Source Apportionment of Ozone and Its Health Effects in North China Plain and Southeast U.S.

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SOURCE APPORTIONMENT OF OZONE AND ITS HEALTH EFFECTS IN NORTH CHINA PLAIN AND SOUTHEAST U.S.

A Dissertation

Submitted to the Graduate Faculty of the Louisiana State University and Agricultural and Mechanical College in partial fulfillment of the requirements for the degree of Doctor of Philosophy

in

The Department of Civil and Environmental Engineering

by

Kaiyu Chen
B.S., China University of Mining and Technology, Beijing, 2014
M.S., China University of Mining and Technology, Beijing, 2017
May 2020
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<th>Description</th>
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<tbody>
<tr>
<td>AERO6</td>
<td>Aerosol module version 6</td>
</tr>
<tr>
<td>AQI</td>
<td>Air Quality index</td>
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<tr>
<td>AQM</td>
<td>Air Quality Models</td>
</tr>
<tr>
<td>BC</td>
<td>Boundary conditions</td>
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<tr>
<td>BenMAP</td>
<td>Benefits Mapping and Analysis Program</td>
</tr>
<tr>
<td>BFM</td>
<td>Brute force method</td>
</tr>
<tr>
<td>BTH</td>
<td>Beijing-Tianjin-Hebei region</td>
</tr>
<tr>
<td>BVOC</td>
<td>Biogenic VOCs</td>
</tr>
<tr>
<td>CAMx</td>
<td>Comprehensive Air Quality Models with Extensions</td>
</tr>
<tr>
<td>CDM</td>
<td>Cardiovascular diseases mortality</td>
</tr>
<tr>
<td>CIESIN</td>
<td>Center for International Earth Science Information Network</td>
</tr>
<tr>
<td>CMAQ</td>
<td>Community Multi-scale Air Quality models</td>
</tr>
<tr>
<td>CNEMC</td>
<td>China National Environmental Monitoring Center</td>
</tr>
<tr>
<td>COPD</td>
<td>Chronic obstructive pulmonary diseases</td>
</tr>
<tr>
<td>CRF</td>
<td>Concentration response function</td>
</tr>
<tr>
<td>CTMs</td>
<td>Chemical transport models</td>
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<tr>
<td>DDM</td>
<td>Decoupled Direct Method</td>
</tr>
<tr>
<td>Acronym</td>
<td>Description</td>
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<tr>
<td>---------</td>
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<tr>
<td>EDGAR</td>
<td>Emission Database for Global Atmospheric Research</td>
</tr>
<tr>
<td>EPA</td>
<td>Environmental Protect Agency</td>
</tr>
<tr>
<td>ER</td>
<td>Emergency room</td>
</tr>
<tr>
<td>FINN</td>
<td>Fire INventory from NCAR</td>
</tr>
<tr>
<td>GE</td>
<td>Gross error</td>
</tr>
<tr>
<td>GEOS-Chem</td>
<td>Goddard Earth Observing System chemical transport model</td>
</tr>
<tr>
<td>HA</td>
<td>Hospital admission</td>
</tr>
<tr>
<td>HDDM</td>
<td>High-order DDM</td>
</tr>
<tr>
<td>IC</td>
<td>Initial condition</td>
</tr>
<tr>
<td>IHD</td>
<td>Ischemic heart disease</td>
</tr>
<tr>
<td>MB</td>
<td>Mean Bias</td>
</tr>
<tr>
<td>MCIP</td>
<td>Meteorology-Chemistry Interface Processor</td>
</tr>
<tr>
<td>MEGAN</td>
<td>Model for Emissions of Gases and Aerosols from Nature</td>
</tr>
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<td>MEIC</td>
<td>Multi-resolution Emission Inventory for China</td>
</tr>
<tr>
<td>MFB</td>
<td>Mean fractional bias</td>
</tr>
<tr>
<td>MFE</td>
<td>Mean fractional error</td>
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<tr>
<td>NAQPMS</td>
<td>Nested Air Quality Prediction Modeling System</td>
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<tr>
<td>NCAR</td>
<td>National Center for Atmospheric Research</td>
</tr>
<tr>
<td>Abbreviation</td>
<td>Description</td>
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<tr>
<td>NCL</td>
<td>NCAR Command Language</td>
</tr>
<tr>
<td>NCP</td>
<td>North China Plain</td>
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<tr>
<td>NMB</td>
<td>Normalized mean bias</td>
</tr>
<tr>
<td>NME</td>
<td>Normalized mean error</td>
</tr>
<tr>
<td>NO&lt;sub&gt;x&lt;/sub&gt;</td>
<td>Nitrogen oxides</td>
</tr>
<tr>
<td>O&lt;sub&gt;3&lt;/sub&gt;</td>
<td>Ozone</td>
</tr>
<tr>
<td>O&lt;sub&gt;3&lt;/sub&gt;N</td>
<td>NO&lt;sub&gt;x&lt;/sub&gt;-related O&lt;sub&gt;3&lt;/sub&gt;</td>
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<tr>
<td>O&lt;sub&gt;3&lt;/sub&gt;V</td>
<td>VOCs-related O&lt;sub&gt;3&lt;/sub&gt;</td>
</tr>
<tr>
<td>O&lt;sub&gt;3&lt;/sub&gt;-BG</td>
<td>O&lt;sub&gt;3&lt;/sub&gt; from background</td>
</tr>
<tr>
<td>O&lt;sub&gt;3&lt;/sub&gt;-EM</td>
<td>O&lt;sub&gt;3&lt;/sub&gt; from emissions</td>
</tr>
<tr>
<td>OMI</td>
<td>Ozone monitoring Instrument</td>
</tr>
<tr>
<td>OSAT</td>
<td>Ozone source apportionment technology</td>
</tr>
<tr>
<td>PRD</td>
<td>Pearl River Delta</td>
</tr>
<tr>
<td>REAS</td>
<td>Regional Emission Inventory in ASia</td>
</tr>
<tr>
<td>REAM</td>
<td>Regional Chemical Transport Model</td>
</tr>
<tr>
<td>RH</td>
<td>Relative humidity</td>
</tr>
<tr>
<td>RDM</td>
<td>Respiratory diseases mortality</td>
</tr>
<tr>
<td>RMSE</td>
<td>Root mean squared error</td>
</tr>
</tbody>
</table>
RR  Relative risk
SUS  Southeast U.S.
STK  Strokes, including both ischemic and hemorrhagic strokes
T    Temperature
VOCs Volatile organic compounds
WD   Wind direction
WHO  World Health Organization
WRF  Weather Research and Forecasting model
WPS  WRF Preprocessing System
WS   Wind speed
YRD  Yellow River Delta
8h-O3 Maximum daily 8 hourly O₃
2R   O₃ two regime scheme
3R   O₃ three regime scheme
Ground-level ozone ($O_3$), as one of six common air pollutants set by National Ambient Air Quality Standards from the U.S. Environmental Protection Agency (EPA), is of great interest due to its health and economical effects. However, $O_3$ contributions from different emission sources are not well understood due to its complicated nonlinear reactions. In this study, $O_3$ source apportionment methods and the applications are firstly reviewed to provide a comprehensive understanding for $O_3$ formations. Application of High-order Decoupled Direct Method (HDDM), brute force method (BFM), $O_3$ source apportionment technology (OSAT) and source-oriented method in $O_3$ simulations are discussed in detail. And applications of different $O_3$ regime schemes are compared with each other. Improved three regime scheme (3R) has better performance in tracking $O_3$ contributions from its precursors. Then, the Community Multi-scale Air Quality (CMAQ) model is applied to predict $O_3$ concentrations in NCP with meteorological conditions generated by the Weather Research and Forecasting (WRF) model. Model performance from using anthropogenic emissions from the updated Emissions Database for Global Atmospheric Research (EDGAR+) and the Multi-resolution Emission Inventory for China (MEIC) are validated. The statistical analysis reveals a better performance from EDGAR+. The source-oriented simulation with 3R technique indicates that $NO_x$ emissions dominate in most regions while contributions from VOCs are higher in megacities than in other regions in NCP. Industry, on-road and energy emissions are major sources, which account for $\sim$75% of total emission-related $O_3$ formation. Emissions from local and surrounding regions are the main $O_3$ contributors and emissions from central China and YRD have strong impacts in peak episodes. $O_3$ simulation and source apportionment in SUS reveal that $NO_x$ emissions from on-road, energy dominate the emission-related $O_3$ while VOCs emissions have less contribution except those from biogenic sectors. Health risk analysis indicates that more
than 0.11 million premature mortalities are associated with O₃ level in NCP due to respiratory (0.04-0.05 million) and cardiovascular (0.07-0.06 million) diseases. A total of 0.03 all-cause premature mortality is estimated for SUS with ~4.6 and ~7.9 thousand from respiratory and cardiovascular diseases, respectively.
Tropospheric ozone (O$_3$), as one of the six common air pollutants identified in the Clean Air Act (CAA), is associated with adverse impacts on air quality, public health and ecosystem. It is mostly referred to severe air pollution, mortality and life year lost from respiratory and cardiovascular diseases, changes of vegetation and crop yield, and impacts on climate and land surface changes $^{1-8}$. In 2015, the U.S. Environmental Protection Agency (EPA) revised the O$_3$ standard to 70 parts per billion (ppb), and they declared that area meeting with the standard is classified as “attainment” area $^9$. Increasing number of days with harmful observations (concentration is higher than threshold of 70 ppb) is reported for both China and the U.S. $^{10-12}$. O$_3$ in the air that people breath in can cause muscle constriction in airways and lead to breathing difficulties when the concentration reaches an unhealthy level. Old people, children and people with asthma are at high risk of suffering O$_3$-related diseases. O$_3$ also attacks sensitive vegetation, causes reduction of photosynthesis and slows plant growth. As a result, vegetation functions are decreased, and the ecological diversity is lost. Both China and U.S. are facing severe O$_3$-related issues. Around 4,700 O$_3$-related mortalities and 36,000 life years lost were reported to be associated with O$_3$ concentrations in U.S. in 2015 $^{13}$. In the same year, around 55,341 to 80,280 mortalities were estimated due to chronic obstructive pulmonary disease (COPD) in China, and the cumulative population exposed to high maximum eight-hour average O$_3$ (8h-O$_3$) concentrations (>100 μg/m$^3$) was estimated to be 816.04 million $^{14}$. O$_3$ level in 2000 induced 6.4%-14.9% yield loss of food crop, and estimated O$_3$ concentration in 2020 would cause 47.4 million metric tons losses of four grain crop production in China $^{15}$.
With increasing attention paid on this specific pollutant, O3 is intensively monitored in different countries and observational data have shown its temporal and spatial variations. An averaged increase rate of 1.13 ± 0.01 ppb/year of 8h-O3 was observed in north of eastern China from 2003 to 2015, and total O3 variations were due to short-term (36.4%), seasonal (57.6%) and long-term (2.2%) changes. Significant increases that averaged 1.7 ppb/year in June and 2.1 ppb/year in July to August during 2003-2015 were also observed in Mt. Tai (China). O3 concentration were also reported exceeding the ambient air quality standard by 100%-200% in major urban centers over China. On the other hand, the U.S. has ineligible O3 issue as well. Though significant decreases of O3 were observed in 83% (summer) and 43 % (spring) of monitoring sites in eastern U.S., increases of springtime O3 were observed in 50% sites in western U.S. Increases of springtime O3 were also observed in western U.S. rural sites by 0.2-0.5 ppb/year while decreases of 8h-O3 were revealed in summertime. Generally, China is experiencing increasing O3 episodes, while the U.S. is experiencing complex seasonally and temporally O3 variations. Observation data offers information to understand historical trend of local O3 variations, but that information is limited within certain geographical range.

Chemical transport models (CTMs) are essential tools for O3 simulation and predict O3 production and destruction involving the chemical and physical dynamic processes in the atmosphere with commonly used chemical mechanisms, such as Carbon Bond and SAPRC. CTMs are widely applied in investigating O3 variations and their responses to changes of climate conditions and emissions. For example, Li, et al. analyzed the chemical productions and transport impacts on diurnal O3 behavior in Mt. Tai (China) in June 2006 by applying the Nested Air Quality Prediction Modeling System (NAQPMS) that indicated that around 60 ppb and 25 ppb afternoon-maximum concentrations were due to regional transport and chemistry production,
respectively. Yang, et al. applied a global 3D Goddard Earth Observing System chemical transport model (GEOS-Chem) by investigating O$_3$ variations under changes of sulfate and nitrate. It was observed that O$_3$ increased in most eastern China in winter, spring and fall when it was dominated by impacts of sulfate while it decreased in summer since nitrate formation played a leading role. Hu, et al. applied the Regional Atmospheric Modeling System-Community Multiple Air Quality (RAMS-CMAQ) model to simulate tropospheric O$_3$ in the North China Plain (NCP) for summer 2015 and found emissions from Shandong and Hebei attributed largest to not only the highest local O$_3$ concentration but also to Beijing and Tianjin. The Community Multi-scale Air Quality model (CMAQ) was also used to estimate O$_3$ response to reduction of anthropogenic emissions in Eastern U.S.. Around 10 to 15 less exceeding days are estimated in Washington, DC as the result of emission reductions since 2002. A regional model (CAMs) nested in GEOS-Chem was applied in estimating background O$_3$ variations in North America and the U.S., and the results indicated an increasing trend of background O$_3$ in western and southwestern U.S which is associated with rising emissions in Asia and Mexico from past 5 decades.

O$_3$ is a secondary pollutant formed by photochemical reactions of nitrogen oxides (NO$_x$) and volatile organic compounds (VOCs). The photolysis of NO$_2$ provides atomic oxygen in forming O$_3$, while VOCs oxidation provides peroxy radicals which helps to convert NO to NO$_2$. Thus, the relative abundances of NO$_x$ and VOCs would greatly affect O$_3$ formation. Based on the sensitivity of O$_3$ to NO$_x$ and VOCs changes, O$_3$ formation would be classified as NO$_x$- or VOCs-limited and switch from each other spatiotemporally. For example, O$_3$ formation in boundary layer in Beijing was proved to be limited by VOCs in haze day while both NO$_x$ and VOCs limited O$_3$ photochemical productions in clean days. An analysis indicated that Boston, Pittsburgh,
Philadelphia and Washington, D.C were under NO\textsubscript{x}-limited condition while New York city was in VOCs-limited regime\textsuperscript{30}. When it is decided as NO\textsubscript{x}- or VOCs- limited, O\textsubscript{3} formation is regarded only sensitive to single precursor, however, limiting condition is changing all the time.

Source apportionment of O\textsubscript{3} is very important for designing control strategies, but it is very challenging since O\textsubscript{3} formation is highly sensitive to its precursors. To better understand O\textsubscript{3} source apportionment, multiple methods were applied to the air quality model to simulate O\textsubscript{3} contribution from its sources. O\textsubscript{3} contributions from neither NO\textsubscript{x} or VOCs have been studied separately by applying High-order Decoupled Direct Method (HDDM), which calculates the sensitivities to perturbations in emissions\textsuperscript{31}. Brute force method (BFM) is another approach to investigate O\textsubscript{3} contribution from specific source by zeroing emissions from a single source\textsuperscript{32}. Besides, O\textsubscript{3} Source Apportionment Technology (OSAT) uses non-reactive tagged tracers in transport and reaction processes to track O\textsubscript{3} sources by splitting the concentration changes based on emission ratios\textsuperscript{33}. Source-oriented methods use reactive-tracers in all chemical and transport processes, it serve as an advanced technique in O\textsubscript{3} source apportionment analysis\textsuperscript{34-36}. O\textsubscript{3} formation is strongly sensitive to concentrations of precursors, and its source contributions are varied spatiotemporally, thus improved source apportionment technique is necessary for more accurate results. The first objective of this study is to overview source apportionment/sensitivity methods including source-oriented methods, OSAT, HDDM and BFM. An overview of current research related to O\textsubscript{3} source apportionment in China will also be conducted to provide a clearer understanding of current O\textsubscript{3} levels and its sources in China. This objective also includes solid evidence to support further studies for better O\textsubscript{3} simulation and source apportionment in China.

CTMs were very useful for understanding O\textsubscript{3}, but the accuracy was highly dependent on emission inventories. Several emission inventories covering China and surrounding regions are
available for different simulation purposes\textsuperscript{37, 38}. Inventories from regional to continental scales, for different pollutant species and emission sectors\textsuperscript{39-43} \textsuperscript{32} were created and were successfully applied in O\textsubscript{3} simulation. Widely used inventories such as Emission Database for Global Atmospheric Research (EDGAR), Multi-resolution Emission Inventory for China (MEIC), MIX, Regional Emission inventory in ASia (REAS) help to analyze air quality in China\textsuperscript{44-49}. However, to a large extent, these inventories are not entirely bottom-up, and they have been created for multiple purposes for simulation, which leads to large uncertainties in simulation results \textsuperscript{50}. EDGAR and MEIC are two most widely used inventories in O\textsubscript{3} simulation in China, while their performances in O\textsubscript{3} simulation vary in years and regions \textsuperscript{41, 51}. \textbf{The second objective of this study is to} validate model performance based on EDGAR and MEIC. Evaluating and improving their performance in O\textsubscript{3} prediction would provide convincing results for a deeper understanding of O\textsubscript{3} formation, health risks, and design of controlling strategies. This objective also supports the next objective in O\textsubscript{3} source apportionment.

Source apportionment of O\textsubscript{3} is very important to quantify source contributions and to design control strategies, but complex nonlinear reactions of O\textsubscript{3} precursors make it a challenge for model simulation. To determine O\textsubscript{3} contribution from NO\textsubscript{x} and VOCs, ratios of photochemical chain reaction production rates, which are widely known as regime indicators, are introduced to classify O\textsubscript{3} contribution. Traditional two regime (2R) approach was implemented in the CMAQ model \textsuperscript{52} by applying indicator production ratio of H\textsubscript{2}O\textsubscript{2}/HNO\textsubscript{3} with correlation coefficients ranging from 0.58 to 0.99. An improved method that applied production ratio indicator of (H\textsubscript{2}O\textsubscript{2}+ROOH)/HNO\textsubscript{3} in three regime scheme (3R) was introduced into CMAQ \textsuperscript{53} and compared with traditional 2R method; results indicated higher contributions from NO\textsubscript{x} in high O\textsubscript{3} concentration regions in China by 5 to 15 ppb. Results also varied when using different source
apportionment methods. The third objective of this study is to use improved source-oriented version of CMAQ for O₃ source apportionment in NCP. O₃ precursors from different emission sources will be tagged as tracers to quantify source contributions during study period. Regional source apportionment will also be conducted in this study to provide evidence for regional transport and their contributions.

O₃ variations are very complicated in the U.S. It was observed that surface O₃ decreased by 6-10 ppb/decade in rural sites based on hourly O₃ mixing ratios from 1989-2007 in eastern U.S.⁵⁴. Though O₃ concentration decreased in eastern U.S. in past decades, an increasing number of days that 8h-O₃ level that were higher than the threshold was also observed in part of the U.S.⁵⁵. O₃ concentration increased by 0.26 ppb/year in western U.S. based on observation data from 1987 to 2004, and springtime O₃ concentrations were increasing since late 1970s. O₃ mixing ratios during 1995-2008 were analyzed and observed to increase; it was reported that the increases of mixing ratios were heavily influenced by direct transport from Asia.⁵⁶ O₃ impacts from emission sources, transport and forming processes and climate conditions were also briefly studied by applying CTMs such as Regional Chemical Transport Model (REAM), GEOS-Chem and CMAQ.⁵⁷-⁶³. Although there are many studies on the U.S., there is no study that comprehensively explain O₃ contribution from each source in SUS. The fourth objective of this study is to apply similar models mentioned in previous objectives to simulate O₃ level and its source apportionment in SUS. O₃ simulation and source apportionment results in SUS will help to understand O₃ spatiotemporal variation patterns, sources of O₃ formation and impact factors under complex climate conditions in this region. Comparison between regions from developed country (SUS) and developing country (NCP) will provides information for differences between these regions.
Human health impacts under certain O\textsubscript{3} level are highly concerned. Short-term exposure to daily 1-hour maximum O\textsubscript{3}, 8h-O\textsubscript{3}, daily and daytime averaged O\textsubscript{3} were all shown to correspond to increase of non-accidental mortality\textsuperscript{64}. Around 70800 premature mortalities were reported through 339 cities in China based on hourly O\textsubscript{3} for the year 2015\textsuperscript{65}. Urbanization also induced increases of O\textsubscript{3}, which resulted in 1,100 O\textsubscript{3}-associated premature mortality in the Pearl River Delta (PRD)\textsuperscript{66}. It was estimated that ~200,000 premature respiratory mortalities in China were associated with long-term exposure while only ~34,000 were estimated in the U.S.\textsuperscript{67}. It was shown that mortality of COPD, congestive heart failure and lung cancer increased by 1.03 (± 0.02) due to long-term exposure to O\textsubscript{3} in U.S. based on data recorded from 2000-2008\textsuperscript{68}. However, less studies focused on this topic in NCP and SUS. Thus, more studies are needed for a comprehensive understanding of the health effects and related sources in these regions\textsuperscript{69}. The last objective of this study is to estimate health risk under simulated O\textsubscript{3} level in NCP and SUS. Premature mortality due to respiratory and cardiovascular diseases will be estimated. Attributions from each emission sources will be also estimated.

With objectives listed above, this study aims to provide a comprehensive understanding of formation, source attribution and health effects of O\textsubscript{3} in NCP and SUS, which would offer information for designing efficient O\textsubscript{3} controlling strategies.
CHAPTER 2. OVERVIEW OF OZONE SOURCE APPORTIONMENT TECHNIQUES

2.1 Introduction

To evaluate and quantify the impacts of emission sources, source apportionment provides spatial and temporal assessments especially in the field of atmospheric science. There is no existing technique that can directly distinguish O$_3$ contribution from its sources by using observation data. It is a challenge for scientists to figure out a reliable method to analyze and quantify the sources of O$_3$. Rapid development of computational resources supports the calculations in full-scale CTMs by combining physical and chemical processes in the atmosphere. It also helps to extend the air quality models (AQM) to further simulate the impacts from sources. This advanced technique is widely used in air quality analysis and applied to estimate O$_3$ contributions from its precursor sources.

Source analysis technique has been applied to estimate air pollution and in support for improving assessments for air pollutions and controlling strategies since 1960s $^{70,71}$. To track air pollutants contribution from specific source, the principal component analysis and the factor analysis methods were initially applied in early studies for aromatic hydrocarbon content and particle compositions $^{72,73}$. Following efforts focused on improving the atmospheric mass-balance model introduced by Miller, et al. $^{74}$ and Winchester and Nifong $^{75}$. Though there were some limitations initially, termed effective variance least squares helped to solve problems $^{76}$. Consequently, many source analysis methods were developed in the following years. Sensitive equations and decoupled direct method (DDM) were recruited as the sensitivity analysis technique in air quality models since 1976 $^{77}$ and 1981$^{78}$. O$_3$ source apportionment technology (OSAT) is an
advanced technique which quantitatively apportions the O₃ pollution concentration at a user specific location and time to emission sources by adding non-reactive tracers. This technique was also compiled into AQMs to measure source contributions. The simplest technique called brute force method (BFM) measures source contributions by conducting simulations with and without given source emissions. An advanced approach, called source-oriented approach, tracks tagged species in emission sources in air quality models, that allows sources contribution to be easily calculated. The above approaches are the most commonly used current techniques in O₃ source apportionment; however, these usually investigate O₃ and its contribution from precursors in high O₃ pollution region.

Source apportionment methods are widely used in distinguishing and quantifying source contributions to O₃. But their abilities and performances are varied since they estimate the contribution in different ways. A comparison of OSAT and DDM indicated that they had a similar agreement of major contributor of O₃ productions in Lake Michigan but OSAT predicted greater relative importance to anthropogenic emissions and boundary concentrations than DDM did. Comparison between OSAT and BFM also declared the similarity of these methods with correlation coefficients ranging from 0.58 to 0.99, but results also indicated that OSAT had a high sensitivity to secondary reactions than BFM. OSAT and DDM agreed well on the top 10 contributors to O₃ formation in eastern U.S. but OSAT indicated more contributions from anthropogenic emissions but results from DDM shown a higher contribution from biogenic emissions. And OSAT predicted more NOₓ-limited regions which were classified as VOCs-limited in DDM. It is also pointed out that OSAT has a better performance in studying source contributions while BFM prefers to reveal the response of changes of emission. These methods are commonly used in O₃ simulations in China since increasing attention were paid to its severe
O_3 pollution. To fully understand source apportionment to O_3 formation, this work examines four main source apportionment methods including DDM, BFM, OSAT and source-oriented methods and their applications in China.

2.2 DDM

DDM, a direct investigation method, is applied in air quality models to calculate the sensitivity coefficient to emission sources. DDM was initially developed in order to solve time-dependent and non-stiff air pollution issues though chemical and meteorological models since 1980s \(^{84}\). Finite-difference approximations were employed in DDM to estimating two or more sensitivity coefficients simultaneously in linear, nonlinear and 3D-CTMs within simulations \(^{85}\). Hakami, et al. \(^{86}\) applied DDM to estimate second- and third-order sensitivity coefficients, which is called higher-order decoupled direct method (HDDM). DDM and HDDM calculate sensitivity coefficients following same functions. The outputs in target space and time period indicate the relationship between pollutant concentrations and perturbations from user specific interests. Following equations give a clear understanding to how HDDM works in air quality models. Advantages of HDDM includes conceptually simpler, higher accurate in calculating first-order sensitivities, and less array storage and lower program computing resources compared to other direct methods.

Equation 1:

$$C_j(x, t) = C_0(x, t) + \Delta \varepsilon_j s_j(1)(x, t) + 0.5 \left( \Delta \varepsilon_j(2)s_j(2)(x, t) \right) + H$$

Equation 2:

$$S_j(x, t) = \frac{\delta C_j(x, t)}{\delta \varepsilon_j(x, t)}$$
Equation 1 and Equation 2 show the basic processes to estimate sensitivity coefficient (S). The $C_j$ in Equation 1: represents concentration of pollutant under perturbation of $j$ in space $x$ and time step of $t$. $C_0$ represent the base concentration (unperturbed) in same space and time. $S_j$ represents the sensitivity coefficient of pollutant $j$ in space of $x$ and time of $t$. $\Delta \varepsilon_j$ is the fractional perturbation of parameter $j$. $s_j(1)$, $\varepsilon_j(2)$ and $s_j(2)$ represent first and second order sensitivity coefficients, which can be calculated by Equation 2. $H$ in Equation 1: represents higher order terms.

Due to its ability in sensitivity analysis, DDM is employed in air quality models to estimated $O_3$ and its impact factors. For example, DDM-3D was coupled with CIT (California/Carnegie Institute of Technology) airshed model and indicated that uncertainty of reaction rate constants have significant impacts on $O_3$ levels in Los Angeles; the results also suggested that uncertainty of $O_3$ prediction depends highly on uncertainty of HNO$_3$ formation rate constants. Jeon, et al. $^87$ applied CMAQ model with DDM-3D technique and found that high $O_3$ concentration in rural area of Chungcheong in the air mass from Seoul was very sensitive to NO$_x$ mainly due to the contribution from VOCs emissions from biogenic sector. Following table summarizes $O_3$ source apportionment simulations in recent decades applying DDM.

<table>
<thead>
<tr>
<th>Model/methods</th>
<th>Study field</th>
<th>Study period</th>
<th>Studied sources</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>CMAQ/DDM</td>
<td>Chungcheong, Korea</td>
<td>Summer in 2009 and 2011</td>
<td>Emissions of NO$_x$ and BVOCs</td>
<td>$^87$</td>
</tr>
<tr>
<td>CIT/DDM</td>
<td>California, U.S.</td>
<td>Aug. 1987</td>
<td>Gas phase reaction rates</td>
<td>$^88$</td>
</tr>
<tr>
<td>CMAQ/DDM</td>
<td>Texas, U.S.</td>
<td>Aug. and Sep. in 2005</td>
<td>Emissions of NO$_x$ and VOCs</td>
<td>$^89$</td>
</tr>
<tr>
<td>CAMx/DDM</td>
<td>Houston, Texas, U.S.</td>
<td>Jun. 2005</td>
<td>Emissions of NO$_x$ and VOCs</td>
<td>$^90$</td>
</tr>
<tr>
<td>CIT/DDM</td>
<td>Mexico–U.S. border</td>
<td>July 1993</td>
<td>Emissions of NO$_x$ and VOCs</td>
<td>$^91$</td>
</tr>
<tr>
<td></td>
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<td>(Table cont’d)</td>
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<tr>
<td>Model/methods</td>
<td>Study field</td>
<td>Study period</td>
<td>Studied sources</td>
<td>References</td>
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</tr>
<tr>
<td>CMAQ/DDM</td>
<td>The U.S.</td>
<td>Jan. and Jul. in 2011</td>
<td>O$_3$ and HCHO precursors</td>
<td>92</td>
</tr>
<tr>
<td>CMAQ/DDM</td>
<td>Central California, U.S.</td>
<td>July in 2007</td>
<td>OH productions</td>
<td>93</td>
</tr>
<tr>
<td>CMAQ/DDM</td>
<td>Southeastern U.S.</td>
<td>Aug. 2000</td>
<td>Emissions of NO$_x$ and VOCs</td>
<td>94</td>
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<tr>
<td>CAMx/DDM</td>
<td>The U.S.</td>
<td>2006</td>
<td>Anthropogenic emissions of NO$_x$ and VOCs</td>
<td>95</td>
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<tr>
<td>CMAQ/DDM</td>
<td>Atlanta, U.S.</td>
<td>2001</td>
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<td>97</td>
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<tr>
<td>CMAQ/DDM</td>
<td>Texas, U.S.</td>
<td>August to September 2006</td>
<td>Emissions of NO$_x$</td>
<td>98</td>
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<tr>
<td>CAMx/DDM</td>
<td>Continental U.S. and eastern U.S.</td>
<td>July 2030</td>
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<td>99</td>
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<tr>
<td>CMAQ/HDDM</td>
<td>East Asia</td>
<td>2007</td>
<td>Emissions of NO$_x$ and VOC</td>
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</tr>
<tr>
<td>MAQSIP/DDM</td>
<td>Central California, U.S.</td>
<td>August 1990</td>
<td>31 organic compounds and CO</td>
<td>101</td>
</tr>
<tr>
<td>CAMx/HDDM</td>
<td>Texas, U.S.</td>
<td>June 2005</td>
<td>Emissions of NO$_x$ and VOCs</td>
<td>90</td>
</tr>
<tr>
<td>CMAQ/DDM</td>
<td>PRD, China</td>
<td>October 2004</td>
<td>Emissions of NO$_x$ and VOCs</td>
<td>102</td>
</tr>
</tbody>
</table>

From Table 1, DDM is widely recruited in source apportionment studies especially applied in CMAQ. The goals of most studies are to assess the relationship between O$_3$ formation and emissions of NO$_x$ and VOCs. However, DDM has its limitations in analyzing sensitivities to secondary air pollutions such as O$_3$; even HDDM has limitations in investigating source contributions through nonlinear reactions. Its ability in simulating O$_3$ source apportionment was studied in 2002 $^{79}$ and indicated that DDM can only explain 70% of O$_3$ concentration through first-order reactions; however, great uncertainties remained for the O$_3$ contributions from higher order reactions. In addition, DDM also takes more simulation resources compared to OSAT if it considers higher order reactions. It is concluded that DDM, as a first order prefer technique, is commonly regarded as source sensitive technique, and may not provide accurate results in O$_3$ source analysis study.
2.3 BFM

CMAQ model and the Comprehensive Air Quality Model with Extensions (CAMx) employed brute force method (BFM) to estimated single source contribution to air pollution\textsuperscript{32,103}. BFM is processed by comparing base simulation with control case. Emissions are remained unchanged in base case while the target emission is removed in control case. The differences between cases indicate the impacts from target sources. BFM is conceptually accurate for linear chemistry and small emission changes. It also directly relates to impacts from emissions controlling measures and also investigates indirect effects such as oxidant-limiting effects\textsuperscript{104}. Besides, BFM has strong ability in investigating the development of emission reduction scenarios, thus it is used in air dispersion modeling\textsuperscript{105}. Though BFM is widely applied in air quality models, most of these studies aim to analyze pollutants such as particulate matter instead of secondary air pollutants. There are limited studies applying BFM as O\textsubscript{3} source apportionment method since it will miss information from secondary reactions after interested emissions are removed. A brief summary of studies applied BFM in O\textsubscript{3} source apportionment is listed in Table 2.

<table>
<thead>
<tr>
<th>Models</th>
<th>Study field</th>
<th>Study period</th>
<th>Studied sources</th>
<th>Reference</th>
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<tbody>
<tr>
<td>NAQPMS</td>
<td>Beijing, China</td>
<td>August 2006</td>
<td>NO\textsubscript{x} and NMVOC</td>
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</tr>
<tr>
<td>CAMx</td>
<td>BTH region, China</td>
<td>Summer 2007</td>
<td>NO\textsubscript{x} and VOCs</td>
<td>107</td>
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<tr>
<td>CAMx</td>
<td>Mexico City Metropolitan Area (MCMA)</td>
<td>1991 to 2006</td>
<td>CO, NO\textsubscript{x} and VOCs</td>
<td>108</td>
</tr>
<tr>
<td>CMAQ</td>
<td>California, U.S.</td>
<td>Summer 2007</td>
<td>NO\textsubscript{x} and VOCs</td>
<td>32</td>
</tr>
<tr>
<td>CAMx</td>
<td>The U.S.</td>
<td>May-September 2011</td>
<td>BVOC</td>
<td>109</td>
</tr>
<tr>
<td>CMAQ</td>
<td>The U.S.</td>
<td>June and April 2011</td>
<td>Emissions from wildfires and prescribed fire</td>
<td>110</td>
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<thead>
<tr>
<th>Models</th>
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<th>Study period</th>
<th>Studied sources</th>
<th>Reference</th>
</tr>
</thead>
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<tr>
<td>CMAQ</td>
<td>Western U.S.</td>
<td>April–October 2007</td>
<td>Background O₃</td>
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<td>STEM-2K1/MM5</td>
<td>Guangdong province, China</td>
<td>March 2001</td>
<td>Emissions from power plant, transport and industry</td>
<td>112</td>
</tr>
<tr>
<td>CMAQ</td>
<td>Southern California, U.S.</td>
<td>July 2005</td>
<td>Seven emission sources</td>
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</tbody>
</table>

BFM is not a truly source apportionment technique, it is widely called as source sensitive method. BFM is not a priority choice in O₃ source apportionment study since its limitations result in unrealistic and undesired changes to source contributions. This method is mainly used in predicting results from changes of O₃ sources, especially in evaluating impacts from emission controlling strategies and climate change\(^{110}\). Most studies listed in Table 2 compared the results from BFM and other source apportionment methods to provides overall source contributions. Besides, this method requires large amount of computational resources to process analysis for multiple contributors.

### 2.4 OSAT

An additional function is needed in photochemical grid models in simulating O₃ formation and presenting source contribution without changing the predictions of total O₃ formation, thus the OSAT was designed in 1995 and first released in CAMx in 1996 to fulfill this purpose \(^{114}\). OSAT generates tracer species in O₃ precursors (NO\(_x\) and VOCs), which allow CAMx to predicts their contributions to O₃ formation simultaneously with O₃ predictions. Four tracers are introduced to represents the proportion of precursors contributions to O₃ formation. Emission tracers from NO\(_x\) and VOCs are grouped as the tracer families which are represented as N\(_i\) and V\(_i\) for source group i for each grid cell in model as shown in equation 1 and 2. Movement of traces would be tracked thus to apportion NO\(_x\) and VOCs emissions. O₃ productions are predicted at given time step and
locations in models, tracer families (O₃Nᵢ and O₃Vᵢ in Equation 3 and Equation 4) are generated simultaneously to estimate the proportion of O₃ formation to emissions of NOₓ and VOCs under certain O₃ regime scheme.

Equation 3:

\[ \sum_{i=1}^{I} N_i = NO_i + NO_2, \quad i=1, 2, 3..., I \]

Equation 4:

\[ \sum_{i=1}^{I} V_i = VOC_s, \quad i=1, 2, 3..., I \]

Equation 5:

\[ \sum_{i=1}^{I} O_3N_i + O_3V_i = O_3, \quad i=1, 2, 3..., I \]

OSAT is improved to advanced version to increase accuracy in calculating O₃ contributions from its sources by considering the feedbacks of reactions in O₃ production and destruction. Tagged atomic oxygen in predicted net O₃ production are traced in deforming process, and O₃ destruction rate due to reactions with species such as HOₓ (OH and HO₂) helps to quantify the potential O₃ reformation. Such improvements were released in 2005 known as OSAT2 with updated version of CAMx ¹¹⁵. A subsequent improvement (OSAT3) was released in 2015 along with CAMx version of 6.3. The odd oxygen in chemical reactions of O₃ reforming processes is tagged with associated source groups, thus regenerated O₃, NO and NO₂ are evaluated. As results, predicted O₃N and O₃V contain information of O₃ reforming, and the accuracy of O₃ source apportionment is improved. This technique is commonly used in recent O₃ source analysis, summary of recent studies applying OSAT is listed in Table 3.
Table 3. Summarization of studies using OSAT in O$_3$ source apportionment.

<table>
<thead>
<tr>
<th>Model</th>
<th>Study field</th>
<th>Study period</th>
<th>Studied sources</th>
<th>Reference</th>
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<td>MM5</td>
<td>PRD, China</td>
<td>Jul. and Nov. 2006</td>
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<tr>
<td>CAMx</td>
<td>Beijing, China</td>
<td>Jul. 2000</td>
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<tr>
<td>CAMx</td>
<td>The U.S.</td>
<td>May. to Sep. 2011</td>
<td>BVOCs emissions</td>
<td>118</td>
</tr>
<tr>
<td>CAMx/CMAQ</td>
<td>The U.S.</td>
<td>2018/2030</td>
<td>Emissions and background O$_3$</td>
<td>83</td>
</tr>
<tr>
<td>MM5</td>
<td>Hong Kong and PRD, China</td>
<td>2006</td>
<td>Regional emission sources</td>
<td>119</td>
</tr>
<tr>
<td>CAMx</td>
<td>The U.S.</td>
<td>2011</td>
<td>Tropospheric and stratospheric O$_3$ contributions</td>
<td>120</td>
</tr>
<tr>
<td>CAMx</td>
<td>YRD, China</td>
<td>2013</td>
<td>Regional emissions and long-range transport</td>
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<tr>
<td>CAMx</td>
<td>Continental North America</td>
<td>2008</td>
<td>Tropospheric and stratospheric O$_3$ contributions</td>
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<tr>
<td>GEOS-Chem/CAMx</td>
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<td>Background O$_3$ contribution</td>
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<tr>
<td>CAMx</td>
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<td>October 2004</td>
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<tr>
<td>CAMx</td>
<td>Europe</td>
<td>2010</td>
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<tr>
<td>CAMx</td>
<td>YRD, China</td>
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<td>VOCs emissions</td>
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<tr>
<td>CAMx</td>
<td>YRD, China</td>
<td>summer 2013</td>
<td>Anthropogenic emission sources</td>
<td>127</td>
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<tr>
<td>CAMx</td>
<td>YRD, China</td>
<td>2013-2017</td>
<td>Transportation and industry emissions</td>
<td>127</td>
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<tr>
<td>CAMx</td>
<td>The U.S.</td>
<td>2025</td>
<td>On road emissions</td>
<td>128</td>
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<tr>
<td>CAMx</td>
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<td>1970-2020</td>
<td>NO$_x$ emissions</td>
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<tr>
<td>CMAQ</td>
<td>The U.S.</td>
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<td>On-road mobile emissions</td>
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</tbody>
</table>

OSAT is an advance technique that tracks transport traces of O$_3$ precursors, thus O$_3$ productions associated with NO$_x$ and VOCs can be calculated for grouped sources. This technique is successfully applied in CTMs and provides reliable evidences for estimate source contributions to O$_3$ pollution. However, this method is highly depended on user specific grouping processes. For example, emission inventories such as EDGAR, MEIC and NEI provide sectoral emissions from different categories, thus, grouped sources are not consisted by varying inventories.
2.5 Source-oriented methods

NO\textsubscript{x} and VOCs are regarded as main precursors of O\textsubscript{3} formation, NO\textsubscript{2} is formed through the oxidation of NO by O\textsubscript{3} while organic peroxy radicals (RO\textsubscript{2}) and hydroperoxy radicals (HO\textsubscript{2}), which play important roles in forming O\textsubscript{3} formation, are formed through reactions of VOCs\textsuperscript{131}. O\textsubscript{3}-oriented technique provides the detailed surface O\textsubscript{3} source apportionment for multiple targets (sources, regions and species) in single simulation in air quality models\textsuperscript{132, 133}. This advanced technique is developed to track O\textsubscript{3} formation by tagging O\textsubscript{3} precursors in their source emissions while air quality model is conducting. As main precursor of O\textsubscript{3}, NO\textsubscript{x} emissions are always tagged in this approach. Detail tagging method is briefly introduced in Zhang and Ying\textsuperscript{134}. Generally, following reactions of Equation 6 and Equation 7, O\textsubscript{3} formation from different sources can be identified.

**Equation 6:**
\[
\text{NO}_{2n} + h\nu \rightarrow \text{NO}_n + \text{O}(3P)_n, \; n=1,2,3\ldots,N
\]

**Equation 7:**
\[
\text{O}(3P)_n + \text{O}_2 \rightarrow \text{O}_3n, \; n=1,2,3\ldots,N
\]

In equation above, superscript \(n\) represents NO\textsubscript{x} emissions from source \(n\), these functions are added in air quality simulation so that O\textsubscript{3} formation in simulation outputs show their source tagged emissions.

As another main precursor, VOCs contributions to O\textsubscript{3} formation is hard to evaluate since their variety of components and intermediate reactions. As recorded in Ying and Krishnan\textsuperscript{135}, reactions of a general reactive hydrocarbon (RH) from emission source \(n\) are tagged to tracking VOCs contributions by following equation:
Equation 8:
\[ \text{RH}_n + \text{HO} \rightarrow \text{RO}_{2n} + \text{H}_2\text{O}, \quad n=1,2,3\ldots, N \]

Equation 9:
\[ \text{RO}_{2n} + \text{NO} \rightarrow \text{NO}_2 + \text{RO}_n, \quad n=1,2,3\ldots, N \]

In these reaction processes, contribution of HO\(_2\) from emission sources can be directly calculated and conversion rate (R) from NO to NO\(_2\) can be determined as F in following equations, thus O\(_3\) apportionment can be estimated.

Equation 10:
\[ F_n = \frac{R(\text{NO}_{2n})}{R(\text{NO}_{2\text{tot}})}, \quad n=1,2,3\ldots, N \]

Equation 11:
\[ O_{3n} = F_n \times O_{3\text{tot}}, \quad n=1,2,3\ldots, N \]

\(R(\text{NO}_{2n})\) in Equation 10 represents conversion rate from source n, \(\text{NO}_{2\text{tot}}\) represents overall NO to NO\(_2\) concentration rate in all VOCs sources. \(O_{3\text{tot}}\) is the predicted overall net O\(_3\) formation rate. O\(_3\) contributions from VOCs emission sources can be calculated by applying above functions in AQMs.

Based on source-oriented technique, O\(_3\) contribution from NO\(_x\) and VOCs emissions can be processed in single simulation, however uncertainties due to nonlinear photochemical reaction rate which greatly varied from different NO\(_x\) and VOCs concentration, multiple classification schemes, such as NO\(_x\)-sensitive, VOCs-sensitive, two-regime (2R) and three-regime (3R), are applied in source oriented simulations to investigate O\(_3\) contribution from NO\(_x\) and VOCs. In following sections, these regime schemes will be brief reviewed.
2.6 O₃ regime schemes

Four regime schemes are discussed in this section. These schemes are mostly used independently in O₃ simulation in which NOₓ or VOCs are determined as dominant precursor. In case where NOₓ is determined as dominant precursor, O₃ formation is attributed to NOₓ emission only; similarly, the same idea for VOCs dominant regions. For example, Zhang and Ying ¹³⁴ studied NOₓ contributions to O₃ in Houston-Galveston-Brazoria (HGB) and Beaumont-Port Arthur (BPA) in the U.S. were determined as NOₓ sensitive regions. However, it is hard to determine whether O₃ production generated in specific periods or regions is relative to NOₓ-sensitive or VOCs-sensitive. 2R scheme is introduced to determine O₃ attribution to NOₓ and VOCs. O₃ production is attributed to either NOₓ or VOCs emissions based on O₃ chemical formation regime. Regime is classified by different indicator ratios. Kwok, et al. ⁵² applied the ratio of production of hydrogen peroxide to nitric acid, to determine if O₃ product occurs in either NOₓ- or VOCs-sensitive chemical regime. Besides, indicator ratio was set to 0.35 based on previous studies ¹³⁶, ¹³⁷. Some other indicators are also applied to identify O₃ sensitivity to NOₓ and VOCs. Ratio of H₂O₂/(O₃+NO₂), HCHO/NOₓ and HCHO/NOₓ were applied to determine VOCs-limited O₃ formation with transit value of 0.02, 0.28 and 1, respectively. ¹³⁸-¹⁴¹. Within these indicators, production rate of H₂O₂/HNO₃ is most widely recruited to identify O₃ sensitivity to NOₓ and VOCs as 2R in recent studies. A summary of recent studies that applied 2R in O₃ source apportionment analysis are listed in Table 4.

Table 4. Summary of studies using 2R scheme in O₃ source apportionment

<table>
<thead>
<tr>
<th>Model</th>
<th>Study field</th>
<th>Study period</th>
<th>Study sources</th>
<th>Reference</th>
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</thead>
<tbody>
<tr>
<td>CAMx</td>
<td>PRD, China</td>
<td>Jun. 26–Jul. 2, 2000</td>
<td>NOₓ and VOCs emissions</td>
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(Table cont’d)
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<tr>
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<td>Diurnal pattern and regional sources</td>
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<td>CCM/CHASER</td>
<td>Japan</td>
<td>1980–2005</td>
<td>Regions of emission sources</td>
<td>144</td>
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<tr>
<td>CMAQ</td>
<td>California, U.S.</td>
<td>Jun. to Jul. 2007</td>
<td>Emissions of NO\textsubscript{x} and VOCs</td>
<td>52</td>
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<tr>
<td>CAMx</td>
<td>YRD, China</td>
<td>2015</td>
<td>Emissions of NO\textsubscript{x} and VOCs</td>
<td>145</td>
</tr>
<tr>
<td>CAMx</td>
<td>YRD, China</td>
<td>Summer 2013</td>
<td>Emissions of NO\textsubscript{x} and VOCs</td>
<td>146</td>
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<tr>
<td>CAMX</td>
<td>PRD, China</td>
<td>2006</td>
<td>Emissions of NO\textsubscript{x} and VOCs</td>
<td>147</td>
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</table>

Though 2R approach is mainly used as current O\textsubscript{3} source analysis method, uncertainties remain. A single threshold (ratio indicator) might not be sufficient since both NO\textsubscript{x} and VOCs control O\textsubscript{3} formation simultaneously. Thus, the transition regime is introduced to improve measurement that O\textsubscript{3} attribute to both NO\textsubscript{x} and VOCs. Thus, 3R scheme is improved to estimate O\textsubscript{3} contributions from transition regime. Based on analysis of O\textsubscript{3} production efficiency and formation kinetics\textsuperscript{136}, production ratio of \((\text{H}_2\text{O}_2+\text{ROOH})/\text{HNO}_3\), as a widely used indicator, was reevaluated based on 2R scheme in SAPRC photochemical mechanism in a model based estimation\textsuperscript{53}. The transition regime is defined when ratio is between 0.047~5.142. 3R regime is updated and validated in 2018, its ability in providing understanding of O\textsubscript{3} attribution to NO\textsubscript{x} and VOCs carried out a higher accurate result O\textsubscript{3} contributions from its sources\textsuperscript{148}.

### 2.7 O\textsubscript{3} source apportionment in China

Severe O\textsubscript{3} pollution is reported in previous studies in eastern China with high 8h-O\textsubscript{3} concentration exceeding the Chinese National Ambient Air Quality Standard (CNAACS) of 82 ppb (160\(\mu\)g/m\textsuperscript{3}) especially in warm and dry summertime\textsuperscript{51}. Many studies analyzed sources of O\textsubscript{3} in China. Generally, a shifting trend from NO\textsubscript{x}-limited to VOCs-limited was observed in rural area as the latitude increases, and NO\textsubscript{x} emissions were estimated as the dominant precursors in southern China while rural regions in north China were classified as VOCs-sensitive area\textsuperscript{149}. Surface O\textsubscript{3} concentration in eastern China was more sensitive to photochemistry while the transport processes...
dominate the O₃ in western regions where the climate conditions such as cloud convections play an important role in forming O₃. Biogenic emissions were listed as one of the major sources that enhance O₃ formation in southeast and east China, and it also shift the dominant precursor from NOₓ to VOCs in these regions.

High O₃ episodes were frequently observed in many Chinese areas such BTH region, YRD, Sichuan Basin and PRD. Increasing O₃ concentrations were proved to associated with growth of NOₓ and VOCs emissions as the result from urbanization and economic development in recent years. It is also revealed that high concentrations in summertime were due to on-road vehicles emission of NOₓ and VOCs. Research has focused on O₃ and its source apportionment in high risk areas to assess the dominant sources. Results are provided as solid evidence for making a strategic policy to reduce O₃ pollution in China.

It was reported that 8h-O₃ concentration in YRD increased from 144 µg/m³ to 168 µg/m³ since 2013 to 2017. Emissions from industry and vehicle sectors were found to be as the major sources. Surface O₃ in Shanghai was briefly analyzed since it was one of the biggest cities in China located in YRD and suffered high summer O₃ concentration by more than 300µg/m³. A regional source apportionment study revealed that Shanghai was greatly affected by local emission which account for ~28.9% of total O₃. Contributions from emissions of surrounding regions also caused significant increases of O₃. Emissions from north Zhejiang provinces were estimated to associate with ~19.9% of total O₃ concentration in Shanghai. Sectoral source apportionment results revealed high contributions from industry (~39.2%), mobile source (~21.3%), biogenic (~13.0%) and power plants (~7.1%) in Shanghai. As one of major sources, biogenic emissions of VOCs were estimated to contribute maximum of 36 µg/m³ O₃ in YRD especially in rural area, it also enhanced daytime O₃ by maximum of ~15 µg/m³.
PRD is another high-risk area where O$_3$ is listed as the major air pollutant. High concentration episodes were always observed in autumn at urban regions with maximum of > 100 ppb$^{160,161}$. Local emissions were evaluated cause more than 50% (maximum of ~70%) of total O$_3$ formation, and mobile emission was the major source for high concentration episodes$^{116}$. Emissions from central and west PRD were transported to south regions and induced high concentration episodes with concentrations higher than 100 ppb under a low air pressure system and slow south wind$^{160}$. VOCs emissions were evaluated as dominant precursors in PRD, species such as p-xylene, 1,2,4-trimethylbenzene, 2-methyl-2-butene, 1-butene and α-pinene were listed as the dominant species. Besides, VOCs emissions were reported associate with ~64.1% of total O$_3$ formation potentials$^{162,163}$. Mobile source (40%) was also estimated as the major source of O$_3$ followed by biogenic emissions (29%)$^{164}$. An analysis in Guangzhou indicated a similar result of contribution from mobile emission while the second source was industrial emission rather than biogenic due to high urbanization and industrialization in this megacity$^{165}$.

As one of most polluted regions, NCP is facing severe O$_3$ pollution due to increasing emissions of NO$_x$ and VOCs. Emissions from Hebei and Shandong provinces enhanced the O$_3$ formation in summertime, which is always referred as the high concentration episode$^{166}$. High O$_3$ concentrations recorded in Beijing ranged from 80 to 159 ppb in urban area during summertime, and the major source was estimated to NO$_x$ emissions especially those from urban area$^{167,168}$. O$_3$ pollution in urban Beijing was also estimated due to emissions from Tianjin and the south Hebei province$^{169}$. Shandong was also reported to enhance O$_3$ concentration in high concentration episodes$^{170}$. Though O$_3$ pollution in NCP is getting worse, there is insufficient data to fully analyze O$_3$ source apportionment in this region. Without solid evidence to quantify the effects from emission sources, no effective controlling strategies could be implemented to reduce O$_3$ pollution.
in NCP; however increasing concern for this issue demands an improvement in air quality in capital regions. Thus, greater effort should be put to analyze O₃ and its source apportionment in NCP.

### 2.8 Conclusions

Four main methods for O₃ source analysis are reviewed in this chapter, and each approach has their own limitations and advantages. As the source sensitive methods, DDM and BFM provide limited information for source contribution from emissions. They miss information from complex nonlinear chemical reactions and potential contributions from removed sources. OSAT offers a much more reliable and simpler way to estimate source contributions to O₃. Tagged tracers help to identify the source contributions. However, non-reactive tracers in this method limit its ability to track source contribution during chemical reactions. An alternative method, the source-oriented approach, clearly quantifies O₃ contribution from its precursors. This method has a strong ability in tracking O₃ formation from non-linear chemical processes, O₃ formation from NOₓ and VOCs are involved. Thus, the tagged sources can be identified in simulation outputs. This method overcomes limitations in methods mentioned above and has been widely accepted in recent O₃ source apportionment studies. Though source-oriented approach has advantages in tracking sources of precursors, limitations also existed. In most case, the study domain is not dominated by single precursor, and is affected by seasons and regions. NOₓ- or VOCs-sensitive simulation might not be able to provide accurate source apportionment. 2R scheme is introduced to fix this issue, which solve most problem, but results would be varied due to application of different indicators. O₃ formations in “transition” regime also lead to uncertainties in 2R scheme. 3R is developed to overcome this issue as it which offers higher accuracy results of contributions from NOₓ and VOCs emissions.
Many studies analyzed O$_3$ source apportionment in China and pointed out that emissions from mobile vehicles, industry and biogenic cause high O$_3$ concentration. O$_3$ sensitivity to NO$_x$ and VOCs were also analyzed. BVOCs was revealed to enhance O$_3$ concentration significantly. However, insufficient studies have been conducted to analyze O$_3$ source apportionment in NCP which is one of the most polluted regions in China. More attention should be put on this area. As one of air pollutants, O$_3$ leads to serious risk in human health and ecological lost. Efforts are needed to improve accuracy in measuring O$_3$ from complex non-linear photochemical processes, such as evaluating a better regime indicator in 3R scheme for different locations. Choosing a reasonable source apportionment method also makes sense in different simulation purposes. Although these methods have their own limitations, they also provide realistic results in each study, which contributes to a better understanding of O$_3$ in the world.
CHAPTER 3. IMPROVING OZONE SIMULATION IN THE NCP

3.1 Introduction

Numerous studies have shown adverse environmental and public health impacts associated with tropospheric O$_3$ pollution $^5, ^{171, 172}$. O$_3$ exposure is associated with respiratory-related hospital admissions, cardiovascular diseases, school day loss, asthma-related emergency department visits, premature mortality, etc. $^{3-6}$. Fann, et al.$^{13}$ revealed that 4700 deaths and 36,000 life-year losses were due to long-term O$_3$ exposure based on O$_3$ concentration in 2005 across the continental United States. In China, around 55 to 80 thousand mortalities in 2015 were attributed to chronic obstructive pulmonary disease (COPD), and a total 816.04 million cumulative population was estimated exposed to 8h-O$_3$ concentrations ($>100 \mu g/m^3$)$^{14, 154}$. O$_3$ level in 2000 also induced 6.4%-14.9% yield loss of food crop, and estimated O$_3$ concentration in 2020 would cause 47.4 million metric tons loss of four grain crops produced in China $^{15}$.

Increasing O$_3$ concentration were reported in many studies. Country scale statistical analysis in 74 cities indicated that 8h- O$_3$ increased from ~69 ppb in 2013 to 75 ppb in 2015, and a 15% increase of non-compliant cities were also revealed with increasing O$_3$ level in China $^{69}$. An average increase rate of 1.13 ± 0.01 ppb/year of 8h- O$_3$ was observed in north of eastern China from 2003 to 2015, and total O$_3$ variations were due to short-term (36.4%), seasonal (57.6%) and long-term (2.2%) changes $^{16}$. About 50% of the days with O$_3$ concentration exceeding 80 ppb in Beijing-Tianjin region (maximum of 170 ppb) were reported during 1983-1986 $^{173}$. Significant increases were also observed in Mt. Tai with an average increase by 1.7 ppb/year in June and by 2.1 ppb/year in July to August during 2003-2015$^{17}$. Recent studies reveal that China is
experiencing severe O₃ pollution, but O₃ variations and its impact factors are not well studied. Lacking comprehensive analysis leads to a challenge in lowering O₃ pollution.

Chemical transport models (CTMs) are commonly used tools to understand the formation and transport of O₃. Li, et al.¹² analyzed the impacts of chemical production and transport on diurnal O₃ behaviors in Mt. Taï and revealed that regional transport and chemistry production contribute ~60 and ~25 ppb, respectively, in afternoon-maximum concentration in June 2006 based on results obtained from the Nested Air Quality Prediction Modeling System (NAQPMS). Yang, et al.²³ applied global three-dimensional Goddard Earth Observing System chemical transport model (GEOS-Chem) to analyze impacts of sulfate and nitrate on surface-layer O₃ concentration in China and indicated that sulfate dominates in O₃ increases while nitrate dominates in O₃ reductions. Hu, et al.²⁴ simulated tropospheric O₃ in the North China Plain (NCP) for 2015 summer by applying the Community Multiscale Air Quality (CMAQ) model and found that emissions from Shandong and Hebei make the largest contribution not only to the highest local O₃ concentration but also to Beijing and Tianjin. They also pointed out that most urban O₃ pollutions are mainly dominated by conditions sensitive to volatile organic components (VOCs), and figured out that emission control strategies in industry, residential and power plant sectors would make significant effects on reducing O₃ concentration. Though O₃ is receiving increasing attention, limited understanding of its variation and impacts require comprehensive analysis in China specially in the NCP.¹⁶, ¹⁷, ¹⁷⁴, ¹⁷⁵

CTMs are very useful for understanding O₃, but the accuracy is highly dependent on emission inventories. Several emission inventories covering China and surrounding regions are available for different simulation purposes.³⁷-³⁸ Inventories from regional to continental scales, for different pollutant species and emission sectors were created and were successfully applied
in O\textsubscript{3} simulation in China, including Emission Database for Global Atmospheric Research (EDGAR), Multi-resolution Emission Inventory for China (MEIC) and Regional Emission inventory in ASia (REAS)\textsuperscript{44-48}. However, to a large extent, these inventories are not entirely from bottom-up, leading to large uncertainties in simulation results\textsuperscript{50}. EDGAR and MEIC are two most widely used inventories in China, while their performances in O\textsubscript{3} simulation vary in years and regions\textsuperscript{41, 51}. Evaluating and improving their performance in O\textsubscript{3} prediction would provide convincing results for deeper understanding of O\textsubscript{3} formation, health risks, and design of controlling strategies.

This study applies the CMAQ model to estimate the pollution level and health risks of O\textsubscript{3} in the NCP during summer 2017 with the anthropogenic emission inventories of MEIC and EDGAR+ (improved version of EDGAR). O\textsubscript{3} variations and the impacts from meteorological conditions and precursors emissions are discussed in detail.

3.2 Methods

3.2.1 Model description

O\textsubscript{3} concentrations are simulated using the CMAQ model v5.0.1\textsuperscript{176, 177} in 12km×12km horizontal resolution domain (Figure 1) that covers NCP including Beijing, Tianjin, Hebei, Shandong, part of Henan, Jiangsu, Anhui and Inner Mongolia (note that the map is generated by using NCAR Command Language (NCL)\textsuperscript{178}). Initial and boundary conditions are both generated by simulation on coarse domain (36 km ×36 km) which covers mainland China and part of surrounding countries. Photochemical mechanism SAPRC-11\textsuperscript{177} and aerosol chemistry mechanism AERO6\textsuperscript{179} are used. The Weather Research and Forecasting (WRF) v 3.7.1\textsuperscript{177, 180, 181} model is applied to generate meteorological inputs with initial and boundary conditions from National Centers for Environmental Prediction (NCEP) FNL (Final) Operational Global Analysis.
Meteorology-Chemistry Interface Processor (MCIP) v4.2 is applied to convert WRF outputs into CMAQ ready meteorological inputs. Different anthropogenic emission inventories are re-gridded to designed domain by using the Spatial Allocator. The Model for emissions of Gases and Aerosols from Nature (MEGAN) is used for biogenic emissions and the Fire Inventory from NCAR (FINN) provides biomass burning emissions.

Figure 1. Simulation domains. Coarse domain (36km by 36km) covers mainland China and part of surrounding countries. NCP (d02) is included as the finer domain (12km by 12km).

3.2.2 Case description

3.2.2.1 EDGAR+ inventory

As precursors of \(O_3\) production \(NO_x\) and VOCs play important roles in \(O_3\) simulation. Two anthropogenic emission inventories with modified \(NO_x\) and VOCs are applied in this study for
comparison. In first scenario, which is referred as “EDGAR+” hereinafter, anthropogenic emissions of VOCs and NO\textsubscript{x} from EDGAR\textsuperscript{186} for China are scaled to 2012 (off-road), 2015 (industry, residential, on-road and energy), and 2016 (industry, residential, on-road and energy for Beijing) to represent as in 2017. Scaling factors for VOCs and NO\textsubscript{x} are shown as in Table 5 and Table 6. On-road emissions are scaled down to the national total given for 2017 in China Vehicle Environmental Management Annual Report (http://dqhj.mee.gov.cn/jdchjgl/zhgltd/201806/P020180604354753261746.pdf). Emissions from energy, residential and industry sectors are scaled down from KNMI (Royal Netherlands Meteorological Institute) DECSO (Daily Emission estimates Constrained by Satellite Observation) based on Ozone Monitoring Instrument (OMI) data\textsuperscript{187, 188} to match year-on-year reduction rate given for 2016 (4%) and 2017 (4.9%) in Government Working report. NO\textsubscript{x} emissions in off-road and agriculture remain as in 2012 since there is not enough evidence to determine scaling factors for them.

Table 5. Scaling factors for VOCs emissions in NCP

<table>
<thead>
<tr>
<th></th>
<th>Agriculture</th>
<th>Residential</th>
<th>Industry</th>
<th>Energy</th>
<th>On-road</th>
<th>Off-road</th>
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<tr>
<td>Beijing</td>
<td>3.64</td>
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<td>1.19</td>
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Table 6. Scaling factor for NO\textsubscript{x} emissions in NCP

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</tr>
</tbody>
</table>

3.2.2.2 MEIC inventory

In another scenario, MEIC\textsuperscript{189} (http://www.meicmodel.org), developed by Tsinghua University, provides monthly NO\textsubscript{x} and VOCs emissions from transportation, residential, power, industry and agriculture in China\textsuperscript{190, 191}. Latest version for 2016 is applied to represent emissions in 2017 for this work. MEIC allows for gridding to user specific domain based on its flexible spatiotemporal and sectoral resolution \textsuperscript{192}. Emission for all sectors are estimated at provincial or county level and allocated to user-specific grids except for power sector which are calculated with unit-based method for individual plants\textsuperscript{15, 193}. In this study, MEIC is applied in CMAQ simulation with same meteorological inputs and model settings as in the EDGAR+ case. Total emissions of NO\textsubscript{x} and VOCs for both scenarios and their differences are shown in Figure 2, while total emission rates from each source are listed in Table 7 and Table 8.
Figure 2. Averaged NO\textsubscript{x} and VOCs emission rates from MEIC and EDGAR+ and their differences (subtracting EDGAR+ by MEIC) in summer 2017. Units are tons/month.

Table 7. NO\textsubscript{x} emission from each source for different inventory in NCP 2017 summer.

<table>
<thead>
<tr>
<th>Source</th>
<th>MEIC (10\textsuperscript{4} ktons/month)</th>
<th>EDGAR+ (10\textsuperscript{4} tons/month)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Agriculture</td>
<td>NA</td>
<td>Agriculture 6.19</td>
</tr>
<tr>
<td>Residential</td>
<td>4.18</td>
<td>Residential 3.57</td>
</tr>
<tr>
<td>Power</td>
<td>60.73</td>
<td>Energy 38.58</td>
</tr>
<tr>
<td>Industry</td>
<td>106.34</td>
<td>Industry 53.41</td>
</tr>
<tr>
<td>Transportation</td>
<td>83.05</td>
<td>On-road 38.10</td>
</tr>
<tr>
<td>NA</td>
<td>NA</td>
<td>Off-road 12.32</td>
</tr>
<tr>
<td>Total</td>
<td>254.30</td>
<td>Total 152.16</td>
</tr>
</tbody>
</table>

Table 8. VOCs emission from each source for different inventory in 2017 summer.

<table>
<thead>
<tr>
<th>Source</th>
<th>MEIC (10\textsuperscript{3} ktons/month)</th>
<th>EDGAR+ (10\textsuperscript{3} ktons/month)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Agriculture</td>
<td>NA</td>
<td>Agriculture 1.90</td>
</tr>
<tr>
<td>Residential</td>
<td>4.21</td>
<td>Residential 3.15</td>
</tr>
<tr>
<td>Power</td>
<td>0.11</td>
<td>Energy 0.35</td>
</tr>
</tbody>
</table>

(Table cont’d)
### 3.4 Results and discussions

#### 3.4.1 Overall performance

Predicted meteorological conditions (temperature (T), wind speed (WS), wind direction (WD) and relative humidity (RH)) from WRF for the simulation period are validated using observed data from National Climate Data Center (NCDC, https://www.ncdc.noaa.gov/). A total of 108 stations are involved. The mean bias (MB), gross error (GE) and root mean squared error (RMSE), as well as mean observation (OBS) and prediction (PRE) of meteorological parameters are shown in Table 9. Statistical results are compared with benchmarks from Emery, et al. 194. Generally, WRF slightly over-predicts temperature and wind speed but underestimates RH in summer. Uncertainties of these biases are believed to result from the model itself including domain resolution, model configuration and parameterization 195. Though biases exist, predictions from WRF are normally accepted in previous work over China with similar statistical results 196, 197.

<table>
<thead>
<tr>
<th></th>
<th>MEIC (10^3 ktons/month)</th>
<th>EDGAR+ (10^3 ktons/month)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Industry</td>
<td>24.77</td>
<td>16.15</td>
</tr>
<tr>
<td>Transportation</td>
<td>6.50</td>
<td>On-road 5.66</td>
</tr>
<tr>
<td>NA</td>
<td>NA</td>
<td>Off-road 0.29</td>
</tr>
<tr>
<td>Total</td>
<td>35.58</td>
<td>Total 27.50</td>
</tr>
</tbody>
</table>

Table 9. Summertime model performances of meteorological conditions in NCP for temperature (T), wind speed (WS), wind direction (WD) and relative humidity (RH).

<table>
<thead>
<tr>
<th></th>
<th>T (℃)</th>
<th>WS (m/s)</th>
<th>WD (°)</th>
<th>RH (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>OBS</td>
<td>24.32</td>
<td>3.27</td>
<td>168.99</td>
<td>63.41</td>
</tr>
<tr>
<td>PRE</td>
<td>25.35</td>
<td>3.82</td>
<td>169.89</td>
<td>58.40</td>
</tr>
<tr>
<td>MB</td>
<td>1.03</td>
<td>0.56</td>
<td>1.71</td>
<td>-5.01</td>
</tr>
<tr>
<td>RMSE</td>
<td>2.72</td>
<td>1.85</td>
<td>58.51</td>
<td>15.3</td>
</tr>
<tr>
<td>GE</td>
<td>2.04</td>
<td>1.42</td>
<td>41.89</td>
<td>11.79</td>
</tr>
</tbody>
</table>

1. Benchmark of MB for T, WS and WD is ±0.5, ±0.5 and ±10, respectively.
2. Benchmark of GE for T, WS and WD is 2, 2 and 30, respectively.
3. Benchmark of RMSE for WS and WD is 2 and 30, respectively.
8h-O₃ observations from CNEMC are used to validate model performance on O₃. Table 10 shows the comparison of model and predicted concentrations in 11 major cities in the NCP from June to August 2017, together with statistics including averaged observations (OBS), averaged predictions (PRE), the mean fractional bias (MFB), the mean fractional error (MFE), the normalized mean error (NME) and the normalized mean bias (NMB). For cities with multiple monitoring stations, averaged concentrations are applied. Different cutoffs for O₃ (from 40 to 60 ppb) are used to analyze the performance of the model as suggested by the US EPA. In this study, 8h-O₃ concentrations higher than 30 ppb are included in analysis based on a previous study.

Table 10. Model performances in 11 major cities in NCP for 8h-O₃ simulation using EDGAR+ (E) and MEIC (M). Units are ppb for OBS and PRE. Bold represents the statistical result exceeds criteria.

<table>
<thead>
<tr>
<th>City</th>
<th>Baoding</th>
<th>Beijing</th>
<th>Datong</th>
<th>Hohhot</th>
<th>Jinan</th>
<th>Shijiazhuang</th>
<th>Taiyuan</th>
<th>Tangshan</th>
<th>Tianjin</th>
<th>Xuzhou</th>
<th>Zhengzhou</th>
</tr>
</thead>
<tbody>
<tr>
<td>OBS</td>
<td>83.13</td>
<td>71.98</td>
<td>63.14</td>
<td>67.53</td>
<td>71.26</td>
<td>72.21</td>
<td>72.38</td>
<td>73.24</td>
<td>70.60</td>
<td>70.71</td>
<td>78.84</td>
</tr>
<tr>
<td>PRE (M)</td>
<td>78.17</td>
<td>80.62</td>
<td>65.17</td>
<td>63.76</td>
<td>71.77</td>
<td>79.10</td>
<td>67.99</td>
<td>51.47</td>
<td>68.19</td>
<td>65.08</td>
<td>74.3</td>
</tr>
<tr>
<td>PRE (E)</td>
<td>73.98</td>
<td>75.35</td>
<td>62.06</td>
<td>61.55</td>
<td>68.51</td>
<td>79.45</td>
<td>69.68</td>
<td>65.83</td>
<td>62.55</td>
<td>62.73</td>
<td>73.75</td>
</tr>
<tr>
<td>MFB (M)</td>
<td>-0.05</td>
<td>0.11</td>
<td>0.05</td>
<td>-0.05</td>
<td>0.03</td>
<td>0.09</td>
<td>-0.05</td>
<td>-0.4</td>
<td>-0.15</td>
<td>-0.07</td>
<td>-0.06</td>
</tr>
<tr>
<td>MFB (E)</td>
<td>-0.09</td>
<td>0.09</td>
<td>-0.03</td>
<td>-0.11</td>
<td>-0.01</td>
<td>0.06</td>
<td>-0.09</td>
<td>-0.17</td>
<td>-0.21</td>
<td>-0.06</td>
<td>-0.05</td>
</tr>
<tr>
<td>MFE (M)</td>
<td>0.20</td>
<td>0.25</td>
<td>0.14</td>
<td>0.16</td>
<td>0.17</td>
<td>0.23</td>
<td>0.19</td>
<td>0.49</td>
<td>0.40</td>
<td>0.21</td>
<td>0.16</td>
</tr>
<tr>
<td>MFE (E)</td>
<td>0.15</td>
<td>0.29</td>
<td>0.14</td>
<td>0.15</td>
<td>0.18</td>
<td>0.16</td>
<td>0.14</td>
<td>0.29</td>
<td>0.3</td>
<td>0.22</td>
<td>0.13</td>
</tr>
<tr>
<td>NME (M)</td>
<td>0.20</td>
<td>0.32</td>
<td>0.17</td>
<td>0.15</td>
<td>0.19</td>
<td>0.26</td>
<td>0.20</td>
<td>0.39</td>
<td>0.39</td>
<td>0.21</td>
<td>0.15</td>
</tr>
<tr>
<td>NME (E)</td>
<td>0.14</td>
<td>0.34</td>
<td>0.15</td>
<td>0.14</td>
<td>0.19</td>
<td>0.17</td>
<td>0.13</td>
<td>0.26</td>
<td>0.26</td>
<td>0.22</td>
<td>0.12</td>
</tr>
<tr>
<td>NMB (M)</td>
<td>-0.02</td>
<td>0.20</td>
<td>0.09</td>
<td>-0.03</td>
<td>0.06</td>
<td>0.15</td>
<td>-0.02</td>
<td>-0.27</td>
<td>-0.01</td>
<td>-0.03</td>
<td>-0.04</td>
</tr>
<tr>
<td>NMB (E)</td>
<td>-0.07</td>
<td>0.17</td>
<td>-0.01</td>
<td>-0.09</td>
<td>0.02</td>
<td>0.09</td>
<td>-0.08</td>
<td>-0.12</td>
<td>-0.15</td>
<td>-0.03</td>
<td>-0.04</td>
</tr>
</tbody>
</table>
Figure 3 and Table 10 indicates that simulations for each inventory generally agree well with observed O$_3$ concentrations in NCP. MEIC always predicts higher O$_3$ concentration than EDGAR+ except in Tangshan and Taiyuan. Over-predictions occur in Beijing, Datong, Jinan and Shijiazhuang for MEIC. It is noted that significant exceedances are observed in Beijing and Shijiazhuang for MEIC. On the other hand, EDGAR+ usually under-predict O$_3$ in this period. The NMB in most cities match the US EPA criteria of $\pm 0.15$ except in Tangshan for MEIC. Similar outcomes are observed in the NME. The NME for both scenarios generally agree well with US EPA suggested criteria of 0.25, but there are 3 and 1 exceedances for MEIC and EDGAR+, respectively. It is noted that the only exceedance in EDGAR+ is 0.29 (Tangshan), but 3 exceedances are observed in MEIC with one extreme case (Tangshan, 0.32). The MFB and MFE in EDGAR+ match suggested criteria of $\pm 0.15$ and 0.35 with only one slight exceedances in Tangshan (MFB of -0.16). The MFB and MFE for MEIC also indicates that model results meet performance goals in most cases except in Tangshan where both indices are not within suggested criteria. Based on statistical results, EDGAR+ has better performance in major cities in NCP. These major cities generally represent the air quality in the NCP, thus, both inventories result in satisfactory model performances and are reliable for further analysis in this study. Though uncertainties of O$_3$ simulation are associated with meteorological field, emissions, model treatment, and configurations, statistical results indicate the CMAQ model is capable of estimating short/long term O$_3$ concentrations variations and effects in NCP.
3.4.2 Temporal and spatial variations

Figure 4 illustrates the comparison of averaged daily 8h-O$_3$ concentration from prediction and observation in 8 major cities in NCP from June to August in 2017. Generally, predicted concentration from EDGAR+ and MEIC agree well with observation. Results from both inventories successfully match the absolute level and temporal variations in major cities, even though biases occur in specific period. It is noted that predictions in late June and early July are mostly lower than observations for most cities (except Shijiazhuang and Zhengzhou) especially
when O₃ concentration is higher than 100 ppb. Unexpected biases exist for many reasons such as uncertainties in meteorological conditions, inventories and model treatment and configuration. In Beijing, under-predictions (~30 ppb) also occur in the beginning of August when O₃ concentrations are ~120 ppb. Over-predictions are observed in late July and early August and part of late August exceeding > 40 ppb. This uncertainty may due to uncertainties in precursor’s emission (such as NO, NO₂ and VOCs) inventories. Simulation in Tianjin indicates that EDGAR+ has higher accuracy in June and July but fail in matching variations in early August. MEIC yields similar predictions before mid-July but result in under-predictions in late July, and it shows a better performance in August than EDGAR+. There are clear differences between EDGAR+ and MEIC in Shijiazhuang before end of July, with MEIC predicting significantly higher concentration (10~30 ppb) than EDGAR+. Both inventories over-predict by ~50 ppb on around July 22nd. Over-predictions are also observed in Jinan during the same period. Another significant over-prediction is observed in Xuzhou at the end of July and beginning of August where the observation is lower than 60 ppb. Simulations in Hohhot generally agree well with observation except two significant under-prediction periods (late June to early July and early August). Zhengzhou also has great agreement with observation except that specific extreme bias occurs in middle June and early August. Generally, EDGAR+ and MEIC predict similar O₃ concentration, and MEIC predicts slightly higher concentration than EDGAR+ in most cities. Comparison between observations and model predictions help to point out that EDGAR+ has better predictions in summertime at most cities.
Figure 4. Average daily 8h-O$_3$ concentration in major cities. Results from EDGAR+ (E) and MEIC (M), observation (Obs) and statistical results (NMB) are shown in each row. Units for O$_3$ concentrations are ppb.

Average diurnal variation of 8h-O$_3$ concentration and corresponding meteorological conditions are shown in Figure 5. In Beijing, MEIC predicts significant higher concentration (~10 to 20 ppb) before noon time (12:00 pm) and lower after 15:00 pm till the sunrise in the next day.
compared with observation data while over-predictions in EDGAR+ are lower (~5 to 10 ppb) than MEIC during the day time compared with MEIC. Both EDGAR+ and MEIC over-predicts the peak value before noon time. In Beijing, EDGAR+ shows a higher sensitivity to temperature since peak concentrations are predicted when the temperature is also high while MEIC always predicts peak concentration ~2 hours ahead of EDGAR+. MEIC and EDGAR+ have similar performance in predicting concentration in Hohhot, and MEIC always predicts ~5 to 10 ppb higher concentration during the nighttime than EDGAR+. In Hohhot, MEIC and EDGAR+ always predict peak values at a similar time around noon time to afternoon (12:00pm – 18:00 pm) and agree well with the observations. MEIC predicts higher concentration during morning to noon time in Jinan, and a significant bias can be observed between MEIC and observation data. In contrast, EDGAR+ has a better accuracy in matching the daily peak value as well as daily variations in Jinan. EDGAR+ predicts lower concentration by ~5 to ~10 ppb in Shijiazhuang then MEIC while both inventories always over-predict peak concentration by ~10 ppb compared to observation data during noon time. Significant under-predictions of ~10 to 20 ppb are observed using both inventories at nighttime. Predictions in Tianjin indicate that both inventories perform well in matching the peak concentration around noon time (12:00 pm) while significant under-predictions are observed at nighttime with a maximum by more than 30 ppb before sunrise (~4:00 am). Predictions in Zhengzhou indicate that MEIC and EDGAR+ yield slightly over-estimates (5 ppb and 10 ppb for EDGAR+ and MEIC, respectively) O₃ concentration in daytime while significantly under-predicting (~10 ppb lower) at night. MEIC predicts ~5 ppb higher O₃ concentration in daytime when EDGAR+ match well with observation data in Xuzhou. However, EDGAR+ has a lower accuracy in predicting concentration before 6:00am, in which MEIC matches well with observed concentration.
Figure 5. Diurnal variations of 8h-O$_3$ from EDGAR+, MEIC and observation (Obs), temperature (T) and relative humidity (RH) in major cities. Units for O$_3$ concentration are ppb, for T are °C, for RH are %.
Generally, MEIC predicts a slightly higher (~5 ppb) concentration than EDGAR+ before noon time (12:00 pm) but not higher or even lower when the temperature is high, and RH is at a low value in the afternoon. It is noted that both inventories predict O\textsubscript{3} peak value well or only slightly higher (< 5 ppb) in diurnal variations. In nighttime, the model predicts lower concentration especially the time before 6 am. In other words, model has better performance in daytime. Variations in all cities indicate that O\textsubscript{3} concentrations are greatly affected by RH and temperature. Diurnal variation also reveals that high O\textsubscript{3} concentration is correlated to high temperature and low RH. In the meantime, it also provides valid evidence that EDGAR+ has a higher accuracy in predicting O\textsubscript{3} concentration in NCP.

Figure 6 shows the spatial distribution of averaged 8h-O\textsubscript{3} concentrations in the summer for MEIC and EDGAR+ and their differences. Overall, O\textsubscript{3} concentration increases from inner land to coastal area, from rural to urban area and around major cities in each province. For both inventories, high O\textsubscript{3} concentrations occur at Beijing, Tianjin, Hebei, coastal Shandong and Jiangsu and junction regions between Hebei, Shanxi and Henan with >100 ppb. It is noted that O\textsubscript{3} concentrations are also very high on surface of Bohai Sea with ~90 ppb. Concentrations in the rest of area range from ~60 to 80 ppb. Compared to MEIC, EDGAR+ predicts higher concentrations in eastern Tianjin, western Hebei, Qingdao and Yantai by ~10 ppb but lower concentration in the rest region, especially in Beijing, northern Shandong and southern Jiangsu by >10 ppb. Generally, MEIC predicts slightly higher O\textsubscript{3} concentrations in most of NCP and ocean surface above the Bohai Sea while EDGAR+ results in higher predictions in part of major cities. The differences between two scenarios are mainly due to emissions as shown in Fig 1. Higher emissions in MEIC induce higher O\textsubscript{3} concentrations in NCP, but since the O\textsubscript{3} formation is not a linear reaction from NO\textsubscript{x} and VOCs,
higher O₃ concentration in EDGAR+ is also due to lower emissions in specific regions such as in western Hebei province. Detailed analysis will be discussed in following sections.

![Image of 8h-O₃ concentrations in NCP for 2017 summer predicted by EDGAR+ and MEIC, and their differences (subtracting EDGAR+ by MEIC). Units are ppb.](image)

**Figure 6.** 8h-O₃ concentrations in NCP for 2017 summer predicted by EDGAR+ and MEIC, and their differences (subtracting EDGAR+ by MEIC). Units are ppb.

### 3.4.3 Peak episodes

There are 3 peak episodes observed during the simulation period including June 14ᵗʰ to 21ˢᵗ, June 22ᵗʰ to 29ᵗʰ and July 8ᵗʰ to 15ᵗʰ (Figure 7). O₃ variations in 8 major cities for these episodes are analyzed. Hourly 8h-O₃ in Figure 7 indicate the variation during peak episodes, in which peak daily 8h-O₃ concentrations are >100 ppb. In Beijing, peak values for each episode are ~120 ppb. Simulation results in June are mostly slightly lower than observation data while over-predictions on June 19ᵗʰ and July 11ᵗʰ with ~30 and 50 ppb higher than peak value, respectively, are shown in S4 and S6 for MEIC. On the other hand, predictions from EDGAR+ match better in these episodes with bias less than ±20 ppb. The model has higher accuracy in predicting high concentrations in Tianjin compared with in Beijing. Most peak values match well with observation as shown in S4 and S5 except on June 14ᵗʰ to 16ᵗʰ when under-prediction occurs in both scenarios. It is noted that over-prediction also existed on June 23ʳᵈ and July 9ᵗʰ though part of observation data is missing for these days. Peak concentrations are also caught in Shijiazhuang except on June 27ᵗʰ. EDGAR+
and MEIC match high concentration during peak episode, but they also over-predict on some days such as June 15\textsuperscript{th}, June 18\textsuperscript{th}, June 26\textsuperscript{th} and July 14\textsuperscript{th}. The peak value on June 15\textsuperscript{th} in Jinan is under-predicted. From July 8\textsuperscript{th} to 15\textsuperscript{th}, simulations mostly agree well with observed concentration with maximum bias on July 10\textsuperscript{th} with around 15-20 ppb. Simulations in Hohhot indicate that predictions from MEIC correspond much more closely to the peak concentration in the study. Similar situation also occurs in Zhengzhou that peak concentrations are matched well on June 25\textsuperscript{th} and July 10\textsuperscript{th} but not on June 20\textsuperscript{th} when prediction are \textasciitilde20 ppb lower. Peak concentrations are under-predicted in Datong on June 15\textsuperscript{th}, 28\textsuperscript{th} and July 13\textsuperscript{th} while predictions during the other peak episodes match well and slightly higher than observations except on June 16\textsuperscript{th} where the simulation results are extremely higher. Spatial plots of 8h-\textsubscript{O\textsubscript{3}} concentrations in 3 episodes (Fig. 6) indicates that EDGAR\textsuperscript{+} predicts higher 8h-\textsubscript{O\textsubscript{3}} than MEIC in most regions especially in west Hebei and the Bohai Sea (\textasciitilde10 to 30 ppb) but lower in some major cities such as Beijing, Tianjin, Shijiazhuang and Jinan by 10 ppb.
Figure 7. Hourly 8h-O$_3$ concentration at major cities for peak episodes. Units are ppb.
Compared with averaged summertime differences in Figure 8, EDGAR+ predicts a higher concentration during peak episodes although its emissions of O3 precursors are lower than those in MEIC. High concentrations occurring during these episodes might be due to specific climate conditions and emissions. Figure 9 shows climate conditions (average temperature (T), relative humidity (RH), wind speeds (WS) and wind directions (WD)) in 3 episodes. Spatial variation of meteorological conditions indicates that high O3 concentrations always occur in locations where the temperature is higher than in the surrounding region such as in south Hebei and north Henan. Low relative humidity and slow wind speed are also observed in these regions to be associated with high O3 concentration. It is obvious that high temperature, low RH and steady low air flow conditions are associated with high O3 production in NCP. However, the opposite situation occurs in Bohai sea where temperature is lower than surrounding area with higher RH and WS. After comparison, it is noted that wind direction has less influence on O3 production then other variables.
Figure 8. Spatial distribution of 8h-O₃ concentrations in 3 peak concentration episodes predicted by EDGAR+ and MEIC, and their differences (subtracting EDGAR+ by MEIC). Units are ppb.
Figure 9. Meteorological conditions in NCP during 3 peak episodes. T represents temperature, RH represents relative humidity, WS represents wind speed, red arrows in the third row represent wind direction, arrow length represents wind speed.

Besides meteorological conditions, emission of O$_3$ precursors also help to explain high concentration occurrences in NCP. Figure 2 (right panel) shows the differences in NO$_x$ and VOCs emissions between EDGAR+ and MEIC which are associated with differences in O$_3$ concentrations in these periods. As emissions are generated using weekly data so the emissions in three peak episodes are same (for five workdays and two weekend days). Significantly lower NO$_x$ emission is noticed in south Hebei, north Henan and northwest and west Shandong in EDGAR+.
while VOCs emission in these regions are not significant lower or ever higher than MEIC. High O₃ concentration in central NCP could mainly be due to NOₓ emissions. lower NOₓ leads to high O₃ concentration when VOCs emission is not too low. However, in Beijing and Tianjin, both NOₓ and VOCs emissions in EDGAR+ are lower than in MEIC. As a result, EDGAR+ predicts lower O₃ in these regions. In south Shandong province, lower NOₓ emission with higher VOCs emission barely change O₃ formation in these regions. Overall, since O₃ concentration is greatly dependent on emission of precursors, changes of NOₓ and VOCs would influence O₃ concentration in different direction. Compared to MEIC, significantly lower (>200 tons/month) of NOₓ and similar (difference within 5 tons/month) VOCs emissions in EDGAR+ induce more O₃ formation; less O₃ is predicted when both NOₓ and VOCs emissions are significantly lower (>200 tons/month and >10 tons/month, respectively); O₃ concentrations are barely changed (within ±10 ppb) when NOₓ emissions are significantly lower (>200 tons/month) and VOCs emissions are significantly higher (>10 tons/month) in EDGAR+. Due to nonlinear reactions of O₃ formation, NOₓ and VOCs play different roles in forming O₃ under different conditions. It is concluded that a higher concentration is always associated with slight lower emission under high temperature, low RH and steady wind field. Though there might be some other reasons that could explain O₃ concentration variations such as solar radiation, cloud accumulation and concentration of particular matters (PM), analyzing impacts from changes of emissions and meteorological conditions helps to figure out the relationship between O₃ and its impact factors, which will provide deeper understanding of their impacts on forming and transporting O₃. It is also offered as evidence for designing strategies and policies to reduce O₃ pollution.
3.5 Conclusions

The WRF/CMAQ modeling system is applied to simulate O\textsubscript{3} concentrations in the NCP during summer 2017 and the results using EDGAR+ and MEIC are compared. Generally, both emission inventories perform well in predicting O\textsubscript{3} concentrations in major cities. Statistical metrics indicate that EDGAR+ performs better with fewer and smaller exceedances of suggested performance criteria compared to MEIC. EDGAR+ is slightly better in representing overall concentrations in NCP while MEIC shows better ability in predicting peak daily 8h-O\textsubscript{3} concentrations. EDGAR+ also shows higher accuracy in matching O\textsubscript{3} concentration in daytime. NO\textsubscript{x} and VOCs emissions play different roles in forming O\textsubscript{3} under different conditions, and high concentrations are always associated with slightly lower emissions under high temperature, low RH and steady wind field.
CHAPTER 4. OZONE SOURCE APPORTIONMENT IN THE NCP

4.1 Introduction

With its adverse impacts on human health, ground-level O$_3$ is receiving increasing attention in recent years in China$^{14,15,69}$. As one of the most polluted regions in China, the NCP is facing severe O$_3$ issues. A report pointed out that more than 50% of the days O$_3$ concentrations were higher than 80 ppb during 1983-1986 in central NCP (Beijing-Tianjin-Hebei region) with peak value of 170 ppb$^{173}$. Many studies also provided evidence that O$_3$ concentration increased from 1980 to 2003, with peak mixing ratio to be up to 286 ppb in Beijing in 2005$^{174,175,202}$. A long-term station recorded O$_3$ concentration in the NCP also indicated an increase of 1.13 ppb/yr during 2003-2015$^{203}$. Both long- and short-term analysis in the NCP show the increasing trend of O$_3$ concentration but not enough studies have analyzed O$_3$ and its sources. Thus, comprehensive analysis is necessary to better understand the impact factors and source of O$_3$ formation in this area.

Chemical transport models (CTMs) are widely used to simulate O$_3$ and understand its sources and impact factors. Source apportionment of O$_3$ is very important to quantify source contributions, which helps to design control strategies. But complex nonlinear reactions of O$_3$ precursors, nitrogen oxides (NO$_x$) and volatile organic compounds (VOCs), make it a challenge for model simulation. To determine O$_3$ contributions from NO$_x$ and VOCs, ratios of photochemical chain reaction production rates, widely known as regime indicators, are introduced to classify O$_3$ contribution. Traditional two regime (2R) approach was implemented in the Community Multi-scale Air Quality (CMAQ) model$^{52}$ by applying indicator ratio of H$_2$O$_2$/HNO$_3$ with correlation coefficients ranging from 0.58 to 0.99. An improved method applied production ratio of
(H₂O₂+ROOH)/HNO₃ as the indicator in three regime scheme (3R) was introduced into CMAQ and compared with traditional 2R method, and results indicated higher contributions from NOₓ in high O₃ concentration regions in China by 5 to 15 ppb. 3R scheme was shown to provide more accurate O₃ contribution from its precursors. Traditional O₃ Source Apportionment Method (OSAT) uses non-reactive tagged tracers in transport and reaction processes to track O₃ sources by splitting the concentration changes based on emission ratios. An improved source-oriented method that applied in CMAQ using reactive-tracers in all processes are also used in O₃ source apportionment. O₃ formation is strongly sensitive to concentrations of precursors, and its source contributions are varied spatiotemporally, thus improved source apportionment technique is necessary for more accurate results. In this study, improved source-oriented version of CMAQ combined with 3R scheme will be applied in simulating O₃ contribution from its precursors.

Due to the ability in irritating respiratory and cardiovascular system, O₃ causes cough, asthma, lung function reduction and other diseases. It was reported that 0.52% and 0.64% increases of daily mortality and cardiovascular/respiratory mortality are associated with 10 ppb increase of weekly O₃ concentration. It was also reported that 10 µg/m³ increases of 8h-O₃ were related to 0.42%, 0.44% and 0.50% increases of non-accidental mortality, cardiovascular mortality and respiratory mortality, respectively, in China. However, there are insufficient studies focusing on O₃ source attribution to these human health risk.

This study will quantify O₃ contribution to sectoral/regional emissions of NOₓ and VOCs by using source-oriented version CMAQ model with improved 3R scheme in NCP. Regional and city-scale analysis provide a comprehensive understanding of source impacts in high O₃ concentration season. Results from this chapter would provide O₃ source contribution for further analysis of O₃ impacts on human health, economic benefits and ecosystem.
4.2 Methods

4.2.1 Model description

O$_3$ concentrations are simulated by applying the CMAQ model (version of 5.0.1) with AERO6 aerosol chemistry mechanism and SAPRC99 photochemical mechanism$^{179, 207}$. The Weather Research and Forecasting (WRF) version of 3.7.1 generates meteorological inputs by using initial condition (ICs) and boundary conditions (BCs) from WRF preprocessing system (WPS), which applies FN1 operational global analysis data from National Center for Atmospheric Research (NCAR, http://dss.ucar.edu/datasets/ds083.2/). Meteorological inputs are converted to CMAQ ready format by using Meteorology-Chemistry Interface Processor (MCIP) v4.2. In this study, improved Emission Database of Gas and Atmospheric Research (EDGAR+), which is validated in previous chapter, provides anthropogenic emissions from sources of agriculture, residential, energy, industrial, off-road and on-road. Biogenic emissions are provided by the Model for Emissions of Gases and Aerosols from Nature (MEGAN) $^{184}$, and Fire Inventory from NCAR (FINN) $^{185}$ is used to generate open-burning (wildfires) emissions. NO$_x$ and VOCs emission from these sectors in NCP are shown in Figure 10 and Figure 11.
Figure 10. Averaged sources of NO\textsubscript{x} emissions in NCP 2017 summer. Units are tons/month.

Figure 11. Averaged sources of VOCs emissions in NCP 2017 summer. Units are tons/month.

Tagged tracers are introduced into source-oriented version CMAQ in this work, which have been successfully applied in many previous studies\textsuperscript{134, 208, 209}. Generally, atomic oxygen (O(3P)) that created in photochemical reaction between O\textsubscript{3} precursors are tagged for each emission sources following reactions, which are recorded in previous works\textsuperscript{135}.

Equation 12:

\[ NO_{2n} \xrightarrow{h\nu} NO_n + O(3P)_n, n = 1, 2, 3 \ldots, N \]
Equation 13:

\[ O(3P)_n + O_2 \rightarrow O_3n, n = 1,2,3 \ldots, N \]

Equation 14:

\[ RH_n + HO \rightarrow R0_{2n} + H_2O, n = 1,2,3 \ldots, N \]

Equation 15:

\[ R0_{2n} + NO \rightarrow NO_{2n} + RO_n, n = 1,2,3 \ldots, N \]

Where \( n \) represents the identification number of emission source, \( N \) represents total number of emission sources. \( NO_2 \) and \( NO \) are tagged for tracking \( NO_x \) attribution while reactive hydrocarbon (RH) are tagged for VOCs. Contribution rate (R) from NO to \( NO_2 \), which is from attribution of \( RO_2 \), can be calculated and presented as \( O_3 \) contribution from VOCs as shown in Equation 16 and Equation 17. \( F_n \) represents contribution from source \( n \), and \( O_{3tot} \) in this equation stands for net \( O_3 \) formation predicted in model. \( O_3 \) contribution from source \( n \) can be calculated following Equation 17 by adding these functions in air quality models.

Equation 16:

\[ F_n = \frac{R(NO_{2n})}{R(NO_{2tot})}, n = 1,2,3 \ldots, N \]

Equation 17:

\[ O_{3n} = F_n \times O_{3tot}, n = 1,2,3 \ldots, N \]

Besides source attribution, \( O_3 \) also sensitive to concentration of its precursors. Traditional approaches classified \( O_3 \) sensitivity to \( NO_x \) and VOCs to \( NO_x \)-limited, VOCs-limited and 2 regime scheme (2R) when the indicator ratio of \( PH_2O_2/PHNO_3 \) is \( \approx 0.35 \). An improved 3 regime (3R) scheme, which is approved provides higher accuracy in predicting \( O_3 \) contribution from \( NO_x \) and
VOCs in high polluted region in China, will be applied in this work. The indicator in this scheme is defined between 0.047~5.142\(^3\), \(O_3\) production in this regime is classified contributions from both NO\(_x\) and VOCs.

4.2.2 Model application

\(O_3\) concentrations are simulated using the CMAQ model v5.0.1 with a coarse domain (36km×36km) covering China (Figure 12) and nested finer domain (12km×12km) covering the NCP, including complete Beijing, Tianjin, Hebei, Shandong and Shanxi and partial of Henan, Jiangsu, Anhui, Inner Mongolia and the three northeast provinces. Both sectoral and regional source apportionment will be conducted in this work. Based on classification in EDGAR+ (improved version of EDGAR as in Chapter 2), biogenic and open-burning sources, emissions are grouped into 8 sources, including agriculture, energy, industrial, residential, on-road, off-road, biogenic and wildfires.

Regional tracers are based on 9 provincial groups as shown in Figure 12, including Beijing, Tianjin, Hebei, Shandong, north (Heilongjiang, Liaoning, Jilin and Inner Mongolia), West (Shaanxi, Shanxi, Xinjiang, Ningxia and Qinghai), YRD (Zhejiang, Jiangsu and Shanghai), central China (Henan, Hubei, Anhui) and others (emissions from other countries and the rest provinces in China). It should be noted that only Beijing, Tianjin, Hebei, Shandong and Shanxi are fully included in the finer domain, thus emission tracers are tagged only on emissions that are involved in this domain.
Figure 12. Simulation domains and regional classifications for emissions. Coarse domain (36km by 36km) covers mainland China and part of surrounding countries. NCP (d02) is included as the finer domain (12km by 12km).

To compare results using different O\textsubscript{3} regime schemes, four scenarios are created to evaluate O\textsubscript{3} contributions from sectoral emission sources. O\textsubscript{3} regime schemes of 1) 3R scheme; 2) 2R scheme; 3) NO\textsubscript{x}-limited scheme and 4) VOCs-limited scheme are applied in source-oriented simulation with same domain and mechanism settings.

4.3 Results and discussions

4.3.1 Overall O\textsubscript{3} in coarse and finer domains

O\textsubscript{3} concentrations in this chapter are generated from CMAQ using same mechanism and settings as in Chapter 2, O\textsubscript{3} source-oriented technique makes no change to overall O\textsubscript{3} predictions, thus model performances are validated, and the results are reliable for further analysis. In Figure 13, summertime 8h-O\textsubscript{3} concentration and its contribution from background (BG) and emissions (EM) in coarse domain are illustrated. It is obvious that NCP and YRD are in the highest
concentration region with more than 80 ppb in summertime. Concentrations in west and south China are lower than 50 ppb except in the Sichuan Basin (~60 ppb), which is known as another high-risk area. From this simulation, most O\textsubscript{3} formation in low concentration area attributes to BG, while anthropogenic and natural emissions have higher contributions to NCP and YRD by more than 50 % (> 40 ppb) of total 8h-O\textsubscript{3}. Emissions play the essential roles in NCP, thus sectoral and regional (provincial) contributions are investigated in following sectors.

Figure 13. Summertime 8h-O\textsubscript{3} concentration in China and their contribution from background (BG) and emissions (EM). Units are ppb.

From Figure 14, YRD, Shandong and Hebei are major sources to NCP, they contribute around 20 ppb to surrounding regions and attribute maximum of 35 ppb locally. Though Beijing and Tianjin have limited city area, emissions from these cities also cause maximum of 20 ppb to local concentration. Contribution from north, central and other regions barely account for high concentration in NCP. Sectoral contribution (Figure 15) reveals that energy and industry are major sources (15-20 ppb) in NCP, followed by on-road (5 ppb) and biogenic emissions (5ppb). Emissions from other sources provide limited O\textsubscript{3} in NCP. It is concluded that emissions have strong effects in NCP and their contributions to O\textsubscript{3} are complicated, thus comprehensive analysis for finer resolution is needed for more clear understanding.
Figure 14. Summer 8h-O$_3$ contribution from regional emission sources in China. Units are ppb.

Figure 15. Summer 8h-O$_3$ contribution from sectoral emission sources in China. Units are ppb.
Figure 16 shows summertime 8h-O$_3$ concentration in NCP and its contributions from BG and EM. Generally, O$_3$ is high in central NCP with ~80 ppb (maximum of ~90 ppb at southwest Hebei and north Henan province). High concentration also occurs in Beijing which is the capital city of China. Background O$_3$ is high in northwestern NCP (~40 ppb) rather than central region (30 ppb). At the meantime, emissions attribute ~40-50 ppb (~50% of total O$_3$) to central NCP, where the concentration is high, but less contributions are illustrated in surrounding regions with lower than 35 ppb (~30%). High contributions from EM are found in Beijing, southwestern Hebei and northwest Henan with maximum contributions are more than 50 ppb (>50%). It is concluded that high concentrations in central NCP are mainly due to emissions rather than background O$_3$. Emissions lead high concentration in NCP, thus comprehensive analysis is needed. Regional and sectoral contribution will be analyzed in following sectors.

![Figure 16](image)

Figure 16. Summertime 8h-O$_3$ concentration in NCP and their contribution from background (BG) and emissions (EM). Units are ppb.

### 4.3.2 Sectoral and regional contribution

Figure 17 reveals sectoral contributions to summertime 8h-O$_3$ concentration. Industry and on-road emissions are major sources in the NCP. Industry contributes to more than 50% (maximum of ~24 ppb) to O$_3$-EM in central NCP (southern Hebei, Shanxi and western Shandong), which accounts for more than 25% of total 8h-O$_3$ in these regions. On-road emissions account for ~30%
of O$_3$-EM in Beijing, Tianjin and central Hebei with maximum of ~50% (~10 ppb). High contributions from energy sector are found at specific cities and regions in southern and southwestern NCP by ~16 ppb, which accounts for maximum of 30% to total O$_3$. Off-road emissions contribute ~6 ppb to O$_3$ along inland water channels in NCP and cause more than 10 ppb O$_3$ above sea surface east to NCP. Residential, agriculture and biogenic emissions cause less than 5 ppb in NCP, respectively. Wildfires also have low contributions except in south western Hebei with maximum of ~5 ppb.

![Figure 17](image1.png)

Figure 17. Summertime 8h-O$_3$ contribution from sectoral emissions in NCP. Units are ppb.

Figure 18 reveals regional contributions to summertime 8h-O$_3$ concentration. O$_3$-EM is generally affected by local emissions. For example, high concentrations in south Hebei, west Shandong, Shanxi and north Henan are greatly dependent on local emissions (~70%) except O$_3$ from background. Local emissions induce ~20 to 30 ppb O$_3$ in high concentration region (with maximum of ~35 ppb). It is noted that local emissions in Beijing and Tianjin provide maximum
of 20 ppb to local O$_3$ formation, and they induce limited effects on each other (less than 5 ppb). Due to being surrounded by Hebei, Beijing and Tianjin are affected by emissions from Hebei significantly with 10% of total O$_3$ from Hebei emissions (~10 ppb). Other provinces in NCP also result in slightly effects on O$_3$ formation in Beijing and Tianjin (less than 5 ppb). Local emissions always result in 10 ppb O$_3$ formation in conjunction area between neighbor provinces. At the meantime, effects from long-distance transport are also observed. For instance, emissions in YRD induce ~10 ppb O$_3$ in whole southwestern Shandong and contribute to ~5 ppb O$_3$ in southeastern Hebei. Emissions from central China also affect O$_3$ concentration in NCP by ~5 to 10 ppb. Emissions from other regions (the rest provinces in China and other countries) have limited impacts in NCP, but they affect O$_3$ formation above ocean surface east to NCP by ~10 ppb.

Figure 18. Summertime 8h-O$_3$ contribution from regional emissions in NCP. Units are ppb.
4.3.3 Source apportionment of O$_3$ precursors

O$_3$ contributions from total NO$_x$ and VOCs emissions are shown in Figure 19. Generally, NO$_x$ accounts for more than 50% (maximum of ~80%) O$_3$-EM in most provinces except Beijing and Tianjin. NO$_x$ contributes to more than 25 ppb O$_3$ formation in NCP, high contributions occur in central NCP, which refers to south Hebei, north Henan and west Shandong with contributions are evaluated to ~40 ppb. It is concluded that NO$_x$ is the major precursor in most NCP while opposite phenomenon is observed at Shijiazhuang and southwestern Tianjin where VOCs dominates O$_3$ formation with more than 20 ppb while NO$_x$ induces ~10 ppb only. VOCs emissions also dominate in specific cities such as Tianjin, Shijiazhuang, Baoding and Qingdao. VOCs contributes less than 10 ppb to O$_3$ in NO$_x$ dominant regions. O$_3$ contributions from NO$_x$ and VOCs emissions (by sectoral and regional groups) are detailed analysis from following discussions.

Figure 19. summer 8h-O$_3$ contribution from NO$_x$ (8h-O$_3$N) and VOCs (8h-O$_3$V) in NCP. Units are ppb.

Figure 20 shows regional contribution of summertime O$_3$ from NO$_x$ and VOCs. Consisted with previous discussion, local emissions (both NO$_x$ and VOCs) dominate local O$_3$ formation. NO$_x$ contributes more than 20 ppb to local O$_3$ in high concentration regions such as south Hebei, north Henan and west Shandong, which account for ~70% of total O$_3$-EM in these regions. It is noted that local NO$_x$ emissions also have significantly impacts to surrounding provinces and regions. For
example, NO\textsubscript{x} emissions from YRD induce \textasciitilde5 to 10 ppb O\textsubscript{3} in Shandong, which accounts for approximately 20% of O\textsubscript{3}-EM. NO\textsubscript{x} dominant O\textsubscript{3} formation lead high concentration in NCP for most provinces except in Beijing and Tianjin. NO\textsubscript{x} accounts maximum of 40% O\textsubscript{3}-EM in Beijing while NO\textsubscript{x} emission from Hebei accounts for 20%. VOCs emission affects less in most NCP compared with NO\textsubscript{x} while VOCs also accounts for more than 30% of total 8h-O\textsubscript{3} in specific regions such as south Tianjin, Shijiazhuang, Tangshan, Taiyuan and Datong. Efforts from VOCs emissions are much more significantly than NO\textsubscript{x}, thus VOCs dominates O\textsubscript{3} formation in these regions.

Figure 20. Summertime NO\textsubscript{x} and VOCs regional contributions to 8h-O\textsubscript{3} concentration. Units are ppb.

Sectoral source apportionment results (Figure 21) reveal that O\textsubscript{3} is mainly relied on NO\textsubscript{x} emissions from all sources except biogenic emissions. Industry emissions induce maximum of \textasciitilde20
ppb O₃ formation related to NOₓ in central NCP. NOₓ emissions from energy sector also induce ~15 ppb in cities in south NCP. NOₓ emissions from on-road and off-road transportation form ~6 and ~9 ppb O₃ in NCP, respectively. It is noted that they also form more than 10 ppb O₃ above sea surface east to NCP. VOCs emissions barely result in O₃ formation (less than 2 ppb) for most sources except the emission from industry and biogenic. VOCs emissions from industry cause 5 to 10 ppb O₃ in specific cities such as Tianjin and Qingdao. High VOCs emissions from industry and on-road transportation help to explain their contributions to O₃ formation. Overall, NOₓ emissions from industry, energy and on-road transportation contribute to greatly in NCP, they provide ~75% of O₃-EM, which account for ~40% of total O₃ in NCP.
Figure 21. Summertime NO\textsubscript{x} and VOCs sectoral contributions to 8h-O\textsubscript{3} concentration. Units are ppb.

4.3.4 Comparison of 3R and other O\textsubscript{3} regime schemes

O\textsubscript{3} contributions from NO\textsubscript{x} and VOCs are calculated using different source analysis techniques. In 3R scenario, NO\textsubscript{x} and VOCs related O\textsubscript{3} formations in transition regime are classified into O\textsubscript{3}N and O\textsubscript{3}V already, respectively. The concentrations and differences between each scenario are shown in Figure 22. Basically, four source-oriented approaches predict same total O\textsubscript{3} concentration in NCP, different attributions to NO\textsubscript{x}, VOCs and background compared with 3R are shown. In first row, results from 3R indicate that high O\textsubscript{3} concentrations are always occurred in central NCP while north and northwest regions are under low concentration.
Figure 22. 8h-O₃ contributions from NOₓ (O₃N), VOCs (O₃V) and background (O₃-BG) in the 3R scenario (first row) and differences with 2R, NOₓ-limited and VOC-limited scenarios (subtracting 3R by the results from each case). Units are ppb.

Due to O₃ formations in NOₓ- and VOCs-limited cases only due to NOₓ and VOCs, thus the differences with 3R are significant. O₃V in VOCs-limited case is much higher (>20 ppb) than in 3R widely in central NCP as well in surface of Bohai Sea. At the meantime, same situation
happens to NO\textsubscript{x}-limited case where O\textsubscript{3} formation is due to NO\textsubscript{x} only, thus O\textsubscript{3}V is significantly lower than in 3R. It is worthy to note that the differences between 3R and 2R provides interesting findings. Generally, 3R predicts lower O\textsubscript{3} contributions from NO\textsubscript{x} emission in NCP except in cities such as Tianjin, Shijiazhuang and Taiyuan where more O\textsubscript{3} formation (~6 ppb) are classified as to from VOCs emissions. As results, 2R predicts more VOCs dominant cities than 3R, O\textsubscript{3} contributions from VOCs are increased in these cities in 2R. Compared to single precursor limited approaches, 3R predicts lower background O\textsubscript{3} by ~ 5 ppb in central NCP. However, 2R has even ~3 ppb lower than 3R in these areas. Due to higher accurate O\textsubscript{3} regime scheme that applied in China, source apportionment results from this work indicate more contributions from NO\textsubscript{x} and less from VOCs in major cities in NCP, these results help to better quantify impacts from emission sources and for more accurate further analysis in O\textsubscript{3}-related impacts on human health, economic benefits and ecosystem.

4.3.5 City scale analysis

Source apportionment analysis in major cities provide detailed evidences for controlling strategies. Emissions and background contributions to total 8h-O\textsubscript{3} in 8 NCP major cities are shown in Table 11. Long-term urbanization and industrial development cause high contribution from background O\textsubscript{3} in NCP\textsuperscript{211}, which accounts for ~50% of total O\textsubscript{3} in these major cities. However, as result of increasing emissions of O\textsubscript{3} precursors (NO\textsubscript{x} and VOCs)\textsuperscript{152, 212}, O\textsubscript{3} contributions from emissions are nonnegligible. Emissions induce ~ 45% to 52% of total O\textsubscript{3} in major cities except in Datong where emissions only account for 35% of total O\textsubscript{3}. There are three peak episodes observed in study period as discussed in chapter 2. O\textsubscript{3} contributions from background O\textsubscript{3} in these periods are slightly higher while significant contributions from emissions are estimated as shown in Table 12. In all studied cities, high O\textsubscript{3} concentrations are associated with emission sources which cause
more than 50% of total O₃ formation (with maximum ~60% in Jinan and Taiyuan). It is concluded that high pollution episodes are mainly due to emissions rather than background O₃ contributions. Sectoral source apportionment results (Figure 23) indicate industrial emission is the major source of O₃-EM, which results in more than 10 ppb O₃ (more than ~33% of O₃-EM, and maximum of 58% (Tianjin)). On-road and energy emissions also strongly affect O₃ concentration. They account for more than 70% (maximum of ~85%) O₃-EM in major cities together with industrial emission. Industry and on-road emissions account for ~65% of total O₃ in Beijing as the results of high population and emissions from mobile vehicles. It is noted that on-road emission has similar attribution as industrial emissions in Beijing while it accounts significantly less in other major cities. Energy emissions in Jinan has similar attribution as industrial emissions while on-road emission has less impact on total O₃-EM. Wildfires, agriculture, residential and biogenic emissions are always having low impacts. Sectoral contributions in high concentration episodes reveal that high O₃ concentration in these periods are caused greatly from emission sources, which cause large amount of O₃ formation. More than 50% of total O₃ (more than 50 ppb) are estimated from emission sources (as shown in right panel for each city in Figure 23). High emission contributions are mainly caused from industry and energy emissions. In all major cities except Datong and Baoding, contribution from industry emissions are increased by ~30 to 50% in high concentration period, which refers to maximum of 10 ppb. Contributions from energy emissions are estimated to more than twice in Baoding and Tangshan compared with regular summertime. It is also noted that contribution from wildfire emissions also has obvious increase in Beijing.
Table 11. Summertime 8h-O\textsubscript{3} contribution from background and emissions. Units are ppb.

<table>
<thead>
<tr>
<th>8h-O\textsubscript{3}</th>
<th>Beijing</th>
<th>Tianjin</th>
<th>Shijiazhuang</th>
<th>Baoding</th>
<th>Tangshan</th>
<th>Jinan</th>
<th>Datong</th>
<th>Taiyuan</th>
</tr>
</thead>
<tbody>
<tr>
<td>Total</td>
<td>73.04</td>
<td>71.89</td>
<td>72.80</td>
<td>74.96</td>
<td>68.8</td>
<td>77.63</td>
<td>60.93</td>
<td>72.18</td>
</tr>
<tr>
<td>BG</td>
<td>37.54</td>
<td>38.21</td>
<td>38.69</td>
<td>37.52</td>
<td>37.27</td>
<td>36.53</td>
<td>39.27</td>
<td>38.87</td>
</tr>
<tr>
<td>EM</td>
<td>35.5</td>
<td>33.68</td>
<td>34.11</td>
<td>37.44</td>
<td>31.53</td>
<td>40.90</td>
<td>21.66</td>
<td>33.31</td>
</tr>
</tbody>
</table>

- EM: O\textsubscript{3} contribution from emissions; BG: contribution from background

Table 12. 8h-O\textsubscript{3} concentration and its contribution from background and emissions in peak episodes. Units are ppb.

<table>
<thead>
<tr>
<th>8h-O\textsubscript{3}</th>
<th>Beijing</th>
<th>Tianjin</th>
<th>Shijiazhuang</th>
<th>Baoding</th>
<th>Tangshan</th>
<th>Jinan</th>
<th>Datong</th>
<th>Taiyuan</th>
</tr>
</thead>
<tbody>
<tr>
<td>Total</td>
<td>96.55</td>
<td>94.24</td>
<td>93.59</td>
<td>94.01</td>
<td>95.57</td>
<td>91.92</td>
<td>66.3</td>
<td>98.05</td>
</tr>
<tr>
<td>BG</td>
<td>41.54</td>
<td>42.48</td>
<td>41.72</td>
<td>41.56</td>
<td>40.22</td>
<td>37.19</td>
<td>39.8</td>
<td>40.24</td>
</tr>
<tr>
<td>EM</td>
<td>55.01</td>
<td>51.76</td>
<td>51.87</td>
<td>52.45</td>
<td>55.35</td>
<td>54.73</td>
<td>26.5</td>
<td>57.81</td>
</tr>
</tbody>
</table>

- EM: O\textsubscript{3} contribution from emissions; BG: contribution from background
Regional source apportionment (Figure 24) reveals the similar results as other studies that local emission would be the major source of O₃-EM. However, impacts from surrounding regions are also nonnegligible. For example, local emission in Beijing accounts for 50% of O₃-EM while emissions from Hebei also induce ~20% of them. Being Surrounded by Hebei makes Beijing very sensitive to emissions from Hebei. However, Tianjin has different situation even if it is also surrounded by Beijing and Hebei. O₃-EM in Tianjin are mainly due to local emissions but less to emissions from surrounding regions. It might be because the geophysical characters in Tianjin that emissions from Hebei and Beijing will be limited locally or spread to ocean surface southeast to Tianjin. Further analysis in needed in future for this. Emissions from north and central China also has slight impacts on O₃-EM in NCP with ~2-6 ppb. Analysis of regional source apportionment indicates an interesting finding. Though contributions from local emission increased, emissions from central China have strong impacts on increasing O₃ concentration in central, south and
southwestern NCP such as in Beijing, Shijiazhuang and Baoding. Contributions from central China are increased to ~10 ppb in these cities. However, emissions from YRD has significant impacts in eastern NCP which refers to Tianjin, Tangshan and major cities in Shandong such as Jinan. Contributions from YRD emissions and local emissions cause high \( \text{O}_3 \) concentration in these episodes. It is also concluded that emissions from Beijing and Tianjin have less impacts on each other in high concentration events but only induce local increases of \( \text{O}_3 \) concentration.

![Figure 24](image.png)

Figure 24. 8h-\( \text{O}_3 \) contributions from regional emissions in major city in summertime (left column) and peak episodes (right column). Units are ppb.

### 4.4 Conclusions

This work applies source apportionment method in simulating \( \text{O}_3 \) concentration and its contributions from natural and anthropogenic emission in NCP for 2017 summer by using source-oriented version of WRF/CMAQ modeling system. Comparison of results from different source apportionment methods indicates the advanced source-oriented method with improve 3R regime scheme increase the accuracy of source apportionment results. Sectoral and regional source
apportionment analysis indicate that industry, energy and on-road emissions are the major sources. Contributions from on-road and industry are significantly increased in peak episodes. Local emissions and emissions from surrounding regions are main sources of O₃ formation. Emissions from central China have significant impacts in Beijing, central, south and southwestern NCP while Tianjin, eastern NCP are more associated with emissions from local and YRD. This work provides information for estimating regional and sectoral contributions to O₃ pollution, which helps to deeper understand the sources of high O₃ concentration. It also offers solid evidences for further estimation of health risk. An effective emission controlling strategies can be designed based on results of this work to reduce O₃ concentration in future.
CHAPTER 5. OZONE SOURCE APPORTIONMENT IN SOUTHEAST U.S.

5.1 Introduction

\( \text{O}_3 \) is a secondary pollutant which is associated with a long-standing air quality problem in the U.S. for decades. Though \( \text{O}_3 \) concentration has significantly decreased through efforts from reducing anthropogenic emissions, many nonattainment events are observed over the U.S., and the \( \text{O}_3 \) concentration has remained higher than NAAQS requested threshold of 70 ppb in some regions. Many studies analyzed \( \text{O}_3 \) variation trends and impact factors in high concentration area over the U.S. A springtime increases of \( \text{O}_3 \) concentration were reported in western U.S. rural area by 0.2-0.5 ppb, while the increases were recorded in wintertime over eastern U.S. Dry deposition was revealed as the primary sink for \( \text{O}_3 \) and it was estimated to be increased in southeastern U.S. The increased air stagnation also induced significantly positive effect to raise \( \text{O}_3 \) concentration associated with dry tropical weather in midwestern U.S. Global warming trend was proved to induce high \( \text{O}_3 \) concentration events in mid-Atlantic region of the U.S. under a 30-years historical analysis.

Increasing concern of \( \text{O}_3 \) pollution requires researcher to analyze sources of \( \text{O}_3 \) formation. Background \( \text{O}_3 \) concentration was estimated to shift maximum \( \text{O}_3 \) event to early summer, and its contribution from global anthropogenic emission was estimated to be increased over the past decades especially in western U.S. Decreases of emission of \( \text{NO}_x \) and VOCs cause a reduction of averaged ambient \( \text{O}_3 \) concentration by \( \sim 22\% \) since 1998. BVOC emission was reported as the major source of VOCs emission in the U.S., which accounted for 75% to 80% of total VOCs emissions. BVOC was classified as a significant contributor to regional \( \text{O}_3 \)
concentration in SUS\textsuperscript{118, 221}. In peak episodes, reductions of NO\textsubscript{x} emissions from mobile vehicles and point source were estimated to cause the largest reductions O\textsubscript{3} concentration in Texas, U.S.\textsuperscript{222}.

O\textsubscript{3} formation is very sensitive to emissions of precursors, thus many approaches were applied to quantify the O\textsubscript{3} source contributions from NO\textsubscript{x} and VOCs. BVOC was estimated as the major precursor of O\textsubscript{3} formation for extreme O\textsubscript{3} events in SUS\textsuperscript{223}. But contributions from other sources are not well studied. This work aims to quantify O\textsubscript{3} sensitivity to precursors and contribution from all emission sources, which will provide information to estimate health impacts, economic benefits and further emission controlling strategies to reduce O\textsubscript{3} concentration so that to match NAAQS requested threshold.

5.2 Methods

5.2.1 Model description

O\textsubscript{3} concentration and its contributions from emission sources are simulated by applying the CMAQ model (version of 5.0.1) with SAPRC99 photochemical mechanism and AERO6 aerosol chemistry\textsuperscript{179, 207}. Meteorological conditions are generated by the Weather Research and Forecasting (WRF) version of 3.7.1 with initial condition (ICs) and boundary conditions (BCs) from WRF preprocessing system (WPS), which is obtained from FNL operational global analysis data from National Center for Atmospheric Research (NCAR, http://dss.ucar.edu/datasets/ds083.2/). Emission Database of Gas and Atmospheric Research (EDGAR) provides anthropogenic emission of 2012 and they are scaled to 2016 based on EPA National Emission Inventory (NEI) Technical Support Document (TSD) (https://www.epa.gov/air-emissions-inventories/2014-national-emissions-inventory-nei-technical-support-document-tds) which includes variation trends of NO\textsubscript{x} and VOCs emissions for each sector from 2012 by state scale. Scale factors for NO\textsubscript{x} and VOCs emissions in SUS are list in
Figure 14 and Figure 15. Biogenic emissions for 2016 are provided by the Model for emissions of Gases and Aerosols from Nature (MEGAN) \textsuperscript{184}, and Fire Inventory from NCAR (FINN) \textsuperscript{185} is used to generate open-burning (wildfires) emissions for simulation period. O\textsubscript{3} source-oriented method is applied in tracking O\textsubscript{3} contribution from emission sources by tagging reactive NO\textsubscript{x} and VOCs tracers as descripted in chapter 3\textsuperscript{134, 208, 209}. Benefits Mapping and Analysis Program (BenMAP) model helps to analyzes health impacts associated with O\textsubscript{3} by applying functions recruited from the published epidemiology literature. These functions calculate health impacts by used value of pollutant concentrations, population, incidence baseline rates and coefficients for different health endpoints, which are from simulation results (pollutant concentration) and BenMAP database, respectively, in every grid in study domain.

Table 13. Scaling factor for NO\textsubscript{x} emissions for major states in SUS.

<table>
<thead>
<tr>
<th></th>
<th>LA</th>
<th>AR</th>
<th>MI</th>
<th>TN</th>
<th>AL</th>
<th>GA</th>
<th>FL</th>
<th>NC</th>
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<tbody>
<tr>
<td>Energy</td>
<td>0.77</td>
<td>0.83</td>
<td>0.45</td>
<td>0.70</td>
<td>0.45</td>
<td>0.46</td>
<td>0.71</td>
<td>0.73</td>
<td>0.42</td>
</tr>
<tr>
<td>Industry</td>
<td>0.74</td>
<td>1.23</td>
<td>1.02</td>
<td>0.91</td>
<td>1.11</td>
<td>0.98</td>
<td>0.81</td>
<td>0.89</td>
<td>0.85</td>
</tr>
<tr>
<td>Residential</td>
<td>0.83</td>
<td>1.79</td>
<td>1.07</td>
<td>1.13</td>
<td>0.68</td>
<td>1.09</td>
<td>1.14</td>
<td>1.11</td>
<td>1.15</td>
</tr>
<tr>
<td>Agriculture</td>
<td>0.91</td>
<td>1.03</td>
<td>0.86</td>
<td>1.25</td>
<td>1.19</td>
<td>1.04</td>
<td>1.23</td>
<td>1.11</td>
<td>1.14</td>
</tr>
<tr>
<td>On-road</td>
<td>0.83</td>
<td>0.74</td>
<td>0.54</td>
<td>0.69</td>
<td>0.73</td>
<td>0.72</td>
<td>0.72</td>
<td>0.67</td>
<td>0.70</td>
</tr>
<tr>
<td>Off-road</td>
<td>0.43</td>
<td>0.84</td>
<td>1.19</td>
<td>0.78</td>
<td>0.98</td>
<td>0.77</td>
<td>0.94</td>
<td>0.82</td>
<td>0.97</td>
</tr>
</tbody>
</table>

Table 14. Scaling factor for VOCs emissions for major states in SUS

<table>
<thead>
<tr>
<th></th>
<th>LA</th>
<th>AR</th>
<th>MI</th>
<th>TN</th>
<th>AL</th>
<th>GA</th>
<th>FL</th>
<th>NC</th>
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</thead>
<tbody>
<tr>
<td>Energy</td>
<td>0.86</td>
<td>0.97</td>
<td>0.92</td>
<td>0.98</td>
<td>1.17</td>
<td>0.96</td>
<td>0.96</td>
<td>0.94</td>
<td>0.80</td>
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<tr>
<td>Industry</td>
<td>0.98</td>
<td>1.22</td>
<td>0.89</td>
<td>0.81</td>
<td>0.82</td>
<td>1.21</td>
<td>0.94</td>
<td>1.11</td>
<td>0.89</td>
</tr>
<tr>
<td>Residential</td>
<td>1.38</td>
<td>1.03</td>
<td>0.48</td>
<td>1.29</td>
<td>1.60</td>
<td>1.74</td>
<td>0.98</td>
<td>1.48</td>
<td>1.46</td>
</tr>
<tr>
<td>Agriculture</td>
<td>1.07</td>
<td>1.12</td>
<td>1.20</td>
<td>1.20</td>
<td>1.09</td>
<td>1.06</td>
<td>0.91</td>
<td>1.15</td>
<td>1.06</td>
</tr>
<tr>
<td>On-road</td>
<td>0.68</td>
<td>0.79</td>
<td>0.62</td>
<td>0.72</td>
<td>0.75</td>
<td>0.73</td>
<td>0.68</td>
<td>0.64</td>
<td>0.79</td>
</tr>
<tr>
<td>Off-road</td>
<td>0.74</td>
<td>0.81</td>
<td>0.85</td>
<td>0.79</td>
<td>0.82</td>
<td>0.78</td>
<td>0.75</td>
<td>0.78</td>
<td>0.78</td>
</tr>
</tbody>
</table>
5.2.2 Model application

O₃ and its source apportionment are simulated in a coarse domain with resolution of 36km covering the U.S. except Alaska and Hawaii. Part of surrounding countries such Canada and Mexico are also included. Nested finer domain covers SUS with resolution of 12km. Finer domain includes Alabama (AL), Arkansas (AR), Florida (FL), Georgia (GA), Louisiana (LA), Mississippi (MI), North Carolina (NC), South Carolina (SC) and Tennessee (TN) and part of neighbor states. Domain settings are shown in Figure 25. Emissions from agriculture, energy, industry, on-road, off-road, residential, biogenic and wildfires are tracked by tagging NOₓ and VOCs species in emissions inputs. Meteorological and emission inputs for June are generated used to predict summertime O₃ behavior in both domains. Three regime scheme (3R) is applied as O₃ sensitivity chemical scheme to precursors of NOₓ and VOCs as described in previous chapter⁵³.
5.3 Results and discussions

5.3.1 Overall O₃ simulations

Summertime 8h-O₃ concentrations in U.S. are simulated and shown in Figure 26, its contributions from background and emission sources are also illustrated. High concentrations occur in western, southwestern and northeastern U.S. with averaged concentration of more than 50 ppb. Highest pollution event is observed in southwest California by concentration of more than 70 ppb. Background O₃ is the major source in western U.S., which provides O₃ formation ranged from 40 to 50 ppb in most west regions. However, contribution from background O₃ is decreased in central and eastern U.S., corresponds to ~30 ppb. Minimum
contribution is observed in SUS with less than 25 ppb. Emissions play essential roles in forming O$_3$ in coastal California and low background contribution area such as central and eastern regions. Maximum contributions are predicted in southwest California and coastal northeastern U.S. by more than 30 ppb. High contribution also occurs around Lake Michigan and Kentucky by ~20 to 30 ppb.

![8h-total](image)

![8h-BG](image)

![8h-EM](image)

Figure 26. Summertime 8h-O$_3$ concentration in U.S. and its contribution from background (BG) and emissions (EM). Units are ppb.

Model performance of O$_3$ predictions in SUS are validated following same suggested statistic criteria introduced in Chapter 2. Predicted O$_3$ concentrations are compared with observation data recorded from a total of 224 monitoring stations in SUS. The statistic results are shown in Table 15. The MFE in all states match well with suggested benchmark of 0.35, but slightly exceedances of MFB are found in GA, NC, SC and TN. The NMB in these regions also exceed suggested criteria. Biases in these states are mainly due to uncertainties in domain edging area. Model slightly overestimates concentrations in SUS, biases are less than 2 ppb in FL, LA and MI, the best performance is found in LA with bias less than 1 ppb. However, model has a significantly overpredictions in part of central and north SUS such as in NC and TN with exceedances of both MFB and NMB. Biases are mainly due to uncertainties from emissions inventories and model resolutions. Overall, 8h-O$_3$ predictions in SUS agree well with observation from a total of 244 monitoring stations in SUS. Results from this simulation are reliable for further analysis. Overall, O$_3$ concentrations in SUS (Figure 27) are less than 50 ppb.
except north and west regions. A decrease trend is found from inner land to coastal area. However, contribution from background is high in the northeastern Gulf of Mexico and coastal Florida and Georgia by ~35-40 ppb but low in inland SUS where ~25-30 ppb O\textsubscript{3} formations are estimated due to background O\textsubscript{3}. It is noted that emissions strongly affect O\textsubscript{3} formation in central and northwest SUS. Detailed analysis is conducted in following section.

Table 15. Model performances in 9 states in SUS for 8h-O\textsubscript{3} simulation. Units are ppb for OBS and PRE. Bold represents the statistical result exceeds criteria.

<table>
<thead>
<tr>
<th></th>
<th>AL</th>
<th>AR</th>
<th>FL</th>
<th>GA</th>
<th>LA</th>
<th>MI</th>
<th>NC</th>
<th>SC</th>
<th>TN</th>
<th>Benchmark</th>
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</thead>
<tbody>
<tr>
<td>OBS</td>
<td>39.13</td>
<td>41.88</td>
<td>36.45</td>
<td>41.31</td>
<td>39.05</td>
<td>41.00</td>
<td>44.39</td>
<td>41.18</td>
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</tr>
<tr>
<td>PRE</td>
<td>45.31</td>
<td>46.93</td>
<td>37.03</td>
<td>50.20</td>
<td>39.24</td>
<td>42.81</td>
<td>53.20</td>
<td>50.40</td>
<td>53.58</td>
<td></td>
</tr>
<tr>
<td>MFB</td>
<td>0.12</td>
<td>0.10</td>
<td>-0.01</td>
<td>0.17</td>
<td>-0.03</td>
<td>0.02</td>
<td>0.17</td>
<td>0.19</td>
<td>0.20</td>
<td>±0.15</td>
</tr>
<tr>
<td>MFE</td>
<td>0.25</td>
<td>0.23</td>
<td>0.28</td>
<td>0.29</td>
<td>0.29</td>
<td>0.23</td>
<td>0.25</td>
<td>0.27</td>
<td>0.27</td>
<td>0.35</td>
</tr>
<tr>
<td>NMB</td>
<td><strong>0.18</strong></td>
<td>0.15</td>
<td>0.04</td>
<td><strong>0.24</strong></td>
<td>0.02</td>
<td>0.07</td>
<td><strong>0.22</strong></td>
<td><strong>0.26</strong></td>
<td><strong>0.27</strong></td>
<td>±0.15</td>
</tr>
</tbody>
</table>

Figure 27. Summertime 8h-O\textsubscript{3} concentration in SUS and its contribution from background (BG) and emissions (EM). Units are ppm.

5.3.2 Source apportionment in SUS

Figure 28 indicates that emissions from NO\textsubscript{x} dominate O\textsubscript{3} formation in SUS and barely O\textsubscript{3} contributions are estimated from VOCs. NO\textsubscript{x} emissions have strong impacts in northwest SUS, they cause more than 20 ppb O\textsubscript{3} formation in this region. Their impacts are significantly reduced from northwest to southeast regions, and they cause less than 10 ppb O\textsubscript{3} in south SUS
and even less than 5 ppb in south Florida. Impacts from VOCs emissions are generally lower than 2 ppb except in specific cities such as in Houston, Dallas and Nashville where ~5 ppb O$_3$ are estimated to associate with VOCs emissions.

Figure 28. 8h-O$_3$ contributions from emissions of NO$_x$ and VOCs. Units are ppb.

Sectoral contributions are shown in Figure 29. More than 10 ppb O$_3$ are from on-road emissions in north SUS, and contributions from on-road emissions are decreased to ~3 ppb in central and south regions. Emissions from energy mainly induce O$_3$ increasing in north and west SUS by 6 to 8 ppb but cause less impacts on central and southeast regions with less than 2 ppb. Industry has slightly lower contribution than energy emissions, it causes ~4 to 6 ppb O$_3$ in specific cities in central and west SUS. Besides, significant contributions from biogenic emissions are found in west and northwest SUS, around 4 ppb O$_3$ are estimated from biogenic sources. It is concluded that on-road emissions are the major sources in SUS followed by emissions from energy, industry and biogenic sector. On-road and biogenic emissions prefer to induce O$_3$ concentration in north and northwest area while emissions from energy and industry have strong impacts on specific cities in north and west SUS.
Figure 29. 8h-O₃ contributions from emission sectors. Units are ppb.

Since O₃-EM in SUS is mainly dominated by NOₓ, a deeper analysis of its source apportionment would carry out a comprehensive understanding. 8h-O₃ contribution from emission sources for NOₓ and VOCs are illustrated in Figure 30. It is noted that VOCs emissions has barely impacts on O₃ formation except the emissions from biogenic and industry. Biogenic emissions are the major sources of VOCs-related O₃, which cause significant impacts in northwestern regions. VOCs industry emissions cause ~ 1 ppb O₃ formation in Houston, Dallas and Atlanta, their impacts on other SUS regions are less than 0.5 ppb. Contributions from NOₓ emission has similar spatial pattern as total source contributions, which means a leading position of on-road emissions followed by energy emissions.
5.3.3 Comparison with China

From the results of previous chapters, anthropogenic emissions induce higher contributions in NCP, which lead average of ~30 ppb O$_3$ in summertime and maximum of more than 50 ppb in peak episodes. However, both anthropogenic emissions of NO$_x$ and VOCs are significantly lower in SUS than in NCP. As shown in

Figure 31, summertime monthly average total NO$_x$ emissions are ~10-20 tons in SUS with maximum of more than 200 tons in megacities such as Houston, Dallas and Atlanta. NO$_x$ emissions are generally higher than 100 tons in central NCP with maximum of more than 300 in specific city such as Beijing, Tianjin and Shijiazhuang. VOCs emissions in NCP also significantly higher than SUS.
Figure 31. Summertime average monthly emissions of NO\textsubscript{x} and VOCs and contribution from anthropogenic sources in SUS. Units are tons/month.

Both NCP and SUS have high energy NO\textsubscript{x} emissions but emissions from other sectors are extremely lower in SUS, especially for on-road, off-road and energy emissions, which are major sources in NCP. High emissions only occur in specific cities in SUS such as Houston, Dallas, and Atlanta while emissions in NCP are generally high in most central regions. It is noted that overall NO\textsubscript{x} emissions are at the low level (by ~10-20 tons/month) in SUS while a decrease trend is found in NCP from south to north (from 50 tons/month to less than 10 tons/month). VOCs emissions from anthropogenic sources are all significantly lower in SUS with a maximum of ~8 tons/month while the high VOCs emissions in NCP are more than 10 tons/month. As the major VOCs contributors in SUS, emissions from on-road and industry are lower than half of them in NCP. Generally, NO\textsubscript{x} and VOCs emissions in SUS are at low levels with only specific high emissions in major cities in each state, and even the high emissions in these cities are much lower than in
most regions in NCP. Emissions in NCP are generally higher in south and central regions. \( \text{O}_3 \) is estimated to sensitive to emissions in both NCP and SUS, differences in emissions cause greatly impacts on \( \text{O}_3 \) formation, thus \( \text{O}_3 \) source apportionment analysis in these regions helps to understand different source contributions under various emission conditions.

Major anthropogenic emission sources are industry, energy and on-road which occupied more than 70% of total \( \text{O}_3 \)-EM in NCP while on-road emissions are the only major anthropogenic source in SUS, less contributions from industry and energy sectors are estimated. Compared to anthropogenic emissions, biogenic emissions contribute less in NCP by causing less than 3 ppb \( \text{O}_3 \) while it becomes one of the major sources in SUS followed by on-road and energy emission. The maximum contribution from biogenic emissions of more than 5 ppb is occurred in western SUS. Contributions from emission sources show different patterns in NCP and SUS, which request an emergent requirement of reducing emissions from industry and energy so that the \( \text{O}_3 \) pollution could be reduced to matching its level in SUS.

5.4 Conclusions

This work simulates summertime \( \text{O}_3 \) concentration in SUS and its contributions from anthropogenic and natural emission sources. Model performances are validated. Though overestimations are remained in northern SUS, simulation results are generally match agree well with observation data and reliable for further analysis. High concentrations are found in north and west regions with the concentration of 8h-\( \text{O}_3 \) higher than 40 ppb. A decrease trend is found from northwest to southeastern coastal regions. Background \( \text{O}_3 \) contributes ~25 to 30 ppb in SUS while emission sources have strong impacts in high concentration regions by inducing ~30 ppb \( \text{O}_3 \) formation. \( \text{O}_3 \) formation in SUS is mainly dominated by \( \text{NO}_x \) while VOCs emissions cause maximum of 5 ppb in Houston, Dallas and Nashville. Major contributors of \( \text{NO}_x \)-related \( \text{O}_3 \)
formation are on-road emissions followed by energy, industry and biogenic emissions while biogenic emissions are major sources of $O_3$V. Comparison between SUS and NCP carries out that anthropogenic emissions cause the high $O_3$ pollution in NCP. Major sources in NCP are industry, energy and on-road emissions while on-road emission is the only major source in SUS. Results of this work provide information for further estimation of health risk analysis and offer solid evidence for designing the controlling strategies to reduce $O_3$ concentration in NCP.
CHAPTER 6. OZONE ASSOCIATED HEALTH RISK ANALYSIS

6.1 Introduction

Ground-level \( \text{O}_3 \), which was listed as one of six major air pollutants as set in NAAQS by EPA, is a highly toxic gas that have harmful effects on human health\textsuperscript{213,226,227}. Inhaling \( \text{O}_3 \) causes irritation, inflammation and constriction to human respiratory system and results in health impacts such as decreases of breathing functions, asthma attacks, hearth attacks and premature mortality\textsuperscript{228,229}. Around 142 thousand premature mortalities were estimated with \( \text{O}_3 \)-related COPD caused by long-term \( \text{O}_3 \) exposure globally\textsuperscript{229}. A total of 9-23 million annul asthma emergency room visits were also reported correspond to \( \text{O}_3 \) pollution around the world. At the meantime, China is shown as one of the most polluted countries that largest impacts from \( \text{O}_3 \)-related health issues were estimated\textsuperscript{230}.

China is experiencing \( \text{O}_3 \) increases issue, a total of 318 cities were revealed to exceed WHO recommended \( \text{O}_3 \) concentration, and 69 of them failed to meet the NAAQS target of China\textsuperscript{231}. Many studies tried to quantify \( \text{O}_3 \) impacts on human health in China. A total of 816.04 million cumulative population was estimated exposed to a circumstance that 8h-\( \text{O}_3 \) concentration is higher than 100 \( \mu \text{g/m}^3 \) in China, which results in around 55 to 80 thousand premature mortality caused by COPD in 2015. At the meanwhile, Beijing, Shandong, YRD, PRD and Sichuan basin were listed as high risk region\textsuperscript{14}. A growth rate of mortality increased from 0.42\% to 1.11\% around China as the result of \( \text{O}_3 \)-related health issue were estimated, which corresponded to 28 to 74 thousand premature mortality\textsuperscript{232}. \( \text{O}_3 \)-related health risk is also detailed analyzed in high \( \text{O}_3 \) risk area. A 39.5\% (1100 deaths) increased of premature mortality was estimated as result of \( \text{O}_3 \)
pollution in PRD. An increase of 10 μg/m³ of 8h-O₃ were associated with 0.55% increases of total mortality in Jiangsu Province. Increases of mortality due to hypertension, coronary diseases and stroke were revealed to associate with 10 μg/m³ increases of 8h-O₃ country wide by 0.60%, 0.24% and 0.29%, respectively. It was reported that more than 3 million respiratory symptoms and 1 million cases of school-loss days would be avoided if O₃ concentration could be controlled to lower than 75 ppb in the U.S. Around 0.11% to 0.27% increases of O₃-related daily mortality were revealed on average across 50 cities in U.S., which were associated with increases of daily 1h-O₃ by average of 4.8 ppb (maximum of 9.6 ppb).

O₃ exposure leads a series of adverse health effects including premature mortalities of respiratory and cardiovascular diseases. The concentration response function (CRF) is widely used in WHO and previous studies to quantify O₃-related health impacts. The change rates of 0.42%, 0.44% and 0.50% of mortality due to non-accidental causes, cardiovascular diseases and respiratory diseases were estimated as the result of an increased 8h-O₃ concentration of 10 μg/m³, respectively. Increase of 10 μg/m³ of daily averaged O₃ concentration was also estimated to cause increase of 0.6% nonaccidental mortality in China. However, there is no study detailed provides O₃-related health impacts in NCP and their contribution from emission sources. Studies in U.S. is also limited in analyzing health impacts from emission sources. This study will recruit results from previous chapters and apply the reliable health analysis methods to estimate O₃-related health risk in NCP and SUS as well as source contribution in these regions. Results of this study provides information to assess health risk caused by human activities and quantify the contributions from emissions sources. Health analysis results would be further used to estimation on economic benefits.
6.2 Methods

China-specific concentration-response functions (CRF)\textsuperscript{242,243} are adapted in this study to estimate the health impacts due to exposure of O\textsubscript{3}. Cardiovascular and respiratory mortalities are calculated in this study. Relative risk (RR) of Cardiovascular and respiratory disease mortalities with a 95\% confidence interval with corresponding 8h-O\textsubscript{3} concentrations are calculated using following equation:

Equation 18:

\[
RR_i = \exp \left[ \gamma (C_i - C_0) \right]
\]

Where i refers to the index of the domain grid. \(\gamma\) is fitted by meta-regression based on the previous epidemiological studies for China\textsuperscript{242}. \(C_i\) and \(C_0\) are the pollution concentration in the target grid and the threshold value, below which will induce no additional risk, respectively. Threshold concentration of 8h-O\textsubscript{3} is 35 ppb (equivalent to 70 \(\mu\)g/m\textsuperscript{3}) in this work\textsuperscript{172}. Extra health impacts are resulted from concentration higher than the threshold value. The health endpoints (E) for CRF is calculated based on following equation:

Equation 19:

\[
E = \sum_i \frac{RR_i - 1}{RR_i} * P_i * F_i
\]

Where \(P_i\) and \(F_i\) refer to population and baseline incidence rate. It is noted that health endpoints in this study include premature mortality due to respiratory diseases (RDM) and cardiovascular diseases (CDM). Major respiratory and cardiovascular diseases including chronic obstructive pulmonary disease (COPD), ischemic heart disease (IHD) and strokes (STK, including both ischemic and hemorrhagic strokes) are also calculated in this analysis. The baseline incidence rates are obtained from the online GBD database (http://vizhub.healthdata.org/gbd-compare/). The
United Nations (UN)-adjusted population distribution for year of 2017 from the Center for International Earth Science Information Network (CIESIN) is used to represent the population exposure.

CRF is a long-term concentration related function, thus simulated summertime 8h-O$_3$ concentrations are scaled to annual concentrations by applying provincial average ratio calculated from observation data recorded in monitoring stations following Equation 20 for each grid.

Equation 20:

$$Annual\ 8h-O_3(S) = Summer\ 8h-O_3\ (S) \times \frac{Annual\ 8h-O_3\ (O)}{Summer\ 8h-O_3\ (O)}$$

S and O in equation (3) refer to concentration from simulation and observation, respectively. Observation data are provided by China National Environmental Monitoring Center (CNEMC, http://113.108.142.147:20035/emcpublish/).

Benefits Mapping and Analysis Program (BenMAP) model helps to estimate the O$_3$-related health risk in SUS. Health endpoints includes mortality (all-cause, respiratory and cardiopulmonary diseases), emergency room (ER) visits (for asthma) and hospital admissions (HA, for all respiratory). Health impacts are calculated by applying recruited function from published epidemiology literature in this model. Health impacts are associated with pollution concentrations, population and incidence baseline rates, which are from results of previous chapters and BenMAP database in U.S.
6.3 Results and discussions

6.3.1 Overall health risk in NCP

Based on discussions in previous chapters, simulation results for O₃ concentrations in NCP are in sufficient agreement with observations to act as basis for health impacts analysis. It is noted that annual 8h-O₃ concentrations are scaled from summertime concentration in this estimation. Health risks are estimated for both MEIC and EDGAR+ simulation results. Health impacts in Beijing, Tianjin, Hebei, Shandong and Shanxi are included in the following discussion while the rest provinces are not included since they are not fully contained in the simulation domain. Results from MEIC and EDGAR+ are listed in Table 16. Due to the higher predicted concentration, MEIC results in a higher risk for all health endpoints. MEIC predicts a total of 0.13 million mortalities for all causes (0.05 million for RDM and 0.08 million for CDM) while EDGAR+ predicts ~0.02 million fewer mortalities than MEIC (total of 0.04 and 0.07 million for RDM and CDM, respectively). COPD is the major disease within RDM, accounting for around 1/3 of total mortality in simulations. Both EDGAR+ and MEIC predict similar relative health impacts in different provinces. Hebei and Shandong have the highest impacts with more than total of 0.04 million mortalities. Shanxi also has high mortality followed by Beijing and Tianjin. With high population, Beijing and Tianjin also have severe health problems under high O₃ concentration. Beijing has ~0.01 million all-cause mortality, which is twice as high as in Tianjin.

Table 16. Provincial health risk analysis results within the NCP. Units for health endpoints are cases.

<table>
<thead>
<tr>
<th>Total mortality</th>
<th>Beijing</th>
<th>Tianjin</th>
<th>Hebei</th>
<th>Shandong</th>
<th>Shanxi</th>
<th>Total</th>
</tr>
</thead>
<tbody>
<tr>
<td>EDGAR+</td>
<td>9536</td>
<td>4809</td>
<td>40902</td>
<td>40840</td>
<td>16302</td>
<td>112390</td>
</tr>
<tr>
<td>MEIC</td>
<td>12062</td>
<td>5395</td>
<td>45460</td>
<td>48602</td>
<td>19022</td>
<td>130541</td>
</tr>
</tbody>
</table>

(Table cont’d)
1. Cardiovascular diseases mortality (CDM); respiratory diseases mortality (RDM); ischemic heart disease (IHD); stroke (STK); chronic obstructive pulmonary disease (COPD).

2. Only Beijing, Tianjin, Hebei, Shandong, Shanxi are completely included in this study, the health result for the rest provinces (Rest) are only refer to the part that included in this study domain.

3. Total mortality includes CDM and RDM only.

Due to higher accuracy of concentration results using EDGAR+, spatial distributions of mortality from each disease in EDGAR+ results are shown in Figure 32. The differences between EDGAR+ and MEIC are also shown in Figure 33. Health endpoints in major cities/provinces are also listed in
Due to the higher predicted concentration, MEIC results in a higher risk for all health endpoints. MEIC predicts a total of 0.13 million mortalities for all causes (0.05 million for RDM and 0.08 million for CDM) while EDGAR+ predicts ~0.02 million fewer mortalities than MEIC (total of 0.04 and 0.07 million for RDM and CDM, respectively). COPD is the major disease within RDM, accounting for around 1/3 of total mortality in simulations. The spatial pattern indicates that adverse impacts usually peak at megacities in the central NCP such as Beijing, Tianjin and Shijiazhuang. Although O$_3$ concentrations are not always extremely high in Beijing, high population density leads to this serious health impacts. Such situations are also observed in capital cities in other provinces such as Zhengzhou, Shijiazhuang as well as some big cities with large population such as Tianjin and Yantai. In north Henan and south Hebei, severe health impacts are also estimated due to the high O$_3$ concentration instead of high population density. However, opposite to central NCP, adverse health impacts are not very serious in coastal regions where O$_3$ concentrations are relatively lower compared to central NCP except in specific high population cities. In north, west and northwest NCP, O$_3$-related health impacts are very low due to both low O$_3$ concentration and population. Figure 33 reveals that EDGAR+ predicts lower health risk than MEIC except in specific cities such as Tangshan, Shijiazhuang, Qingdao and Taiyuan by 10~20 cases/grid. It is significant that EDGAR+ predicts lower mortality (20 cases/grid) in Beijing, where EDGAR+ has higher accuracy in predicting O$_3$. It is believed that EDGAR+ also predicts health risk more accurately than MEIC.
Table 17. Provincial health risk analysis results within the NCP. Units for health endpoints are cases.

<table>
<thead>
<tr>
<th>Province</th>
<th>Beijing</th>
<th>Tianjin</th>
<th>Hebei</th>
<th>Shandong</th>
<th>Shanxi</th>
<th>Total</th>
</tr>
</thead>
<tbody>
<tr>
<td>Total mortality</td>
<td>EDGAR+</td>
<td>9536</td>
<td>4809</td>
<td>40902</td>
<td>40840</td>
<td>16302</td>
</tr>
<tr>
<td>CDM</td>
<td>MEIC</td>
<td>12062</td>
<td>5395</td>
<td>45460</td>
<td>48602</td>
<td>19022</td>
</tr>
<tr>
<td>RDM</td>
<td>EDGAR+</td>
<td>5884</td>
<td>2975</td>
<td>25276</td>
<td>25341</td>
<td>10130</td>
</tr>
<tr>
<td>COPD</td>
<td>MEIC</td>
<td>7389</td>
<td>3324</td>
<td>27991</td>
<td>29964</td>
<td>11750</td>
</tr>
<tr>
<td>IHD</td>
<td>EDGAR+</td>
<td>3652</td>
<td>1834</td>
<td>15626</td>
<td>15499</td>
<td>6172</td>
</tr>
<tr>
<td>STK</td>
<td>MEIC</td>
<td>4673</td>
<td>2071</td>
<td>17469</td>
<td>18638</td>
<td>7272</td>
</tr>
<tr>
<td>COPD</td>
<td>EDGAR+</td>
<td>3582</td>
<td>1798</td>
<td>15325</td>
<td>15200</td>
<td>6054</td>
</tr>
<tr>
<td>MEIC</td>
<td>4583</td>
<td>2031</td>
<td>17132</td>
<td>18279</td>
<td>7132</td>
<td>49157</td>
</tr>
<tr>
<td>IHD</td>
<td>EDGAR+</td>
<td>2796</td>
<td>1614</td>
<td>12011</td>
<td>12042</td>
<td>4814</td>
</tr>
<tr>
<td>MEIC</td>
<td>3511</td>
<td>1580</td>
<td>13301</td>
<td>14239</td>
<td>5583</td>
<td>38214</td>
</tr>
<tr>
<td>STK</td>
<td>EDGAR+</td>
<td>2745</td>
<td>1388</td>
<td>11792</td>
<td>11822</td>
<td>4726</td>
</tr>
<tr>
<td>MEIC</td>
<td>3447</td>
<td>1551</td>
<td>13058</td>
<td>13978</td>
<td>5481</td>
<td>37515</td>
</tr>
</tbody>
</table>

1. Cardiovascular diseases mortality (CDM); respiratory diseases mortality (RDM); ischemic heart disease (IHD); stroke (STK); chronic obstructive pulmonary disease (COPD).
2. Only Beijing, Tianjin, Hebei, Shandong, Shanxi are completely included in this study, the health result for the rest provinces (Rest) are only refer to the part that included in this study domain.
3. Total mortality includes CDM and RDM only.
Figure 32. Health end point results of five O₃-associated diseases. Total shows the total mortality due to O₃-related diseases including RDM, CDM COPD, IHD and STK. Units are cases/grid.
Figure 33. Difference of health endpoints between EDGAR+ and MEIC (subtracting EDGAR+ by MEIC). Units are cases/grid.

Health outcomes from EDGAR+ and MEIC are compared with others’ studies for China as shown in Table 18. Most studies used similar function (CRF) to estimate health risk with different corresponding concentrations and thresholds. Mostly, 8h-O\textsubscript{3} is used as the concentration metric in the CRF with a threshold of 75.2 μg/m\textsuperscript{3}. This study uses a slightly lower threshold (70 μg/m\textsuperscript{3}) which is validated and successfully used in previous works\textsuperscript{172, 235}. Though the national health impacts from other studies are calculated for different years by using varied thresholds, this
comparison also indicates that NCP is a high-risk region in China. EDGAR+ and MEIC predict ~0.04 and ~0.05 million respiratory mortalities, respectively, for five provinces in the NCP, which account for ~50% to 70% of national respiratory mortalities linked to results in Maji, et al. COPD mortality also amounts for ~61% of national-wide impacts estimated by Liu, et al.

Table 18. Comparison of health outcome with previous studies

<table>
<thead>
<tr>
<th>Study domain (target year)</th>
<th>Corresponding concentration</th>
<th>Threshold</th>
<th>Health endpoint</th>
<th>Estimated mortality</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>NCP (2017)</td>
<td>8h-(\text{O}_3)</td>
<td>70 (\mu)g/m(^3)</td>
<td>Respiratory and cardiovascular diseases</td>
<td>112,390</td>
<td>EDGAR+(^1)</td>
</tr>
<tr>
<td>NCP (2017)</td>
<td>8h-(\text{O}_3)</td>
<td>70 (\mu)g/m(^3)</td>
<td>Respiratory and cardiovascular diseases</td>
<td>130,541</td>
<td>MEIC (^1)</td>
</tr>
<tr>
<td>China (2016)</td>
<td>8h-(\text{O}_3)</td>
<td>75.2 (\mu)g/m(^3)</td>
<td>Respiratory morality</td>
<td>69,536–74,233</td>
<td>(244)</td>
</tr>
<tr>
<td>China (2015)</td>
<td>8h-(\text{O}_3)</td>
<td>100 (\mu)g/m(^3)</td>
<td>COPD mortality</td>
<td>55,341–80,280</td>
<td>(154)</td>
</tr>
<tr>
<td>China (2000)</td>
<td>1h-(\text{O}_3)</td>
<td>75.2 (\mu)g/m(^3)</td>
<td>Premature all-cause mortality(^2)</td>
<td>70,000–150,000</td>
<td>(245)</td>
</tr>
<tr>
<td>China (2010)</td>
<td>1h-(\text{O}_3)</td>
<td>75.2 (\mu)g/m(^3)</td>
<td>Respiratory morality</td>
<td>300,000</td>
<td>(246)</td>
</tr>
<tr>
<td>Urban China (2015)</td>
<td>8h-(\text{O}_3)</td>
<td>50 (\mu)g/m(^3)</td>
<td>Premature all-cause mortality</td>
<td>70,800</td>
<td>(247)</td>
</tr>
</tbody>
</table>

1. Results from this predicted concentration in this work.
2. All-cause mortality includes all \(\text{O}_3\)-related diseases

6.3.2 Health risk contribution from emissions sources for NCP

Health risk contribution from emissions of NO\(_x\) and VOCs are shown in Figure 34, these results are from predicted \(\text{O}_3\) concentration by using EDGAR+ which has slightly better accuracy.
in matching averaged O\textsubscript{3} concentration in NCP. Emission-related O\textsubscript{3} causes \(~46.5\%\) of total premature mortality while the rest of them are due to background O\textsubscript{3} (53.5\%). It is noted that NO\textsubscript{x} is the major source in NCP while both NO\textsubscript{x} and VOCs have great impacts on megacities such as Beijing, Tianjin and Shijiazhuang where have high level of both population and O\textsubscript{3} pollution. For major cities/provinces in NCP, total of 52,346 premature mortalities are estimated due to emissions. NO\textsubscript{x} emissions cause 82.5\% of emission-related premature mortality, correspond to 43,211 deaths. Hebei and Shandong provinces have highest premature mortality, a total of 19.16 and 19.02 thousand deaths are estimated due to emissions, a total of 5 thousand mortalities are estimated for Beijing. Source contributions to mortality are shown in Figure 35, which is associated with concentration distribution. Industry, energy and on-road emissions are major sources that cause 79\% of the total emission-related mortality. Emissions from Central China, Hebei and Shandong provinces are the major sources of O\textsubscript{3}-related premature mortality, they cause a total of 55\% emission-related premature mortality. Spatial distribution of regional and sectoral emissions contributions (Figure 36) indicates that local emissions are the major health issue sources, and emissions in Hebei, Shandong and central China cause high health risk to central NCP, they cause large amount mortality in central NCP. At the meantime, high contributions from emissions from Beijing and Tianjin are also due to large population in these cities. Figure 36 also shows that industry, energy, on- and off-road emissions are major sources in central and south NCP.
Figure 34. Spatial contributions from NO$_x$ and VOCs emissions to premature mortality. Units are cases/grid cell.

Figure 35. Regional (left) and sectoral (right) emission contribution ratios to total premature mortality.
Figure 36. Spatial contribution of health impacts from regional (left) and sectoral (right) emission sources. Units are cases/grid cell.

6.3.3 Health risk analysis in SUS and comparison with NCP

O3-related health endpoints are calculated and shown in Figure 37. All-cause mortality, respiratory mortality and cardiovascular mortality are calculated based on simulation results in chapter 5. A total of ~35 thousand all-cause mortalities are estimated due to long-term exposure to O3. Cardiovascular and respiratory diseases cause 7913 and 4605 mortalities, account for ~22% and ~13% of all-cause mortalities.
mortality, respectively. High risk is estimated to associate with population density. Megacities such as Houston, Dallas, Atlanta and Orlando are estimated as high risk area, with more than 40 premature mortality cases are calculated in each grid. More than 20 thousand ER visits and 6.5 million HA are estimated in this work. These results reveal that even O$_3$ concentration is at a low level, it remains a great potential risk for people who is sensitive to O$_3$-related diseases. Contribution of O$_3$-related health impacts from O$_3$ sources are shown in Figure 38. Emissions cause a total of 12663 premature mortalities in SUS, account to 35% of total O$_3$-related impacts. As major sources, on-road emission cause 39% of emission-related health impact followed by emissions from energy (20%) and biogenic (14%).

Figure 37. O$_3$-related health risk in SUS. First row represents the estimated premature mortality, bottom row refers to the estimated impacts cases for ER visits and HA. Units are cases/grid.
Figure 38. All-cause mortality contributions from BG and emission sources. Right panel shows the contribution of emission related impacts from emission sources.

Results in SUS are compared with health impacts in NCP. Generally, less health impacts are estimated in SUS than in NCP since lower level of both O₃ concentration. Besides, population density is another reason for this phenomenon. Population is high in big cities for both scenarios such as Houston, Dallas, Atlanta, Beijing, Tianjin and Shijiazhuang where the O₃ concentrations are also relative higher than other cities (Figure 39). But NCP has large amount population in central and south regions which refer to Hebei, Henan and Shandong provinces, where the population remains in a high level. Population in rural SUS is in a significantly lower level, which is equal to ~10% as in NCP, thus less health impacts are estimated in these regions. Different incidence rates also help to explain the differences as shown in Table 19. NCP has more than twice respiratory incidence rate than SUS and has a similar cardiovascular diseases incidence rate of mortality. However, though less people suffered from respiratory diseases, large amount people has high risk in cardiovascular diseases, which leads high mortality of CDM in SUS.
Figure 39. Population in SUS (left) and NCP (right). Population data are both for 2015.

Table 19. Incidence of mortality of respiratory (RDM) and cardiovascular (CDM) diseases. Units are cases per 100,000 people.

<table>
<thead>
<tr>
<th></th>
<th>SUS</th>
<th>NCP</th>
</tr>
</thead>
<tbody>
<tr>
<td>RMD</td>
<td>18-40</td>
<td>~82</td>
</tr>
<tr>
<td>CMD</td>
<td>220-360</td>
<td>~78</td>
</tr>
</tbody>
</table>

- Incidence rates are calculated based on dataset recruited in BenMAP and GBD.

### 6.4 Conclusions

This chapter detailed analyzed O₃-related health risk in NCP and SUS. A total of ~ 0.11 million and 0.12 million premature mortalities are estimated by using different emission inventories in NCP. A major contribution from COPD is estimated to account for ~33.3% of total mortality. Emission-related health impacts account for ~46.5% of total mortality in NCP based on simulation from EDGAR+. Emissions from Hebei and Shandong dominate the impacts in high risk area (central NCP). Emissions from industry, energy and on-road sectors correspond to 79% of emission-related mortality in this study. Health risk analysis in SUS indicate that nature and anthropogenic emissions have less contribution to O₃-related health problems, the major source is the background O₃. In emission-related mortality, on-road emissions are the major sources followed by energy and biogenic emissions. Differences between NCP and SUS are mainly due to
different emissions, population and incidence rates. This simulation quantifies the health risk contribution from emission sources, which can be used in further estimation of economic loss and helps to deeper understand impacts from O$_3$ pollution.
CHAPTER 7. CONCLUSIONS

This study builds a fully understanding of current O$_3$ pollution in China and approaches in estimating source contributions firstly. Then a comprehensive analysis of O$_3$, its impact factors and source apportionment is conducted for 2017 summertime in NCP. A source apportionment analysis was also conducted for SUS for comparison with NCP. This study provides valuable results for designing O$_3$ controlling strategies in China. At the end, O$_3$-related health risk analysis in the last chapter, which helps to quantify health impacts from current O$_3$ pollution and their contributions from emissions sources.

Chapter 2 provides a brief overview of four major O$_3$ source apportionment approaches including DDM, BFM, OSAT and source-oriented methods. These methods are developed to quantify impacts from user specific sources by different ways. Each method has its own advantages and limitations. DDM has limitation in estimate contribution through high order chemical reactions, which causes significant uncertainty in tracking source contributions from secondary pollutants such as O$_3$. BMF can quantify effects of emission control policies in lowing O$_3$ but it is not a quantifying method to estimate current contribution from emissions sources. Both OSAT and O$_3$-oriented method are commonly used to quantify O$_3$ contribution from emission sources. But without the reactive tracer, OSAT misses information through O$_3$ forming processes and causes limitations in the result. Thus O$_3$-oriented method would be a better approach, which is applied in following chapters to quantify emission impacts on O$_3$ concentration. Overview of current O$_3$ source apportionment studies in China provides a clear result that China is experiencing severe O$_3$ pollution and the O$_3$ concentration is increasing in recent years. Anthropogenic emission of NO$_x$ and VOCs and their effects on O$_3$ formation are commonly studied in China, but there is no a
sufficient study provides a comprehensive understanding in NCP where is one of the high O$_3$ risk area in China.

CTMs are a widely used method to analyze O$_3$ behaviors, but uncertainty remains in its sensitivity to emission inventory. To fully understand O$_3$ pollution in NCP, Chapter 3 simulates 2017 summertime O$_3$ concentration in NCP by using WRF/CMAQ system and compare the performances from using different emission inventories, this objective aims to evaluated performances from different inventories and improves simulation accuracy. In this chapter, model performances are validated, performances in EDGAR+ and MEIC are compared with each other. Statistical results reveal that EDGAR+ has an overall better performance in both regional scales and city scale while MEIC has better ability in predicting peak O$_3$ value. Summertime O$_3$ concentration are estimated higher than ~70 ppb in major cities in NCP. Significantly high concentrations are found in Beijing, Tianjin, south Hebei, west Shandong and north Henan with maximum of ~90 ppb, and these regions are classified as high risk area. O$_3$ analysis of diurnal and peak episodes indicates that high concentrations are always associated with slightly lower emissions under high temperature, low RH and steady wind field. Emissions could lead significant variations of O$_3$ predictions. Compare to MEIC, significant lower (<200 tons/month) of NO$_x$ and similar (difference within ±5 tons/month) VOCs emissions in EDGAR+ induce more O$_3$ formation; less O$_3$ is predicted when both NO$_x$ and VOCs emissions are significantly lower (<200 tons/month and <10 tons/month, respectively); O$_3$ concentrations are barely changed (within ±10 ppb) when NO$_x$ emissions are significantly lower (<200 tons/month) and VOCs emissions are significantly higher (>10 tons/month) in EDGAR+.

The source apportionment analysis of 2017 summertime O$_3$ in NCP is conducted in Chapter 4. Due to its better accuracy in matching overall O$_3$ concentration and spatiotemporal variations,
EDGAR+ is applied in this simulation. This objective aims to deeper understand effects from emission sources. O₃ contributions from emission sources are quantified by sectoral and regional analysis. Overall, emission sources contribute ~30%-50% to total O₃ concentration in NCP, and the contributions are increased to ~50%-60% in peak episodes when O₃ concentration is higher than ~90 ppb in major cities. NOₓ emissions are estimated to dominate O₃ concentrations in most NCP while VOCs emissions have significant impacts in megacities such as Tianjin and Shijiazhuang. Emissions from industry sector are the major contributors to O₃ formation followed by energy and on-road emissions, and they cause ~75% of total emission-related O₃ formation in study period. Local emissions are classified as the major contributors while impacts of emissions from surrounding regions are also important. Emissions from Hebei, Shandong and central China are the major sources of high concentration in NCP. In addition, emissions from central China have significant impacts in Beijing, central, south and southwestern NCP while Tianjin, western NCP are more associated with emissions from local and YRD especially in high concentration episodes.

Source apportionment study in SUS is conducted in Chapter 5, O₃ concentrations are predicted by using scaled EDGAR inventory. Similar analysis methods as used as in NCP scenario help to detailed analyze sectoral contribution to O₃ formation from emission sources. The results are compared to NCP to understand the differences between developing and developed countries. Both NCP and SUS have general high sensitivity to NOₓ emission than to VOCs. High contributions are always found in megacities in NCP and SUS where NOₓ emissions are high in these regions. It is different to NCP that anthropogenic emissions have significantly less contributions in SUS while contribution from biogenic emissions dominate the O₃ formation especially in Florida. Biogenic emissions are generally have slightly impacts in NCP. The main
reason of this phenomenon is the low anthropogenic emissions in SUS. Total NO\textsubscript{x} and VOCs emissions in SUS are much lower than in NCP. Though most anthropogenic emissions are low, contribution from on-road emissions also cause ~5-8 ppb O\textsubscript{3} in SUS.

O\textsubscript{3}-related health risk analysis are shown in Chapter 6 for both NCP and SUS and their contributions from emission sources. Generally, the health impacts are calculated associate with pollution concentration, population and baseline incidence rates. Estimating functions are from previous epidemiological studies that indicate a certain threshold of O\textsubscript{3} concentration, beyond which will cause additional adverse health effects. Health impacts due to emission sources are quantified. There are total of ~0.11 thousand premature mortalities due to respiratory and cardiovascular diseases estimated in NCP based on EDGAR+ while MEIC predicts slightly higher (by 0.12 thousand) mortality for same period. COPD is the major disease that causes ~40% of total premature mortality. Source contribution results are consisted with concentration results in chapter 5. NO\textsubscript{x} emissions cause 82.5% of emission-related premature mortality, correspond to 43,211 deaths. Industry, energy and on-road emissions cause ~79% of emission-related premature mortality. Emissions from central China, Hebei and Shandong provinces are the major regional sources that cause ~55% of total death. It is noted that emissions from Beijing and Tianjin also has high contribution to local premature mortality even their contributions to concentration is not that high, the main reason is the high population in these regions. A total of 35175 all-cause mortalities are estimated in this study for SUS, which is mainly due to respiratory (4605) and cardiovascular (7913) diseases. a total of 22 thousand ER visits and 6.5 million hospital admissions indicates that even O\textsubscript{3} concentration is not at a high value, its impact on human health remains significantly. Health impacts in SUS are mainly from on-road, energy and biogenic emissions, which account for ~73% of total emission-related mortality.
This work details overview O₃ source apportionment methods and applies in analyzing O₃ behaviors in NCP and SUS and their source contributions. Though extensive work has been done to deeper understand O₃ in NCP and SUS, there are still uncertainties remain to be improved in future. A year-long improvement of emission inventory should be conducted to provide long-term O₃ simulation in both high and low concentration seasons and thus to increase accurate of the results from source apportionment and health risk analysis. Furthermore, to measure the long-term O₃ behavior and its impacts, simulation period should be extent to decades in cases. Historical and future potential changes would lead a deeper understanding of O₃ pollution. To comprehensive analyze current O₃ pollution in China, a national wide investigation is also needed to fully evaluate emission contributions not only in high risk regions but also in increasing developing regions such as south and southeastern China, where emissions structures are different with NCP and so as to their contributions. Finally, a further study on O₃-related impacts on economic and ecosystem should be processed to evaluate the total impacts from O₃ pollution.
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VITA

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