models. This objective involves understanding how temperature influences VOC emissions from anthropogenic sources, such as fuel and solvent evaporation and industrial processes, and encapsulating these relationships in theoretically or empirically derived functions. These functions are subsequently integrated into a regional atmospheric chemistry model to quantify the impacts of temperature-sensitive anthropogenic VOCs on surface ozone pollution. The simulation results are validated against observational data to ensure their reliability and applicability in the ambient atmosphere. The findings from this objective underscore a new interaction pathway between air quality and meteorology, carrying significant implications for air quality in a future warmer climate.

- 2. Compare and understand the differences in simulated ozone formation with different complexity degrees of VOC chemistry. This objective involves conducting a comparative analysis of various VOC chemical mechanisms using a box model. By evaluating how different levels of chemical complexity influence reaction pathways and the accuracy of ozone predictions, critical intermediates and reactions essential for accurate simulations will be identified. This analysis will clarify the trade-offs between model complexity and computational efficiency, ultimately guiding the development of more effective modeling strategies for ozone formation.
- **3.** Enhance representation of RO_x chemistry in a regional air pollution model. This objective focuses on improving ozone prediction accuracy in a regional atmospheric chemistry model by refining the production yield of methylglyoxal (MGLY), which plays a crucial role in aromatic RO₂ chemistry. Integrating this enhancement into the WRF-GC regional air quality model aims to improve ozone simulations in urban areas, thereby supporting more effective air quality management and climate change mitigation efforts.

By achieving these aims, this research seeks to advance the field of atmospheric modeling, providing more reliable tools for predicting air quality and informing policies to reduce ozone pollution and protect public health. The outcomes of this thesis will contribute to a better understanding of the complex interactions between VOC emissions and chemistry, and ozone formation, ultimately leading to more effective strategies for managing regional air pollution.

1.3 Thesis layout

Chapter 2 provides an overview of surface ozone pollution and trends in China, summarizes the photochemical processes involved in ozone formation, and highlights the needs for accurately simulating surface ozone for effective pollution control and public health protection. Chapter 3 describes the models and data used in this research, including the WRF-GC model for regional air

quality simulations and the DSMACC box model for detailed chemical mechanism analysis. Chapter 4 details the methodology for developing a parameterization for the temperature dependence of anthropogenic VOC emissions and its integration into air quality models. Chapter 5 analyses different chemical mechanisms in a box model to assess how varying chemical complexities affect ozone prediction accuracy. This chapter identifies key intermediates and reactions for accurate ozone simulations and discusses trade-offs between model complexity and computational efficiency. Chapter 6 improves ozone prediction accuracy by tuning methylglyoxal yields from photochemical reactions of its precursors in the WRF-GC model to better represent organic peroxy radical formation and net ozone production. The effectiveness of this approach is demonstrated through urban case studies in China. Chapter 7 interprets findings within existing literature and their impact on atmospheric modeling and air quality management, and summarizes contributions, addresses limitations, and suggests future research. Modeling advancements are also highlighted, and recommendations are offered for improving air quality and public health.

2. Background

2.1 Ozone in the Troposphere

Ozone (O₃) is a vital component of the atmosphere, with multifaceted impacts on climate, human health, and ecosystems. The stratosphere is a layer of Earth's atmosphere located above the troposphere, extending from about 10 to 15 kilometres to 50 kilometres in altitude. The ozone in the stratosphere is primarily concentrated at altitudes between approximately 15 to 35 kilometres. The ozone layer in the stratosphere absorbs nearly all the Sun's ultraviolet (UV) radiation in the 240 nm to 290 nm range and about 90% of the UV radiation in the 290 nm to 320 nm range. This absorption shields Earth's surface from excessive UV radiation, thereby protecting life on Earth from conditions such as skin cancer in humans and damage to aquatic ecosystems. Ozone's absorption of the solar UV radiation also warms the stratosphere, creating a temperature inversion that characterizes the tropopause (Wallace et al., 2006; Jacob, 1999).

In the troposphere, ozone is a major greenhouse gas and an important oxidant of reduced chemicals. The troposphere is the lowest layer of Earth's atmosphere, extending from the surface up to about 8 to 15 kilometres in altitude. Ozone in the troposphere is primarily concentrated at altitudes of about 10 to 15 kilometres. At the surface, ozone is an air pollutant harmful to human health, responsible for an estimated annual premature mortality of 290,000 from 1990 to 2019 (Hu et al., 2024; Murray et al., 2020; GBD 2019). Surface ozone also damages cells and stomata of plants, jeopardizing ecosystem health and decreasing crop yields (Morgan et al., 2003; Reich and Amundson, 1985). Therefore, comprehending the factors that determine the budget, distribution, and impacts of tropospheric ozone is pivotal for tackling air pollution and mitigating its detrimental effects.

2.1.1 Ozone budget: production, destruction, transportation, and deposition

The budget of tropospheric O_3 is influenced by its transport, chemical production and loss, and deposition to the surface. Table 2.1 summarizes the global tropospheric ozone budgets from published studies. Ozone is a secondary species that is not directly emitted into the atmosphere but formed through photochemical reactions (Hu et al., 2017; Zeng et al., 2010; Stevenson et al., 2006;

Roelofs and Lelieveld, 1997). In the presence of sunlight, precursors (VOC, NO_x, and CO) undergo complex reactions that ultimately lead to the formation of ozone. Ozone is chemically depleted in the atmosphere by reactions with other chemicals such as NO₂, VOCs, and halogens. Ozone also undergoes photolysis reactions where it absorbs solar radiation and breaks down into O_2 and oxygen atoms. Additionally, ozone may deposit to the Earth's surface via both dry and wet processes.

Reference		Young et al, 2013	Griffiths et al., 2021			
1	Models	15 models from ACCMIP	5 models from ACCMIP 5 models from CMIIP6		5 models from CMIIP6	
Simul	ation period	2000	1850 1980 20		2000	
Sources	Chemical production	5110 ± 606	2901±932	4490±1305	5283±1798	
[Tg yr ⁻¹]	STE	552 ± 168	_	_	-	
Sinks [Tg yr ⁻¹] Dry	Chemical loss	4668 ± 727	2437±480	3481±363	3948±379	
	Dry deposition	1003 ± 200	622±222	988±434	1075±514	
Tropospheric burden [Tg yr ⁻¹]		337 ± 23	247±36	325±30	347±30	
Tropospheric lifetime [days]		22.3 ± 2.0	29.5±21	26.4±1.2	25.5±22	

Table 2.1 (Global	budgets	of tro	posp	oheric	ozone
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The transport of ozone in the atmosphere is a complex process involving the movement of ozone molecules both horizontally and vertically, including advection, convection, and diffusion. Advection refers to the horizontal transport of ozone by horizontal winds, moving ozone from areas of high concentrations, such as urban or industrial regions, to rural and remote areas of lower concentrations. Convection causes the vertical movement of ozone. One of the key components in the vertical movement of ozone is the stratosphere-troposphere exchange (STE). The STE has strong seasonal variation. In the mid-latitudes, the STE is most pronounced in spring because of the tropopause folding associated with frontal systems (Wang et al., 2023; Škerlak et al., 2014). The contribution of stratospheric ozone to tropospheric ozone typically ranges from 20% to 50%, depending on the season, region, and meteorological conditions (Williams et al., 2019; Lelieveld and Dentener, 2000). Deep convective events, such as thunderstorms, can also facilitate the transport of ozone from the stratosphere to the troposphere. Diffusion describes the random movement of ozone molecules driven by turbulence and Brownian motion.

Aside from chemical loss (Section 2.2), ozone is removed from the atmosphere through deposition processes. Dry deposition refers to the transfer of molecules from the atmosphere to the Earth's surface in the absence of precipitation. For ozone, dry deposition is mainly driven by turbulent diffusion and may occur over a variety of surfaces, including water, soil, vegetation, and manmade structures. As ozone molecules are transported to approach these surfaces, they enter the surface layer, where wind speed decreases and the transport of ozone is largely influenced by molecular diffusion. Upon reaching the surface, ozone molecules can be absorbed by plants through stomata, react with chemicals on the surface of soil or water, or be absorbed into water bodies (Fowler et al., 2011; Cieslik, 2004; Fowler et al., 2001). Wet deposition is the process where precipitation, such as rain or snow, falls to the Earth's surface, capturing and transporting soluble pollutants along with it. The contribution of wet deposition to ozone removal is relatively small due to ozone's limited solubility (Hu et al., 2017; Wild et al., 2007).

2.1.2 Tropospheric ozone as a greenhouse gas and source of OH

Tropospheric ozone is a significant greenhouse gas that plays a crucial role in the Earth's energy balance. It absorbs the infrared (IR) radiation emitted by the Earth's surface and emits IR radiation at a lower temperature, thereby contributing to global warming. According to the Sixth Assessment Report (AR6) from the Intergovernmental Panel on Climate Change (IPCC) (Forster et al., 2021), the effective radiative forcing (ERF) for total O₃ in 2019 relative to the radiative balance of 1750 is estimated to be 0.47 W m⁻², with a 5%-95% range of 0.24 to 0.70 W m⁻² (Figure 2.1, Forster et al., 2021). Contribution of stratospheric and tropospheric ozone to positive radiative forcing is surpassed only by CO₂ and methane. Compared to the Fourth Assessment Report (AR4) and the Fifth Assessment Report (AR5), the AR6 provided an updated assessment of ERF from stratospheric and tropospheric ozone. The ERF of total ozone estimated in AR6 (1970-2019) increased by 0.17 W m⁻² from the estimates in AR4 (1970-2005) (Table 2.2, Forster et al., 2021).



Figure 2.1 Change in effective radiative forcing (ERF) from 1750 to 2019 by contributing forcing agents (carbon dioxide, other well-mixed greenhouse gases (WMGHGs), total ozone, stratospheric water vapour, surface albedo, contrails and aviation-induced.

	AR4	AR5	AR6
	(1750–2005)	(1750–2011)	(1750–2019)
Tropospheric	0.35	0.40	
ozone	[0.25 to 0.65]	[0.20 to 0.60]	0.47
Stratospheric	-0.05	-0.05	[0.24 to 0.71]
ozone	[-0.15 to 0.05]	[-0.15 to 0.05]	

Table 2.2 Summary table of effective radiative forcing (ERF, units: W m⁻²) estimates for AR4, AR5 and AR6 from IPCC. Ranges shown are 5–95%. (Forster et al., 2021, section 7.3.5, Table 7.8)

In the troposphere, ozone also serves as an important source of OH, which is the dominant atmospheric oxidant. Photolysis of ozone by solar radiation (\leq 320 nm wavelength) generates O(¹D) radicals, which then react with water vapor to produce two OH radicals. These OH radicals may react with air pollutants, such as CO and toxic VOCs, eventually transforming them into less toxic components and effectively cleaning the atmosphere. The oxidation of CH₄ by OH reduces its atmospheric lifetime, thereby mitigating its greenhouse effect. At the same time, the oxidation of organic and inorganic chemicals by OH leads to the formation of oxidized secondary products. For example, the OH oxidation of VOCs and semi- and intermediate volatility compounds, leads to the formation of ozone and SOA. The cycles of production and consumption of OH influence atmospheric chemistry and climate dynamics. Therefore, ozone, as the primary source of OH, indirectly influences atmospheric temperature, atmospheric oxidation capacity, and air quality.

2.1.3 The health and ecosystem hazards of tropospheric ozone

Tropospheric ozone also poses significant risks to human health and ecosystems. In terms of human health, short-term exposure to high concentrations of ozone can lead to acute health issues, such as severe asthma attacks (Goodman et al., 2018), and may also exacerbate existing respiratory conditions or trigger new ones (Kumagai et al., 2017; Yang et al., 2016; Koren et al., 1989). Short-term exposure ozone exposure can also increase coronary mortality, particularly affecting children,

the elderly, and individuals with pre-existing respiratory conditions (Nuvolone et al., 2013). Additionally, short-term exposure contributes to heart disease development, including atherosclerosis, and raises the risk of serious events like heart attacks and strokes (Xia et al., 2018). Long-term exposure to low concentrations of ozone is associated with an increased risk of cardiovascular diseases, partly due to the oxidative stress it induces (Niu et al., 2022; Cakmak et al., 2016). Previous studies have found positive associations between ozone exposure and mortality from Parkinson's disease, dementia, stroke, and multiple sclerosis (Zhao et al., 2021). Long-term ozone exposure could result in premature death (Lim et al., 2019). According to the Global Burden of Disease Study 2019, ozone exposure is estimated to have resulted in 210,000 deaths globally in 1990, increasing to 370,000 by 2019 (Hu et al., 2024; Murray et al., 2020).

Concerning plant life, tropospheric ozone can have severe impacts on photosynthesis. Ozone damages plant cells and stomata, the tiny openings on leaves that facilitate gas exchange. This damage disrupts the photosynthetic process, leading to reduced plant growth and crop yields (Morgan et al., 2003; Reich and Amundson, 1985). This is a significant concern for society, where crop yield is directly tied to food security and economic stability. Additionally, ozone-induced damage weakens plants' defence mechanisms, making them more susceptible to pests, diseases, and other environmental stressors, such as drought or extreme temperatures. This vulnerability can lead to declines in plant health (Iriti and Faoro, 2009; Sandermann, 1996). The damages to plants would futher lead to losses in biodiversity and shifts in ecosystem dynamics (Grulke et al., 2020).

2.2 Ozone formation in the troposphere

Tropospheric ozone is formed via a set of complex photochemical reactions (Sillman et al., 1995; Krupa et al., 1988). Ozone is formed by the combination of oxygen atoms and oxygen (Eq. 2.1).

$$0_2 + 0 + M \rightarrow 0_3 + M$$
 (2.1)

where M denotes a collision partner, not affected by the reaction.

In the stratosphere, atomic oxygen O is produced via the photolysis of O₂ by ultraviolet (UV) radiation ($\lambda \le 240$ nm) (Eq. 2.2). Ozone can also be photolyzed by UV radiation ($\lambda \le 320$ nm) and decompose into oxygen molecule and atomic oxygen (Eq. 2.3).

$$0_2 + hv \to 0 + 0 \qquad (\lambda \le 240 \text{nm}) \tag{2.2}$$

$$0_3 + hv \to 0_2 + 0(^{1}D) \quad (\lambda \le 320nm)$$
 (2.3)

In the troposphere, with much less high-energy UV radiation available, the atomic oxygen is supplied by photolysis of NO_2 (Eq. 2.4). The formed ozone reacts with NO to regenerate NO_2 (Eq. 2.5).

$$NO_2 + hv \rightarrow NO + 0$$
 $(\lambda \le 424 \text{ nm})$ (2.4)

$$0_3 + NO \rightarrow NO_2 + O_2 \tag{2.5}$$

(Eq. 2.1), (Eq. 2.4) and (Eq. 2.5) form a rapid null circle of NO, NO₂, O_3 in the troposphere, and the ozone concentrations will reach a steady state without other reactions (the production rates of ozone equal to destruction rates of ozone).

The formation of ozone is initiated by the production of HO_x ($HO_x \equiv OH + HO_2$). The O¹D formed by (Eq. 2.3) react with H₂O to generate OH

$$O(^{1}D) + M \rightarrow O(^{3}P) + M$$
 (2.6)

$$O(^{1}D) + H_{2}O \rightarrow 2OH$$
 (2.7)

The oxidation of OH with hydrocarbons (RH) propagated the reaction chain. RH includes methane and Non-Methane Volatile Organic Compounds (NMVOCs). RH is emitted into the atmosphere from natural or anthropogenic sources. When RH is oxidized by the OH radical, an H is extracted by OH to form R radicals. R rapidly forms RO₂ with oxygen molecules in the atmosphere (Eq. 2.8). As the molecular size of hydrocarbons increases, their reactivity with OH radicals generally rises, driven by the greater number of C-H bonds available for hydrogen abstraction by OH. Unsaturated hydrocarbons are particularly reactive because OH can rapidly add to the C=C double bonds.

$$RH + OH + O_2 \rightarrow RO_2 + H_2O \tag{2.8}$$

 RO_2 are organic peroxy radicals. In regions with high anthropogenic pollution, the concentrations of NO_x are typically elevated. RO_2 reacts with NO, yielding an organic oxy radical RO and NO_2

$$\mathrm{RO}_2 + \mathrm{NO} \to \mathrm{NO}_2 + \mathrm{RO} \tag{2.9}$$

RO can also react with O₂, producing a carbonyl compound (R'CHO)

$$RO + O_2 \rightarrow R'CHO + HO_2 \tag{2.10}$$

The HO₂ then reacts with NO to generate NO₂ and OH.

$$\mathrm{HO}_2 + \mathrm{NO} \to \mathrm{NO}_2 + \mathrm{OH} \tag{2.11}$$

The carbonyl compound R'CHO may either photolyze to produce HO_x (branching the chain) or react with OH to continue the chain propagation.

Following these reactions, the photolysis of NO₂ leads to the production of ozone and NO. NO participates in reaction (Eq. 2.8) – (Eq. 2.11) and generates NO₂. OH reacts with RH and subsequently reformed by HO₂+NO. In the above reactions, the HO_x and NO_x radicals are not consumed; rather, they act as catalysts, propagating the chain reactions to produce ozone reformed hydrocarbons. This process represents a crucial pathway for the generation of ozone from hydrocarbons in the troposphere. The net reaction is

$$RH + 4O_2 \rightarrow R'CHO + 2O_3 + H_2O$$
 (2.12)

The chain reactions that produce ozone are terminated when either the HO_x or NO_x radicals are removed (Eq. 2.13-2.16):

$$HO_2 + HO_2 \to H_2O_2 + O_2$$
 (2.13)

$$OH + NO_2 + M \rightarrow HNO_3 + M \tag{2.14}$$

$$\mathrm{RO}_2 + \mathrm{NO}_2 + \mathrm{M} \leftrightarrow \mathrm{RO}_2 \mathrm{NO}_2 + \mathrm{M} \tag{2.15}$$

$$\mathrm{HO}_2 + \mathrm{RO}_2 \rightarrow \mathrm{ROOH} + \mathrm{O}_2 \tag{2.16}$$

HNO₃, RO₂NO₂, H₂O₂, and ROOH are all soluble in water and may therefore be removed by deposition. They may also undergo photolysis, allowing NO_x to return to the system.

2.3 Ozone formation regimes

In polluted atmosphere, the chain propagation of ozone production is efficient and the radicals are in steady state. Reaction rates of (Eq. 2.8-2.11) are assumed equal, reactions (Eq. 2.9) and (Eq. 2.11) generate NO_2 that result in the ozone formation, so the ozone production rates can be expressed as

$$P_{O_3} = k_{Eq.2.9}[RO_2][NO] + k_{Eq.2.11}[HO_2][NO]$$
(2.17)

The production and loss rates of the radicals are the same and given by

$$P_{0_3} = 2k_{\text{Eq.2.11}}[\text{H0}_2][\text{N0}]$$
(2.18)

(Eq. 2.11) produces OH and (Eq. 2.8) destroy OH, so the production and loss rates of OH can be expressed as:

$$P_{\rm OH} = k_{\rm Eq.2.11} [\rm HO_2] [\rm NO]$$
 (2.19)

$$L_{\rm OH} = k_{\rm Eq.2.8}[\rm RH][\rm OH]$$
 (2.20)

 $P_{\text{OH}} = L_{\text{OH}}$, thus $k_{\text{Eq.2.11}}[\text{HO}_2][\text{NO}] = k_{\text{Eq.2.8}}[\text{RH}][\text{OH}]$, the concentration of OH is given by

$$[OH] = k_{Eq.2.11}[HO_2][NO] / k_{Eq.2.8}[RH]$$
(2.21)

The HO_x radicals are in steady state, and the production rates and loss rates of HO_x are equal, (Eq. 2.13) and (Eq. 2.14) destroy HO_x, so

$$L_{\rm HO_x} = k_{\rm Eq.2.13} [\rm HO_2]^2 + k_{\rm Eq.2.14} [\rm OH] [\rm NO_2] [\rm M]$$
(2.22)

According to $P_{HO_x} = L_{HO_x}$, the production rates of HO_x

$$P_{\rm HO_x} = k_{\rm Eq.2.13} [\rm HO_2]^2 + k_{\rm Eq.2.14} [\rm OH] [\rm NO_2] [\rm M]$$
(2.23)

In low NO_x condition, the reaction rates of (Eq. 2.13) are much greater than reaction rates of (Eq. 2.14), and the radicals are mainly removed by (Eq. 2.13), so if $k_{Eq.2.14}$ [OH][NO₂][M] in (Eq. 2.23) can be ignored, the production rates of HO_x could be simplified as

$$P_{\rm HO_x} = k_{\rm Eq.2.13} [\rm HO_2]^2$$
(2.24)

So $[HO_2] = (P_{HO_x} / k_{Eq.2.13})^{1/2}$, the production rates of ozone (Eq. 2.17) are equal to

$$P_{O_3} = 2k_{Eq.2.11}[NO](P_{HO_x}/k_{Eq.2.13})^{1/2}$$
 (2.25)

(Eq. 2.25) indicates that the production rates of ozone are positively related to the concentrations of NO in a low NO_x environment but is independent of hydrocarbons. In this case, the O_3 production rate is limited by the supply of NO_x, thus it is called NO_x-limited regime.

When NO_x concentrations are high, the reaction rates of (Eq. 2.14) are much greater than reaction rates of (Eq. 2.13), so the radicals are mainly removed by (Eq. 2.14), the production rates of HO_x can be simplified as

$$P_{\rm HO_x} = k_{\rm Eq.2.14} [\rm OH] [\rm NO_2] [\rm M]$$
(2.26)

So that $[OH] = P_{HO_x}/k_{Eq.2.14}[NO_2][M]$, which can then be replaced into (Eq. 2.21) to give:

$$[HO_2] = (P_{HO_x} k_{Eq.2.8} [RH]) / (k_{Eq.2.14} k_{Eq.2.11} [NO_2] [M] [NO])$$
(2.27)

Then replacing $[HO_2]$ in the production rates of ozone (Eq. 2.18) gives:

$$P_{O_3} = (2k_{Eq.2.11}k_{Eq.2.8}[RH][NO]P_{HO_x})/(k_{Eq.2.14}k_{Eq.2.11}[NO_2][M][NO])$$
$$= (2k_{Eq.2.8}P_{HO_x}[RH])/(k_{Eq.2.14}[NO_2][M])$$
(2.27)

In Eq. 2.27, the production rates are positively related to the concentrations of RH and are negatively related to the concentrations of NO_2 . This case is called the VOC-limited regime, because the O_3 production rate is limited by the supply of hydrocarbons.

These relationships between concentrations of ozone and precursors can expressed by O₃-isopleths using EKMA (Empirical Kinetic Modeling Approach) (Sillman et al., 1990). In the classical EKMA approach, the calculations are based on chemical box models, which simulates that air transported from the region of most intense source emissions (such as a city centre) to the downwind point of maximum ozone accumulation. Such box models ignore any specific mixing effects which might occur during transport. They are implemented many times starting from different initial air pollutant concentrations in the source region, which allows the results to be shown as Figure 2.2. The approach is used to determine an optimal air pollution strategy to reduce ozone.



Figure 2.2 O_3 -isopleths calculated by EKMA approach. The axes are the initial VOC and NO_x concentrations. An ozone isopleth diagram characteristically exhibits a diagonal ridge from the lower left to the upper right corner of the graph. The corresponding VOC/NO_x ratio is typically about 8:1. (Finlayson-Pitts et al., 1999, Section 6, Figure 16.14)

For VOC/NO_x ratios that are large and to the right of the ridge line, the system is NO_x-limited. In this region of an isopleth, there is an ample supply of RO₂ and HO₂ to convert NO to NO₂. The only important tropospheric source of ozone is the photolysis of NO₂. In this regime, the ozone concentration is sensitive to change of available NO_x rather than that of VOC.

For VOC/NO_x ratios that are small to the left of the ridge line, the system is VOC-limited. The radicals that propagate VOC oxidation and NO-to-NO₂ conversion are scavenged by the relatively high concentrations of NO_x. The NO₂ effectively competes with the VOC for the OH radical, the rate of ozone formation is determined by the rate of the reaction of VOC with OH. In this regime, the ozone concentration is sensitive to change of VOC, and it is also inversely proportional to NO_x.

2.4 Tropospheric ozone pollution in China

2.4.1 Historical trends and status

With rapid industrialization and urbanization, surface ozone pollution has emerged as a significant environmental and public health issue in China over the past few years. Observations from the China National Environmental Monitoring Center (CNEMC) reveal a consistent rise in surface ozone levels nationwide (MEE, 2024). Silver et al. (2018) found that the annual mean maximum daily 8-hour average (MDA8) ozone had a positive median trend of 4.6 μ g m⁻³ per year across over 1000 stations in China. The percentage of days exceeding the World Health Organization (WHO) Air Quality Guideline for MDA8 ozone (100 μ g m⁻³) rose from 9.8% in 2015 to 12.4% in 2017. From 2013 to 2019, the mean increase in the MDA8 ozone during summer was 1.9 ppb per year (Figure 2.3, Li et al., 2020). In response to ongoing concerns about ozone pollution, the Chinese government released the "Three-Year Action Plan for Winning the Blue Sky Defense Battle" in 2018, which explicitly addressed control measures for both VOCs and NO_x. While this initiative had some success in curbing increases in ozone concentrations, high levels persist (Zheng et al., 2018a). The average MDA8 ozone across 339 cities was recorded at 144 μ g m⁻³ in 2023, still exceeding WHO guidelines despite a slight decrease compared to previous years (MEE, 2024).

The trend of ozone pollution is closely linked to precursor emissions. Emission inventories estimate that anthropogenic NMVOC emissions in China increased from 9.76 Tg in 1990 to 28.5 Tg in 2017 (Li et al., 2019a). NO_x emissions rose by a factor of 5.46 from 1980 to 2015; however, since 2013, there has been a significant decline in NO_x levels due to government interventions such as the "Air Pollution Prevention and Control Action Plan" (Li et al., 2024; Sun et al., 2018).

This plan primarily aimed at reducing $PM_{2.5}$ and PM_{10} levels, which also indirectly affected ozone precursor emissions. Between 2013 and 2019, $PM_{2.5}$ levels decreased by an 49%, while NO_x emissions dropped by approximately 25%-30%. Despite these reductions, NMVOC emissions did not show a downward trend (Zheng et al., 2018a, Figure 2.4). The significant reduction in NO_x emissions, combined with a slight increase in VOC emissions, may have contributed to the rise in ozone under VOC-limited conditions.

In addition to precursor emissions, meteorological factors play a crucial role in influencing ozone trends (Lin et al., 2021; Hu et al., 2021). Research indicates that natural factors accounted for approximately 44% of the upward trend in tropospheric column ozone and about 27% for surface ozone over Southern China from 2006 to 2016, with solar radiation cycles identified as a primary driver of long-term increases (Chen et al., 2020). In Tianjin, a city in the North China Plain (NCP), afternoon temperatures and morning solar radiation were found to be key meteorological factors controlling O₃ levels from 2009 to 2015 (Yang et al., 2019). Rising temperatures have emerged as a major driver of increased summer ozone concentrations in the NCP over the 2013 to 2019, with enhanced wind speeds also contributing (Li et al., 2020).

Other factors, such as heterogeneous chemistry, further influence changes in ozone trends. Research has shown that the most significant cause of increasing ozone levels in the NCP appears to be the decrease in $PM_{2.5}$ concentrations. This occurs because $PM_{2.5}$ particles (e.g., those containing transition metal ions like Cu^{2+}/Fe^{3+}) serve as a sink for HO₂ radicals through heterogeneous catalytic reactions on aerosol surfaces. With fewer $PM_{2.5}$ particles, the loss rate of HO₂ decreases, leading to more HO₂ reacting with NO_x to produce ozone (Li et al., 2019b). Similar findings have shown that continued reduction of particulate matter emissions has somewhat offset efforts to control ozone pollution because $PM_{2.5}$ can inhibit its formation by removing radicals on particle surfaces and affecting aerosol radiative effects that lower photolysis rates (Liu et al., 2023). Additionally, Gao et al. (2022) reported that reductions in aerosols contribute significantly to worsening winter ozone pollution in the Beijing-Tianjin-Hebei (BTH) area. Therefore, more effective measures are needed to control VOC emissions; their correlation with rising ozone levels underscores the complex relationship between human activities and tropospheric ozone pollution.



Figure 2.3 Summer (June, July, August) concentrations of (**a**) maximum MDA8 ozone, (**b**) mean MDA8 ozone, (**c**) maximum PM_{2.5}, and mean (**d**) PM_{2.5} for 2013–2019 in China. Rectangles denote four megacity clusters: North China Plain (NCP), Yangtze River Delta (YRD), Pearl River Delta (PRD), and Sichuan Basin (SCB) (Li et al., 2020, Section 3, Figure 1).


Figure 2.4 Anthropogenic emissions trends from 2010 to 2017 by sectors in China. The species include (a) SO₂, (b) NO_x, (c) NMVOCs, (d) NH₃, (e) CO, (f) TSP (the particulate matter with an aerodynamic diameter of 100 μ m or less), (g) PM₁₀, (h) PM_{2.5}, (i) BC, (j) OC, and (k) CO₂. Emissions are divided into six source sectors: power, industry, residential, transportation, agriculture, and solvent use. The stacked columns represent the actual emissions data; upright triangles represent emission scenarios that assuming activity is kept frozen at 2010 levels; inverted triangle represent emission scenarios that assuming pollution control frozen at 2010 levels. (Zheng et al., 2018a, Sector 3, Figure 3)

2.4.2 Spatial and temporal variation

Ozone pollution in China exhibits significant spatial variability. Spatially, higher ozone levels are typically observed close to urban and industrial regions where precursor emissions are abundant. In mega urban agglomerations such as the Beijing-Tianjin-Hebei (BTH), Yangtze River Delta (YRD), and Pearl River Delta (PRD) regions, surface ozone pollution has become more urgent

(Chan et al., 2008). From 2013–2017, there were over 27 days per year on average with air quality worse than grade II standard, and ozone hot spots (annual average MDA8 > 50 ppb and exceedance > 40 days) were mainly in eastern China, especially the NCP and the YRD, due to high concentrations of ozone precursors from human activities (Lu et al., 2018). These densely populated areas, characterized by intensive industrial operations and heavy traffic volumes, serve as focal points for VOC emissions, thereby exacerbating ozone pollution levels (Li et al., 2014). However, ozone can also be transported over long distances, affecting rural and downwind areas. The spatial coherence between regions marked by elevated VOC emissions and heightened ozone pollution highlights the pivotal role of VOC as primary precursors in the atmospheric chemistry processes.

Ozone concentrations also display distinct seasonal and diurnal patterns. Seasonally, levels are generally higher during the warmer months, particularly from April to September (Wang et al., 2022; Lu et al., 2018; Wang et al., 2011). Notably, the timing of peak ozone concentrations varies by region: in northern China, peaks typically occur in summer, while in southern China, they are more common in autumn or spring (Gao et al., 2020). Diurnally, ozone levels usually reach their highest point in the afternoon when sunlight and temperatures peak. These conditions facilitate the photochemical reactions responsible for ozone formation. However, various meteorological factors such as solar radiation and wind direction, can influence the exact timing of this diurnal peak, potentially shifting it to earlier in the day or later into the evening (Xu et al., 2021).

2.4.3 Policy and mitigation efforts

To address the growing ozone pollution problem, China has implemented several policies and measures aimed at reducing precursor emissions. In 2013, the State Council of China released the 'Air Pollution Prevention and Control Action Plan', which set clear targets for improving air quality by 2017, including reducing $PM_{2.5}$ concentrations in key regions such as BTH, YRD and PRD. Specific measures included strict vehicle emission standards and other initiatives. While the primary goal was to reduce concentrations of $PM_{2.5}$, PM_{10} , and other major pollutants. These measures also indirectly addressed ozone pollution by optimizing the energy structure to reduce coal consumption and increase the use of clean energy, thereby lowering emissions of NO_x and

VOC, both of which are precursors to ozone. Additionally, promoting new energy vehicles, phasing out old vehicles, and reducing NO_x and VOC emissions from vehicle exhaust, as well as implementing stringent emission standards to control industrial emissions, were part of these efforts.

In 2018, the State Council released the 'Three-Year Action Plan for Winning the Blue Sky Defense Battle', further advancing air quality improvement with the goal of achieving over 80% of good air quality days in cities at the prefecture level and above by 2020, and significantly reducing $PM_{2.5}$ concentrations. This policy explicitly addressed ozone pollution control with measures including strengthening VOC management through comprehensive treatment in key industries, promoting the use of low-VOC raw materials, and implementing leak detection and repair (LDAR) systems. Strengthening NO_x control by strictly controlling emissions from key industries such as coal-fired power plants, steel, and petrochemicals, and promoting low-nitrogen combustion technologies was also emphasized. Enhancing vehicle emission control by accelerating the phase-out of old diesel trucks, promoting the use of new energy vehicles, and strictly implementing vehicle emission standards to reduce NO_x and VOC emissions from vehicle exhaust were key components. Furthermore, regional joint prevention and control efforts were strengthened, particularly in BTH, YRD, and the Fenwei Plain (FP), to control emissions of ozone precursors.

In addition to these plans, various phased policies and measures have been implemented, including stricter vehicle emission standards, the promotion of cleaner fuels and technologies, enhanced industrial emission controls, and efforts to reduce VOC emissions from various sources. Regional air quality management plans have also been developed to coordinate actions across different provinces and cities. Despite these efforts, achieving significant reductions in ozone levels remains challenging due to the complex and non-linear nature of ozone chemistry. Continued research and monitoring are essential to improve our understanding of ozone formation mechanisms and to develop effective mitigation strategies.

In summary, the emissions of anthropogenic VOCs (AVOCs) in China pose challenges for understanding, predicting, and managing ozone pollution. Several key unknowns drive the motivation for this research. For instance, the temperature dependence of VOC emissions is not fully quantified across diverse sources, limiting our ability to predict how climate variations will impact air quality and ozone formation. In Chapter 4, the influenced of temperature to AVOC emissions from different sources were explored. Understanding these interactions is essential for effective mitigation strategies, as it helps identify which sectors and specific VOC species should be prioritized for emission management. Another critical issue in current understanding of ozone is the unclear characterization of high-reactivity AVOCs from certain source. Specifically, the representation of aromatics from industrial and transportation sources within atmospheric chemistry models remains inadequate. This lack of clarity hinders our understanding of their role in ozone formation and complicates predictions related to air quality. In Chapters 5 and 6 of this study, these gaps are analysed and optimization methods for better representation of aromatics in regional air quality models are proposed. By emphasizing the urgent need to improve the characterization and understanding of VOC emissions in China, this research aims to strengthen air quality models, and inform policy decisions.

3. Model and data descriptions

In this chapter, a brief overview of the models and data used in this study are provided. The WRF-GC model (Feng et al., 2021; Lin et al. 2020) is an online coupled regional meteorology-air quality model; the structure of the WRF-GC model and its meteorological component (WRF, Skamarock et al., 2008) and chemical component (GEOS-Chem, Bey et al., 2001) are described. WRF-GC is used to develop the module describing the temperature dependence of AVOC emissions and to evaluate the impacts of that temperature dependence on regional ozone, as discussed in Chapter 4. In Chapter 5, the Dynamically Simple Model of Atmospheric Chemical Complexity box model (DSMACC) is driven with gas-phase photochemical mechanisms of various degrees of complexity to investigate how the representation of aromatic photochemical mechanisms impacts the simulation of ozone formation. The findings in Chapter 5 are further evaluated on a regional scale using the WRF-GC model. More details regarding the model setup and specific chemical schemes will be provided in the relevant chapters.

This chapter also introduces the data utilized in this study. Regional emission inventories of natural and anthropogenic precursors are described. The initial and boundary inputs and meteorological datasets used for nudging the WRF-GC simulations are briefly described. Observations used for model evaluation and hypothesis testing, including surface ozone observations in China and satellite observations of tropospheric NO₂ and formaldehyde concentrations are also summarized.

3.1 The WRF-GC regional meteorology-air quality model

3.1.1 Overview of WRF-GC

WRF-GC (https://atmoschem.org.cn/index.php?title=WRF-GC; Lin et al., 2020; Feng et al., 2021) is coupling of the Weather Research an online and Forecasting (WRF, https://www.mmm.ucar.edu/models/wrf; Skamarock et al., 2008) regional meteorological model and the GEOS-Chem atmospheric chemistry model (http://www.GEOS-Chem.org; Bey et al., 2001). Figure 3.1 describes the WRF-GC model structure. The WRF model drives the GEOS-Chem model with simulated meteorological conditions at each chemical timestep. In turn, GEOS-Chem simulates atmospheric chemical conditions, including speciated aerosol mass concentrations, which may feedback to affect WRF meteorology if aerosol-radiation interactions (ARI) and aerosol-cloud interactions (ACI) are enabled. The two models exchange simulated meteorological and chemical variables through the WRF-GC coupler, consisting of the State Conversion Module, the State Management Module, and the GEOS-Chem Column Interface. In particular, both the WRF and GEOS-Chem model completely retain their respective native code and can be independently updated.

WRF-GC v0.1 was first released in January 2019, followed by a more mature and stable version 1.0 in autumn 2019 (Lin et al., 2020). The release of WRF-GC v2.0 included important capabilities, including nested-domain modeling, online lightning NO_x emissions, and ARI and ACI (Feng et al. 2021). The latest WRF-GC version 3.0 supports GEOS-Chem 14.1.1, KPP 3.0.0, and HEMCO 3.6.2, alongside WRF version 4.4 compatibility. Technical updates in WRF-GC v3.0 involved refining infrastructure for specialized simulations, improving diagnostic capabilities with pNETCDF, and streamlining the recompilation process. For this study, WRF-GC v2.0 and WRF-GC v3.0 are used.

WRF-GC has been employed in a number of regional atmospheric chemistry and air quality studies, and evaluations of the model against observations has demonstrated WRF-GC's reasonable capability at simulating urban to regional scale atmospheric chemistry and meteorology-chemistry interactions. Liu et al. (2023) showed that WRF-GC reproduced the diurnal variations of the planetary boundary layer heights and vertical ozone profiles at Houston, Texas during the TRACER-AQ campaign. Xu et al. (2022) reported that the integration of Hg simulation in the WRF-GC-Hg v1.0 model accurately depicted the elevated mercury wet deposition in the southeastern United States, aligning closely with observations. Additionally, WRF-GC exhibited strong performance in replicating surface VOC concentrations and pollutant, underscoring its reliability and versatility in evaluating air quality (Jia et al., 2023; Zhang et al., 2020). In the City of Shenzhen in Southern China, WRF-GC's simulation of the surface ozone-meteorology relationship demonstrated strong spatial (r = 0.81) and temporal (r = 0.82) correlations with observations (Zhang et al., 2023).



WRF-GC Model (v2.0, two-way)

Figure 3.1 (a) Architectural overview of the WRF-GC coupled model (v2.0). The WRF-GC coupler (all parts shown in red) includes interfaces to the two parent models, as well as the two-way coupling modules (shown in orange). The parent models (shown in gray) are standard codes downloaded from their sources, without any modifications. (b) Flow diagram of the aerosol–radiation and aerosol–cloud interactions in the WRF-GC coupled model (v2.0) (Feng et al., 2021, Section 2, Figure 1).

3.1.1 The WRF meteorological model

WRF-GC incorporates the WRF model as its meteorology module (Skamarock et al., 2008). WRF is widely used in simulating meteorology with high spatial and temporal resolution, incorporating physics parameterizations and data assimilation techniques to provide detailed and accurate forecasts for various weather conditions. The WRF module can operate independently as a weather forecasting model or be coupled online with chemical modules. For example, WRF-Chem (<u>https://ruc.noaa.gov/wrf/wrf-chem</u>) and WRF-CMAQ (<u>https://www.epa.gov/cmaq/wrf-cmaq-model</u>) are atmospheric chemistry transport models that embed different chemical processes within the WRF framework, chemical and meteorological processes in the real atmosphere occur simultaneously and interact with each other.

WRF includes several steps to ensure accurate simulation and forecasting.

a) Preprocessing

The WRF Preprocessing System (WPS) is responsible for preparing the input data required for running the model. WPS runs three main tools sequentially: 'geogrid', 'ungrib', and 'metgrid'. Firstly, 'geogrid' is used to prepare geographical data such as terrain, land use types, and land cover. This tool interpolates and remaps the geographical data onto the horizontal and vertical grids of the WRF model. Secondly, ungrib is employed to decompress and decode atmospheric observation data, typically sourced from weather stations, satellites, or other data sources. 'ungrib' decodes this data into a format recognizable by the WRF model. Lastly, 'metgrid' is utilized to interpolate meteorological field data onto the WRF model's horizontal and vertical grids, generating the necessary boundary and initial conditions for model runs. 'metgrid' handles horizontal and vertical interpolation as well as inconsistencies between terrain heights and meteorological field data.



Figure 3.2 Workflow flow between the WPS programs (WRF v4.5 User Guide, Section: The WRF Preprocessing System (WPS))

b) Initialization and boundary conditions

Initialization establish initial states for key variables governing atmosphere, land surface, and oceans. Proper initialization ensures that the model starts with realistic conditions, enabling accurate simulations of weather patterns, climate phenomena, and interactions between different components of the Earth system. Land surface initialization sets parameters like soil moisture, temperature, and land cover, impacting energy balance, water cycle, and weather patterns (Sellers et al., 1997; Bonan, 1995).

Defining key boundary conditions shapes the behaviour of simulated atmospheres. Lateral boundaries allow external influences on impact weather patterns, integrating surrounding effects. Top boundaries govern interactions with the upper atmosphere, necessitating precise parameters like temperature and humidity for accurate vertical atmospheric processes. Surface boundaries regulate the dynamic interplay between the atmosphere and Earth's surface, accounting for factors such as surface roughness and vegetation cover that influence heat, moisture, and momentum exchange. These conditions collectively shape atmospheric dynamics, ensuring models capture the complex interactions between different components of the Earth system. The data used for initial and boundary condition in this study is introduced in Section 3.3.1.

c) Physical parameterization schemes

Physical parameterization schemes cover a range of processes including convection, boundary layer dynamics, radiation transfer, and cloud microphysics. In this study, several key parameterization schemes are employed in WRF-GC, as outlined in Table 3.1.

Processes	Physical parameterization schemes
Microphysics	Morrison two-moment (Morrison et al., 2009)
Longwave radiation	RRTMG (Iacono et al., 2008)
Shortwave radiation	RRTMG (Iacono et al., 2008)
Surface layer	MM5 Monin-Obukhov (Jimenez et al., 2012)
Land surface	Noah (Chen and Dudhia, 2001)
Planetary boundary layer	MYNN2 (Nakanishi and Niino, 2006)
Cumulus parameterization	New Tiedtke (Tiedtke et al., 1989)

Table 3.1 Physical parameterizations used in the WRF-GC simulations in this study

The Morrison two-moment scheme (Morrison et al., 2009) simulates cloud and precipitation processes in the WRF model. Within the WRF model, diverse cloud microphysics schemes are available, focusing on water vapour, clouds, and precipitation treatment. These schemes fall into single-moment and double-moment parameterization categories. The Morrison scheme, a double-moment method, handles six hydrometeor types and offers customization options for graupel/hail treatment to precise modeling of cloud and precipitation evolution. It uses a gamma distribution to represent particle size distribution, derived from mixing ratios and number concentrations.

RRTMG is an improved version of the Rapid Radiative Transfer Model (RRTM) (Iacono et al., 2008). RRTMG utilizes the correlated k-distribution technique to compute atmospheric radiation

fluxes, providing a more accurate representation of radiation transfer at different wavelengths. Additionally, RRTMG employs the Monte Carlo Independent Column Approximation (MCICA) algorithm to simulate the impact of cloud overlap characteristics at sub-grid scales, enhancing the model's ability to capture cloud radiation effects. The RRTMG scheme also accounts for the radiative effects of various aerosols such as organic carbon, black carbon, sulfate, sea salt, dust, and stratospheric aerosols (Tegen et al., 1999).

The MM5 Monin-Obukhov scheme integrates the Monin-Obukhov similarity theory into its boundary layer parameterization schemes to compute friction velocity and exchange coefficients within the near-surface layer (Jimenez et al., 2012). This computational approach facilitates the accurate estimation of heat and water vapor fluxes in both land surface and planetary boundary layer processes. The updated MM5 scheme incorporates stability functions to enhance the calculation of near-surface exchange coefficients, thereby improving its versatility across a wide range of atmospheric stability conditions. Furthermore, by considering surface characteristics such as land cover type, vegetation, and soil moisture, the scheme effectively considers their impacts on the heat and water vapor exchange processes.

The Noah Land Surface Model, a widely utilized parameterization scheme in atmospheric models, integrates principles from hydrology, ecology, and soil physics to simulate energy and water processes on land surfaces. Developed jointly by National Centers for Environmental Prediction (NCEP) and National Center for Atmospheric Research (NCAR), the Noah Land Surface Model evolved from the OSU Land Surface Model (Chen and Dudhia, 2001) and enables forecasting of canopy humidity, snow cover fraction, frozen soil, vegetation types, and fractional vegetation cover. This model, based on a 4-layer soil temperature and humidity scheme with depths at 10 cm, 30 cm, 60 cm, and 100 cm, considers variables such as soil temperature, humidity, vegetation cover, snow cover, and their interactions with the atmosphere. It accounts for processes like precipitation, evapo-transpiration, runoff, and soil moisture dynamics.

The Mellor-Yamada-Nakanishi-Niino Level 2.5 hybrid parameterization scheme (MYNN2) is used for simulating boundary layer and cloud microphysical processes, focusing on turbulent motion and energy transfer within the boundary layer (Nakanishi and Niino, 2006). This layer influenced by surface properties, often contains concentrated pollutants. Turbulence in this region

facilitates the transport, mixing, and exchange of heat, moisture, momentum, and pollutants, impacting regions beyond the immediate boundary layer. MYNN2 determine the boundary layer's height and structure by defining flux profiles in the mixed and stable layers. They evaluate boundary layer processes' effects on the atmosphere by calculating flux tendencies of temperature, moisture, momentum, and pollutants throughout the atmospheric column.

The New Tiedtke scheme is a convection parameterization utilized to simulate convective processes in the atmosphere, incorporating atmospheric turbulence and vertical motion to aid in modeling convective clouds and precipitation based on its original version (Tiedtke et al., 1989). Widely adopted in atmospheric models, this scheme improves the representation of convective phenomena, enhancing the modeling of convective processes. This enhanced version of the Tiedtke parameterization focuses on refining cloud microphysical processes, particularly in precipitation modeling, by parameterizing cloud formation, development, and dissipation processes, considering variables such as cloud water content, cloud droplet number concentration, and cloud particle size distribution. Notably, the New Tiedtke scheme refines precipitation simulation to accurately depict the occurrence and intensity of precipitation events, distinguishing between various precipitation types like rain, snow, and hail, and capturing their spatial distribution patterns.

3.1.2 The GEOS-Chem chemical model

WRF-GC integrates the GEOS-Chem model as its chemical module. GEOS-Chem is a global 3D atmospheric chemical transport model driven by meteorological input from the Goddard Earth Observing System (GEOS) of the National Aeronautics and Space Administration (NASA) Global Modeling and Assimilation Office (Bey et al., 2001). It is a widely used chemical transport model in atmospheric science, enables a comprehensive simulation of pollutant sources, chemical reactions, transport processes, and removal mechanisms in the atmosphere. The independent GEOS-Chem model is typically driven by reanalysis meteorological data. These data include parameters such as atmospheric pressure, temperature, humidity, wind speed, and wind direction. While in WRF-GC, WRF modules provide online meteorological simulations for GEOS-Chem.

The GEOS-Chem model involves several key steps. Initially, the model is initialized with atmospheric composition data, emissions, and meteorological fields. Subsequently, GEOS-Chem simulates the transport of gases and particles in the atmosphere through processes including advection, diffusion, and convection, driven by meteorological data. Chemical reactions among species are then computed using a chemical mechanism to represent atmospheric compound interactions. Emissions from various sources are integrated into the model, and processes like deposition account for pollutant removal.

a) Emissions

In GEOS-Chem, emissions of various chemical species from different sources are handled by the Harmonized Emissions Component (HEMCO) emission scheme (Lin et al., 2021). Developed collaboratively by Harvard University and NASA, HEMCO enables the integration of emissions data from multiple inventories and sources. Firstly, HEMCO reads emissions data from different sources, such as anthropogenic activities, biomass burning, biogenic emissions, and other sources. These data include spatial and temporal information on the emissions of various chemical species. HEMCO then processes the emissions data and distributes them spatially and temporally across the model grid. This step involves interpolating emissions data to the model resolution and accounting for factors such as emission factors, activity levels, and meteorological conditions. Finally, HEMCO integrates the processed emissions data into the GEOS-Chem model, where they interact with atmospheric chemistry and transport processes.

Designed as a modular component, HEMCO enables the flexible incorporation of different emissions datasets and sources. In Chapter 4 of this study, the temperature-dependent parameterization module is developed for AVOC within the HEMCO in WRF-GC.

b) Chemistry mechanism

GEOS-Chem provides a chemical mechanism that simulate the interactions among various chemical species in the atmosphere. GEOS-Chem encompasses a diverse range of atmospheric components, including gases, aerosols, radicals, and reactive trace gases, distributed across a 3D grid covering the Earth's atmosphere. GEOS-Chem simulates chemical reactions between these species using a system of differential equations that are solved numerically. These reactions include gas-phase reactions, heterogeneous reactions, and photolysis (Shah et al., 2023; Bates et

al., 2021; Kwon et al., 2021; Bates and Jacob, 2019). The model integrates these chemical transformations with meteorological data, incorporating factors such as temperature, pressure, humidity. These meteorological variables play a crucial role in influencing the rates of chemical reactions within the model. GEOS-Chem advances in time steps, updating the concentrations of each chemical species at every grid point based on the simulated chemical reactions and prevailing meteorological conditions. The chemical mechanisms used in this study are described in more detail in Chapter 5.2.

c) Photolysis scheme

FAST-JX is integrated into the GEOS-Chem model to enhance the simulation of photochemical processes involving trace gases and aerosols (Eastham et al., 2014). FAST-JX computes photolysis rates for various atmospheric species, taking into account the effects of aerosols on radiation. First, GEOS-Chem loads essential meteorological and chemical data, including temperature, humidity, and radiation. Based on initial conditions, the calculation of photolysis rates relies on the decomposition of solar radiation into different wavelength intervals. For each gas involved in photolysis reactions, FAST-JX uses predefined photolysis cross sections and quantum yields. These parameters, typically derived from experimental data, describe the ability of gases to undergo photolysis at specific wavelength. These rates are dynamically influenced by solar radiation, aerosol concentrations, and other environmental factors. At each time step, FAST-JX computes the interactions between gases and aerosols, including adsorption, reactions, and release of gases. FAST-JX continuously updates the photolysis rates, accounting for changes in atmospheric conditions such as variations in solar intensity and dynamic aerosol characteristics. GEOS-Chem utilizes the updated photolysis rates and the results of gas-aerosol interactions to perform calculations of gas-phase and aerosol-phase chemical reactions, including the generation and consumption of various chemical species.

3.1.3 DSMACC box model

The Dynamically Simple Model of Atmospheric Chemical Complexity (DSMACC) is a box model used for simulating atmospheric chemistry (<u>https://github.com/barronh/DSMACC</u>). Chemical mechanisms such as Master Chemical Mechanism (MCM), GEOS-Chem could be applied in DSMACC. DSMACC is a simplified model that used to study the complex interactions of various chemical species in a controlled environment. It is a model that represents the atmosphere as a single box, rather than a 3D grid, and atmospheric transport processes are neglected. DSMACC simulates the chemical reactions that occur among gas-phase species. These reactions are represented by a set of differential equations, which are solved numerically. This simplification allows for more rapid simulations and makes it easier to isolate specific processes for study (Womack et al., 2019; Stone et al., 2018; Zhou et al., 2014; Stone et al., 2011; Emmerson and Evans, 2009). Like other models, DSMACC advances in time steps, updating the concentrations of each chemical species based on the simulated chemical reactions.

The Kinetic PreProcessor (KPP) is a crucial component of the DSMACC box model, used to generate numerical code for simulating chemical kinetics in atmospheric models (Damian et al., 2002). It's designed to handle the complexity of atmospheric chemistry, which involves hundreds to thousands of reactions among many species. The user provides a list of chemical species and reactions in a specific format. This includes the reaction rates, which can be functions of factors like temperature and solar radiation. KPP processes this list and generates a system of ordinary differential equations (ODEs) that represent the chemical kinetics of the system. Then KPP generates Fortran or C code that can solve this system of ODEs, typically using methods like the Rosenbrock or Gear methods, which are designed to handle stiff systems of equations. The generated code is integrated into the DSMACC model. When the model is run, it uses the code to calculate the changes in concentrations of each chemical species over time, based on the specified reactions and their rates. Finally, the model produces output data that includes the concentrations of each chemical species at each time step.

3.2 Emission inventories

Emission inventories play a critical role in atmospheric chemistry modeling. They provide data on the types and quantities of pollutants being released into the atmosphere from various sources, both natural and anthropogenic. This information is essential for accurately simulating the distribution and concentration of atmospheric pollutants, as well as their chemical transformations and interactions. In this study, WRF-GC simulation domain mainly focuses on mainland China. There are some inventories applied in this study.

3.2.1 The Multi-resolution Emission Inventory for China (MEIC)

For anthropogenic emissions, two different inventories are applied. Over mainland China, the primary study area, the Multi-resolution Emission Inventory for China (MEIC, <u>http://meicmodel.org.cn</u>) is used. MEIC is a comprehensive, high-resolution emission inventory that provides detailed and reliable data on a wide range of pollutants, including SO₂, NO_x, CO, CO₂, NMVOCs, NH₃, PM (Li et al., 2019a; Li et al., 2017). Covering various sectors including power, industry, transportation and residential, the MEIC allows for a detailed analysis of the sources of air pollution in China (Peng et al., 2019; Liu et al., 2015; Zheng et al., 2015). Notably, it provides data at a high spatial resolution of $0.25^{\circ} \times 0.25^{\circ}$ for the entire country and offers monthly data, enabling the examination of seasonal variations in emissions. The MEIC includes historical emission data from 1970 and projects future emissions up to 2050 under different scenarios (Tong et al., 2020).

The development MEIC follows a systematic process that begins with the collection of activity data, which represents the number of human activities leading to emissions, gathered from various sources such as government statistics, industry reports, and scientific studies (Shen et al., 2015; Huo et al., 2012). This is followed by determining emission factors, representative values that connect the quantity of a pollutant released to the atmosphere with an associated activity. The emissions are then calculated by multiplying the activity data with the emission factors for each source of pollution and each type of pollutant. Subsequently, these calculated emissions are distributed spatially and temporally, assigning the emissions to specific locations based on the

source and specific times based on when the emissions occur, using techniques like geographic information systems and statistical modeling. The final step involves validating the emission inventory by comparing it with other data sources like air quality measurements and other emission inventories, followed by regular updates to incorporate new data and research findings (Geng et al., 2017; Wang et al., 2012).

3.2.2 Mosaic Asian anthropogenic emission inventory (MIX)

For areas of Asia outside mainland China, the Mosaic Asian anthropogenic emission inventory (MIX, <u>http://meicmodel.org.cn</u>) is applied. MIX is a comprehensive emission inventory for Asia, integrating the available inventories for major sectors like power, industry, residential, transportation, and agriculture, and pollutants such as SO₂, NO_x, CO, NMVOCs, NH₃, PM (Li et al., 2017). Covering emissions from 2008 onward for countries in East, South, Southeast, and West Asia, the MIX is widely applied in air quality modeling studies (Kurokawa et al., 2013; Lee et al., 2011; Lu et al., 2011). The creation process involves collecting, evaluating, and integrating multiple existing emission inventories, including regional, national, and sector-specific inventories, including harmonizing the data in terms of units, spatial resolution, temporal resolution, and other parameters. Emissions for are distributed spatially across the Asian continent using detailed geographic, allowing for high-resolution mapping, and temporally, with monthly, weekly, and hourly profiles each sector and pollutant, providing a detailed trend of air pollution.

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

Biogenic emissions are provided with the Model of Emissions of Gases and Aerosols from Nature (MEGAN, Guenther et al., 2012). MEGAN is a global model that calculates the emission rates of VOCs, other gases, and particles from terrestrial ecosystems into the atmosphere. Designed for standalone use or integration into regional and global atmospheric chemistry, air quality, and climate models, MEGAN considers factors influencing biogenic emissions, including light

intensity, temperature, vegetation type, leaf area index, and soil moisture. It estimates emissions from a diverse vegetation source, including trees, shrubs, grasses, and crops, and covers a wide spectrum of compounds such as isoprene, monoterpenes, sesquiterpenes, other VOCs, carbon dioxide, and methane. The model employs a detailed process-based approach to estimate emissions, calculating the emission potential for each type of vegetation and compound and adjusting it based on environmental conditions. It also integrates a canopy environment model to simulate the physical and chemical environment within a plant canopy, thereby influencing emissions.

3.2.4 Other emission inventories

Global Fire Emissions Database version 4 (GFED4) is utilized to account for emissions from biomass burning, including wildfires and agricultural fires, which are significant sources of pollutants such as CO₂, CO, NO_x, VOCs, and PM (Giglio et al., 2013). The GFED4 dataset provides comprehensive information on emissions from various ecosystems, including forests, grasslands, and croplands, detailing the spatial distribution, temporal variations, and types of pollutants released during fires. Dust emissions are calculated using the AFCID (Anthropogenic Fugitive, Combustion, and Industrial Dust). The AFCID inventory specifically addresses residual anthropogenic primary PM_{2.5} emissions, excluding organic mass and black carbon, and has been refined using global data from the ECLIPSE dataset alongside regional inventories from India and China (Philip et al., 2017). Ship emissions are incorporated based on the CEDS (Community Emissions Data System). The CEDS inventory includes ship emissions for a range of species, including SO₂, NO_x, CO, NMVOCs, NH₃, BC, OC, CO₂, and CH₄ (Hoesly et al., 2018). Aircraft emissions are calculated using the Aircraft Emissions Inventory Code (AEIC), which includes species such as NO, CO, hydrocarbons (Simone et al., 2013).

3.3 Data

3.3.1 NCEP FNL dataset

In this study, the National Centers for Environmental Prediction (NCEP) Final (FNL) Operational Global Analysis dataset (<u>https://rda.ucar.edu/datasets/d083002</u>) provides meteorology initial and boundary conditions for WRF-GC simulation. This dataset is generated by NCEP, which is part of NOAA in the United States. This product is from the Global Data Assimilation System (GDAS), which continuously collects observational data from the Global Telecommunications System (GTS), satellite data, and numerical weather prediction models. One of the key strengths of the NCEP FNL dataset is its high spatial and temporal resolution, providing detailed information on atmospheric conditions around the world. The NCEP FNL dataset includes a range of atmospheric variables such as temperature, humidity, wind speed, and pressure at various levels in the atmosphere. NCEP FNL dataset is on 1-degree by 1-degree grids prepared operationally every six hours. The dataset covers the time range from 1997 to the present day. The analyses are accessible across various levels from 10 hPa to 1000 hPa.

3.3.2 Chemical initial and boundary conditions for driving WRF-GC simulations

WRF-GC as a regional model, requires chemical initial conditions (IC) and boundary conditions (BC) for species. The accurate setting of IC and BC is crucial for capturing the intricate dynamics of chemical species within the atmosphere. IC establishes the simulation's starting point by defining the initial concentrations and spatial distributions of various chemical species. BC, on the other hand, regulates the model's interaction with the external environment, including factors such as air inflow and outflow at the model domain boundaries and the exchange of substances between the simulation domain and its surroundings.

In this study, both BC and IC are derived from the global simulation results of the GEOS-Chem model. GEOS-Chem model at a resolution of 2×2.5 degrees is utilized, running it for the year

preceding the WRF-GC simulation time to ensure the mixing of ozone concentrations. The output from the GEOS-Chem simulation was employed as input conditions for the chemical module of the WRF-GC model. The species simulated in GEOS-Chem are completely consistent with those in WRF-GC, thus eliminating errors in species mapping.

3.3.3 Surface ozone observations in China

The surface ozone observations used in this study are from the China National Environmental Monitoring Center (CNEMC, <u>http://www.cnemc.cn</u>) network, which is responsible for monitoring surface air pollutants in mainland China under the supervision of the Ministry of Ecology and Environment (MEE, formerly known as the Ministry of Environmental Protection (MEP) before 2018, <u>http://www.mep.gov.cn</u>). The network has been operational since 2013, initially monitoring in 74 major cities and expanding to cover 3867 sites by 2022. The observations record the air quality situation in Chinese cities and have been widely utilized in recent studies. The dataset is archived at <u>https://quotsoft.net/air</u>, includes hourly concentration measurements of O₃, CO, NO₂, SO₂, PM_{2.5}, and PM₁₀.

3.1.2 Satellite observations of tropospheric NO₂ and formaldehyde column concentrations

Satellite-observed formaldehyde-to-NO2 column concentration ratios (FNR) have been used as a qualitative indicator for the regional ozone photochemical regime (Jin et al., 2017; Duncan et al., 2010) in this study. Level 3 Cloud-Screened Tropospheric Column NO₂ product (0.25° resolution, https://doi.org/10.5067/Aura/OMI/DATA3007, Krotkov et al., 2019) and the Total Column Daily 3 Level Weighted Mean Global **HCHO** product (0.1°) resolution, https://doi.org/10.5067/Aura/OMI/DATA3010, Chance, 2019) from the Ozone Monitoring Instrument (OMI) are used in this study. OMI is a satellite-based sensor designed to monitor and measure various atmospheric parameters related to air quality and ozone concentrations in the Earth's atmosphere. Launched aboard NASA's Aura satellite in 2004, OMI provides data including ozone, nitrogen dioxide, sulfur dioxide, formaldehyde, and aerosols. OMI operates by measuring the sunlight reflected and scattered by the Earth's atmosphere and surface. By analyzing the ultraviolet and visible light spectra, OMI can detect and quantify the presence of different pollutants and trace gases in the atmosphere. This high-resolution instrument offers global coverage and provides detailed information on the distribution and variability of atmospheric pollutants daily. The data collected by OMI is widely used in atmospheric research, air quality monitoring, and climate studies (Hammer et al., 2016; Duncan et al., 2010).

4. Impact of temperaturedependent evaporative anthropogenic VOC emissions on regional ozone pollution

4.1 Introduction

VOCs that contribute to surface ozone pollution originate from a variety of anthropogenic, biogenic, and biomass burning sources (Wang et al., 2021a). Among these sources, the emissions of biogenic VOCs (BVOCs), including most importantly isoprene, exacerbate ozone pollution events. This is because the warm and sunny conditions that facilitate ozone photochemical production also enhance BVOC emissions (Guenther et al., 2012). This meteorology-chemistry connection is well understood and is accounted for in most air quality models (Fu et al., 2019).

In contrast, the emissions of anthropogenic VOCs (AVOCs) are also sensitive to ambient temperature, however the potential impacts of this sensitivity on regional surface ozone have not been fully explored. Temperature variations affect both the intensities of anthropogenic activities and the emission factors of AVOCs from those activities. For instance, power generation increases at both high and low ambient temperatures due to power demands for cooling and heating (Tian et al., 2012). This weather-driven variation of anthropogenic activities has been accounted for in emission inventories on monthly to seasonal scales. Much less is known about the temperature dependence of AVOC emission factors, particularly the enhanced evaporation of AVOCs in warm weather. Many studies have shown that high ambient temperatures substantially increased the fugitive evaporative emissions of AVOCs from petrochemical processing, vehicles, as well as the use of solvents (e.g., painting/coating, dry cleaning, and printing (Cetin et al., 2003; Niu et al., 2021; Li et al., 2019a; Qi et al., 2019; Zheng et al., 2018b; Rubin et al., 2006)). Niu et al. (2021) observed that in summer, the ambient levels of VOCs and oxygenated VOCs (OVOCs) associated with printing and dry cleaning were 20 to 40 times higher than their respective winter levels in a central Chinese city. Since the volatility of AVOC species vary, the temperature dependency of evaporative AVOC emissions also affect the composition and reactivity of AVOCs in the ambient air (Song et al., 2019). Na et al. (2005) observed that warm weather enhanced the evaporative emissions of aromatics from vehicles in Seoul, Korea, and that the ozone formation potential (OFP) of VOCs from vehicular evaporative emissions was 40% higher than that from vehicular exhaust gases in summer. Gu et al. (2020) incorporated into a box model a 1% increase of AVOC emissions per 3 °C rise in

ambient temperature and found that this temperature dependence of AVOCs increased the simulated surface ozone concentrations by 2 ppb in urban Shanghai when the daily maximum temperature was 41 °C.

The impacts of temperature-dependent evaporative AVOC emissions on surface ozone have not been quantified on a regional scale. A key challenge is that the temperature dependency of AVOCs emitted from different sources has not been formulated and represented in regional models. In this chapter, parameterizations are developed for the temperature dependencies of evaporative AVOC emissions from transportation, solvent use, and other non-solvent-use industrial activities (hereafter referred to as 'NSI activities'). These parameterizations are tested in a regional air quality model to evaluate the responses of summertime surface ozone to temperature-dependent AVOC emissions in the BTH area of China. Finally, the simulated ozone-temperature sensitivities as driven by evaporative AVOC emissions and by BVOC emissions are compared, respectively, to better understand the role of temperature-dependent emissions in regional air quality-meteorology interactions in China.

4.2 Methodology

4.2.1 Simulations of surface ozone in the BTH area using the WRF-GC model

WRF-GC regional air quality model (v2.0, described in Section 3.1) (Feng et al., 2021; Lin et al., 2020) is employed to simulate surface ozone concentrations over China. Simulations were conducted between May 28th and July 5th 2017 with the first 4 days of the simulation considered as model spin-up and discounted from analyses. This period was simulated because June and July are the months with most frequent ozone exceedances over the BTH area, although evaporative AVOC emissions are sensitive to temperature in all seasons. Also, the constraint for temperature dependency of NSI emissions were based on a most recent published observation in 2017 (Song et al., 2019). A single domain of 27-km horizontal resolution and 50 vertical layers was used (Figure 4.1). WRF-GC used the O₃-VOC-NO_x-aerosol-halogen

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chemical mechanism from GEOS-Chem v12.8.1, which was supplemented with the photochemical mechanism of aromatics from GEOS-Chem v13.0.0 (Wang et al., 2021a; Bates et al., 2021). Meteorological initial and boundary conditions were from the National Centers for Environmental Prediction Final Operational Global Analysis (NCEP FNL, 1° resolution). The simulated winds, temperature, and water vapour mixing ratios above the planetary boundary layer were nudged with the NCEP FNL data every 6 hours. Aerosol feedback to meteorology were disabled to further ensure that the meteorological conditions in all simulations were identical. Chemical boundary conditions were from a standard full-chemistry simulation using GEOS-Chem v12.8.1 (Bay et al., 2001). Table 4.1 summarizes the physical configurations used in the simulations.



Figure 4.1 Domain of the WRF-GC simulations used in this study with a horizontal resolution of 27 km.

Table 4.2 Design of WRF-GC sensitivity simulations

Sensitivity simulations	VOC emission rates	
BASE	Standard emission inventories with temperature-independent AVOC emissions and temperature-dependent BVOC emissions.	
AVOC(T)	Same as the BASE except AVOC emissions are temperature-dependent	
BVOC(NT)	Same as the BASE except BVOC emissions are temperature-independent	



Figure 4.2. Monthly mean emissions of (a) representative AVOC species from transportation (top), solvent use (middle), and NSI activities (bottom) and (b) biogenic isoprene during the simulation period.

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Monthly mean anthropogenic pollutant emissions within Mainland China were from the Multiresolution Emission Inventory for China (MEIC, <u>http://www.meicmodel.org</u>) for the year 2017, which included emissions from power generation, industries (distinguishing the solvent use and non-solvent-use sub-sectors), transportation (including on-road and off-road), and residential activities at 0.25° resolution (Li et al., 2014). Anthropogenic emissions for the rest of the simulated domain were from a mosaic Asian anthropogenic emission inventory for year 2010 (Li et al., 2017). Biomass burning emissions were from the Global Fire Emissions Dataset version 4.1 with small fires (GFED4s) (van der Werf et al., 2017). Meteorology-dependent BVOC emissions (MEGAN v2.0) (Guenther et al., 2012) and soil- and lightning-NO_x emissions (Hudman et al., 2012; Murray et al., 2012) were calculated online in WRF-GC. Figure 4.2 shows the monthly mean VOC emissions over the BTH area during the simulation period. AVOC emissions from transportation, solvent use, and NSI activities generally overlapped in space, reflecting the collocation of population, vehicles, and industrial activities over this area. The BVOC emissions were highest over Beijing, Tianjin, and the northeastern parts of Hebei, reflecting the denser vegetation in these areas relative to other parts of the BTH.

Three sensitivity simulations were conducted to elucidate the impacts of temperature-dependent VOC emissions on surface ozone (Table 4.2). The BASE simulation was driven by meteorology-dependent BVOC emissions, as well as temperature-independent AVOC emissions with prescribed weekday/weekend and diurnal temporal patterns to represent the anthropogenic activity variations independent of daily meteorological variations. The AVOC(T) simulation was identical to the BASE simulation, except that the hourly AVOC emissions were further dependent on hourly ambient temperature as described in Section 4.2.2 below. A BVOC(NT) simulation was also conducted, which was identical to the BASE simulation, except the dependence of BVOC emissions on daily temperature variations were disabled. Instead, BVOC emissions were driven by the monthly mean temperature for each model grid cell. The simulated ozone differences between the AVOC(T) and the BASE experiments allowed isolation of the impacts of temperature-dependent evaporative AVOC emissions, while the simulated ozone differences between the BASE and BVOC(NT) experiments allowed isolation of the impacts of temperature-dependent BVOC emissions.

4.2.2 Parameterizations for the temperature dependency of evaporative AVOC emissions for use in a regional air quality model

Several studies have derived the theoretical or empirical temperature dependence of evaporative VOC emissions from different anthropogenic sources (Romagnuolo et al., 2019; Atkins, 1998). Evaporative AVOC emissions from transportation mostly involved the vapour losses from bulk storage devices (Liu et al., 2017); these evaporative fluxes took the form of Eq. (4.1) (Huang et al., 2022; Romagnuolo et al., 2019; Yamada et al., 2018; Huang et al., 2015; Yamada et al., 2015; Atkins, 1998) analogous to the Clausius-Clapeyron equation:

$$E_1 = \frac{A_1}{T} \exp\left(\frac{-B_1}{T}\right) \tag{4.1}$$

where E_1 was the evaporative VOC emission flux from transportation (unit: kg m⁻² s⁻¹), and *T* was the ambient temperature (unit: K). A_1 (unit: kg m⁻² s⁻¹ K) and B_1 (unit: K) were empirical temperature-dependency parameters; B_1 was analogous to the ratio between the enthalpy and the specific gas constant ($\Delta H_{evp}/R$) in the Clausius-Clapeyron equation.

The evaporative VOC emissions associated with solvent use often involves evaporation from large surface areas, such as a painted or coated surface. Huang et al. (2015) derived the form of evaporative fluxes from such surfaces based on statistical physics:

$$E_2 = \frac{A_2}{\sqrt{T}} \exp\left(\frac{-B_2}{T}\right) \tag{4.2}$$

where E_2 was the evaporative VOC flux associated with solvent use (unit: kg m⁻² s⁻¹). A_2 (unit: kg m⁻² s⁻¹ K^{1/2}) and B_2 (unit: K) were the temperature-dependency parameters. In contrast to the 1/*T* term on the right-hand-side of Eq. (4.1), the bulk exponential temperature dependence of Eq. (4.2) was modulated by a $1/\sqrt{T}$ term. This dependence was traced to the kinetic energy distribution of molecules bound to a surface by adsorption (Huang et al., 2015).

For the evaporative VOC emissions from NSI activities, there has not been systematic measurements of their temperature dependencies. Song et al. (2019) used a positive matrix factorization (PMF) model to quantitatively attribute their observed ambient VOC

concentrations in an industrial city to different sources. This observed linear temperature dependence for the ambient VOC concentrations associated with NSI activities is used here (Eq. 4.3):

$$E_3 = A_3 T + B_3 \tag{4.3}$$

where E_3 was the evaporative VOC emission from NSI activities (unit: kg m⁻² s⁻¹). A_3 (unit: kg m⁻² s⁻¹ K⁻¹) and B_3 (unit: kg m⁻² s⁻¹) were empirically derived parameters.

It was further assumed that the monthly mean AVOC emissions used in the BASE simulation represented the emission fluxes for the monthly mean temperature (\overline{T}_g) of model grid g. Given the temperature dependence forms of Eqs. (4.1) to (4.3), the temperature sensitivity factor of evaporative AVOC emissions, $f_{i,t,g}(T_{t,g})$, is derived, which describes the ratio of AVOC flux from source *i* at a given temperature $T_{t,g}$, relative to the AVOC flux at monthly mean temperature \overline{T}_g (Eqs. 4.4a-4.4c):

$$f_{i=1,t,g}(T_{t,g}) = \frac{\overline{T}_g}{T_{t,g}} \times \exp\left(\frac{B_1}{\overline{T}_g} - \frac{B_1}{T_{t,g}}\right)$$
(4.4a)

$$f_{i=2,t,g}(T_{t,g}) = \sqrt{\frac{\overline{T}_g}{T_{t,g}}} \cdot \exp\left(\frac{B_2}{\overline{T}_g} - \frac{B_2}{T_{t,g}}\right)$$
(4.4b)

$$f_{i=3,t,g}(T_{t,g}) = \frac{A_3 T_{t,g} + B_3}{A_3 \overline{T}_g + B_3}$$
(4.4c)

where *i* represents the different sources (*i* = 1 for transportation; *i* = 2 for solvent use; *i* = 3 for NSI activities). A_1 and A_2 from Eqs (4.1) and (4.2) are eliminated. The parameter values in Eqs (4.4a-4.4c) can be determined empirically to represent the emissions associated with the prevailing technology of source *i*. A literature review was undertaken to select parameter values most representative of Chinese conditions in 2017 (Table 4.3). The empirical value of B_1 and its uncertainty ($1.6\pm0.5\times10^4$ K) for China V standard light-duty gasoline car was adopted, which accounted for 87% (MEE, 2019) of the total number of vehicles in China in 2015 (Huang et al., 2022). For evaporative emissions from solvent use, an experimental value of B_2 ($4.9\pm1.0\times10^3$

K) for formaldehyde (Tan et al., 2021) was applied, whose emission from building materials had a temperature dependency similar to that of other common solvents (Xiong et al., 2013). A_3 (0.1±0.01 kg m⁻² s⁻¹ K⁻¹) and B_3 (26.6±4.0 kg m⁻² s⁻¹) and their uncertainty ranges were fitted from Song et al. (2019) based on measurements in a Northern Chinese city in 2017. The uncertainties associated with the temperature sensitivity factor in Table 4.3 stem from various sources and are discussed in Section 4.4. The uncertainties associated with the temperature sensitivity factor were not incorporated in the simulations conducted in this study.

Table 4.3 Temperature sensitivity factors $(f_{i,t,g}(T_{t,g}))$ of evaporative AVOC emissions used in this study. Temperatures are in units of K.

Sources	Temperature sensitivity factor $f_{i,t,g}(T_{t,g})$
Fugitive emissions from transportation (Huang et al., 2022)	$f_{i=1,t,g}(T_{t,g}) = \frac{\overline{T}_g}{T_{t,g}} \exp\left(\frac{1.6 \pm 0.5 \times 10^4}{\overline{T}_g} - \frac{1.6 \pm 0.5 \times 10^4}{T_{t,g}}\right)$
Solvent use (Tan et al., 2021)	$f_{i=2,t,g}(T_{t,g}) = \sqrt{\frac{\overline{T}_g}{T_{t,g}}} \cdot \exp\left(\frac{4.9 \pm 1.0 \times 10^3}{\overline{T}_g} - \frac{4.9 \pm 1.0 \times 10^3}{T_{t,g}}\right)$
Other non-solvent- use industrial (NSI) activities (Song et al, 2019)	$f_{i=3,t,g}(T_{t,g}) = \frac{0.1 \pm 0.01 \times T_{t,g} - 26.6 \pm 4.0}{0.1 \pm 0.01 \times \overline{T}_g - 26.6 \pm 4.0}$

The temperature sensitivity factors were applied to the AVOC(T) simulation to represent the variation of AVOC emissions as perturbed by hourly ambient temperatures (Eq. 4.5):

$$E_{i,j,t,g} = c_{i,j,g} [f_{i,t,g}(T_{t,g}) \cdot \gamma_i + (1 - \gamma_i)] E_{0,i,j,t,g}$$
(4.5)

 $E_{i,j,t,g}$ was the emission rate of AVOC species j from source i for model grid g at time t. $E_{0,i,j,t,g}$ was the temperature-independent emission rate of species j in the BASE simulation. $T_{t,g}$ was the surface air temperature for model grid g at time t, and $f_{i,t,g}(T_{t,g})$ was the corresponding temperature sensitivity factor for source i. y_i is defined as the evaporable (i.e., ambienttemperature-sensitive) fraction of AVOC emissions from source *i*, which was the fugitive fraction of AVOC emissions from that source (Liang et al, 2024). Non-fugitive AVOC emissions, such as the tailpipe exhaust from vehicles, are more affected by the temperature within engines and less affected by ambient temperature. For transportation emissions, $\gamma_1 = 0.39$ is assumed based on emission tests for Chinese passenger vehicles and trucks in the year 2015 (Liu et al., 2017). The same temperature sensitivity is assumed for both on-road and off-road vehicles, because all vehicles could release evaporative AVOC emissions during hot soak loss (gasoline evaporation after engine shutdown), diurnal breathing loss, refueling loss, and running loss (Liu et al., 2017). For AVOC emissions from solvent use (i = 2) and NSI activities $(i = 3), \gamma_i = 1$ is assumed because (1) the emissions associated with solvent use were mostly fugitive, and (2) the temperature sensitivity factor adopted for NSI emissions were from the observed variation of ambient VOC concentrations and accounted for the fugitive fraction implicitly. The temperature sensitivity of AVOC emissions is nonlinear, so the inclusion of temperature sensitivity factors would alter the total emissions in the AVOC(T) simulation during the warm period. The normalizing factor $(c_{i,j,g})$ is applied to each model grid, such that, for species *j*, the sum of emissions from source *i* during the simulation period in the AVOC(T) simulation $(\sum_{t} E_{i,j,t,g})$ was identical to the sum of emissions from that source in the BASE simulation ($\sum_{t} E_{0,i,j,t,g}$) (Figure 4.2). This normalization ensured that the simulated differences in surface ozone were only driven by the temperature-induced variability of evaporative AVOC emissions.

4.2.3 Calculation of OFP driven by temperature sensitivity of VOC

The ozone formation potential (OFP) is a widely used metric to quantify the total photochemical production of ozone from individual VOC species throughout its entire photochemical cascade (Carter, 1994). For unit emission of a VOC species *j* released into a boundary layer box of known volume, its OFP is the product of its emission and its emission-based maximum increment reactivity (*MIR_j*; unit: g O₃ g⁻¹ VOC) (Li et al., 2019a; Wu et al., 2017; Zheng et al., 2009). Assuming that the local photochemical conditions (e.g., oxidant levels, actinic fluxes) were unchanged, the local change of OFP of species *j* at model grid *g* at time *t* ($\Delta OFP_{i,j,t,g}$; unit: g O₃) would be proportional to the local change of its emission $\Delta E_{i,j,t,g}$ (unit: g VOC s⁻¹):

$$\Delta OFP_{i,j,t,g} = \Delta E_{i,j,t,g} \times MIR_j \tag{4.6}$$

MIR_j values calculated for Chinese cities from previous studies were adopted here (Zhang et al., 2022; Zhang et al., 2021; Carter, 2010).

4.2.4 Surface observations of ozone concentrations and meteorological conditions, and satellite observations of tropospheric NO₂ and formaldehyde column concentrations

Model results are evaluated with hourly measurements of surface ozone concentrations at 91 sites in 13 cities in the BTH area during summer 2017. The measurements were managed by the National Environmental Monitoring Centre (http://www.cnemc.cn, last accessed: March 30th, 2023). A consistent data quality control protocol (Wang et al., 2021a; Lu et al., 2018) was applied to the hourly measurements and they were averaged onto the model grids for comparison with the simulations. Hourly meteorological data downloaded from the National Centers for Environmental Information (NCEI, http://www.ncdc.noaa.gov, last accessed: January 10th, 2024) is used to evaluate the simulated meteorology.

Satellite-observed formaldehyde to NO₂ column concentration ratios (FNR) have been used as a qualitative indicator for the regional ozone photochemical regime (Jin et al., 2017; Ducan et al., 2010; Martin et al., 2004). Level 3 Cloud-Screened Tropospheric Column NO₂ product (0.25° resolution) (Krotkov et al., 2019) and the Total Column Daily Level 3 Weighted Mean Global HCHO product (0.1° resolution) (Chance, 2019) from the Ozone Monitoring Instrument (OMI, nadir overpass time at approximately 13:45 local time) are used to calculate observed FNR over the BTH area in summer 2017. Both datasets were interpolated to 0.25° resolution for analysis.

4.3 Results

4.3.1 Evaluation of surface ozone concentrations simulated by the BASE experiment

The performance of WRF-GC in simulating the observed meteorological conditions and surface ozone concentrations during June 1st and July 5th 2017 is first evaluated. The WRF-GC simulations, nudged with NCEP reanalysis data, reproduced the spatiotemporal variability of observed surface temperature and relative humidity (Figures 4.3, 4.4). The BASE simulation reproduced the spatial distribution of MDA8 ozone concentrations over the BTH area (Figure 4.5, spatial correlation r = 0.64). The simulated MDA8 ozone concentration over the BTH area during this period averaged 179±40 µg m⁻³, in good agreement with the observations in terms of mean (160±38 µg m⁻³) and variability (Figure 4.6, temporal correlation r = 0.79). Observed BTH-mean MDA8 ozone concentrations exceeded the national air quality standard of 160 µg m⁻³ during June 14th to 21st (hereafter referred to as Episode 1) and during June 25th to July 5th (Episode 2). The BASE simulation correctly simulated 17 out of these 19 ozone exceedance days in the BTH area (Figure 4.6), which formed the basis for the subsequent analyses. However, the model tended to underestimate ozone abundances on exceedance days and the mid-day ozone concentrations (Figure 4.6), potentially reflecting a subdued sensitivity of ozone to temperature in the BASE simulation.



Figure 4.3 Spatial distribution of mean observed (symbols) and simulated (filled contours) (a) surface temperature, (b) surface relative humidity from the BASE experiment over the BTH area during June 1^{st} to July 5^{th} , 2017. The averaged observed and simulated meteorological variables and the spatial correlations (*r*) during the simulated period are shown inset.



Figure 4.4 Time series of mean observed (symbols) and simulated (filled contours) (a) surface temperature, (b) surface relative humidity from the BASE experiment over the BTH area during June 1^{st} to July 5^{th} , 2017. The averaged observed and simulated meteorological variables and the spatial correlations (*r*) during the simulated period are shown inset.

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Figure 4.5 (a) Spatial distribution of mean observed (symbols) and simulated (filled contours) MDA8 ozone concentrations from the BASE experiment over the BTH area during June 1st to July 5th, 2017. The averaged observed and simulated MDA8 ozone concentrations (units: μ g m⁻³) and the spatial correlation (*r*) are shown inset. (b) Province/ cities in Beijing (red lines), Tianjin (green lines) and Hebei (blue lines).



Figure 4.6 Time series of the observed (black line) and simulated (red line, BASE simulation) hourly ozone concentrations over the BTH area between June 1st and July 5th, 2017. The observed and simulated MDA8 ozone are shown with grey and blue lines, respectively. The mean ozone concentrations (\pm standard deviations) and the temporal correlation (r) between observed and simulated hourly ozone concentrations during the simulated period are shown in the figure.
4.3.2 Simulated temperature-dependencies of regional anthropogenic and biogenic VOC emissions

Figure 4.7 shows $[\gamma_i \cdot f_{i,t,g}(T_{t,g}) + (1 - \gamma_i)]$ from Eq. (4.5), which was the parameterized effective temperature sensitivity of the total (evaporative and non-evaporative) AVOC flux from source *i*, assuming a monthly mean temperature \overline{T}_g of 298 K at model grid *g*. The shaded areas represent the ranges of uncertainty associated with the empirical parameters used in Eq. (4.4a-4.4c) (Table 4.3). The AVOC emissions from transportation increase only weakly with increasing temperature below \overline{T}_g but increased sharply with temperature above \overline{T}_g . At 10 K above \overline{T}_g , the AVOC flux from transportation was a factor 2.8 times larger than the flux at \overline{T}_g . In contrast, the AVOC fluxes associated with solvent use and NSI activities increased roughly linearly with temperature. At 10 K above \overline{T}_g , the AVOC fluxes at \overline{T}_g . The AVOC species from transportation and solvent-use emissions consisted of high fractions of alkenes and aromatics of high OFPs. It is hypothesized that the temperature sensitivity of the AVOC emissions from transportation and solvent use may substantially aggravate surface ozone pollution during anomalously warm weather.



Figure 4.7 The effective temperature sensitivity of total AVOC emissions from transportation (i = 1, light purple), solvent use (i = 2, blue), and NSI activities (i = 3, yellow) for a model grid g at time t, relative to the monthly mean temperature of $\overline{T}_g = 298$ K for that grid. The grey dashed lines mark the ratios of AVOC emissions at 308 K relative to their emissions at 298 K. The shaded areas represent the ranges of uncertainty associated with the empirical parameters in Eq (4).

Figure 4.8a shows the daily variations of BTH-averaged AVOC and BVOC emissions in response to daily temperature variations, as simulated by the WRF-GC sensitivity experiments. During the study period, the daily mean temperature over the BTH area varied between 291 K and 304 K. In particular, the pollution Episodes 1 and 2 both corresponded to periods of anomalously warm temperature. Daily temperature variations caused the BTH-wide daily AVOC emissions from the three anthropogenic sectors to vary substantially by -39% to 35% relative to their respective monthly means. For the entire BTH area, the temporal correlations between BTH-mean daily temperature and BTH-wide AVOC emissions from the three sectors were 0.92, 0.97, and 0.98, respectively. The overall sensitivity of total (from all sectors) AVOC emissions to temperature was 6.25% K⁻¹ over the BTH during the simulated period.

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Transportation AVOC emissions contributed the most to this overall temperature sensitivity (9.7% K⁻¹), especially on warm days. Solvent use and NSI activities contributed 5.8% K⁻¹ and 3.4% K⁻¹, respectively, to the overall temperature sensitivity of total AVOC emissions. In comparison, daily temperature variations drove a daily BVOC emission variability between - 67% and 61%, resulting in a temperature sensitivity of 11.2% K⁻¹ and temporal correlation against daily temperature r = 0.97. In short, the temperature sensitivity of total AVOC emissions was comparable in magnitude to the temperature sensitivity of BVOC on a BTH-wide regional scale.



Figure 4.8. (a) Time series of simulated daily surface air temperature (grey dashed line), daily variations of BTH-mean VOC emissions from anthropogenic and biogenic sources relative to their respective monthly means (bars), and the simulated MDA8 ozone responses to temperature-dependent anthropogenic (red dots and whiskers) and biogenic (green dots and whiskers) VOC emissions. (b) Time series of simulated 10-m wind speeds (W10, grey dashed line with triangles), downward shortwave radiation fluxes (SWDOWN, pink dashed line with squares), and planetary boundary layer height (PBLH, blue dashed line with diamonds) over the BTH area during the simulation period. The time periods of two ozone exceedance episodes are shaded in blue (Episode 1) and yellow (Episode 2).

4.3.4 Simulated responses of surface ozone to temperature-dependent VOC emissions

Figure 4.8a also shows the responses of BTH MDA8 ozone to the temperature-dependent AVOC and BVOC emissions, represented by the simulated ozone differences between the AVOC(T) and the BASE experiments, and by the differences between the BASE and the BVOC(NT) experiments, respectively. The monthly mean MDA8 ozone over the BTH area in the AVOC(T) (159 \pm 42 µg m⁻³) and BVOC(NT) (161 \pm 32 µg m⁻³) simulations were similar to that in the BASE simulation ($160 \pm 38 \ \mu g \ m^{-3}$), which is due to the monthly mean VOC emissions being constrained to the same values in all simulations. The non-linear impacts on the simulated ozone differences were small, because in all simulations: (1) the OH concentrations were relatively similar (less than 10% difference, Figure 4.9a), (2) the ozone production in most of the BTH cities were NO_x-saturated (discussed in Section 3.4), and (3) RO₂ were mainly produced by the photolysis of oxygenated products of AVOCs and BVOCs. The inclusion of AVOC's temperature-dependence enhanced the daily variability of ozone, as shown by the -7.6 μ g m⁻³ (June 3rd) to 6.6 μ g m⁻³ (June 30th) difference relative to the BASE simulation (Figure 4.8a), and this inclusion also slightly improved the temporal correlation of daily simulated MDA8 ozone concentrations with the observations in 9 out of 13 cities in the BTH area (Figure 4.10). The daily ozone variability induced by AVOC-temperature relationship was found to be comparable to the daily ozone variability induced by the BVOCtemperature relationship (-13.5 µg m⁻³ on June 3rd to 10.1 µg m⁻³ June 30th; Figure 4.8a). Temperature-enhanced AVOC and BVOC emissions both contributed to exacerbating ozone exceedances during the warm periods of Episodes 1 and 2. During the cool period between June 3rd and June 8th, both AVOC and BVOC emissions were subdued, resulting in comparable contributions to the decreased surface ozone concentrations.

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Figure 4.9. Percent differences of the simulated surface mean (a) OH concentrations and (b) H_2O_2/HNO_3 ratios in the AVOC(T) experiment relative to those in the BASE experiment.



Observed MDA8 O₃ [µg m⁻³]

Figure 4.10 Comparison of the daily simulated MDA8 ozone concentrations in the BASE (blue) and AVOC(T) (red) experiments against the observations for 13 cities in the BTH area during the simulation period. The solid lines are the reduced-major axis regression lines; the

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slopes and intercepts are shown inset. Also shown are the mean slopes of the regression lines for 13 cities. The grey dashed lines indicate the 1:1 line. The city names are labelled in red if the inclusion of temperature-enhanced evaporative AVOC emissions in the model improved the temporal correlation of daily simulated MDA8 ozone concentrations with the observations.

The responses of surface ozone to temperature-enhanced VOC emissions were also modulated by other meteorological variables (Figure 4.8b), reflecting the complex meteorological control on pollutant emissions, advection, accumulation, and photochemistry. During the Episode 2, the daily maximum temperature over the BTH was 3.5 K above the monthly mean, and the MDA8 ozone enhancements due to temperature-dependent AVOC and BVOC emissions were $6.1 \,\mu g \,\mathrm{m}^{-3}$ and $8.5 \,\mu g \,\mathrm{m}^{-3}$, respectively. Episode 2 was marked by strong downward shortwave radiation flux (> 340 W m⁻²), low surface wind speeds (< 3 m s⁻¹), and relatively low planetary boundary layer heights (< 1000 m), all of which were favourable conditions for the accumulation of ozone precursors and their local photochemical production of ozone (Li et al., 2020; Wang et al., 2017). In contrast, during Episode 1, the response of MDA8 ozone to temperature-enhanced VOC was slightly subdued, partly because the high temperatures lasted shorter than they did during Episode 2. Additionally, the high planetary boundary layer heights (12% above the monthly mean) and enhanced surface winds (19% above the monthly mean) during Episode 1 both promoted the dispersion of ozone and its precursors, such that the impacts of temperature-enhanced anthropogenic and biogenic VOC emissions on local ozone production were both diminished.



Figure 4.11 The spatial distributions of mean OFP enhancements (unit: g O₃) driven by temperature-dependent (a) AVOC and (b) BVOC emissions during Episode 2. Also shown are the spatial distributions of simulated mean MDA8 ozone enhancements (unit: μ g m⁻³) driven by temperature-dependent (c) AVOC and (d) BVOC emissions.

An analysis was conducted to examine how temperature-dependent VOC emissions from various sectors contributed to surface ozone pollution during Episode 2. Figure 4.11 shows the spatial distributions of the OFP enhancements during Episode 2 driven by temperaturedependent AVOC and BVOC emissions, respectively. The OFP enhancements associated with increased AVOC emissions were highest over Beijing, Tianjin, Tangshan, and Baoding (Figure 4.12). The simulated ozone enhancements associated with increased AVOCs were spatially consistent with the corresponding OFP enhancements, with largest ozone enhancements exceeding $6 \ \mu g \ m^{-3}$ over the four aforementioned cities (Figure 4.11a, 11c). In contrast, the OFP enhancements associated with temperature-dependent BVOC emissions were spatially correlated with increased isoprene emissions (Figure 4.11b, 4.2b), but the simulated ozone enhancements were slightly displaced to the northwest of the BTH area (Figures 11d, 4.2b). This displacement was because the oxidation of isoprene first produced its intermediate products, such as methacrolein and methyl vinyl ketone, formaldehyde, and acetaldehyde, which in turn photochemically form ozone (Bates et al., 2019). All of these intermediate products have lifetimes ranging from a few hours to a day, which were longer than that of isoprene. As a result, these products were transported downwind by the surface easterly and southerly winds (Figure 4.13), and the eventual ozone formation were spatially displaced and

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lagged behind the initial oxidation of isoprene by several hours. In contrast, the photochemical production of ozone from highly reactive alkenes (e.g., propene) and aromatics (e.g., m-xylenes) began immediately after the initial oxidation of these precursors (Sakamoto et al., 2022). This difference in the ozone production timescales from reactive AVOCs and from isoprene is consistent with evidence from chamber experiments. Compared to BVOCs, the temperature-dependent AVOC emissions have a more localized impact on surface ozone. In the WRF-GC model for the simulation period, the inclusion of temperature-sensitive AVOC emissions led to less than 10% perturbation on the regional OH levels (Figure 4.9a); the difference in the simulated biogenic secondary organic aerosol abundance was also small (Figure 4.14).



Figure 4.12 Temperature-enhanced emissions of (a) representative AVOC species from transportation (top), NSI activities (middle), and solvent use (bottom) and (b) biogenic isoprene during Episode 2, relative to their respective monthly mean emissions (Figure 4.2).

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Figure 4.13 Mean surface (10 m) wind over the BTH area during Episode 2.



Figure 4.14. Percent difference of biogenic secondary organic aerosol concentrations produced by isoprene epoxydiols (IEPOXSOA) in the AVOC(T) experiment compared with that simulated in the BASE experiment during the simulation period.

Figure 4.15 compares the temperature-induced OFP enhancements contributed by different AVOC and BVOC species and sectors over Beijing, Tianjin, and Hebei, respectively, during Episode 2. The temperature dependencies of BVOCs and AVOCs contributed comparably to the OFP enhancements over Beijing and Tianjin, but BVOCs contributed twice as much OFP enhancements than AVOCs over Hebei. Averaged over the three cities and provinces, the temperature-enhanced OFP associated with AVOCs was mostly associated with transportation (50%) and solvent-use (40%) emissions, with only minor contributions from NSI activities (10%), confirming the earlier hypothesis. In terms of chemical species, short-lived aromatics (including toluene and xylenes, mostly from solvent-use emissions) were the largest contributors (45%) to the anthropogenic OFP enhancements, followed by $\geq C_3$ alkenes (largely from transportation) and $\geq C_4$ alkenes (from both transportation and solvent-use emissions). These results indicated that, over areas with strong AVOC emissions, selectively reducing the evaporative emissions of highly reactive species from transportation and solvent use would mitigate the local ozone pollution associated with warm temperatures.



Figure 4.15. The OFP enhancements driven by temperature-dependent VOC emissions over Beijing (left), Tianjin (middle), and Hebei (right) during Episode 2. The source sectors are color-coded. The OFP enhancements from the top-five-contributing AVOC species are also shown. The OFP for each city/province is the sum of episode-averaged OFP for all grids within that city/province.

4.3.5 Ozone-temperature relationship as driven by temperature-dependent VOC emissions

An analysis was performed to determine whether and how the inclusion of temperaturedependent AVOC emissions enhanced the representation of the ambient ozone-meteorology relationship in the model. Figure 4.16 shows the simulated MDA8 ozone enhancements (Δ MDA8O₃) driven by temperature-dependent AVOC and BVOC emissions, respectively, as a function of mean afternoon (13:00-17:00) temperature anomaly (Δ T) for cities in the BTH area. The ozone-temperature sensitivity (*k*) is defined as the slope of the reduced-major axis regression line of Δ MDA8O₃ versus Δ T. The temperature dependency of AVOC emissions drove simulated ozone-temperature sensitivities (*k*_A) of 1.0 to 1.8 µg m⁻³ K⁻¹, which were on average 70% of the total simulated ozone-temperature sensitivity driven by the temperature dependency of BVOCs emissions (*k*_B = 1.7 to 2.4 µg m⁻³ K⁻¹).

A potential relationship between the variable values of k_A and k_B across BTH cities and the local ozone production regime in each city is investigated. The simulated FNRs from the AVOC(T) experiment were spatially consistent with the OMI-observed FNRs (Figure 4.17), indicating that the model reproduced the spatial difference of the ozone production regimes over the BTH area.



Figure 4.16. Scatter plots of the simulated responses of MDA8 ozone (Δ MDA8O₃) to temperature-enhanced AVOC (orange) and BVOC (green) emissions versus afternoon (13:00-17:00) temperature (Δ T) for each city in the BTH area. The solid lines are the reduced-major axis regression lines. The ozone-temperature sensitivity driven by temperature-enhanced AVOC (k_A) and BVOC (k_B) emissions are defined as the slope of these regression lines. Units of k: μ g m⁻³ K⁻¹.



Figure 4.17 (a) Observed FNR values from OMI; (b) Simulated FNR values from the BASE experiment during the simulation period.

Furthermore, both the simulated FNR and H₂O₂/HNO₃ ratios (Ye et al., 2016) were not significantly different in the BASE and AVOC(T) experiments, indicating that the regime of ozone production was not substantially altered by the inclusion of temperature-sensitive AVOC emissions (Figure 4.9b). Figure 4.18 shows the simulated values of k_A and k_B and their ratios versus the OMI-observed FNR values over model grids with surface ozone measurements during the study period. Previous model studies over East China have shown that FNR < 2.3 and FNR > 4.2 respectively indicated local ozone production to be NO_x-saturated (or VOC-sensitive) and NO_x-sensitive, while an FNR value between 2.3 and 4.2 indicated ozone production to be in a transitional regime (Wang et al., 2021b).⁴ Based on these thresholds, ozone production in most of the 13 cities in the BTH area were VOC-sensitive (Figure 4.18). The k_B values across BTH cities were not significantly correlated with FNR, which may be due in part to the delayed ozone production from isoprene oxidation (discussed in Section 3.3). However, k_A values (r = -0.48, two-tail *p*-value < 0.005) and k_A/k_B values (r = -0.67, two-tail *p*-value < 10⁻⁴) across BTH cities were negatively correlated with FNRs. These negative correlations indicated that, in cities where ozone production was severely saturated with NO_x emissions and

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thus highly sensitive to VOC emissions, the localized production of ozone from temperaturedependent AVOC emissions would contribute more substantially to the overall ozonetemperature relationship, compared to the cities with FNR > 2.3, such as Zhangjiakou and Chengde (Figures 5 and S13). In these latter cities, the ozone production was in the transitional regime and less sensitive to increased VOC emissions; as such, both k_A and k_A/k_B were relatively small in Zhangjiakou and Chengde (Figure 4.18).



Figure 4.18. The simulated ozone-temperature sensitivities for each city in the BTH area as driven by temperature-enhanced (a) AVOC emissions (k_A) and (b) BVOC emissions (k_B), and (c) the ratio of k_A/k_B versus the FNR values observed by OMI. Also shown are (d) the observed ozone-temperature sensitivity for each city (observed MDA8 ozone anomaly versus afternoon

(13:00-17:00) temperature anomaly during ozone episodes). The symbols are outlined in red if the inclusion of temperature-enhanced evaporative AVOC emissions in the model improved the simulated overall ozone-temperature sensitivity on ozone exceedance days. The gray dashed line represents the threshold between a NO_x-saturated (VOC-sensitive) regime and a transition regime for ozone photochemical production.

The observed surface ozone-temperature sensitivity over the BTH cities on ozone exceedance (MDA8 ozone > 160 µg m⁻³) days (9.8±2 µg m⁻³ K⁻¹, Figure 4.19) were larger than the sum of k_A and k_B , indicating that there were other coupling mechanisms between temperature and ozone pollution at play, in addition to the temperature dependencies of AVOC and BVOC emissions explored in this study. These other coupling mechanisms may include the actinic flux-dependency of BVOC emissions, the temperature-dependency of soil NO_x emissions, surface stagnation and boundary layer compression associated with subsidence and anticyclonic weather, advection of ozone from other parts of Eastern China, and faster photochemical reactions and less ozone removal under warm and dry weather (Wang et al., 2021c; Fu et al., 2019; Porter et al., 2019; Fu et al., 2015). Nevertheless, the inclusion of the temperature-dependent AVOC emissions in model improved the simulated ozone-temperature sensitivities (from $8.3\pm1 \ \mu g \ m^{-3} \ K^{-1}$ in the BASE experiment to $9.5\pm1 \ \mu g \ m^{-3} \ K^{-1}$ in the AVOC(T) experiment) over the BTH area as a whole and at most BTH cities on ozone exceedance days (Figures 4.19).



T anomaly [K]

Figure 4.19 Scatter plots of the MDA8 ozone anomaly versus afternoon (13:00-17:00) temperature anomaly for each city on ozone exceedance days. The solid lines are the reduced-major axis regression lines. The ozone-temperature sensitivities (*k*) in the observations (black), as simulated in the BASE experiment without temperature-dependent AVOC emissions (blue), and as simulated in the AVOC(T) experiment with temperature-dependent AVOC emissions (orange) are shown inset. The city names are labelled in red if the inclusion of temperature-enhanced evaporative AVOC emissions in the model improved the simulated overall ozone-temperature sensitivity. Units of *k*: μ g m⁻³ K⁻¹.

4.4 Summary and discussion

The parameterizations derived for the temperature dependency of evaporative AVOC emissions involve uncertainties arising from several aspects, including the scarcity of observational constraints on the temperature dependence of individual sources and species, as well as the continued change of emission control policies in China. For example, the same temperature sensitivity for evaporative emissions is assumed from on-road and off-road vehicles, but the fuel types and emission regulations for these vehicles are in fact different (Lu et al., 2018; Zheng et al., 2018a). For NSI emissions, the use of parameters derived from the source-apportionment study of Song et al. (2019) may be sensitive to their measurements and apportionment techniques. In addition, the Chinese government has promulgated stronger control policies on AVOC emissions since 2021 (MEE, 2021). Emission standards for vehicles have also tightened (MEE, 2016), and in many cities a significant portion of on-road fleet has become electrical (CSC, 2020). These changes likely have substantial impacts on evaporative AVOC emissions. However, measurements in 2021 showed that fugitive emissions still constituted more than half of the total VOC emissions from several industrial processes, including coating (Liang et al., 2024).⁵ More measurements representative of current technologies is urgently needed to reduce the uncertainties of the parameters in Table 4.3 and better represent the temperature sensitivities of evaporative emissions of AVOC species from individual sources in China.

Application of the parametrizations derived here in regional models could help improve air quality forecasts and accentuate targets for emission reduction, providing policy-makers with effective guidance in air quality management. A persistent issue in current air quality models is the tendency to underestimate high ozone pollution events (Yang et al., 2023; Petersen et al., 2019). It has been demonstrated that incorporating the temperature-dependency of evaporative AVOC emissions into the model help rectify this underestimation by improving the simulated ozone-temperature sensitivity, especially in major cities. The findings in this Chapter also highlighted the need to strengthen the control of evaporative emissions of high-reactivity AVOC species, including higher alkenes and aromatics, which is already an emission reduction priority set by the Chinese Ministry of Ecology and Environment (MEE, 2022). Furthermore, reducing evaporative AVOC emissions on hot days, such as temporarily suspending vehicular

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and industrial refueling, open-air painting, and asphalt laying may be viable emergency response measures to mitigate ozone exceedance episodes in urban areas.

This chapter has also highlighted a previously under-explored factor in the "climate change penalty" of surface ozone pollution, which is the deterioration of ozone air quality as a result of climate warming even when anthropogenic activities remain unchanged. Studies have shown that global warming may increase the frequency and intensities of heatwaves and urban heat island effects (Perkins-Kirkpatrick et al., 2020; Fu et al., 2019), such that the impacts of temperature-dependent AVOC emissions on ozone may become more pronounced in the future. Other underestimated or unrepresented natural and anthropogenic emissions of ozone precursors, such as soil-NO_x emissions⁶ (Wang et al., 2021c) and emissions associated with urban greening practices (Schlaerth et al., 2023; Yu et al., 2022; Gunawardena et al., 2017), may also cause complex ozone-temperature sensitivities. These linkages between air pollution and meteorology should be considered in projection of long-term air quality trends to better inform long-term emission reduction goals.

5. Improving aromaticchemistry representationin a box model framework

5.1 Introduction

Peroxy radicals RO_x ($RO_x \equiv OH + HO_2 + RO_2$) are highly reactive components in the VOC oxidation progress, playing a pivotal role in the formation of O₃ and SOA, particularly in regions with elevated concentrations of NO_x and significant ozone pollution. The budget of RO_x radicals is predominantly governed by local chemical reactions rather than transport processes due to their high reactivity and short atmospheric lifetimes. In the presence of NO_x, RO_x radicals initiate and propagate the oxidation of VOCs and CO, leading to the production of ozone as a secondary pollutant (see Chapter 2.2). OH-initiated oxidation of VOCs involves the abstraction of hydrogen atoms or the addition of OH to double bonds, forming RO₂. Under high-NO_x conditions, RO_2 primarily reacts with NO to form NO₂, which subsequently photolyzes, leading to the formation of ozone. The concentration and reactivity of RO_x species are thus critical determinants of the rate and extent of ozone production. In contrast, under low-NO_x conditions, RO_2 tends to react with other RO_2 radicals, resulting in the formation of oxygenated VOCs (OVOCs) with higher molecular weights, potentially contributing to SOA formation. Consequently, areas with substantial NO_x emissions from traffic, industrial activities, and power generation often experience elevated ozone levels, contributing to deterioration of air quality and adverse health effects.

Despite the crucial role of RO_x radicals, their representation is often insufficient in current atmospheric models. Several factors contribute to this deficiency. Firstly, modelling the photochemical cascade of VOCs poses significant challenges due to the vast number of species and pathways involved, and the complexity of RO_x chemical reactions is often inadequately captured in atmospheric models. The near explicit chemical mechanism MCM, includes 142 non-methane VOCs, encompassing more than ten thousand reactions to describe the real atmospheric processes (Bloss et al., 2005). Accurately representing this chemistry in models is computationally intensive. Therefore, most current atmospheric models employ simplified chemical schemes, such as GEOS-Chem (Bey et al., 2001), and the CRI (Jenkin et al., 2008), SAPRC (Carter et al., 2010) mechanisms. These mechanisms utilize lumping strategies to simplify the representation of VOCs by grouping them based on similar behaviours. These strategies include lumping by reactivity, where abundant, long-lived species are explicitly represented while assuming that short-lived, reactive species oxidize locally to form products such as ozone or SOA. Other strategies involve lumping by reaction pathways, product similarity, or by ignoring minor species altogether. For

example, MCM v3.3.1. includes 18 aromatic species and approximately 5,000 reactions, while GEOS-Chem includes 3 aromatics species and fewer than 100 reactions. These simplified mechanisms condense the complex processes into a smaller number of reactions, which reduce the computational load but also the accuracy of the simulations. The different complexity can lead to significant discrepancies in the simulated concentrations of RO_x (Emmerson et al., 2009; Zong et al., 2018; Qu et al., 2021).

Additionally, limited understanding of RO_x chemistry also contributes to the inadequate representation of RO_x in models. In the PMTACS-NY campaign, Ren et al. (2003) found that daytime OH radicals were underestimated by a factor of 1.1, while HO₂ was underestimated by factors of 2–20 at NO mixing ratios above 20 ppb. Similar findings were reported in Tokyo during wintertime (Kanaya et al., 2007). Lu et al. (2013) pointed out that current chemical mechanisms lack an OH source under low NO_x conditions. In Beijing's BEST-ONE campaign, Tan et al. (2018) highlighted that HO₂ and RO₂ concentrations were underestimated by factors up to 5 during high NO_x pollution episodes. Additionally, Zhang et al. (2022) found consistent underestimations of HO₂ in Shanghai's winter, suggesting missing primary peroxy radical sources. These studies indicate that limited understanding of chemical processes is a key reason for the underrepresentation of RO_x radicals in models.

Furthermore, emission uncertainty significantly impacts the accurate representation of RO_x chemistry. For instance, NMVOC emissions in Asia for 2000 had an estimated uncertainty of $\pm 130\%$ (Streets et al., 2003), while updated inventories for China show uncertainties ranging from $\pm 68\%$ to $\pm 78\%$ (Li et al., 2019a). These uncertainties arise from unreliable data on scattered area sources and discrepancies in methods, particularly regarding solvent use and industrial processes (Wu et al., 2016). Wang et al. (2014) revealed that a 68% increase or decrease in anthropogenic NMVOC emissions could lead to significant changes in OH, HO₂, and RO₂ concentrations across regions in China.

As societal demands for more precise and accurate air quality simulations increase, the accurate representation of RO_x generated from the oxidation of VOCs has become a crucial requirement for atmospheric models, especially from highly reactive VOCs such as aromatics. Aromatics such as benzene, toluene, and xylenes, are significant contributors to the formation of SOA and ozone (Wu

et al., 2017; Zheng et al., 2009; Hakami et al., 2004). These compounds are primarily emitted from a variety of anthropogenic sources, including vehicle exhaust, industry, and residential activities (Li et al., 2017). In urban areas, where traffic emissions and industrial activities are concentrated, the concentrations of aromatic hydrocarbons can be particularly high, making them a major concern for air quality management (Gao et al., 2021; Shao et al., 2016). Once released into the atmosphere, aromatic undergo complex oxidation reactions initiated by reactive species such as OH. The oxidation of aromatics leads to the formation of RO_x radicals, and these participate in further reactions that contribute to the production of ozone and SOA. However, condensed aromatics mechanisms are usually employed in atmospheric models, and some lumped species may not react locally but are instead transported, leading to discrepancies between the goals of precise air quality simulations and the chemical representations used (Qu et al., 2021).

Considering the balance between ozone simulation accuracy and computational efficiency, it is crucial to identify key intermediates or reactions and thoroughly characterize their chemical behaviours to enhance the accuracy of atmospheric models. Among these intermediates, methylglyoxal (MGLY) stands out due to its formation during the oxidation of VOCs, particularly aromatics. Larger aromatic molecules undergo a series of reactions, often starting with the addition of OH followed by several oxidation steps. Stepwise degradation following ring-opening mechanisms can lead to the direct generation of MGLY. Wagner et al., (2003) found MGLY is one of the major sources of RO_x in the chemical scheme of toluene oxidation, and ozone is highly sensitive to changes in MGLY concentrations. MGLY has also been shown to be a major source of RO_2 production, accounting for over 50% of the total RO_2 generated in certain atmospheric conditions (Qu et al., 2021). These findings underscore the importance of MGLY in the atmospheric degradation of aromatics and subsequent impact on ozone formation.

This chapter provides insights into the limitations of condensed chemical mechanisms in simulating RO_x chemistry and presents practical solutions to enhance the accuracy of atmospheric models. The photochemical differences between a near-explicit gas-phase chemical mechanism and two lumped mechanisms with varying complexities are quantified. Differences in simulated oxidation pathways and role of MGLY in forming key RO_x species is assessed. Additionally, potential parameterizations are explored to address the lack of complexity in lumped schemes while maintaining computational efficiency. This chapter particularly emphasizes the role of

aromatic compounds as significant ozone precursors in urban environments that are often oversimplified in current models. These scientific inquiries are conducted within a box model framework to minimize complexities associated with atmospheric transport. Findings from this chapter will be applied in Chapter 6 to a 3-D regional atmospheric chemistry model to assess the impacts of VOC-chemistry complexity on regional air quality.

5.2 Methodology

5.2.1 Site and measurements

Measurements at the Atmospheric Observation Supersite of Shenzhen (AOSS, 22.60 °N, 113.98 °E) are utilized as the input data for box model simulations using the DSMACC box model (see Chapter 3 for basic model description). The AOSS is located in the Shenzhen Graduate School of Peking University, Guangdong, in a typical urban environment. The observation instruments were placed on the top floor of the building, with the sampling inlets approximately 25 m from the ground. The site is surrounded by campus buildings, apartments, and scattered green spaces, with a medium-traffic road approximately 100 metres away. The measurements used in this study were made during 15th to 20th September 2022, which included an ozone air pollution episode.

Ambient VOC concentrations were measured using a proton-transfer-reaction time-of-flight mass spectrometry (PTR–TOF–MS) instrument. Other pollutants measured included O_3 , NO_x , $PM_{2.5}$, PM_{10} , SO_2 , and CO. Previous research indicated that the measured concentrations of $PM_{2.5}$ and VOCs at this site were comparable to the average observed levels of these species at other locations in the PRD region (Louie et al., 2013; Huang et al., 2018). As such, the pollutant concentrations measured at this site is representative of the pollutant levels in Shenzhen city. Meteorological data, including temperature, relative humidity, wind speed, wind direction was also measured on-site. More measurement details can be found in previous published studies (Li et al., 2024; Xia et al., 2023; Xia et al., 2021).

During the study period, the average observed VOC/NOx (ppbv/ppbv) ratio at this site was 3.2. The photochemical production of ozone in Chinese megacity clusters, such as the NCP, YRD, and PRD, are currently in the VOC-limited regime, although some studies have indicated a gradual migration toward the transitional regime as a result of the strong control of NO_x emissions in recent years (Ren et al., 2022; Wang et al., 2021b). Previous studies indicate that in cities within the PRD, such as Shenzhen and Guangzhou, the ozone formation mechanism is VOC-limited (An et al., 2024; Yu et al., 2020; Zou et al., 2015).



Figure 5.1 (a) Shenzhen is located on the southeast coast of China; (b) the sampling site of this study and its surrounding environment in the Pearl River Delta region (satellite images from Google Earth) (Xia et al., 2021, Section 2, Figure 1).

5.2.2 Gas-phase chemistry mechanisms for aromatic compounds

In this study, three gas-phase chemical mechanisms of varying complexity for aromatic compounds are applied in box model simulations. These three mechanisms are the Master Chemical Mechanism (MCM v3.3.1, Bloss et al., 2005), the Common Representative Intermediates Mechanism (CRI v2.2, Jenkin et al., 2008) and the chemical mechanism in the GEOS-Chem chemical transport model v14.1.0 (Bey et al., 2001). These mechanisms are briefly described below.

a) Master Chemical Mechanism (MCM)

The MCM (<u>https://mcm.york.ac.uk/MCM/</u>) is a near-explicit gas-phase photochemical mechanism of VOCs (Bloss et al., 2005). MCM facilitates investigations requiring a comprehensive

representation of chemistry, such as the distributions of speciated radicals and intermediates formed during VOC degradation.

MCM v3.3.1 described the photochemical cascade of methane and 142 NMVOC precursors, encompassing a total of 17,224 reactions involving 5,832 distinct chemical species. Among these, 18 aromatic precursors were included in MCM v3.3.1: benzene, toluene, xylenes, other alkyl benzenes, styrene, and benzaldehyde. In MCM v3.3.1, the photochemical oxidation of the aromatic precursors was described by 5,000 reactions, engaging around 1,900 species, including over 400 RO₂ species.

b) Common Representative Intermediates Mechanism (CRI)

The CRI v2.2 mechanism (<u>https://mcm.york.ac.uk/CRI/;</u> Jenkin et al., 2008) was developed based on the MCM characterizes ozone formation from methane and 115 NMVOCs. It consists of 1,268 reactions involving 445 unique species. Similar to the MCM, it encompasses 18 aromatic species but efficiently describes their chemistry using just over 400 reactions, involving fewer than 200 species.

The CRI lumps VOCs that contain the same number of reactive bonds (i.e., C-C and C-H). The number of these reactive bonds in VOC is referred to as the CRI index. This lumping principle assumes that the potential for ozone formation from a given VOC correlates with the number of reactive bonds it contains. For instance, consider the oxidation of simple VOCs CH_4 , C_2H_6 and C_2H_4 .

For the oxidation of methane under high-NO_x conditions, the total O_3 yield during oxidation to CO_2 and H_2O is proportional to the number of reactive bonds in the parent molecule (C-H and C-C). In the case of methane, the overall reaction can be represented as:

$$CH_4 + 80_2 \rightarrow CO_2 + 2H_2O + 4O_3$$
 (5.1)

resulting in four O₃ molecules.

Similarly, the oxidation of ethane and ethene under high-NO_x conditions forms seven molecules and six molecules of O_3 ,

$$C_2H_6 + 14O_2 \rightarrow 2CO_2 + 3H_2O + 7O_3$$
 (5.2)

$$C_2H_4 + 12O_2 \rightarrow 2CO_2 + 2H_2O + 6O_3$$
(5.3)

Ozone generation begins with the oxidation of VOCs by OH, producing RO₂ and HO₂, which convert NO to NO₂. Tropospheric ozone is formed through the photolysis of NO₂, releasing atomic oxygen that combines with O₂ to create ozone. Thus, the conversion of NO to NO₂ during VOC oxidation directly affects ozone levels. The CRI mechanism uses the number of reactive bonds in closed-shell intermediates as an index to evaluate potential NO to NO₂ conversions in subsequent OH-initiated and NOx-catalyzed degradation.

Figure 5.2 shows the pathways for complete oxidation of C_1 – C_6 alkanes, grouping common intermediates with the same CRI index. For example, '19' in RN₁₉O₂ and '16' in CARB₁₆ indicate the number of NO to NO₂ conversions possible during complete degradation via this pathway. By employing these indexes, the CRI mechanism simplifies detailed chemistry for larger VOCs and provides computational savings by representing multiple species with a single index.



Figure 5.2 The representation of the OH-initiated, NO_x-catalyzed degradation chemistry for C_1 - C_6 alkanes in CRI v2. (Jenkin et al., 2008, Section 1, Figure 2)

c) GEOS-Chem v14.1.0 chemical mechanism

The gas-phase chemical mechanism in the GEOS-Chem v14.1.0 model (https://github.com/GEOSchem/GEOS-Chem/releases/tag/14.1.0; Bey et al., 2001) includes 290 chemical species, involving a total of 650 gas-phase chemical reactions. Additionally, GEOS-Chem also contains 157 photolysis reactions and 94 heterogeneous reactions. VOC precursors in GEOS-Chem includes ALK4, BENZ, C_2H_2 , C_2H_4 , C_2H_6 , C_3H_8 , CH4, ISOP, LIMO, MTPA, MTPO, NAP, PRPE, TOLU, XYLE. In this chapter, only the gas-phase chemistry and photolysis reactions were applied in the DSMACC box model.

Compared to the MCM mechanism, VOC species in GEOS-Chem are highly lumped to reduce complexity and computational burden. This method allows for a reasonable representation of atmospheric chemical processes on regional and global scales. Chemical species in GEOS-Chem are often lumped based on similarities in reactivity, sources, or sinks. For example, in GEOS-Chem, alkanes include specific species such as methane, ethane, and propane, while alkanes with carbon numbers greater than or equal to 4 are collectively lumped as ALK4. Similarly, alkenes with carbon numbers greater than or equal to 3 are lumped as PRPE. This lumping approach is particularly useful for simulating complex chemical reactions in global atmospheric models but result in inaccurate representation of chemical reactions.

The gas-phase chemistry of aromatics in GEOS-Chem v14.1.0 were taken from RACM (Goliff et al., 2013) and includes 3 precursors: benzene, toluene, and xylenes. Notably, xylene species are not differentiated into individual isomers such as o-xylene, m-xylene, and p-xylene. Instead, the chemical reactions involving xylene are represented using mean parameters of these three xylenes. This approach may introduce discrepancies in the overall reactivity of xylene species in the atmosphere.

5.2.3 Design of DSMACC box model experiments

The DSMACC box model (see Chapter 3) was used to conduct sensitivity simulations, with the goal of exploring the impacts of chemical complexity on simulated aromatic chemistry and ozone formation. This study focuses on specific reactions involving benzene, toluene, o-xylene, m-/p-

xylene, and RO_2 species associated with the oxidation of those aromatic precursors. Table 5.1 summarizes sensitivity simulations, and the chemical mechanisms used. In all cases, the gas-phase chemistry for non-aromatic species is identical and taken from GEOS-Chem v14.1.0. For aromatic chemistry, three different mechanisms of varying degrees of complexity are used. MCM v3.3.1 is used to represent the most complex chemical mechanism, providing a comprehensive description of the oxidation processes of aromatic compounds. CRI is a moderately degenerated representation of aromatic chemistry based on MCM. GEOS-Chem v14.1.0 employs a lumping approach and represent the most simplified mechanism. Based on the findings of analyses, this study further experimented with modifying the yields of MGLY from xylene, toluene, AROMP₅ (Generic C₅ product from aromatic oxidation) in the GEOS-Chem mechanism to compensate for its lack of complexity. Specifically, the yields of MGLY from xylene, toluene, AROMP₅ were increased by factors of 1.5 and 2.0, respectively, and sensitivity simulations were conducted to evaluate their effects on RO_x concentrations and ozone production rates.

The simulation configurations for all cases were identical except for the aromatic chemical mechanisms. All model simulations were constrained with measured ambient temperature and concentrations of observable precursors and products, including NO₂, CO, SO₂, O₃, o-xylene, m-/p-xylenes, benzene, toluene, C₂H₆, C₂H₄, C₂H₂, C₃H₈, ALK₄ (\geq C₄ alkanes), PRPE (\geq C₃ alkenes), isoprene, acetaldehyde, and acetone. The concentrations of lumped VOCs are the sum of concentrations of individual species comprising that lumped VOC category (Table 5.2). The simulation period from 15th to 20th September 2022. In DSMACC simulations, the concentrations of species at each hour were obtained by running forwards under constraints until a steady state has been reached.

To assess the sensitivity of radical chemistry and ozone formation under different levels of NO_x , further sensitivity simulations were conducted by constraining the NO_x levels between 10% to 90% of the observed levels. The mean observed NO_2 concentrations in AOSS is 13.5 ppb. The mean VOC/NO_x concentrations in these sensitivity simulations range from 3.2 ppb to 29.6 ppb, representing different conditions.

Cases	Aromatics mechanism	Non-aromatics mechanism		
GC_NA	no aromatics mechanism			
GC	GEOS-Chem v14.1.0			
	GEOS-Chem v14.1.0, yield of			
GC_MGx1.5	MGLY from xylene, toluene, AROMP5 multiplied by 1.5	GEOS Chem y14.1.0		
	GEOS-Chem v14.1.0, yield of			
GC_MGx2	MGLY from xylene, toluene, AROMP ₅ multiplied by 2.0			
CRI	CRI v2.2			
МСМ	MCM v3.3.1			

Table 5.1 Description	of chemical	mechanisms	used in	model cases.	
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GEOS-Chem Category	Species measured			
	Isobutane			
	n-Butane			
	Cyclopentane			
	Isopentane			
	n-Pentane			
	2,2-Dimethylbutane			
	2,3-Dimethylbutane			
	2-Methylpentane			
	3-Methylpentane			
	n-Hexane			
	2,4-Dimethylpentane			
	Methylcyclopentane			
	2-Methylhexane			
ALK4 (204 aikaiies)	Cyclohexane			
	3-Methylhexane			
	2,2,4-trimethylpentane			
	n-Heptane			
	Methylcyclohexane			
	2,3,4-trimethylpentane			
	2-Methylheptane			
	3-Methylheptane			
	n-Octane			
	n-Nonane			
	Decane			
	Undecane			
	Dodecane			
	Propylene			
PRPE (≥C3 alkenes)	trans-2-Butene			
	n-Butene			

Table 5.2 Lumped VOC species considered in the box model simulations and their categorization in the GEOS-Chem mechanism.

ALD2 (>C ₂ aldehvdes)	Acetaldehvde
	Isoprene
	cis-2-Pentene
	trans-2-Pentene
	1-Pentene
	Butadiene
	Isobutylene
	cis-2-Butene

Table 5.3 Constrained species and mean concentrations used for the box model simulation period.

Species	NO_2	СО	SO_2	O ₃	o-Xylene	m-Xylene	p-Xylene	Benzene	Toluene
Concentrations (ppb)	13.5	439	2.17	65.6	0.21	0.25	0.28	0.27	2.61
Species	C ₂ H ₆	C ₂ H ₄	C_2H_2	C ₃ H ₈	ALK₄ (≥C₄ alkanes)	PRPE (≥C₃ alkenes)	Acetaldehyde	Acetone	Isoprene
Concentrations (ppb)	2.07	0.89	1.27	3.04	9.02	0.46	1.75	5.31	0.20

5.2.4 Calculation of the simulated ozone net production rate

The simulated net ozone production rate is the simulated difference between the total ozone production rate and the total ozone loss rate. The total ozone production rate refers to the sum of all reaction rates that produce ozone. In the troposphere, NO₂ dissociates under solar ultraviolet light to yield NO and atomic oxygen. Atomic oxygen rapidly reacts with molecular oxygen to generate ozone. Ozone also reacts with NO to form NO₂ and oxygen (Chapter 2). A photostationary state among NO, NO₂, and O₃, therefore results in a null cycle and no net ozone formation. However, The RO₂ and HO₂ in the atmosphere compete with O₃ to consume NO to generate NO₂, result in O₃ production. Therefore, the instantaneous production of ozone in the troposphere can be represented by the kinetic rate equations of RO₂+NO and HO₂+NO as:

$$P(O_3) = \sum k_{RO_{2,i}+NO}[RO_{2,i}][NO] + k_{HO_2+NO}[HO_2][NO]$$
(5.4)

where $[RO_{2,i}]$ and $[HO_2]$ are proxy radical concentrations of RO₂ and HO₂. The footnote *i* represents different RO₂ species. The constants *k* are rate coefficients of the corresponding reactions.

The ozone loss rate refers to the sum of all reaction rates that consume ozone. OH, HO₂, and alkenes will react with ozone. Photolysis of ozone by UV radiation in the <320 nm range produces $O(^{1}D)$, which react with H₂O to generate two OH radicals, leading to net ozone loss. At the same time, a competing reaction relaxes $O(^{1}D)$ to $O(^{3}P)$, whose further reaction with O₂ reforms ozone and result in no net ozone loss. The loss rate of ozone in atmosphere can be calculated by Eq. (5.5):

$$L(O_3) = k_{OH+O_3}[OH][O_3] + k_{HO_2+O_3}[HO_2][O_3] + k_{alkenes+O_3}[alkenes][O_3]$$

$$+k_{0^{1}D+H_{2}0}[0^{1}D][H_{2}0] +$$
(5.5)

The instantaneous net production of ozone is calculated by the difference between ozone production and loss, as shown by Eq. (5.6).

$$P_{net}(O_3) = P(O_3) - L(O_3)$$
(5.6)

In this study, we evaluated the ozone formation capacity of different mechanisms by comparing these indicators.

5.3 Results

5.3.1 Condensed aromatic chemistry underestimates RO_x radical abundance

The inclusion of aromatic photochemistry significantly amplifies the concentrations of RO_x radicals (Figure 5.3a-c). Relative to the GC_NA case, which excludes aromatics photochemistry, the inclusion of aromatic reactions increases daytime concentrations of RO₂, HO₂, and OH by 8.0 $\pm 1.0 \times 10^7$ molecules cm⁻³, $1.2 \pm 0.1 \times 10^8$ molecules cm⁻³, and $1.3 \pm 0.3 \times 10^6$ molecules cm⁻³, respectively. This corresponds to enhancements of 57% $\pm 10\%$, 44% $\pm 7\%$, and 10% $\pm 3\%$, respectively, with the uncertainties indicating standard deviations derived from three simulation cases.

Aromatic chemistry plays a substantial role in shaping the diurnal profiles of RO_x radicals (Figure 5.3d-f). When the production of radicals from non-aromatic sources is discounted, aromatic chemistry contributes to $35\% \pm 4\%$ of RO₂, $30\% \pm 3\%$ of HO₂, and $9\% \pm 2\%$ of OH in the full chemical mechanism simulations. The contribution of aromatic chemistry to total RO₂ and HO₂ peaks in the afternoon, coinciding with the maximum solar radiation intensity. However, the OH enhancements resulting from aromatic chemistry diminish in the early afternoon, likely due to the accumulation of OVOCs produced earlier in the day, which serve as a significant OH sink.

The comparison between simplified aromatics mechanisms and MCM aromatics chemistry reveals significant discrepancies in radical simulations (Figure 5.3g-i). Specifically, the CRI and GEOS-Chem mechanisms underestimate total RO₂ by 23% and 28%, respectively, compared to the MCM mechanism, with the largest discrepancies occurring in the afternoon. Similarly, HO₂ is underestimated by 16% and 21%, primarily during midday, compared to the MCM results. For OH, CRI and GEOS-Chem simulations are 43% and 24% lower than MCM results, respectively, with the largest deviations observed in the morning. The GEOS-Chem case also demonstrates a slight overestimation of OH relative to the MCM case in the afternoon. These findings highlight the importance of accurately representing aromatic chemistry in atmospheric models, as simplified mechanisms may lead to significant biases in radical simulations.



Figure 5.3 Simulated concentrations of (a) RO₂, (b) HO₂, (c) OH radicals during daytime (08:00-19:00) by different mechanisms. Enhanced (d) RO₂, (e) HO₂, (f) OH radicals by aromatic chemistry during daytime (08:00-19:00), compared to GC_NA case. Differences in simulated concentrations of (g) RO₂, (h) HO₂, (i) OH radicals during daytime (08:00-19:00) by each aromatic mechanism compared to the MCM aromatics mechanism. The simulation results are depicted by the blue line (MCM), purple line (CRI), orange line (GEOS-Chem), and grey line (GC_NA). The values below "To GC_NA" indicate the percentage increase of concentrations compared to the GC_NA case. The values below "Contri." represent the percentage contribution of aromatic chemistry to the total radical concentrations. The values below "To MCM" indicate the percentage underestimation compared to the MCM case. These concentrations represent the mean daytime simulations during the simulation period in units of molecules cm⁻³.

Figure 5.4 illustrates the simulated contributions of individual RO₂ species to the total RO₂ enhancement resulting from aromatic photochemistry. CH₃O₂ and CH₃CO₃ are the predominant contributors across all three aromatic schemes, consistent with previous findings (Qu et al., 2021). On average, CH₃CO₃ and CH₃O₂ together account for 49% of the total RO₂, with CH₃CO₃ contributing 11% and CH₃O₂ contributing 38%. The top five other aromatics-related RO₂ species (designated as a whole as AROMRO₂) combined contribute 20% to 30% to the overall RO₂ enhancement.



Figure 5.4 Compositions of the RO₂ enhancements simulated with the three different aromatic photochemical mechanisms (left: MCM case; centre: CRI case; right: GC case), relative to the simulation without aromatic chemistry (GC_NA case). For all cases, the left bars represent the relative contributions of CH_3O_2 (dark blue) and CH_3CO_3 (grey blue) radicals, while the coloured segments in the right bars illustrate the top five other RO2 species with largest relative contributions to total RO₂ enhancements. Note that GC_AROMRO₂ is a lumped species representing all other generic peroxy radical from aromatic oxidation in GEOS-Chem.
Table 5.4 provides details on the top five AROMRO₂ species in the MCM. These species are explicitly formed through the oxidation of benzene, toluene, and xylenes by OH and subsequent reactions. The most significant contributor is TLBIPERO₂ (6%, C₇H₉O₅, from toluene + OH), followed by MECOACETO₂ (C₄H₅O₅), MALANHYO₂ (C₄H₃O₆), C₆H₅O₂ (from C₆H₅O and C₆H₅CO₃), and TLFUO₂ (from C₅H₆O₂), each contributing approximately 2% to the RO₂ enhancement. Contributions from other AROMRO2 species cumulatively account for an additional 17%.

CRI exhibits a more simplified classification of AROMRO₂ species compared to MCM, representing fewer species overall. Table 5.5 lists the top five AROMRO₂ contributors in CRI, with the largest being RA₁₆O₂ (9%) and RN10O₂ (5%). RA₁₆O₂ is primarily produced in the initial reaction between toluene and OH, serving as an intermediate that can generate up to 16 molecules of O₃ if completely oxidized. Similarly, RN₁₀O₂ is a C₃ intermediate capable of forming up to 10 molecules of O₃ upon complete degradation. In addition to these top five contributors, the remaining AROMRO₂ species account for an additional 3% of the RO₂ enhancement. Overall, CRI shows good consistency with MCM regarding carbon number, sources, and proportions of the top five AROMRO₂ contributors (i.e., the distribution among C₄, C₆, and C₇ RO₂ radicals). However, it lacks representation for C₅ AROMRO₂ and overestimates the contribution from C₃ AROMRO₂.

The chemical mechanism in GEOS-Chem represents the photochemistry of aromatics with the highest degree of lumping. The RO₂ species from aromatic oxidation are represented by only 5 species: BRO₂ (first generation RO₂ from benzene), TRO₂ (first generation RO₂ from toluene), XRO₂ (first generation RO₂ from xylenes), BZCO₃ (benzoylperoxy radical RO₂, from benzaldehyde and tolualdehyde), BENZO₂ (C₆H₅O₂, from benzoylperoxy radical, benzaldehyde and tolualdehyde, C₆H₅O radical), GC_AROMRO₂ (lumped species representing all other generic peroxy radicals from aromatic oxidation that do not contain carbon). Among these, BRO₂, TRO₂, and XRO₂ are used for tracking aromatic oxidation in secondary organic aerosol formation and do not actually participate in subsequent photochemistry and ozone formation. The species participating in subsequent ozone formation reactions are BZCO₃, BENZO₂, and GC_AROMRO₂, contributing 0.2%, 1%, and 18% to the total RO₂ enhancements, respectively.

RO_2	Contribution	formula	Structure	Primary precursors
TLBIPERO ₂	6%	C7H9O5	HO	Toluene
MECOACETO ₂	2%	C4H5O5	Å, Å, °,.	ACCOMECO ₃ (C ₅ H ₅ O ₆)
MALANHYO ₂	2%	C ₄ H ₃ O ₆	но с о	MALANHY (C4H2O3)
C ₆ H ₅ O ₂	2%	C ₆ H ₅ O ₂		C ₆ H ₅ O C ₆ H ₅ CO ₃
TLFUO ₂	2%	C ₅ H ₇ O ₅		TLFUONE (C ₅ H ₆ O ₂)

Table 5.5 Top 5 increased AROMRO2 in the CRI simulation

RO ₂	Contribution	# of C	Precursors
RA16O2	9%	C ₇	Toluene
RN ₁₀ O ₂	5%	C ₃	UDCARB ₁₁
R N ₁₀ O ₂	/1%	C	UDCARB ₁₄
K (1302	70	C4	CARB ₁₃
RA ₁₉ AO ₂	3%	C ₆	Xylene
RN16O2	2%	C ₆	CARB ₁₆

5.3.2 Condensed aromatic chemistry underestimates ozone production rates

Figure 5.5 shows the enhancement of reaction rates of RO₂+NO, HO₂+NO, ozone loss and net ozone production simulated with aromatic photochemical mechanisms of different complexity, compared to the GC_NA case. Averaged over the three mechanisms, the simulated reaction rates of RO₂+NO increased by 46% \pm 8% during the daytime, relative to the simulation without aromatic photochemistry. The simulated enhancement of RO₂+NO reaction rate in the MCM was the largest, averaging 9 ppb h⁻¹ in a daytime and peaking at 15 ppb h⁻¹ in the afternoon. Similarly, the simulated enhancements of HO₂+NO reaction rates were 33 \pm 4% averaged over the three mechanisms. At the same time, the increased OH and HO₂ concentrations also accelerated ozone loss via the reactions O₃+OH and HO₂+O₃. Overall, the inclusion of aromatic photochemistry increases the reaction rates of net ozone production rates by 35% \pm 5% on average and peaking at 33 ppb h⁻¹ in the MCM case.

The photochemical complexity of aromatic oxidation mechanism also impacts the reactions rates of net ozone production. Figure 5.5a reveals that both the CRI and GEOS-Chem mechanisms inadequately represent the reaction rates of total RO₂ + NO compared with MCM, showing a shortfall of -32% (CRI) and -27% (GEOS-Chem), respectively. The biases in the simulated HO₂ + NO reaction rates relative to that simulated by the MCM are -20% (CRI) and -18% (GEOS-Chem) (Figure 5.5b). The simulated rates of ozone loss are also undervalued in CRI (30%) and GEOS-Chem (15%) (Figure 5.5c). Overall, the underestimation of simulated net ozone production reaction rates by the CRI and GEOS-Chem mechanisms were 26% and 22%, respectively, and peaking at -10 ppb h⁻¹ (CRI) and -8 ppb h⁻¹ (GEOS-Chem) around midday (Figure 5.5d). Although the presentation of aromatics oxidation of CRI is more complicated than GEOS-Chem, their simulated net ozone production rates in our box model experiments are similar. These findings underscore the limitations of the condensed chemistry in accurately capturing ozone formation processes.



Figure 5.5 Increase of simulated reaction rates of (a) total RO_2+NO , (b) HO_2+NO , (c) ozone loss, (d) ozone net production during daytime (08:00-19:00), relative to GC_NA case simulation. The reaction rates depicted by the blue line (MCM), purple line (CRI), and orange line (GEOS-Chem), illustrate the differences compared to a mechanism that excludes aromatic chemistry. These reaction rates represent the mean daytime simulations during the simulation period.

5.3.3 Key differences in simulated products and pathways using different mechanisms

Given the significant impacts of chemical mechanism complexity on simulated radicals and ozone formation, the pathways contributing to these impacts are further analysed. Figure 5.6 illustrates the differences in concentrations of CH₃O₂, CH₃CO₃, and GC_AROMRO₂ simulated by the CRI and GEOS-Chem mechanisms, relative to those simulated by the MCM. Compared to the MCM, the CRI and GEOS-Chem mechanisms underestimated the daytime average CH₃O₂ concentrations by 35% and 39%, respectively. These underpredictions are more substantial during the midday and early afternoon hours, when photochemical activities are strongest, reaching up to 54% (CRI) and -52% (GEOS-Chem) at peak times. The difference in simulated CH₃O₂ concentrations between the CRI and the GEOS-Chem are also largest in the afternoon. For CH₃CO₃, the daytime average concentrations simulated by the CRI and the GEOS-Chem mechanisms were similar, but both are lower than that simulated by the MCM by 38% $\pm 2\%$.

For the sum of concentrations of other RO₂ species associated with aromatic photochemistry, the concentrations simulated by CRI aligned closely with those from MCM, differing by less than 1% throughout the day. This consistency can be attributed to CRI's lumping approach. While CRI groups intermediate with the same number of reactive bonds, it effectively retains the process by which large hydrocarbon molecules progressively break carbon bonds into smaller ones, thereby characterizing the carbon conservation during aromatic hydrocarbon oxidation. The contributions, carbon numbers, and sources of the top five increased AROMRO₂ species presented in Tables 5.4 and Table 5.5 support this point. CRI demonstrates characterization for C₇, C₆, and C₄ AROMRO₂ species. Although its representation of C₅ AROMRO₂ is limited, this shortcoming is compensated for by an overestimation of C₃ AROMRO₂ contributions. Therefore, CRI generally reproduces the overall abundance of RO₂ species as represented in MCM.

In comparison, the GEOS-Chem mechanism underestimates the daytime average concentration of AROMRO₂ by 17% relative to the MCM, showing a minor overestimation in the morning but substantial underestimation throughout the rest of the day. The MCM explicitly represented the photochemistry of benzene, toluene, and xylenes with approximately 170 individual RO₂ species and numerous intermediate non-radical products with varying carbon counts and reactivities. In contrast, GEOS-Chem employs AROMP₄ and AROMP₅ to represent generic first-generation C₄ and C₅ products from the OH-oxidation of aromatics, lumping the resulting RO₂ species into only three categories: BZCO₃, BENZO₂, and GC_AROMRO₂. Notably, GC_AROMRO₂ primarily serves to recycle HO_x and NO₂ back into the system, leading to a lack of strict carbon conservation. Consequently, GEOS-Chem does not exhibit stepwise degradation during aromatic oxidation. The generation of aromatic intermediates in GEOS-Chem is independent, with their yields reliant on parameters from chamber experiments. This simplification reduces the complexity of aromatic chemistry pathway and results in insufficient representation of reaction coefficients, product yields, and subsequent reactions.



Figure 5.6 The underestimation of simulated concentrations of (a) CH₃O₂, (b) CH₃CO₃, and (c) AROMRO₂ during daytime hours (08:00-19:00), relative to MCM case simulation. The differences are illustrated by the blue line (MCM), purple line (CRI), and orange line (GEOS-Chem).

Further analysis of the sources and sinks in aromatic chemistry simulations indicates that the underestimations of CH₃O₂ and CH₃CO₃ in the GEOS-Chem mechanism are directly linked to inaccuracies in the simulated concentrations of methylglyoxal (MGLY). Table 5.6 compares the simulated daytime photochemical source and sink of key products and RO₂ species in the MCM, CRI, GC. CH₃O₂ and CH₃CO₃ are the most abundant simulated RO₂ species in all cases, as well as the two largest contributors to the RO₂ enhancement as a result of aromatic photochemistry (Figure 5.4). In all simulations, approximately 58% of CH₃CO₃ is produced from MGLY's oxidation by OH or photolysis of MGLY. Subsequently, 66% of the CH₃CO₃ reacts with NO and HO₂ to generate CH₃O₂, which constitute 85% of the CH₃O₂ source. This finding indicates that MGLY is the dominant precursor for both CH₃O₂ and CH₃CO₃. Figure 5.7a compares the simulated concentrations of MGLY in the CRI and GEOS-Chem mechanisms, relative to that simulated by the MCM. As a result of differences in representation of aromatic chemistry, the CRI and GEOS-Chem mechanisms underestimated daytime MGLY abundances by 60% and 51%, respectively.

Species	Source	Contribut	ion Sink C	Contribution
GU CO	(common) MGLY + OH> CH ₃ CO ₃ + CO	46%	(common) $CH_3CO_3 + NO - CO_2 + CH_3O_2 + NO$	O ₂ 66%
CH ₃ CO ₃	(common) MGLY> CH ₃ CO ₃ + CO + HO ₂	12%	(common) CH ₃ CO ₃ + NO ₂ > PAN	32%
CH ₃ O ₂	(common) CH ₃ CO ₃ + NO> CO ₂ + CH ₃ O ₂ + NO	O ₂ 85%		
	(MCM) C ₅ CO1 ₄ CO ₂ > MALANHY + CH ₃ O ₂	6%	$(\text{common}) \text{ CH}_3\text{O}_2 + \text{NO}> \text{NO}_2 + \text{HO}_2 + \text{CH}_2\text{O}$	65%
	(CRI) UDCARB ₁₁ + OH> ANHY + CH ₃ O ₂	13%		
	$(GC) CH_4 + OH> CH_3O_2 + H_2O$	3%	(common) $CH_3O_2 + NO_2> MPN$	32%
HO ₂	(common) $CH_3O_2 + NO \rightarrow NO_2 + HO_2 + CH_2O_2$	23%		
	$(common) OH + CH_2O> CO + HO_2 + H_2O$	11%	(common) NO + HO ₂ > OH + NO ₂	85%
	(CRI) $C_2H_5O_2 + NO \rightarrow ALD_2 + NO_2 + HO_2$	11%		
	(GC) OTHRO ₂ + NO> $ALD_2 + NO_2 + HO_2$	10%		100/
	(GC) AROMRO ₂ + NO> NO ₂ + HO ₂	15%	$(\text{common}) O + HO_2 \longrightarrow OH + O_2$	10%
011	(common) NO + HO ₂ > OH + NO ₂	81%	$(\text{common}) \text{ OH} + \text{CH}_2\text{O} \dashrightarrow \text{CO} + \text{HO}_2 + \text{H}_2\text{O}$	12%
OH	(common) $O + HO_2 \rightarrow OH + O_2$	10%	(common) TOLUENE+OH>AROMRO ₂	10%
	(common) $CH_3O_2 + NO \rightarrow NO_2 + HO_2 + CH_2O_2$	76%	(common) $OH + CH_2O \rightarrow CO + HO_2 + H_2O$	65%
CH ₂ O		220	(common) $O + CH_2O \rightarrow CO + OH + HO_2$	24%
	$(CRI) HOCH_2CH_2O_2 + NO> CH_2O$	23%	(common) $CH_2O \rightarrow H + CO + HO_2$	4%

Table 5.6 Primary sources and	sinks of s	pecies in a	aromatics chemistry	^v simulation
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* The table lists the primary sources and sinks that accounting for a large proportion from aromatics chemistry rather than the whole mechanism. A source or sink marked with 'common' indicates that it is included in the MCM, CRI, and GEOS-Chem, and its contribution represents the average contribution of these three mechanism simulations. If a mechanism name is marked before the source or sink, it indicates that the source or sink only exists in that mechanism.



Figure 5.7 Differences of simulated concentrations of (a) MGLY, (b) CH₂O, (c) PAN, during daytime (08:00-19:00) are presented in units of molecules cm^{-3.} The differences of simulated concentrations depicted by the blue line (MCM), purple line (CRI), and orange line (GEOS-Chem), illustrate the differences compared to concentrations simulated using MCM.

Table 5.7 presents the sources of MGLY that contribute over 1% and sinks of MGLY in MCM box model simulations. In the MCM, MGLY is produced from over 70 reactions downstream of aromatic oxidation, with 22 sources contributing more than 1% each. Within the MCM mechanism, 38% MGLY originates from C_4 (23%) and C_5 (15%) compounds that are common produced by various aromatics; 27% MGLY comes from toluene and its oxidation products (C_5 and C_7 compounds), while 24% is derived from the oxidation products of xylene ($C_4 - C_8$ compounds). The chemical sinks of MGLY are oxidation by OH (79%) and photolysis (21%), which are the same across simulations with different aromatic chemical mechanisms.

Table 5.8 presents the sources and contributions of MGLY in CRI mechanisms. In the CRI, the sources of MGLY contributing over 1% are limited to five reactions. Among these, 55% of the reactants are first-generation oxidation products of toluene, while 41% originate from first-generation oxidation products of xylene. Additionally, Table 5.6 shows that the sink of MGLY simulated by CRI align with those from the MCM mechanism. This indicates that the CRI mechanism emphasizes MGLY sources from first-generation products of toluene and xylene, thus the potential underestimation of MGLY in the CRI may be due to insufficient contributions from C_4 and C_5 sources.

In the GEOS-Chem mechanism, 23% of MGLY is produced directly as a first-generation product from the OH-oxidation of xylenes, and 18% is produced from the OH-oxidation of toluene. Additionally, 50% of MGLY is generated through the oxidation of C₅ compounds (AROMP₅), some of which formed during the ring cleavage of aromatics. This suggests that the primary sources and contributions of MGLY in GEOS-Chem are more aligned with those in the MCM mechanism compared to CRI. However, GEOS-Chem still lacks contributions from C₄ compounds. Furthermore, the overall sink of MGLY in GEOS-Chem is consistent with those simulated by MCM. Consequently, it can be inferred that the underestimation of MGLY in GEOS-Chem may be due to missing C₄ sources and inaccuracy yields.

Furthermore, the primary sources of MGLY in MCM and CRI indicate that its production is NO_x sensitive (Tables 5.7 and 5.8). The reaction between $CO_2H_3CO_3$ and NO accounts for 21% of MGLY production from C₄ intermediates, explicitly highlighting the NO_x sensitivity of MGLY production through the chemical reaction pathways in MCM. In CRI, this NO_x sensitivity is amplified, as the reaction of $RA_{16}O_2$ with NO contributes 54% to the MGLY source from first-generation RO₂ derived from toluene. However, in GEOS-Chem's characterization of MGLY sources, there is no indication of NO_x sensitivity (Table 5.9).

Precursors	Source of MGLY in MCM	Contributions
C_4	$CO_2H_3CO_3 + NO \rightarrow MGLY + NO_2 + HO_2$	21%
(23%)	$CO_2H_3CO_3 \rightarrow MGLY + HO_2$	2%
	$C_5COO_2NO_2 + OH \rightarrow MGLY + 2 CO + NO_2$	6%
G	$C_5CO_{14}CO_2 \Rightarrow MGLY + CO + HO_2$	4%
C_5 (1.40/.)	$C_3MCODBCO_2 \rightarrow MGLY + CO + HO_2$	2%
(14%)	$C_4M_2ALOHO \rightarrow MGLY + GLYOX + HO_2$	2%
	$C_3MCODBPAN + OH → MGLY + 2 CO + NO_2$	1%
	TLBIPERO → BZFUONE + MGLY + HO ₂	9%
toluene	TLBIPERO → MALDIAL + MGLY + HO ₂	9%
(27%)	C₅DICARBO → MGLY + GLYOX + HO ₂	6%
	TLEMUCO → EPXC ₄ DIAL + MGLY + HO ₂	2%
xylene	C_3 MDIALO → MGLY + CO + HO ₂	5%
	DMKOHO \rightarrow 2 MGLY + HO ₂	4%
	MXYBIPERO \rightarrow MGLY + C ₄ MDIAL + HO ₂	2%
	MXYBIPERO \rightarrow MGLY + C ₅ DICARB + HO ₂	2%
	MXYBIPERO \rightarrow PXYFUONE + MGLY + HO ₂	2%
	OXYBIPERO \rightarrow MGLY + C ₅ DICARB + HO ₂	2%
(24%)	OXYBIPERO → TLFUONE + MGLY + HO ₂	2%
	PXYBIPERO → PXYFUONE + MGLY + HO ₂	2%
	PXYBIPERO → MGLY + C ₄ MDIAL + HO ₂	2%
	$MXYMUCO \rightarrow EPXMC_4DIAL + MGLY + HO_2$	2%
	TLCOBIPEOH + OH → MALDIALCO ₃ + MGLY	1%
-	Sink of MGLY in MCM	Contributions
	$MGLY + OH \rightarrow CH_3CO_3 + CO$	77%
-	MGLY \rightarrow CH ₃ CO ₃ + CO + HO ₂	23%

Table 3.7 Sources and sinks of WOLT in WOW aromatics chemistry	Table 5.7 Sources and	nd sinks of MGLY	in MCM aromatic	s chemistry
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Precursors	Source of MGLY (CARB ₆) in CRI	Contributions
toluene	$RA_{16}O_2 + NO \rightarrow UDCARB_8 + CARB_6 + NO_2 + HO_2$	54%
(55%)	$RA_{16}O_2 \rightarrow UDCARB_8 + CARB_6 + HO_2$	1%
vylono	$RA_{19}BO_2 + NO \rightarrow UDCARB_{11} + CARB_6 + NO_2 + HO_2$	23%
(41%)	$RA_{19}NO_3 + OH \rightarrow UDCARB1_1 + CARB_6 + NO_2$	16%
	$RA_{19}OOH + OH \rightarrow UDCARB_{11} + CARB_6 + OH$	2%
-	Sink of MGLY (CARB6) in CRI	Contributions
-	$CARB_6 + OH \rightarrow CH_3CO_3 + CO$	76%
-	$CARB_6 \rightarrow CH_3CO_3 + CO + HO_2$	24%

Table 5.8 Source and sink of MGLY	(CARB ₆) in CRI aromatics chemistry
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Table 5.9 Source and sink of MGLY in GEOS-Chem aromatics chemistry

Precusors	Source of MGLY in GEOS-Chem	Contributions
	$TOLU + OH \rightarrow TRO_2 + 0.06 \text{ BALD} + 0.19 \text{ CSL} + 0.06 \text{ BALD} + 0.19 \text{ CSL} + 0.06 \text{ BALD} + 0.019 \text{ CSL} + 0.019 C$	
Toluene	$0.3 \ AROMP_5 + 0.68 \ AROMP_4 + 0.81 \ AROMRO_2 + \\$	190/
(18%) 0.12 GLYX + 0.12 MGLY + 0.04 MVK + 0.27 CO		18%
	$+ 0.19 \text{ HO}_2$	
	$XYLE + OH \rightarrow XRO_2 + 0.06 \text{ BALD} + 0.15 \text{ CSL} + 0.06 \text{ BALD} + 0.15 \text{ CSL} + 0.06 \text{ BALD} + 0.015 \text{ CSL} + 0.015 C$	
Xylene	0.56 AROMP ₅ + 0.28 AROMP ₄ + 0.85 AROMRO ₂	220/
(23%)	+ 0.1 GLYX + 0.2 MGLY + 0.04 MVK + 0.3 CO +	23%
	0.15 HO ₂ + 0.45 RCOOH	
	$AROMP_5 + OH \rightarrow 0.1 HCOOH + 0.15 ACTA + 0.6$	
C	MGLY + 0.33 RCO ₃ + 0.25 CO + 0.25 OH + 0.33	25%
C_5	$HO_2 + 0.52 RCOOH$	
(50%)	$AROMP_5 + O_3 \rightarrow 0.2 HCOOH + 0.3 ACTA + 0.95$	2504
	$GLYC + 0.6 \; MGLY + 0.5 \; CO + 0.1 \; OH + 0.1 \; HO_2$	25%
-	Sink of MGLY in GEOS-Chem	Contributions
	$MGLY + OH \rightarrow CH_3CO_3 + CO$	81%
	$MGLY \rightarrow CH_3CO_3 + CO + HO_2$	19%

Table 5.6 shows that discrepancies in simulated CH_3O_2 from aromatic chemistry also affect the predictions of HO₂ and OH. Budget calculations for HO₂ indicate that 23% of HO₂ generated from the oxidation of aromatics results from the reaction of CH_3O_2 with NO. Therefore, the underestimation of CH_3O_2 can directly influence the simulated concentrations of HO₂ and its subsequent chemistry, including its reaction with NO to form ozone. In addition to HO₂, CH_2O is also underestimated in both the CRI and GEOS-Chem mechanisms by 30% ± 12% (Figure 5.7b), as 65% of the sink for CH_3O_2 leads to the formation of CH_2O in aromatic chemistry. Furthermore, 81% of OH sources in aromatic chemistry arise from the reaction between HO₂ and NO, meaning that the underestimation of OH is directly linked to low concentrations of HO₂. Additionally, a significant sink for CH_3CO_3 is its conversion to PAN; thus, the underestimation of CH_3CO_3 in both CRI and GEOS-Chem mechanisms of HO₂. Additionally, a 5.7c).

Figure 5.8 summarizes the analyses above and illustrates the reaction chains responsible for the simulated differences in RO₂ species and ozone formation between the simplified chemical mechanisms of CRI and GEOS-Chem, relative to those simulated by MCM. Under high NO_x conditions, the entire reaction chain begins with the oxidation of aromatics by OH, leading to a series of RO₂ species, among which CH₃CO₃ and CH₃O₂ are the most abundant. In MCM simulations, the predominant AROMRO₂ (6%) is the first-generation RO₂ from toluene (C₇), while C₇, C₅, and C₄ AROMRO₂ contribute 2%, 4%, and 2%, respectively. However, CRI underestimates the contribution of C₅ AROMRO₂ while overestimating that of C₃ AROMRO₂. This compensation effect allows CRI's total simulated concentration of AROMRO₂ to align well with MCM simulations. Regarding CH₃CO₃ and CH₃O₂, CRI significantly underestimates their concentrations due to an underestimation of their primary source, MGLY. This likely stems from CRI only accounting for MGLY contributions from toluene and xylene while neglecting significant contributions from C₄ and C₅ intermediates.

In contrast, GEOS-Chem's mechanism does not adequately reflect the gradual breaking of carbon bonds in large aromatic molecules or ring-opening processes, leading to violations of carbon conservation and an overall underestimation of AROMRO₂. Similar to CRI, GEOS-Chem also severely underestimates CH₃CO₃ and CH₃O₂ due to its own underestimation of MGLY. However, GEOS-Chem performs better than CRI in characterizing MGLY sources since it includes contributions from toluene, xylene, and C_5 ; yet it still lacks representation for sources from C_4 intermediates, which can lead to simulation biases for MGLY. Consequently, this results in a relatively independent generation of MGLY whose yield is heavily dependent on chamber experimental parameters.

Ultimately, both CRI and GEOS-Chem's underestimation of MGLY leads to further underestimations of CH₃O₂ and CH₃CO₃ concentrations, subsequently impacting downstream reaction chains. Specifically, the reaction between CH₃O₂ and NO produces CH₂O and HO₂, both are significant contributors to ozone formation. Additionally, the reaction between HO₂ and NO accounts for 81% of the OH source in aromatic chemistry; another 10% is related to HO₂ (via O + HO₂). Moreover, the reaction between CH₃CO₃ and NO₂ generates PAN, and this process is also affected by the underestimation of CH₃CO₃. As a result, the intensity of RO_x-driven chemistry simulated by simplified aromatics mechanism is underestimated, leading to an underpredicted rate of ozone formation.



Figure 5.8 Reactions chain described the species transformation in aromatics chemistry. The arrows represent the conversion of reactants to products. The percentages indicated in red illustrate the contribution of each source reactions to its corresponding product.

5.3.4 Optimizing the MGLY yield to improve simulation of RO_x radicals

The analyses above showed that, in our simulated urban atmospheric environment: (1) MGLY is the largest source of CH_3CO_3 and CH_3O_2 , the two most abundant RO_2 species; (2) MGLY is mostly produced from the oxidation of aromatics, both during the initial ring-cleavage stage and downstream of intermediate products. Therefore, it is hypothesized that tuning the yield of MGLY from aromatic oxidation may be a way to compensate for the insufficient simulation of RO_x chemistry in the CRI and the GEOS-Chem mechanism.

Figure 5.9 compares the simulated differences in concentrations of key OVOCs and RO₂ species in the CRI and GEOS-Chem mechanisms, relative to those simulated in the MCM, as well as results from two sensitivity simulations in which the MGLY yields from aromatics in the GEOS-Chem mechanism are scaled by 1.5 and 2.0 (GC_MGx1.5 and GC_MGx2 in Table 5.1), respectively. The effective yield of MGLY from toluene and xylenes in the original GEOS-Chem mechanism was 0.12 and 0.2 for our urban atmospheric environment setting. Scaling the MGLY yields from aromatics (TOLU+OH, XYLE+OH, AROMP5, AROMP5+OH, and AROMP5+O3 reactions) by factors of 1.5 and 2, respectively, led to near-linear reductions of the simulated biases in MGLY concentrations, relative to the MCM. The simulated biases of total RO₂ concentrations decreased from -28% in the GC case to -15% in the GC_MGx1.5 case and -1% in the GC_MGx2 case, respectively (Figure 5.8d). The simulated concentrations of CH₃O₂ and CH₃CO₃ in the GC_MGx1.5 and GC_MGx2 cases are both closer to those simulated by the MCM; although in the case of GC_MGx2, the CH₃O₂ and CH₃CO₃ concentrations are higher than that of the MCM. Scaling the MGLY yield in GEOS-Chem's aromatic chemistry by a factor of 1.5 also significantly improved the concentrations of HO₂, OH, and PAN (Figures 5.9e-g). Compared to the MCM, the original GC underestimate HO₂ by 16%, OH by 24%, and PAN by up to 38%; these biases are reduced to 2%, 1%, and 18%, respectively, in GC_MGx1.5. However, scaling the MGLY yield by a factor of 2 leads to overestimation of HO₂, OH, and PAN by 12%, 22%, and 4%, respectively.



Figure 5.9 Differences of simulated concentrations of (a) MGLY, (b) CH₃CO₃, (c) CH₃O₂, (d) total RO₂, (e) HO₂, (f) OH, (g) PAN, (h) CH₂O during daytime (08:00-19:00) are presented in units of molecules cm^{-3.} The differences of simulated concentrations depicted by the blue line (MCM), orange line (GEOS-Chem), green line (optimized GEOS-Chem with 1.5-fold MGLY yield), and red line (optimized GEOS-Chem with 2.0 fold MGLY yield), illustrate the differences compared to concentrations simulated using MCM.

Further analysis focuses on how the improved simulations of RO₂ and other radicals obtained by scaling MGLY yield in the GEOS-Chem model propagate to affect subsequent ozone formation rates. Figure 5.10 compares the rates of ozone production reactions from RO₂ + NO or HO₂ + NO, the rates of ozone loss, and the net ozone production rates simulated by all sensitivity simulations in Table 5.1. As discussed in Sections 5.3.1 and 5.3.2, the simulated ozone production from individual RO₂ + NO and HO₂ + NO reactions, as well as the simulated ozone loss rate and net production rate, are all substantially larger in the MCM case than in the CRI and GC cases. In comparison to MCM, the original GEOS-Chem mechanism underestimates the daytime average reaction rates of CH₃O₂ + NO (-44%, Figure 5.10a), CH₃CO₃ + NO (-41%, Figure 5.10b), total RO₂ + NO (-27%, Figure 5.10c), and HO₂ + NO (-18%, Figure 5.10d). Scaling the MGLY yield

from aromatics by 1.5 (GC_MGx1.5 case) compensates for the inadequate photochemical production of RO₂ and HO₂ in GEOS-Chem, thereby rectifying the ozone production rates from RO₂ + NO and HO₂ + NO reactions, and substantially reducing the simulated biases of daytime average rates for CH₃O₂ + NO (-27%), CH₃CO₃ + NO (-21%), total RO₂ + NO (-15%), and HO₂ + NO (-6%). Scaling the MGLY yield from aromatics by 2.0 (GC_MGx2 case) also improves overall simulated RO₂ + NO and HO₂ + NO reaction rates but slightly overshoots CH₃CO₃ + NO and HO₂ + NO rates compared to MCM. At the same time, the GC_MGx2 case simulates a slightly faster ozone loss compared to MCM (Figure 5.10e). The overall effect is that the net ozone production rate (daytime average of 18 ppb h⁻¹, Figure 5.10f) in the GC_MGx2 case is most consistent with that simulated by MCM (daytime average ppb h⁻¹). These findings confirm that optimizing MGLY yield leads to significant enhancements in simulating aromatic RO_x chemistry and ozone formation.



Figure 5.10 Simulated reaction rates of (a) total $CH_3O_2 + NO$, (b) $CH_3CO_3 + NO$, (c) total $RO_2 + NO$, (d) $HO_2 + NO$, (e) ozone loss, and (f) ozone net production during daytime (08:00-19:00 local time) are presented in units of ppb h⁻¹. The differences in simulated concentrations depicted by the blue line (MCM), orange line (GEOS-Chem), green line (GC_MGx1.5), and red line (GC_MGx2) illustrate the differences in simulated reaction rates compared to those simulated using MCM.

5.3.5 Optimizing the MGLY yield across a range of NO_x conditions

As discussed in Section 5.3.3, the MCM and CRI explicitly represent the impacts of NO_x on photochemical pathways by allowing RO_2+NO_x reactions to compete with RO_2+RO_2 and RO_2+HO_2 reactions. In contrast, the GEOS-Chem mechanisms make different assumptions about the abundance of NO_x in the ambient air that it simulates. This section further explores how these different assumptions manifest in how the MGLY-yield adjustment affect simulated aromatic photochemistry. To this end, a series of sensitivity experiments are conducted with NO_x concentrations ranging from 10% to 100% of the observed value, corresponding to VOC/ NO_x mixing ratios of 29.6 to 3.2.

Figure 5.11 compares the afternoon (13:00-17:00 local time) mean simulated ozone production and loss rates from the different chemical mechanisms as a function of NO₂ concentrations. These comparisons were represented as ratios compared to the reaction rates simulated by the MCM. Both the CRI and the GEOS-Chem mechanisms show large biases compared to the MCM at NO_x levels <40% of the observed values, reflecting the fact that these two simplified chemical mechanisms mainly assumed that their reacting environments to be high in NO_x. At between 40% to 70% NO_x, the CRI and GEOS-Chem simulated RO₂+NO and HO₂+NO reaction rates were closest to those simulated by the MCM. At the same time, at below 70% NO_x, both the CRI and GEOS-Chem mechanisms both overestimated ozone loss. The combined effect was that both the CRI and GEOS-Chem underestimated net ozone production by more than 3% across all NO_x levels.

Scaling the MGLY yields in GEOS-Chem by factors of 1.5 and 2.0 improved the simulated total RO₂+NO reaction rate, the HO₂+NO reaction rate, and the O₃ loss rate to within 5% differences relative to the MCM for NO_x levels >30% of the observed value. This in turn reduced the simulated biases in ozone net production rates to $<\pm1\%$ relative to the MCM. Overall, experiments where the MGLY yield was scaled up by a factor of 1.5 show best consistency with MCM simulations across conditions ranging from 20% to 100% NO_x, with an average ratio of 0.99.

Under conditions with NO_x concentrations below 70%, the CRI simulation shows greater sensitivity in net ozone production compared to the GEOS-Chem simulation. Table 5.8 shows the MGLY generation in the CRI mechanism is sensitive to NO_x levels, while GEOS-Chem does not capture this sensitivity (Table 5.9). Previous studies have shown that MGLY yields from toluene and xylene decrease with increasing NO₂ concentrations, with mean representative yields estimated at 0.22 for toluene and 0.34 for xylene in the ambient atmosphere (Nishino et al., 2010). Similarly, NO_x dependency of MGLY yields were observed in chamber experiments, and the yields of MGLY were 0.18 for toluene oxidation and 0.37-0.45 for m-xylene oxidation across NO_x levels spanning 5 ppb to 60 ppb (He et al. 2023a). The yields of MGLY in the GC_MGx2 simulation (0.24 for toluene, 0.4 for xylene) align better with these experimental results, compared to that applied in standard GEOS-Chem mechanism (0.12 for toluene, 0.2 for xylene). However, the optimized mechanisms still lack the representation of NO_x sensitivity of MGLY production.



Figure 5.11 Ratios of simulated rates of (a) total RO_2+NO , (b) HO_2+NO , (c) O_3 loss, and (d) net O_3 production using different chemical mechanisms relative to those simulated by the MCM under a range of NO_x concentrations. The NO_x concentrations are shown as percentages relative to the observed NO_2 concentrations; the corresponding VOC/NO_x ratios are shown on the top x-axis.

5.4 Discussion

This chapter shows that MGLY serves as a key intermeiate organic VOC (OVOC) species in the photochemical oxidation of aromatics by acting as the dominant precursor of RO₂ in aromatic photochemistry, which affects subsequent ozone production. In this way, MGLY acts as a valve regulating the flow of carbon in the photochemical cascade of aromatics. Because of this role played by MGLY, its yield from aromatics can also serve as a tuneable parameter for reprsenting aromatic RO₂ chemistry in simplified chemical mechanisms. Using the yield of MGLY from aromatics as tuneable parameter offers several advantages. Firstly, compared to other species, MGLY is easier to tune in models. This is because most current chemical loss of MGLY to form RO₂ is well-defined. Other higher intermediates (\geq C₃) are typically lumped to varying degrees in different mechanisms. Secondly, according to the MCM, MGLY is an upstream product of RO₂ from aromatics and a direct precursor of CH₃O₂ and CH₃CO₃, making it impact directly on downstream RO_x abundance. Last but not least, concentrations of MGLY in chambers and in the ambient air can be measured with several techniques, such as the PTR-MS, and these observational constraints can be used to tune the yield.

There are some limitations in the initial work presented in this chapter. First, box models simplify the complex atmospheric system. However, this approach may overlook critical factors such as transport and meteorological effects, which significantly influence species concentrations. Furthermore, the simulations in this chapter only consider gas-phase mechanisms and cannot accurately describe heterogeneous reactions (e.g., RO₂ and HO₂ reactions on particle surfaces). This simplification may lead to overestimated RO₂ lifetimes and ozone contributions, particularly under NO_x-saturated conditions where aerosol interactions rapidly consume RO₂ (Pye et al., 2019). Second, the species concentration data in this study are limited to a single site under specific NO_x conditions which may affect the applicability of proposed MGLY tuning approach. Additionally, while the MCM serves as a reference for evaluating chemical reactions, it does not incorporate recent experimental findings on reaction pathways. For example, it underestimates aromatic oxidation branching ratios (Zaytsev et al., 2019; Bloss et al., 2005; Jenkin et al., 2003) and fails to describe autoxidation pathways of highly oxygenated organic molecules from multi-substituted aromatics such as trimethylbenzenes (Molteni et al., 2018).

5.5 Summary

The chapter has investigated the impact of aromatic chemistry schemes with different complexities on simulated RO_x and net ozone production rates in atmospheric photochemical processes. The results indicate that the presence of aromatic compounds significantly elevates simulated RO_x concentrations, with a mean increase of $57 \pm 9\%$ in total RO₂, $44 \pm 5\%$ in HO₂, and $10 \pm 2\%$ in OH during daytime. The uncertainties indicating standard deviations derived from three simulation cases. However, the GEOS-Chem and CRI mechanisms show underestimations of $23\% \pm 5\%$ and $29\% \pm 10\%$ in total RO_x compared with the explicit MCM scheme. The reaction rates of RO₂ + NO and HO₂ + NO are notably higher when aromatics are included, leading to an average increase in net ozone production rates by $35\% \pm 5\%$, reaching up to 33 ppb h⁻¹ in the afternoon. However, GEOS-Chem and CRI mechanisms show underestimations of approximately 22% and 24% in net ozone production, highlighting the limitations of simplified mechanisms' ability to accurately capture ozone formation processes.

Further investigation into discrepancies among simulations using different chemical mechanisms revealed that both CRI and GEOS-Chem underestimate the key species CH_3O_2 by about $37\% \pm 2\%$ and CH_3CO_3 by approximately $38\% \pm 2\%$. This underestimation is attributed to oversimplifications in their chemical representations, particularly regarding their precursor MGLY. The analysis has identified that the yield of MGLY significantly influences downstream reactions leading to RO_x formation. Specifically, MGLY contributes to an increase in CH_3CO_3 and CH_3O_2 concentrations by enhancing their production, and thereby increase the production of CH_2O , HO_2 and OH.

The simulation of MGLY in GEOS-Chem and CRI reveals notable differences compared to the MCM mechanism. In MCM, MGLY is produced from over 70 reactions, with significant contributions from C_4 (23%) and C_5 (15%) compounds, as well as various oxidation products of toluene and xylene. There are 22 sources that contribute more than 1% each. In contrast, CRI identifies only five key reactions for MGLY production, primarily from first-generation oxidation products of toluene (55%) and xylene (41%), which may lead to an underestimation of MGLY due to insufficient representation of C₄ and C₅ sources. GEOS-Chem shows a different profile, with MGLY mainly produced from the OH-oxidation of xylenes (23%) and toluene (18%), but it lacks contributions from C₄ compounds altogether. Additionally, while both MCM and CRI demonstrate

 NO_x sensitivity in MGLY production, particularly through specific reactions involving $CO_2H_3CO_3$ and NO in MCM and $RA_{16}O_2$ with NO in CRI; GEOS-Chem does not exhibit this sensitivity in its characterization of MGLY sources. Despite these differences, the sinks for MGLY are consistent across all three mechanisms, primarily through oxidation by OH and photolysis.

To address these shortcomings in simplified mechanisms, this work proposes optimizing the yield of MGLY within GEOS-Chem. Adjustments lead to improved simulations of RO_x, reducing underestimations from $23\%\pm5\%$ to $6\%\pm7\%$ (GC_MGx1.5) and to $-11\%\pm10\%$ (GC_MGx2). The optimized mechanisms of increasing MGLY yield by scaling of 1.5 align more closely with MCM predictions across 20% to 100% NO_x concentration levels, achieving agreement ratios of up to 0.99. Under conditions with NO_x below 70%, CRI demonstrates greater NOx sensitivity in net ozone production than GEOS-Chem, primarily due to MGLY production reactions in CRI being significantly influenced by NO_x, while those in GEOS-Chem are not. These findings underscore the importance of accurately representing aromatic chemistry in atmospheric models to enhance our understanding of photochemical processes and improve predictions related to air quality and ozone formation.

Given the limitations in Section 5.4, future work should validate the MGLY optimization approach in regional models that incorporate transport, meteorological effects, and heterogeneous chemistry across urban and rural NO_x environment. Such validation is essential to evaluate the method's robustness under realistic atmospheric conditions.

6. Improving RO_x chemistry representation in a regional model

6.1 Introduction

As societal demand for more precise and accurate air quality simulations continues to grow, models are being developed to operate at finer resolutions to capture complex atmospheric dynamics at smaller scales. However, despite advancements in resolution, many models still rely on simplified chemical mechanisms. These highly lumped representations exhibit significant limitations at finer resolutions, as some lumped species are influenced not only by local reactions but also by transport processes, leading to a disconnect between the goals of precise air quality simulation and the chemical representation within the models.

The results presented in Chapter 5 highlight the critical importance of methylglyoxal (MGLY) in aromatic chemistry within box model simulations and its potential role as a regulator of RO_x in condensed chemical mechanisms. These RO_x radicals are essential for ozone production, particularly near urban areas where NO_x is often saturated while ozone production is limited by VOCs. However, several limitations exist within box model simulations. They fail to account for key processes such as transportation, deposition, and heterogeneous reactions occurring on surfaces or within aerosol particles. This lack of consideration can lead to oversimplified representations of atmospheric chemistry, especially in complex environments. Furthermore, box model simulations are typically observation-based and represent the VOC/NO_x environment at a single site, which may not capture spatial variability present in larger urban or regional contexts. The complexity of China's ozone regime arises from diverse pollution sources, varying meteorological conditions, and intricate interactions among different chemical species. Thus, further validation through regional model simulations is essential to ensure that findings from box models can be reliably applied to broader contexts.

Recent studies indicate that surface ozone pollution has been increasing in areas experiencing rapid industrialization and urbanization (Silver et al., 2018; Wang et al., 2022). The Beijing-Tianjin-Hebei (BTH), Yangtze River Delta (YRD), and Pearl River Delta (PRD) urban agglomerations are key economic regions in China, representing the country's major industrial, commercial, and technological hubs while also facing significant environmental pollution challenges. According to Report on the State of the Ecology and Environment in China 2023 (MEE, 2024), the 90th percentile concentration of MDA8 ozone are 181 µg m⁻³ in BTH, 158 µg m⁻³ in YRD, and 160 µg

 m^{-3} in cities like Shenzhen within PRD. These concentrations significantly exceed those found in other regions of China. One of the drivers behind this severe ozone pollution is the high AVOC emissions from these three urban agglomerations. Li et al. (2019) revealed aromatic species emissions accounted for a substantial 33% of total anthropogenic VOC emissions in China, 2017, making them the largest chemical group emitted. Furthermore, among the top 30 contributing species to ozone formation, the OFP proportions of aromatics have increased dramatically from 20% in 1990 to an 50% by 2017. Moreover, the ozone formation mechanism in these urban agglomerations has been predominantly VOC-limited since 2013 (Zhang et al., 2024). Although there was an expansion of transition mechanisms aimed at controlling regional emissions, the overall situation remains characterized by NO_x-saturated conditions (Lu et al., 2019). These findings highlight the complex interplay between VOCs and NO_x emissions in exacerbating air quality issues within these urban agglomerations.

Based on the findings from Chapter 5, this chapter aims to address the underrepresentation of RO_x chemistry in atmospheric models with condensed mechanisms like GEOS-Chem. The optimized MGLY yield derived from box model experiments will be incorporated into the WRF-GC regional model to evaluate its effectiveness in simulating ozone production in urban environments across China characterized by high VOC and NO_x emissions. By optimizing MGLY yields, this chapter aim to improve simulation accuracy for RO_2 species and rates of ozone formation while maintaining computational efficiency. This enhanced representation of atmospheric chemistry is crucial for informing more effective strategies for predicting and managing ozone pollution.

6.2 Method

6.2.1 Regional model simulations

To assess whether the optimized MGLY yield enhances the simulation of RO_x chemistry in regional models, three different cases with varying aromatic chemical mechanisms were designed (Table 6.1). The chemical mechanisms align with those implemented in DSMACC (Section 5.2.3).

The MCM case served as the control run, employing the aromatic chemistry from MCM v3.3.1, which includes five aromatic precursors, approximately 200 RO₂ species, and around 2000 reactions. In the GC case, the aromatic mechanism was based on the standard GEOS-Chem v4.1.0, incorporating three aromatic precursors, 44 RO₂ species, and 44 reaction equations. The differences between the aromatic mechanisms in GEOS-Chem v4.1.0 and MCM v3.3.1 are detailed in Section 5.2.2. In the GC_MG×1.5 case, the MGLY yield was increased by a factor of 1.5 compared to the GC case. For all cases, the non-aromatic mechanism was derived from the standard GEOS-Chem v14.1.0.

Cases		GC	GC_MG×1.5	MCM
	Version Description	GEOS-Chem v14.1.0	GEOS-Chem v14.1.0, yields of MGLY from xylene, toluene, AROMP ₅ multiplied by 1.5	MCM v3.3.1
Aromatics mechanism	Precursors	benzene, xylene, toluene	benzene, xylene, toluene	benzene, o-xylene, m-xylene, p-xylene, toluene
	Number of RO ₂	8	8	~200
	Number of reactions	44	44	~2000
Non- aromatics mechanism	Version Description		GEOS-Chem v14.1.0	

 Table 6.1 Chemical mechanisms description of cases.

The regional air quality model WRF-GC (v3.0) (Lin et al., 2020; Feng et al., 2021) is used to compare the differences of mechanisms in terms of simulating surface ozone over China. WRF-GC is an online coupling of the Weather Research and Forecasting (WRF v4.4, <u>https://www.mmm.ucar.edu/models/wrf</u>) (Skamarock et al., 2021) meteorological model and the GEOS-Chem atmospheric chemistry model (v14.1.0, <u>http://www.geos-chem.org/</u>) (Bey et al., 2001) (see Chapter 3 for further details). Monthly mean anthropogenic pollutant emissions within Mainland China were taken from the Multi-resolution Emission Inventory for China (MEIC, <u>http://www.meicmodel.org</u>) for the year 2019 at 0.25° resolution (Li et al., 2014; Zheng et al., 2018). Anthropogenic emissions for the rest of the simulated domain were from a mosaic Asian anthropogenic emission inventory for year 2010 (Li et al., 2017). Biomass burning emissions were from the Global Fire Emissions Dataset version 4.1 with small fires (GFED4s) (van der Werf et al., 2017). Meteorology-dependent BVOC emissions (MEGAN v2.0) (Guenther et al., 2012) and soil- and lightning-NO_x emissions (Hudman et al., 2012; Murray et al., 2012) were calculated online in WRF-GC.

The simulations are conducted between September 20th to 30th 2019 with the first 4 days of the simulation considered as model spin-up and discounted from analyses. A single domain of 27-km horizontal resolution and 50 vertical layers is used (Figure 6.1). Meteorological initial and boundary conditions were from the National Centers for Environmental Prediction Final Operational Global Analysis (NCEP FNL, 1° resolution). The simulated winds, temperature, and water vapour mixing ratios above the planetary boundary layer were nudged with the NCEP FNL data every 6 hours. Table 3.1 summarizes the physical configurations used in our simulations. Chemical boundary conditions were from a standard full-chemistry simulation using GEOS-Chem v14.1.0 (Bey et al., 2001).



Figure 6.1 Domain of the WRF-GC simulations used in this study with a horizontal resolution of 27 km.

6.2.2 Ozone observations

The performance of the WRF-GC model in simulating surface ozone concentrations during the study period is evaluated using surface ozone measurements obtained from the National Environmental Monitoring Centre (<u>http://www.cnemc.cn</u>, last accessed: March 12th, 2024). This evaluation involves a comparison between hourly model simulations and measurements collected from a total of 376 monitoring sites across three key regions: 77 sites in the BTH, 205 sites in the YRD, and 94 sites in the PRD. To ensure data integrity and reliability, a consistent data quality control protocol, as outlined by Wang et al. (2021a) and Lu et al. (2018), is applied to all hourly measurements. This protocol includes steps such as removing outliers.

6.3 Results

6.3.1 Model evaluation

In the MCM case simulations, the temporal variation of MDA8 ozone concentrations aligns well with observational data (Figure 6.2). In the BTH region, the simulated MDA8 ozone concentration averages 86±16 ppb, slightly higher than the observed value of 79±11 ppb, with a correlation of r = 0.92, indicating a strong agreement. In the YRD region, the simulated and observed MDA8 ozone concentrations are 80±4 ppb and 75±7 ppb, respectively, with a lower correlation of r =0.56. In the PRD region, the simulated and observed MDA8 ozone are 101±6 ppb and 89±4 ppb, with a correlation of r = 0.84. Observations indicate that during the simulation period, there were 5 days, 2 days and 7 days of ozone pollution events (MDA8 ozone concentrations exceeding the national air quality standard of 80 ppb) in BTH, YRD, and PRD regions respectively. The MCM case simulation successfully predicted 4 out of 5 exceedance events in BTH and 1 out of 2 exceedance events in YRD. MCM case simulation accurately predicted all exceedance events in PRD. Simulated MDA8 ozone suggests that the model substantially underestimates ozone pollution events in BTH and YRD regions. The simulated hourly nighttime ozone in the three regions is overestimated compared to the observations, indicating that the simulation bias may also stem from factors such as background ozone concentration and boundary layer dynamics. (He et al., 2023b; Li et al., 2018).

Figure 6.3 shows the spatial distribution of simulated ozone concentrations from the MCM case, compared against surface observations from September 24th to 30th, 2019. The simulation successfully reproduces the spatial distribution of MDA8 ozone concentrations across three key regions. The spatial correlation coefficients indicate a strong agreement, with values of r=0.66 for BTH, r=0.62 for YRD, and r=0.74 for PRD. Overall, the MCM case simulation exhibits good consistency with observed surface ozone abundances in areas which this study is focused, supporting further analysis of ozone dynamics and processes.



Figure 6.2 Time series of the observed (black line) and simulated (red line, MCM case) hourly ozone concentrations over the BTH, YRD and PRD areas between September 24th and September 30th, 2019. The observed and simulated MDA8 ozone are shown with grey and blue lines, respectively. The mean ozone concentrations (\pm standard deviations) and the temporal correlation (r) between observed and simulated hourly ozone concentrations during the simulated period are shown in the figure.



Figure 6.3 Spatial distribution of mean observed (symbols) and simulated (filled contours) MDA8 ozone concentrations simulated by WRF-GC over China during between September 24th and September 30th, 2019. The averaged observed and simulated MDA8 ozone concentrations (units: ppb) and the correlation (r) are shown inset.

6.3.2 Surface spatial evaluation of impacts of different model representations of RO_x chemistry over China

Figure 6.4 presents the surface spatial distribution of average concentration differences for MGLY, total RO₂, HO₂, and OH during the afternoon (13:00–17:00) across the simulation period. The differences are shown for the GC case relative to the MCM case (left column) and for the GC_MG×1.5 case relative to the MCM case (right column). The results indicate that the standard GEOS-Chem model underpredicts concentrations of MGLY compared with MCM, particularly in urban areas with significant aromatic emissions. Aromatic emissions are most enhanced in urban agglomerations such as BTH, YRD, and PRD regions in China, with monthly emission rates of 2.6×10^{-11} kg m⁻² s⁻¹, 3.2×10^{-11} kg m⁻² s⁻¹, and 3.4×10^{-11} kg m⁻² s⁻¹ respectively (Figure 6.5). This underestimation of MGLY aligns with the pattern of aromatic emissions, with the largest discrepancy observed in BTH, reaching up to 0.57 ppb (Figure 6.4a). The total RO₂ concentrations are underestimated in GC by as much as 3×10^{-3} ppb across China (Figure 6.4c). The spatial

distribution of underestimation for HO₂ exhibits similar patterns (Figure 6.4e) with MGLY. RO₂ and HO₂ come from the oxidation of aromatics and the intermediates in this process; the simplification of aromatic mechanisms results in insufficient simulation of RO₂ and HO₂, which is consistent with results in Chapter 5. The reaction of HO₂ and NO is one of the main sources of OH under high NO_x conditions (Chapter 5.3.3), thus the spatial distribution of underestimation for OH is similar to that of HO₂ in China's urban agglomerations (Figure 6.4g). In summary, RO_x is poorly represented in the condensed mechanism due to simplifications in the model, especially in regions with abundant aromatic emissions.

Figure 6.4 also indicates that the underestimation of simulated RO_x improves by increasing the MGLY yield produced in the aromatic chemistry. A factor 1.5 times increase in MGLY yield within GEOS-Chem reduced the maximum underestimation of MGLY concentrations from 0.57 to 0.42 ppb compared with MCM (Figure 6.4b). The predicted differences are also diminished for total RO₂, HO₂ and OH concentrations across BTH, YRD and PRD regions (Figures 6.4d, 6.4f and 6.4h). Although RO_x concentrations are more severely underestimated in some regions of GC_MG×1.5, increasing the MGLY yield to improve the representation of RO_x chemistry proves effective for major urban regions in China.

Figure 6.6 illustrates the mean afternoon (13:00–17:00) concentration differences of CH₃CO₃ and CH₃O₂ between the GC and MCM cases, as well as between the GC_MG×1.5 and MCM cases, across the simulation period. CH₃CO₃ and CH₃O₂, key RO₂ species derived from MGLY, account for approximately 50% of total RO₂ (Chapter 5). The maximum underestimation was reduced from 3.4×10^{-4} ppb to 1.7×10^{-4} ppb for CH₃CO₃ and from 1.2×10^{-3} ppb to 6.2×10^{-4} ppb for CH₃O₂ (Figures 6.6a and 6.6c). Although in areas with low aromatic emissions, CH₃CO₃ and CH₃O₂ concentrations are slightly overestimated, the increased MGLY production effectively enhances in regions with high aromatic emissions (Figures 6.6b and 6.6d).

Figure 6.7 compares the mean afternoon (13:00-17:00) concentrations of NO, NO₂ and PAN across the simulation period, highlighting the differences between the GC and MCM cases (left column) and between the GC_MG×1.5 and MCM cases (right column). The low concentrations of RO₂ and HO₂ in the condensed mechanism result in slow reactions between peroxyl radicals and NO, leading to an overestimation of NO concentrations in standard GEOS-Chem compared to

simulations using MCM aromatic chemistry (Figure 6.7a). Increasing the MGLY yield significantly decreases NO concentrations (Figure 6.7b), with a similar change observed for NO₂, which also decreases in GC_MG×1.5 case. Additionally, reactions between CH₃CO₃ and NO₂ produce PAN, which transports NO_x from urban areas to downwind regions. Consequently, underestimated CH₃CO₃ in GEOS-Chem simulations lead to inadequate PAN generation (Figure 6.6a and 6.7e). The underestimation of PAN in standard GEOS-Chem is improved in GC_MG×1.5 from -0.5 ppb to -0.3 ppb. These differences highlight that when RO_x chemistry is inadequately represented, more NO_y is stored as NO_x rather than PAN in the model.

Other downstream products in the RO_x chain such as CH₂O are also underestimated in standard GEOS-Chem due to low estimates of RO_x compared to MCM. As analysed in Chapter 5.3.3, $CH_3O_2 + NO$ serves as a primary source for CH₂O within aromatic chemistry. The underestimation of CH₃O₂ led to a maximum underestimate of CH₂O by up to 0.83 ppb in China, while increasing MGLY yield improved this because a greater participation rate of CH₃CO₂ reacting with NO to form CH₂O.

Increasing the MGLY yield by a factor of 1.5 significantly improves the underestimations of ozone concentrations. Figure 6.8c shows differences in mean afternoon (13:00-17:00) ozone concentrations between standard GEOS-Chem and MCM throughout the simulation period. As the final product in the RO_x chain, ozone's underestimation aligns with the pattern of RO_x underestimation, averaging 0.6 ppb across China and reaching a maximum underestimation of up to 10.8 ppb. Simulated ozone in GC_MG×1.5 closely aligned with simulations in MCM case, reducing the maximum underestimation to 8.2 ppb. The improvement in ozone is attributed to increased abundance of RO₂ and HO₂ species that facilitate conversion of NO to NO₂, and subsequent photolysis of NO₂ to further promote ozone formation. Photolysis of CH₂O within the RO_x chain also contributes positively to ozone generation.



Figure 6.4 Spatial distribution of average concentration differences for MGLY, total RO₂, HO₂, and OH in the afternoon (13:00–17:00) during the simulation period. The left column shows differences between the GC case and the MCM case, and the right column shows differences between the GC_MG×1.5 case and the MCM case. The maximum and average differences across China are labelled within each subplot.



Figure 6.5 Monthly mean aromatics emissions flux of (a) xylene, (b) toluene, (c) benzene in September 2019 from MEIC (units: kg m⁻² s⁻¹).



Figure 6.6 Spatial distribution of average concentration differences for CH_3CO_3 and CH_3O_2 in the afternoon (13:00–17:00) during the simulation period. The left column shows differences between the GC case and the MCM case, and the right column shows differences between the GC_MG×1.5 case and the MCM case. The maximum and average differences across China are labelled within each subplot.



Figure 6.7 Spatial distribution of average concentration differences for NO, NO₂ and PAN in the afternoon (13:00–17:00) during the simulation period. The left column shows differences between the GC case and the MCM case, and the right column shows differences between the GC_MG×1.5 case and the MCM case. The maximum and average differences across China are labelled within each subplot.


Figure 6.8 Spatial distribution of average concentration differences for CH_2O and O_3 in the afternoon (13:00–17:00) during the simulation period. The left column shows differences between the GC case and the MCM case, and the right column shows differences between the GC_MG×1.5 case and the MCM case. The maximum and average differences across China are labelled within each subplot.

6.3.3 Vertical distribution of reactive species in response to MGLY yield variations in major urban agglomerations in China

The increase in MGLY yield exerts a significant influence on both surface-level and vertical RO_x chemistry. As shown in Figure 6.9a (GC-MCM), the GC case underestimates MGLY concentrations not only at the surface but also in the atmosphere above, particularly below 400 metres at midday, with an underestimation of approximately 0.1 ppb compared to the MCM case. This behaviour can be attributed to the relatively long lifetime of MGLY (several hours), which facilitates its vertical transport through boundary layer mixing. Similarly, Figure 6.10a and 6.10c reveal that CH₃CO₃ and CH₃O₂ concentrations in the GC case are also underestimated below 700 metres. However, above 700 metres, the GC case slightly overestimates these species compared to the MCM case. Total RO₂ concentrations in the GC case are systematically underestimated across all altitudes during daytime (Figure 6.9c). The GC_MG×1.5 case, which incorporates an enhanced MGLY yield, mitigates these underestimations for MGLY, CH₃CO₃, CH₃O₂, and total RO₂ (Figures 6.9b and 6.9d), highlighting the sensitivity of these species to MGLY production.

The vertical profiles of HO₂ and OH exhibit more complex patterns. At the surface, both HO₂ and OH are underestimated in the GC case, while at higher altitudes, the GC case overestimates these species compared to the MCM case, particularly in the afternoon (Figures 6.9e and 6.9g). The vertical gradient suggests the strong dependence of HO₂ and OH on photochemical processes and vertical transport. The GC_MG×1.5 case improves the underestimation of HO₂ and OH at the surface but slightly exacerbates their overestimation at higher altitudes by approximately 3% (Figures 6.11b and 6.11d). These results suggests that while enhanced MGLY yield improves surface-level chemistry, it may introduce additional complexities in the vertical distribution of reactive species.

Figure 6.12a (GC-MCM) demonstrates that NO concentrations are overestimated in the GC case compared to the MCM case, particularly below 600 metres during the morning. The enhanced MGLY yield in the GC_MG×1.5 case increases NO consumption, alleviating this overestimation. Figure 6.12c and 6.12d reveal that NO₂ is also overestimated in the GC case in the lower atmosphere, consistent with the photochemical linkage between NO and NO₂. However, in the GC_MG×1.5 case, the increased MGLY yield reduces NO₂ levels due to accelerated reactions with

peroxyacetyl radicals, which also improves the underestimation of PAN in the GC case (Figures 6.12e and 6.12f). These results suggest that increased MGLY production positively impacts NO_x chemistry, likely through its role in RO_x cycling and NO_x chemistry.

In Figure 6.13a (GC-MCM), CH₂O concentrations are significantly underestimated in the morning and midday, particularly below 700 metres, with a maximum difference of -0.12 ppb. The enhanced MGLY yield in the GC_MG×1.5 case increases CH₂O concentrations during these periods (Figure 6.13b). Similarly, O₃ concentrations in the GC case are underestimated in the afternoon, particularly below 600 metres, with a maximum difference of approximately 2 ppb (Figure 6.13c). The enhanced MGLY yield significantly increases O₃ concentrations, although an underestimation of around 1 ppb persists below 400 metres (Figure 6.13b). These improvements highlight the role of MGLY as a precursor to CH₂O and O₃ and its influence on photochemical reactions.

These results demonstrate that MGLY production plays a critical role in shaping the spatial and temporal distribution of key atmospheric species, including RO₂, HO₂, OH, NO, NO₂, PAN, CH₂O, and O₃. The GC case systematically underestimates concentrations of many species in the lower atmosphere, while the enhanced MGLY yield in the GC_MG×1.5 case mitigates these biases, particularly at the surface. However, the vertical distribution of reactive species such as HO₂ and OH becomes more complex, with overestimations at higher altitudes.



Figure 6.9 Mean diurnal vertical profiles of concentration differences for MGLY, total RO₂, HO₂, and OH during the simulation period, averaged over the BTH, YRD and PRD regions. The first column shows differences between the GC case and the MCM case, and the second column shows differences between the GC_MG×1.5 case and the MCM case.



Figure 6.10 Mean diurnal vertical profiles of concentration differences for CH_3CO_3 and CH_3O_2 during the simulation period, averaged over the BTH, YRD and PRD regions. The first column shows differences between the GC case and the MCM case, and the second column shows differences between the GC_MG×1.5 case and the MCM case.



Figure 6.11 Mean diurnal vertical profiles of concentration differences percentage for HO_2 and OH during the simulation period, averaged over the BTH, YRD and PRD regions. The first column shows differences between the GC case and the MCM case, and the second column shows differences between the GC_MG×1.5 case and the GC case.



Figure 6.12 Mean diurnal vertical profiles of concentration differences for NO, NO₂ and PAN during the simulation period, averaged over the BTH, YRD and PRD regions. The first column shows differences between the GC case and the MCM case, and the second column shows differences between the GC_MG×1.5 case and the MCM case.



Figure 6.13 Mean diurnal vertical profiles of concentration differences for CH_2O and O_3 during the simulation period, averaged over the BTH, YRD and PRD regions. The first column shows differences between the GC case and the MCM case, and the second column shows differences between the GC_MG×1.5 case and the MCM case.

6.3.4 Evaluation of improvement of surface RO_x chemistry and ozone simulation in major urban agglomerations in China

Figure 6.14 displays the mean ratios of surface species concentrations simulated by standard GEOS-Chem, GC_MG×1.5, and MCM in the BTH, YRD, and PRD regions. The standard model shows a significant shortfall in representing MGLY, with an underestimation of -34%, leading to an average underestimation of approximately 7% for CH₃CO₃ and about 5% for CH₃O₂ across these areas. The optimized mechanism significantly reduced these biases to 2% for CH₃CO₃ and 1% for CH₃O₂, indicating substantial improvements in simulating these key RO₂ species. Consequently, the overall underestimation of total RO₂ decreased from 5% to 3%. However, the

remaining underestimation of total RO₂ concentrations may be attributed to insufficient simulation of AROMRO₂ species; as analysed in Chapter 5, GEOS-Chem lacks the capability to accurately represent various AROMRO₂ generated during the degradation processes of aromatics. This limitation suggests that further enhancements are needed to fully capture the dynamics of RO₂ species in urban environments. For HO₂ and OH, a 1.5-fold increase in MGLY yield led to a slight overestimation of approximately 1%. Overall, this optimization significantly improved the characterization of RO_x chemistry.

Similar enhancements were observed for CH_2O ; while the standard models underestimated CH_2O by around 4%, the GC_MG×1.5 simulations demonstrated significant improvements, with concentration ratios of CH_2O in the BTH, YRD, and PRD regions reaching up to 0.98 when compared to MCM simulations. This improvement indicates that the optimized mechanism not only addresses the biases in RO_2 species but also enhances the representation of key carbonyl compounds like formaldehyde.

The improvements in NO_y simulations, particularly the reduction in NO₂ overestimations and the notable 15% enhancement in PAN representation, indicate a more accurate depiction of NO_x chemistry in urban environments. PAN is a stable reservoir species in the storage and transport of nitrogen oxides by sequestering NO_x during photochemical processes and releasing it in regions with lower reactivity. The GC_MG×1.5 simulations improved the conversion of NO₂ to PAN, reflecting a more accurate simulation of interactions between NO_x and organic radicals. This advancement enhances the atmospheric redistribution of nitrogen oxides and potentially improves the representation of secondary pollutant formation.

The simulation of ozone in the BTH, YRD, and PRD regions has significantly improved, with the average underestimation of afternoon O_3 reduced from 0.6 ppb to 0.3 ppb. Previously, this underestimation in the standard GEOS-Chem model reached as high as 10.8 ppb (Figure 6.4). This enhancement is primarily attributed to linked improvements of all underestimated species and radicals within the RO_x chain. This also indicates that the photochemical mechanisms governing ozone formation in these three major urban clusters are primarily VOC-limited. The increased representation of OVOCs MGLY, has enhanced the representation of RO_x dynamics, facilitating the conversion of NO to NO₂ through RO₂ and HO₂ radicals. This optimization ultimately promotes ozone formation by improving the efficiency of photochemical reactions in these regions.



Figure 6.14 Comparison of species concentrations simulated by standard GEOS-Chem (GC case), optimized GEOS-Chem (GC_MG×1.5 case, with MGLY yield increased to 1.5-fold), and the MCM in three major urban agglomerations in BTH, YRD, and PRD. Green dots represent the ratio of species concentrations simulated by the GC case to that simulated by the MCM case. Red dots represent the ratio of species concentrations simulated by the GC_MG×1.5 case to that simulated by the MCM case. The error bars indicate the standard deviation of the ratio differences across the regions, and the ratios are calculated as the mean value of each grid within these areas.

6.4 Discussion and summary

This section examines the impacts of different RO_x chemistry representations in China, highlighting significant underestimations in the standard GEOS-Chem model compared to the MCM. Key species like MGLY, RO₂, HO₂, and OH are notably underpredicted in urban areas with high aromatic emissions. The maximum discrepancy for MGLY reached 0.57 ppb. Increasing the MGLY yield by 1.5 times significantly improves predictions, reducing this underestimation to 0.42 ppb and enhancing concentrations of RO₂, HO₂, and OH. This adjustment also helps correct overestimations of NO levels and improves PAN generation. Ozone concentrations show similar patterns of underestimation, averaging a 0.6 ppb deficit across China and reaching up to 10.8 ppb at maximum; this is reduced to 8.2 ppb with higher MGLY yields. Overall, these findings emphasize that better representation of ROx chemistry is crucial for accurate predictions of key atmospheric species and pollutants in urban areas.

The vertical analysis further emphasizes the importance of accurately representing MGLY and RO_x chemistry in both surface and atmospheric layers. In the GC case, MGLY concentrations are underestimated not only at the surface but also in the lower atmosphere. This vertical transport of MGLY highlights the need to consider boundary layer dynamics in model simulations. Similarly, CH_3CO_3 and CH_3O_2 exhibit underestimations below 700 metres but slight overestimations at higher altitudes, reflecting the complex interplay between photochemical processes and vertical mixing. The GC_MG×1.5 case mitigates these biases, improving the vertical distribution of RO_x , NO_x , CH_2O and O_3 .

In major urban agglomerations in China (BTH, YRD, PRD), significant improvements of surface RO_x chemistry and ozone simulation were observed. The standard GEOS-Chem model underestimated MGLY by 34%, leading to 7% and 5% underestimations for CH₃CO₃ and CH₃O₂. Increasing MGLY yield by 1.5 times reduced these biases to 2% and 1%, respectively, with total RO₂ underestimation decreasing from 5% to 3%. HO₂ and OH showed a slight overestimation of about 1%, but overall RO_x characterization improved. CH₂O's underestimation dropped from around 4% to 2% compared to MCM simulations. NO was overestimated by 4%, but NO₂ and PAN simulations improved, with PAN showing a notable enhancement of 15%. Afternoon O₃ underestimation decreased from 2% to 1%. These improvements indicate that photochemical mechanisms governing ozone formation are primarily VOC-limited, enhancing the efficiency of ozone formation through better RO_x dynamics.

Furthermore, the transition from VOC-limited to NO_x -limited regimes in China poses significant challenges for ozone forecasting. In urban areas like BTH, YRD, and PRD, ozone formation is VOC-limited, but there is an expansion of the transition regime, characterized by conditions where ozone formation shifts from VOC-limited to NO_x -limited (Zhang et al., 2024; Lu et al., 2019). The current approach of enhancing MGLY yield, effective in VOC-limited areas, shows limited improvement in suburban regions with higher NO_x concentrations (Section 6.3.2). As transition regime expand, this method's applicability may diminish, highlighting the need for more robust mechanisms to address the transition regime.

In conclusion, this study highlights that in China's major urban agglomerations, MGLY serves as a tuneable knob to modulate aromatic RO_x photochemistry, significantly influencing the formation of key atmospheric species. These findings underscore the necessity of continuously refining atmospheric models to enhance air quality predictions and inform effective environmental policies and management strategies.

7. Conclusions

7.1 Overview of main results

This doctoral thesis was aimed at addressing some of the challenges associated with understanding the impact of VOCs on ozone formation, specifically on regional scales in China. The ultimate objective was to enhance our modelling capabilities of VOC contributions to ozone formation, thereby offering insights for air quality management strategies. The specific objectives of this thesis were as follows:

Objective 1: Develop a parameterization to represent the temperature-dependent AVOC emissions for use in atmospheric chemistry models.

Existing models typically employ static AVOC emission factors that do not account for temperature fluctuations, leading to potential inaccuracies in atmospheric chemistry models. In Chapter 4, a parameterization that captures the temperature dependence of AVOC emissions from solvent use, NSI and transportation sources was developed. By integrating this parameterization into a regional atmospheric chemistry model, the impacts of temperature-sensitive VOCs on surface ozone pollution were quantified across a region of China.

The non-linear temperature sensitivity of AVOC and BVOC emissions revealed patterns across sources. AVOC emissions from transportation exhibited weak increases below the monthly mean temperature (298 K) but surged sharply above this threshold, reaching 2.8 times baseline levels at 10 K above the mean. In contrast, AVOC emissions from solvent use rose to 1.7 and 1.3 times their baseline values, respectively, at the same temperature increase. Over a typical warm-season temperature range of 291 K to 304 K, the overall temperature sensitivity of total AVOC emissions in the BTH area was 6.25% K⁻¹, with transportation contributing the most (9.7% K⁻¹), followed by solvent use (5.8% K⁻¹) and NSI activities (3.4% K⁻¹). BVOC emissions exhibited even higher temperature sensitivity (11.2% K⁻¹). Both AVOC and BVOC emissions demonstrated strong correlations with daily temperature.

The response of surface ozone to temperature-dependent AVOC and BVOC emissions exhibited spatial patterns. Over the temperature range of 291 K to 304 K, temperature-enhanced AVOC emissions significantly increased daily ozone variability, with differences ranging from -7.6 μ g m⁻³ to 6.6 μ g m⁻³ relative to baseline simulations, averaging 1.3 μ g m⁻³ K⁻¹. Similarly, BVOC

emissions driven by temperature changes induced ozone variability from -13.5 µg m⁻³ to 10.1 µg m⁻³, averaging 2 µg m⁻³ K⁻¹. Both AVOC and BVOC emissions exacerbated ozone exceedances during warm periods but their contributions diminished during cooler periods. Spatially, AVOC-related ozone enhancements were localized over urban areas like Beijing, Tianjin, Tangshan, and Baoding, driven by reactive alkenes and aromatics with immediate ozone production. In contrast, BVOC-related ozone enhancements were displaced northwest due to the longer lifetimes of isoprene oxidation products, which were transported downwind. Over the BTH region, AVOC contributions to OFP were dominated by transportation (50%) and solvent use (40%), with short-lived aromatics and alkenes being the most reactive species. BVOCs contributed comparably to OFP in urban areas but doubled AVOC contributions in less urbanized regions like Hebei. Overall, temperature-sensitive AVOC emissions had a more localized impact on ozone, while BVOCs influenced broader regional ozone formation. Therefore, urban air quality modeling and management should place greater emphasis on considering the temperature sensitivity of AVOCs.

The inclusion of temperature-dependent AVOC emissions improved the representation of the ambient ozone-meteorology relationship in the model. Temperature-sensitive AVOC emissions contributed to ozone-temperature sensitivities (k_A) of 1.0–1.8 µg m⁻³ K⁻¹, approximately 0.7 times the sensitivity driven by BVOC emissions ($k_B = 1.7-2.4 \mu g m^{-3} K^{-1}$). This effect was most pronounced in NO_x-saturated (VOC-limited) cities, where k_A and the ratio k_A/k_B exhibited negative correlations with FNR values. On ozone exceedance days (MDA8 ozone > 160 µg m⁻³), incorporating temperature-dependent AVOC emissions increased the overall simulated ozone-temperature sensitivity from $8.3 \pm 1 \mu g m^{-3} K^{-1}$ (BASE) to $9.5 \pm 1 \mu g m^{-3} K^{-1}$ (AVOC(T)), aligning more closely with observed sensitivities ($9.8 \pm 2 \mu g m^{-3} K^{-1}$). Overall, the inclusion of temperature-dependent AVOC emissions enhanced the model's accuracy, particularly in VOC-sensitive urban areas.

The findings highlight the need to account for temperature sensitivities in emission inventories and air quality models, especially in regions prone to high ozone concentrations. For environmental policy, the findings emphasize the importance of targeted measures to reduce emissions of reactive AVOC species, particularly from transportation and solvent use, especially during warmer periods. Such measures can effectively mitigate localized ozone pollution and enhance urban air quality.

Objective 2: Compare and understand the differences in simulated ozone formation with different degrees of VOC chemical complexity.

Many models still rely on highly lumped chemical mechanisms due to computational resource limitations. However, simplified mechanisms often overlook key reactions and intermediates essential for accurate ozone simulations. Chapter 5 conducted a comparative analysis using a box model to investigate how the chemical complexity of aromatics influences RO_x chemistry and ozone formation, identifying critical intermediates that affect ozone production pathways. It further proposes a parameterization to address the shortcomings in simulating RO_x chemistry within condensed mechanisms.

The findings indicated that the presence of aromatic compounds significantly enhanced simulated RO_x concentrations, with mean increases of $57 \pm 9\%$ in total RO₂, $44 \pm 5\%$ in HO₂, and $10 \pm 2\%$ in OH during daytime. The inclusion of aromatics led to a substantial increase in net ozone production rates by an average of $35\% \pm 5\%$, reaching up to 33 ppb h⁻¹ in the afternoon. However, both the GEOS-Chem and CRI mechanisms exhibited underestimations of total RO_x by approximately $23\% \pm 5\%$ and $29\% \pm 10\%$, respectively, when compared to the explicit MCM. GEOS-Chem and CRI mechanisms underestimated net ozone production by about 22% and 24%, respectively, highlighting their limitations in accurately capturing ozone formation processes.

Further analysis revealed that both CRI and GEOS-Chem underestimated key species such as CH_3O_2 by approximately $37\% \pm 2\%$ and CH_3CO_3 by around $38\% \pm 2\%$. This underestimation was largely due to oversimplifications regarding their precursor MGLY. The study identified that MGLY yield significantly influenced downstream reactions leading to RO_x formation; specifically, it enhanced the production of CH_3CO_3 and CH_3O_2 while also increasing concentrations of CH_2O , HO_2 , and OH.

The simulations showed notable differences in MGLY production across mechanisms. In MCM, MGLY was generated from over 70 reactions with significant contributions from C₄ (23%) and C₅ (15%) compounds as well as various oxidation products of toluene and xylene. In contrast, CRI identified only five key reactions for MGLY production that primarily came from first-generation oxidation products of toluene (55%) and xylene (41%), which may have led to an underestimation due to insufficient representation of C₄ and C₅ sources. GEOS-Chem presented a different profile

where MGLY was mainly produced from the OH-oxidation of xylenes (23%) and toluene (18%), lacking contributions from C₄ compounds altogether. While both MCM and CRI demonstrated NO_x sensitivity in MGLY production through specific reactions involving $CO_2H_3CO_3$ with NO in MCM and RA₁₆O₂ with NO in CRI, GEOS-Chem did not exhibit the NO_x sensitivity.

To address these shortcomings within simplified mechanisms, this work proposed optimizing the yield of MGLY within GEOS-Chem. Adjustments led to improved simulations of RO_x concentrations, and the underestimations were reduced from $23\% \pm 5\%$ to just $6\% \pm 7\%$ when scaling MGLY yields by a factor of 1.5, achieving agreement ratios with MCM predictions to 0.99 across varying 20%-100% NO_x levels. Under conditions where NO_x levels were below 70%, CRI demonstrated greater sensitivity in net ozone production compared to GEOS-Chem due primarily to its more responsive characterization of MGLY production influenced by NO_x levels.

In summary, this chapter emphasizes MGLY's key role as an intermediate OVOC species; it acts as a tuneable knob regulating carbon flow within aromatic photochemical cascades due to its upstream production characteristics relative to higher intermediates ($\geq C_3$). This tuneable parameter offers advantages such as ease of adjustment within models since MGLY is typically represented explicitly rather than lumped with other species.

Objective 3: Enhance representation of RO_x chemistry in a regional air pollution model.

Chapter 5 highlighted the crucial role of MGLY in regulating RO_x radicals, revealing that box model simulations had limitations due to their inability to account for key processes such as transportation, heterogeneous reactions, and representing varying VOC/NO_x environments. Chapter 6 incorporated optimized MGLY yields into the WRF-GC regional model to evaluate their effectiveness in simulating ozone production in urban areas of China. It assessed the spatial impacts of different model representations of RO_x chemistry across the country and quantified enhancements in both RO_x chemistry and ozone predictions, particularly in major urban agglomerations like BTH, YRD, and PRD.

In the spatial evaluation of surface RO_x chemistry models over China, the study found that the standard GEOS-Chem aromatics mechanism significantly underestimated concentrations of

MGLY, total RO₂, HO₂, and OH, especially in urban areas like BTH, YRD, and PRD, compared to that simulated by MCM aromatics mechanism. Increasing MGLY yield by 1.5 times reduced its maximum underestimation from 0.57 ppb to 0.42 ppb and improved predictions for total RO₂, HO₂, and OH. This adjustment also led to a reduction in NO concentrations and enhanced PAN generation. Key RO₂ species such as CH₃CO₃ and CH₃O₂ saw significant improvements in their underestimations. The study noted that low RO_x estimates previously resulted in overestimated NO levels and inadequate PAN generation; however, increasing MGLY yield addressed these issues. Importantly, ozone underestimation improved from a maximum of 10.8 ppb in the standard model to 8.2 ppb with the optimized mechanism, linked to increased RO₂ and HO₂ facilitating NO conversion to NO₂ and promoting ozone formation through photolysis processes involving CH₂O within the RO_x chain.

Inaccurate MGLY representation also impacts atmospheric simulations above the surface. The standard GEOS-Chem aromatics mechanism underestimates MGLY, CH₃CO₃, CH₃O₂, and total RO₂ concentrations below 700 metres compared to the MCM aromatics mechanism. Increasing the MGLY yield mitigates these underestimations relative to MCM, particularly at the surface, but slightly exacerbates overestimations of HO₂ and OH at higher altitudes by approximately 3%. NO and NO₂ concentrations in the standard GEOS-Chem mechanism are overestimated below 600 metres relative to MCM, but the enhanced MGLY yield reduces these biases by improving NO consumption and PAN simulations. CH₂O and O₃ concentrations in the standard GEOS-Chem mechanism are also underestimated relative to MCM, with the enhanced MGLY yield increasing CH₂O and O₃ levels, though a 1 ppb O₃ underestimation relative to MCM persists below 400 metres.

In the evaluation of mean surface RO_x chemistry and ozone simulation improvements in major urban agglomerations in China, the study revealed that the standard GEOS-Chem aromatics mechanism underestimated MGLY by 34% compared to the MCM aromatics mechanism, leading to average underestimations of 7% for CH3CO3 and 5% for CH3O2 relative to MCM aromatics mechanism. Increasing MGLY yield by a factor 1.5 in GEOS-Chem reduced these biases to 2% and 1%, respectively, while the total RO2 underestimation relative to MCM decreased from 5% to 3%. Although some underestimation remained due to limitations in representing AROMRO₂ species, formaldehyde representation in GEOS-Chem improved substantially. NO was still overestimated by 4% relative to MCM, but PAN simulations in GEOS-Chem showed a notable

enhancement of 15% compared to the standard GEOS-Chem aromatics mechanism. The simulation of ozone concentrations in GEOS-Chem also improved, with afternoon O_3 underestimation relative to observations reduced from 0.6 ppb to 0.3 ppb. This improvement was linked to better representation of RO_x dynamics in GEOS-Chem, indicating that ozone formation mechanisms were primarily VOC-limited and enhanced by increased MGLY levels facilitating NO conversion to NO₂ through RO₂ and HO₂ radicals.

This study addresses the trade-off between model simplicity and accuracy in atmospheric chemistry by tuning MGLY yields within the GEOS-Chem mechanism. This adjustment enhances the efficiency of regional scale simulations while maintaining the accuracy of air quality models. By refining the representation of MGLY, the simulation of key species like CH₃CO₃, HO₂, NO, and O₃ are improved, particularly in VOC-limited urban areas such as BTH, YRD, and PRD. The findings highlight the potential of targeted adjustments to improve pollutant simulations, nitrogen cycling, and atmospheric oxidative capacity, offering a perspective for developing more robust and efficient modelling techniques to address urban ozone pollution.

The findings also emphasize that controlling primary emissions of MGLY and its key VOC precursors, such as aromatics, can effectively mitigate ozone pollution. By targeting these specific precursors, policymakers can implement focused emission control measures, especially in VOC-limited regions where ozone formation is highly sensitive to VOC levels.

7.2 Future work

Chapter 4 established a preliminary parameterization in HEMCO to represent the relationship between anthropogenic AVOC emissions and temperature, assessing the impact of temperature sensitivity on AVOC emissions. This parameterization should be further optimized into a more universal form that can be applied across various atmospheric models (Guenther et al., 2012). Such an advancement will facilitate the integration of temperature sensitivity into air quality simulations, thereby enhancing their accuracy and reliability.

While Chapter 4 provided parameterization of the temperature dependence of AVOC emissions from solvent use, transportation, and non-solvent use industries, many relationships between

specific species or source categories remain unclear (Song et al., 2019; Liang et al., 2024). For instance, Qin et al. (2025) proposed the temperature sensitivity of AVOC emissions from volatile chemical products (VCPs); however, AVOC emissions from VCPs have not yet been incorporated into most atmospheric models, and their temperature sensitivity remains highly uncertain (Coggon et al., 2021; McDonald et al., 2018). Additionally, the current approach in Chapter 4, which applies the same temperature sensitivity to all VOC species, is limited by the fact that different VOC species exhibit varying volatilities and emission characteristics. Future work should focus on measuring or extracting observational data to better characterize the relationship between AVOC emissions and temperature across diverse sources. This could involve targeted field studies or advanced remote sensing techniques to gather comprehensive datasets that inform model development. Such efforts will help refine emission parameterizations and reduce uncertainties in predicting temperature-dependent AVOC emissions.

Conducting scenario analyses under projected climate change conditions will provide a clearer understanding of how shifts in temperature patterns may alter VOC emissions and subsequent ozone production dynamics (Perkins-Kirkpatrick et al., 2020; Fu et al., 2019). Future studies should also consider multi-pollutant interactions, examining how various pollutants (e.g., PM_{2.5}) interact with VOCs under different environmental conditions to influence overall air quality (Li et al., 2019b). Integrating these findings into global climate models will help predict how AVOC emissions and their ozone-forming potential will evolve under future climate scenarios. As global temperatures rise, the temperature sensitivity of VOC emissions and their impact on ozone formation may intensify, particularly in rapidly urbanizing regions.

Chapter 5 highlighted the critical role of MGLY in regulating RO_x chemistry within aromatic photochemical cascades, demonstrating its importance as a tuneable intermediate for accurate ozone simulations. Future research should focus on integrating ground-based MGLY observations into atmospheric models to refine its production and loss processes, thereby improving ozone and SOA forecasting accuracy (Liu et al., 2020; Ling et al., 2020; Fu et al., 2008). Additionally, further investigation into the relationship between MGLY and NO_x is essential to elucidate ozone formation mechanisms and VOC oxidation pathways, particularly under varying environmental conditions. Beyond aromatics, future work should explore whether similar "knob" effects exist in other VOC chemistries, such as isoprene oxidation, to identify key intermediates that regulate these processes (Bates et al., 2019).

In summary, future research should optimize temperature-dependent AVOC emission parameterizations, integrate VCP emissions, and refine MGLY representation in models. Investigating multi-pollutant interactions and climate change impacts on VOC emissions will enhance air quality predictions. Exploring "knob" effects in isoprene oxidation and other VOC chemistries. These efforts will advance the ability to predict and mitigate the impacts of VOC emissions on air quality and climate change.

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