Source apportionment of summertime ozone in China using a source-oriented chemical transport model

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ABSTRACT

Contributions of industries, power plants, residential, transportation, open burning, and biogenic sectors to summertime ozone (O\textsubscript{3}) in China in August 2013 are quantified using an improved O\textsubscript{3} source apportionment method implemented in a source-oriented Community Multiscale Air Quality (CMAQ) model. The new O\textsubscript{3} source apportionment method attributes in-situ O\textsubscript{3} formed in each time step to nitrogen oxides (NO\textsubscript{x}) and volatile organic compounds (VOCs) with a new attribution scheme that considers NO\textsubscript{x}-VOC-O\textsubscript{3} formation sensitivity in NO\textsubscript{x}-limited, transition, and VOC-limited regimes (three regimes, 3R). This represents an improvement from the traditional 2R source apportionment models, in which O\textsubscript{3} formation sensitivity is divided into two-regimes (2R), either NO\textsubscript{x}-limited or VOC-limited. An expanded source-oriented gas phase chemical mechanism is developed to concurrently track NO\textsubscript{x} and primary VOCs and their oxidation products from different sources. The source-resolved NO\textsubscript{2} photolysis rates and the NO to NO\textsubscript{2} conversion rates by peroxy radicals from the source-oriented chemical mechanism are then used to apportion O\textsubscript{3} to NO\textsubscript{x} (O\textsubscript{3}-NO\textsubscript{x}) and VOCs (O\textsubscript{3}-VOC) from different emission sources.

Industries, transportation, power plants and biogenic sources are the major emission sectors to O\textsubscript{3}. High industrial O\textsubscript{3}-NO\textsubscript{x} (8–15 ppb; 20–25% of total O\textsubscript{3}) is mainly located in north and northeast China, the Yantze River Delta (YRD) and part of the Sichuan Basin (SCB). Transportation O\textsubscript{3}-NO\textsubscript{x} accounts for 10–15% of total O\textsubscript{3} in most urban areas. Power plants’ contributions to O\textsubscript{3}-NO\textsubscript{x} (10–15%) are mostly located in Shanxi, Shaanxi, Ningxia and part of Shandong and Jiangsu. The contribution of soil NO\textsubscript{x} to O\textsubscript{3}-NO\textsubscript{x} is highest in regions in west, central and south China with less direct anthropogenic emission influences. VOC-limited grid cells are mostly located at urban cores and large city clusters in the YRD and Pearl River Delta (PRD) regions. Biogenic and industrial sectors are the most important emission sectors that contribute to O\textsubscript{3}-VOC, accounting for more than 85% of the O\textsubscript{3}-VOC in China. In north and east provinces, more than 50% of the O\textsubscript{3} is non-background, with the provinces in north China having higher overall O\textsubscript{3}. The Beijing-Tianjin-Hebei (BTH) region has an area-averaged 8-hr O\textsubscript{3} of 75 ppb in August 2013 and about half is non-background. Contributions of industries, transportation, power and biogenic sources to non-background O\textsubscript{3} are 37%, 22%, 13% and 23%, respectively. The relative contribution of biogenic emissions to non-background O\textsubscript{3} is lower on high 8-hr O\textsubscript{3} days. The 2R and 3R approaches show significant differences in assessing the relative importance of O\textsubscript{3}-NO\textsubscript{x} and O\textsubscript{3}-VOC, with the 3R regime approach predicting lower O\textsubscript{3}-NO\textsubscript{x} but higher O\textsubscript{3}-VOC. The new source allocation method for O\textsubscript{3}-VOC can lead to up to 10% differences for industrial and biogenic sectors.

1. Introduction

High concentrations of tropospheric ozone (O\textsubscript{3}) can cause significant health problems on human, such as irritation of the respiratory system and aggravation of asthma (Brauer et al., 2016; Li et al., 2015; Lippmann, 1993; Liu et al., 2013). Exposure to high concentrations of O\textsubscript{3} is also known to have adverse effects on crops and ecosystems (Feng et al., 2015; Madronich et al., 2015). While fine particulate matter (PM\textsubscript{2.5}) has been the pollutant of focus in recent years in China, O\textsubscript{3} concentrations in many urban areas are high (Wang et al., 2017) with
increasing trends (Ma et al., 2016; Ou et al., 2016; Shao et al., 2006), and are projected to continue to rise (Wang et al., 2013). Thus, as O3 pollution gradually becomes more serious, identification and quantification of the sources that contribute to O3 formation is essential in formulating cost-effective emission control policies.

As the O3 formation reactions in the troposphere involve a variety of volatile organic compounds (VOCs) and nitrogen oxides (NOx, NO + NO2) and are highly nonlinear, different apportionment approaches tend to yield different results due to their different underlying assumptions (Cohan and Napelenok, 2011). Existing O3 formation and source apportionment studies in China mostly focused on three densely populated metropolitan areas, the Beijing-Tianjin-Hebei (BTH) region, the Yangtze River Delta (YRD) and the Pearl River Delta (PRD). Most of the studies used emission-based chemical transport models (CTMs) to investigate the complex source-receptor relationships between O3 in target areas and O3 precursors from different sources and source regions. Source contributions to O3 was studied using regular CTMs with a brute-force (BF) method that excludes emissions from one source sector at a time and compares the resulted O3 concentrations with a base case simulation (Feng et al., 2016; Li et al., 2017). However, due to non-linear dependence of O3 on precursor concentrations, the BF approach for O3 is usually considered less accurate due to its underlying linear assumption. Qu et al. (2014) attempted to improve the BF method by introducing additional simulations that remove more than one source at a time in order to estimate non-linear interactions. However, 32 regional CTM simulations are needed to fully determine contributions from 5 sectors, making it inefficient to apply the technique in long-term simulations. Dunker (2015) showed that source apportionment calculations of secondary pollutants such as ozone can be done by gradually changing the precursor emissions using a path-integral approach but the results depend on the assumptions of how precursor emissions are reduced.

A summary of previous O3 source apportionment studies can be found in Table S4. Wang et al. (2009), Li et al. (2012) and Li et al. (2016) applied the O3 Source Apportionment Technology (OSAT) in the Comprehensive Air Quality Model with Extensions (CAMx) to study local and regional contributions to O3 in Beijing (summer 2000), the PRD region (summer and fall 2006) and the YRD region (summer 2013), respectively. The OSAT attributes in-situ O3 formation to either NOx or VOC sources based on the value of an indicator that determines O3 formation sensitivity regime as NOx or VOC-limited. Non-reactive tracers are used to track NOx and VOCs related O3 attributed to different sectors or source regions. A technique similar to OSAT has been incorporated into the coupled Weather Research and Forecasting/Chemistry (WRF/Chem) model by Gao et al. (2016) to attribute O3 to local and regional sources in the YRD region in May 2013. In Beijing, mobile and industrial sources are two leading sources of O3 followed by point and biogenic sources, as reported by Wang et al. (2009). In the PRD region, OSAT reported that motor vehicles and area source were the most important sources, and contributions from point and biogenic sources were also important (Li et al., 2012). In all these studies, it was found that a significant fraction of O3 can be attributed to regional transport. This is not surprising because of the relatively small target areas used in these studies and the relatively long atmospheric life time of O3 and its precursors. A comprehensive source apportionment study that reports source contributions to O3 in the entire China is needed to provide a complete understanding.

In OSAT and similar source apportionment techniques that classify in-situ O3 formation into either NOx or VOC-limited regimes, misallocation of O3 to NOx and VOC sources can occur if in-situ O3 formation is in a transition regime where both NOx and VOC changes can lead to perturbation of O3 formation in the same direction (Kwok et al., 2015). Wang et al. (2019) improved the traditional two-regime (2R) approach with a three-regime (3R) approach. O3 formation sensitivity is classified into VOC-limited, transition and NOx-limited regimes. In the transition regime, O3 formation is proportionally attributed to NOx and VOC sources depending on the relative sensitivity of O3 to NOx and VOC changes. Using this improved approach, Wang et al. (2019) defined threshold indicator values for the transition regimes and illustrated that during summertime a significant fraction of O3 formation occurs in the transitional regime. Approximately 20–30% of non-background O3 formed in the BTH regions previously attributed to VOCs should be attributed to NOx instead. However, detailed source apportionment simulations were not conducted thus it is unclear how this change in NOx and VOC attributions can affect source apportionment results.

The objective of this study is to determine the contributions of major anthropogenic (industries, power plants, residential and transportation) and biogenic sources to summertime O3 in the whole China using the improved O3 attribution scheme in a regional CTM. Source contributions to O3 from these sectors are quantified for each province. Differences in source apportionment of O3 using the traditional 2R approach and the improved 3R approach are also evaluated. In addition, differences in source contributions to O3 during high and low O3 periods are compared to improve the understanding of the cause of high O3 days.

2. Methods

2.1. Attributing in-situ O3 to NOx and/or VOCs based on a three-regime classification

An improved attribution of in-situ O3 to NOx and VOCs based on the 3R NOx-VOC-O3 sensitivity regime classification scheme (Wang et al., 2019) is implemented into a modified Community Multiscale Air Quality (CMAQ) model (version 5.0.1) (Appel et al., 2013; Byun and Schere, 2006; Foley et al., 2010) in this study. In summary, the 3R scheme classifies in-situ O3 formation at each grid cell into one of the three regimes, VOC-limited, transition and NOx-limited, based on the value of a regime indicator. While the regime transition values for several different regime indicators were reported in the literature, the regime indicator R defined in equation (1) is used in the current study:

\[ R = \frac{P_{H2O2} + P_{ROOH}}{P_{HNO3}} \]  

where \( P_{H2O2} \) is the formation rate of hydrogen peroxide (H2O2); \( P_{ROOH} \) is the formation rate of organic peroxyde (ROOH), and \( P_{HNO3} \) is the formation rate of nitric acid (HNO3) in each chemistry time step. The threshold values for the start (Rts, i.e. switching from VOC-limited to transition regime) and end (Rte, i.e. switching from transition to NOx-limited regime) of the transition regime for this indicator are 0.047 and 0.142 (Wang et al., 2019), respectively. These threshold values are derived based sensitivity simulations for summer 2013 that cover all regions of China where significant ozone formation is predicted. Subsequently, the same set of threshold values is applied in all regions in this study. Similar to the traditional 2R classification used in previous O3 source apportionment models (Kwok et al., 2015, and the references therein), when the in-situ O3 formation is considered in the NOx-limited (R > Rts) or VOC-limited (R < Rts) regime, the newly formed O3 is attributed entirely to NOx and VOC sources. However, when the O3 formation is in the transition regime (Rts ≤ R ≤ Rte), in-situ O3 is attributed to both NOx and VOC sources. The fraction of O3 formed in the transition regime attributed to NOx (FNOx) can be expressed in equations (2) and (3), both are functions of the indicator R:

\[ F_{NOx} = 3.718R, \quad R_{ts} \leq R < R_{tx} \]  
\[ F_{NOx} = R/(1.049R + 0.136), \quad R_{tx} \leq R \leq R_{te} \]
Fig. 1. Average source contributions to 8-hr O$_3$ attributed to NO$_x$ (O$_3$ NO$_x$, column 1), VOCs (O$_3$ VOC, column 3), and to 8-hr O$_3$ formed in the transition regime attributed to NO$_x$ (O$_3$ NO$_x$ TRS, column 2) and VOCs (O$_3$ VOC TRS, column 4). Emissions from different sectors in other countries are combined and considered as a single class. The IC/BC contributions are O$_3$ formed attributed to NO$_x$ and VOCs entered the domain through initial and boundary conditions. O$_3$ directly enters the domain through initial and boundary conditions are referred to as “background” O$_3$ and is not included in the IC/BC class. Units are ppb.
for O₃ attribution is evaluated against a stepwise brute-force (BF) method by Wang et al. (2019). The stepwise BF uses a series of perturbation simulations which alternatively reducing NOₓ and VOC emissions until zero to determine the contributions of NOₓ and VOCs to ozone. The 3R method shows better agreement with the stepwise BF results than the traditional 2R approach that does not consider the transition regime.

2.2. Source apportionment of O₃

Once the amount of in-situ O₃ attributed to NOₓ (henceforth O₃_{NOₓ}) and VOCs (henceforth O₃_{VOC}) are determined, they need to be apportioned to different NOₓ and VOC sources accordingly. In this study, concentrations of O₃_{NOₓ} and O₃_{VOC} from different sources are tracked using non-reactive O₃ tracers. The concentrations of these tracers are not updated during the regular gas phase chemistry time step but are updated afterwards based on the O₃ production and removal rate as well as the concentrations of the NOₓ and VOCs from different sources, which are actively tracked in the gas phase chemistry using additional model species. The source-oriented framework to actively track NOₓ and VOC sources from different sources is summarized in the next section. In the following, the approach to apportion in-situ O₃ formation to different NOₓ and VOC sources, which is mostly based on the method used by Kwok et al. (2015), is described.

The first step in the calculation is to calculate the intermediate concentrations of O₃ attributed to NOₓ (O₃_{NOₓ,i}) and VOC (O₃_{VOC,i}) from the ith source by considering the O₃ production (P_{O₃}, ppb/time step), as shown in equations (4) and (5):

\[ O_{3,NOx,i}^{int} = O_{3,NOx,i-\Delta t} + P_{O₃} F_{NOx,i} S_{NOx,i} \quad i = 1, \ldots, N_i \]

\[ O_{3, VOC,i}^{int} = O_{3, VOC,i-\Delta t} + P_{O₃} (1 - F_{NOx,i}) S_{VOC,i} \quad i = 1, \ldots, N_i \]

where i is the source index; the superscript int indicates intermediate concentrations, and superscript t-\Delta t denotes concentrations from the previous time step; \( F_{NOx} \) is the attribution function defined in equations (2) and (3); \( F_{NOx} \) is zero when \( R < R_{ts} \) and \( F_{NOx} = 1 \) when \( R > R_{te} \); \( S_{NOx,i} \) and \( S_{VOC,i} \) are source apportionment functions to apportion incremental O₃_{NOₓ} and O₃_{VOC} to the ith source of NOₓ and VOCs, respectively. In this study, \( S_{NOx} \) and \( S_{VOC} \) are calculated using equations (6) and (7):

\[ S_{NOx,i} = \frac{P_{NOx,NOx,i}}{\sum_{j=1}^{N_i} P_{NOx,NOx,j}} \]

\[ S_{VOC,j} = \frac{P_{NOx,VOC,j} + \sum_{j=1}^{N_r} P_{NOx,RO,RO,j}} {\sum_{j=1}^{N_r} \left(P_{NOx,RO,RO,j} + \sum_{j=1}^{N_r} P_{NOx,RO,RO,j} \right)} \]

where \( P_{NOx,NOx,i} \) is the formation of O³⁻⁻⁻ radical from photolysis of NO₂ from the ith source; \( P_{NOx,VOC,j} \) and \( P_{NOx,RO,RO,j} \) are the formation of NO₂ due to NO reacting with HO₂ and organic peroxy radicals (RO₂) generated from degradation of organic compounds from the ith source, respectively, and j is peroxy radical index. \( N_r \) is the total number of different RO₂ radicals in the photochemical mechanism. Using NO₂ photolysis rate to differentiate local and background O₃ was first used by Zhang and Ying (2011). Using NO to NO₂ conversion by organic peroxy radicals has been suggested and applied by Ying and Krishnan (2010) to study contributions of different VOC sources to O₃ formation in southeast Texas.

In the traditional source apportionment method, \( S_{NOx} \) and \( S_{VOC} \) are
calculated using total NOx and maximum incremental reactivity (MIR) weighted VOC concentrations, as shown in equations (6a) and (7a):

\[
S_{\text{NOx},i} = \frac{C_{\text{NOx},i} + C_{\text{NOx},j}}{\sum (C_{\text{NOx},i} + C_{\text{NOx},j})}
\]

(6a)

\[
S_{\text{VOC},i} = \frac{\sum (C_{\text{VOC},i} + MIR_j)}{\sum (\sum (C_{\text{VOC},i} + MIR_j))}
\]

(7a)

where \(N_c\) is the number of VOCs included in the calculation, \(C_{\text{VOC},j,i}\) is the concentration of the \(j\)th VOC from the \(i\)th source, and \(MIR_j\) is the maximum incremental reactivity of the \(j\)th VOC. \(C_{\text{NOx},i}\), and \(C_{\text{NOx},j}\) are concentrations of NO and NO\(_2\) from the \(i\)th source, respectively. The MIR values for the VOC species included in equation (7)' are listed in Table S1. The differences in the expected source apportionment results due to different source attribution functions are discussed in Section 5.2.

The intermediate concentrations are then used to update the concentrations of \(O_3\)NO\(_x\),\(i\) and \(O_3\)VOC\(i\) by including the \(O_3\) removal terms, as shown in equations (8) and (9):

\[
O_{3\_NOx,ij} = O_3\_NOx^{int}_{ij} - D_{O3} \sum_{i=1}^{N_c} (O_3\_NOx^{int}_{ij} + O_3\_VOC^{int}_{ij}), \quad i = 1,2,...N_c
\]

(8)

\[
O_{3\_VOC,ij} = O_3\_VOC^{int}_{ij} - D_{O3} \sum_{i=1}^{N_c} (O_3\_NOx^{int}_{ij} + O_3\_VOC^{int}_{ij}), \quad i = 1,2,...N_c
\]

(9)

where \(D_{O3}\) is the in-situ \(O_3\) removal rate. To quantify contributions of different sources to \(O_3\) formed in the transition regime, another set of \(O_3\) tracers \(O_3\)TRS\(_{NOx}\),\(i\) and \(O_3\)TRS\(_{VOC}\),\(i\) are included in the analysis. Equations to update their concentrations are similar to equations (4)–(9) and are not repeated here.

Equations (8) and (9) do not use bulk \(O_3\) in denominators. When background ozone reacts with NO, it is not permanently removed as the NO\(_2\) forms from the \(O_3 + NO\) reaction will lead to re-formation of \(O_3\) in the photolytic cycle, and this reformed \(O_3\) should be still be considered as background. However, in the current approach, \(O_3\) formation is always attributed to some emission sources, as shown in equations (4) and (5). Thus, equations (8) and (9) should not use the bulk \(O_3\) to avoid incorrectly attributing background ozone to emission sources.

2.3. Source apportionment of NO\(_x\) and VOCs

The source-resolved formation rates needed for equations (6) and (7) and the concentrations of NO\(_x\) and VOC\(_s\) needed for equations (6)' and (7)' are calculated at each chemistry time step using an expanded source-oriented photochemical mechanism that tracks the emissions of NO\(_x\) and VOC\(_s\) from different sources and their reaction products using reactive source-tagged species. Reactions of these source-tagged species are generated based on the reactions of their corresponding non-tagged species. The source-oriented approach using reactive tagged species has been applied previously to the NO\(_x\) related reactions for source apportionment of nitrate aerosol (Zhang et al., 2012) and to VOC\(_s\) related reactions for source apportionment of SOA (Wang et al., 2018). In this study, a modified lumped SAPRC-11 mechanism (Carter and Heo, 2013; Ying et al., 2015) was expanded to simultaneously track NO\(_x\) primary VOC\(_s\) and their reaction products from two separate sources. The entire expanded reaction system includes 1356 reactions and 350 species. A few reactions to explain the concept are provided below. Reaction sets (RS1), (RS2) and (RS3) show examples of the reactions of NO\(_x\) species, organic peroxy and hydroperoxyl radicals, and double tagged species with both NO\(_x\) and VOC precursors, respectively:

\[
\text{OH} + \text{NO}_2^{x1} = \text{HNO}_3^{x1}
\]
OH + NO₂ → HNO₃⁺
MEO₂⁺ + NOₓ = NO₂⁺ + HCHO⁺ + HO₂⁺
MEO₂⁺ + NOₓ = NO₂⁺ + HCHO⁺ + HO₂⁺
MEO₂⁺ + NOₓ = NO₂⁺ + HCHO⁺ + HO₂⁺
MEO₂⁺ + NOₓ = NO₂⁺ + HCHO⁺ + HO₂⁺

OH₂ species produced from the RO₂ + NO reaction has the same source tag as its RO₂ precursor. PAN is a double-tagged species so that the correct sources of MECO₃ and NO₂ can be determined during its thermal decomposition reaction.

While this source-oriented approach can be applied to develop mechanisms with more than two groups of tagged species, the number of reactions increases rapidly due to reactions with multiple tag-species such as RS₂ and RS₃. Thus, as an illustration of concept, it is limited to two sources in this study. For source apportionment calculations for N sources, N model simulations need to be carried out. In each simulation, emissions from one explicit source are tracked using X₁ species, and emissions from all other sources, including initial and boundary conditions, are lumped and treated as X₂ species.

Table 1

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<th>Province</th>
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<th>NB ppb</th>
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*Ind.: industry; Res.: residential; Transp.: transportation; Power: Power plants; OB: open burning; Biog.: biogenic; Other Count.: other countries; IC/BC: initial and boundary conditions.

Fig. 4. Average 8-hr O₃ concentrations on (a) high O₃ days (8-hr O₃ > 80 ppb) and (b) low O₃ days (8-hr O₃ within 40 and 80 ppb) during August 2013. The red box marks the region with high O₃ concentrations where differences in source contributions between high and low ozone days are shown in Fig. 5. (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)
3. Model application

The source-oriented CMAQ model was applied to determine source contributions to O₃ in China in August 2013. The model domain has a horizontal resolution of 36 × 36 km² and covers China and surrounding areas (Fig. S1). Meteorological inputs for the CMAQ model were generated using the Weather Research and Forecasting (WRF) model version 3.6.1, driven by initial and boundary conditions based on the FNL reanalysis data from the National Centers for Environmental Prediction (NCEP). Anthropogenic emissions in China were based on the Multi-resolution Emission Inventory for China (MEIC) version 1.0, which groups emissions into four sectors, industries, residential, power plants and transportation. Open burning emissions were generated using an inhouse program using inputs from the FINN inventory from the National Center for Atmospheric Research (NCAR) (Wiedinmyer et al., 2011). Emissions from biogenic sources were generated using MEGAN v2.1. The Regional Emission inventory in ASia v2.1 (REAS2) (Kurokawa et al., 2013) was used to generate emissions for other countries in the model domain. The CMAQ vertical domain is divided into 18 layers with increasing layer thickness. The surface layer is ∼35 m and the total height is approximately 10 km. The initial and boundary conditions for the simulation were based on the CMAQ default profiles which represent unpolluted continental condition. More details of the meteorological and emission processing for this episode can be found in Hu et al. (2016). The capability of this WRF/CMAQ setup in reproducing observed pollutant concentrations, including O₃, PM₂.₅, VOCs, and PM₁₀ primary and secondary components has been extensively evaluated in previous studies (Hu et al., 2015, 2016, 2017; Shi et al., 2017; Ying et al., 2018). The mean normalized bias (MNB) and mean normalized error (MNE) of hourly O₃ (> 60 ppb) for four representative cities are shown in Fig. 3. The overall model performance for August is also acceptable, with MNB = 0.06 and MNE = 0.30 for 1-h peak O₃.

In this study, source contributions to regional O₃ were determined for industries, residential, power plants, transportation, open burning and biogenic sources. In addition, contributions to O₃ due to NOₓ and VOCs emissions from other countries and from initial and boundary conditions were also explicitly determined. The background O₃ concentration at each grid was estimated by the difference between the overall concentration and the sum of the source-resolved O₃ (i.e. non-background O₃). Thus, the non-background O₃ includes O₃ due to NOₓ
and VOCs from the anthropogenic and biogenic emission sources in China, from other countries and from initial and boundary conditions. The indirectly calculated background O₃ provides an estimation of the amount of O₃ directly entering the domain via initial and boundary conditions.

Two sets of source apportionment calculations were performed. One used the 3R approach described in Section 2 and other used the traditional 2R approach with a threshold value of 0.5 (Tonnesen and Dennis, 2000) to determine whether O₃ formation in the NOₓ or VOC-limited regime. Both sets of simulations used the O₃-sensitivity regime indicator as defined in equation (1), and the source apportionment function equations (6) and (7).

4. Results

4.1. Regional source apportionment of O₃

Fig. 1 and Fig. S2 show the regional concentrations and fractional contributions of August monthly average 8-hr O₃ attributed to different sources of NOₓ and VOCs. Industries, transportation, power and biogenic sources are four major emission sectors that contribute to O₃_NOₓ with different spatial distributions. This is consistent with the source
The apportionment of NOx results shown in Fig. S3. The high O3_NOx areas of the industrial sector (generally 8–15 ppb or approximately 20–25% of total O3, with a maximum concentration of 30 ppb) are mainly located in north and northeast China (Liaoning, Hebei, and Shandong; locations of the provinces in China can be found in Fig. S1), central China, the YRD and part of the SGB. The O3_NOx attributed to the transportation sector reaches a maximum of 18 ppb, with a spatial distribution similar to that of the industrial sector. For power sector, the high O3_NOx regions are located in Shanxi, Shaanxi, Ningxia and part of Shandong and Jiangsu with 10–15% relative contributions to total O3.

In mountainous regions in west, central and south China, especially the areas with low NOx emissions from anthropogenic sources, O3 formation is in the NOx-limited regime. Biogenic NO (i.e. NO emitted from microbial activities in the soil) can contribute to a significant fraction (as high as 30–40%) of total NO2 (see Fig. S3). O3 attributed to biogenic NOx in these areas reaches as high as 10–15% of total O3 and a maximum concentration of 12 ppb. The O3_NOx formed in the transition regime (O3_NOx_TRS) accounts for a significant fraction of the total O3_NOx (column 2 in Fig. 1), mostly in the high O3 concentration areas in north, central and east China. The source contributions to O3_NOx averaged for each province can be found in Table S2.

O3 attributed to VOCs does not have a regional distribution as broad as that attributed to NOx. This is because most of the VOC-limited grid cells are located at urban cores in big cities as well as some large city clusters in the YRD and PRD regions (Wang et al., 2019). The transition areas with more O3 formation attributed to VOC sources are mostly located in the urban areas near the VOC-limited grid cells. Biogenic and industrial sectors are the most important emission sectors that contribute to O3_VOC. The high contributions of the industrial sector to VOCs are likely due to emissions from solvent utilization processes (Wang et al., 2018). The high concentration areas of the biogenic sector are located in Shandong, Jiangsu, Henan and Anhui with the highest fraction to total O3 of ~20%. It is interesting to note that this does not agree with the spatial distribution of the emissions of biogenic VOCs.

Fig. 7. Monthly averaged source contributions to O3_NOx, O3_VOC and total non-background O3 in Beijing, Shanghai, Guangzhou and Chengdu estimated by the 3R and 2R approaches. Numbers at the center of the pie charts are average concentrations in ppb.
Understanding the cause of high O$_3$ concentrations in northern, eastern and southeast China, using the MOZART leads to less than 10 ppb increase in the total O$_3$ concentrations. The differences are larger in several western provinces. Thus, the amount of background O$_3$ in these regions might be underestimated.

4.2. Time series of source contributions to O$_3$

Fig. 3 shows the diurnal and day-to-day variation and source apportionment of hourly O$_3$NOx, O$_3$ VOC and total non-background O$_3$ (O$_3$NOx + O$_3$VOC) in four megacities: Beijing, Shanghai, Guangzhou and Chengdu in August 2013. Overall, the model predictions reproduced observed diurnal and day-to-day variations although several O$_3$ peaks were underpredicted. This good agreement between observations and predictions provides confidence in the predicted source apportionment results. Hourly concentrations of O$_3$NOx can reach high concentrations in all four cities, with peak O$_3$NOx approaching 80 ppb in Beijing, Shanghai and Chengdu on several days. Peak O$_3$NOx in Guangzhou is usually low although on a few days it can reach 40–50 ppb. Industries and transportation are the two major contributors in all four cities. Power plants contributions are significant in three of the four cities except Chengdu, where transportation sector contributions are on par with the industrial sector. Concentrations of O$_3$VOC are lower than O$_3$NOx in general. Peak hourly concentrations reach ~20 ppb with contributions mostly due to industrial and biogenic sources. In Shanghai, contributions to O$_3$VOC due to industrial sources can be much higher on high O$_3$ days, reaching 40 ppb in several days, which leads to overall O$_3$VOC concentrations of approximately 60 ppb. The biogenic sector is a more significant contributor in Beijing and Chengdu with the highest values ~15 ppb and ~20 ppb, respectively. On several days, contributions of open burning to O$_3$VOC are also predicted, with a highest hourly concentration of approximately 20 ppb in Shanghai on August 6. When both O$_3$NOx and O$_3$VOC are included, non-background O$_3$ can be responsible for as much as 60–70% of total O$_3$ on high O$_3$ days in Beijing, Guangzhou and Chengdu. In Shanghai, this fraction can be as high as 80%.

4.3. Differences in source contributions on low and high O$_3$ days

A sensitivity simulation using boundary conditions derived from the Model for Ozone and Related Chemical Tracers (MOZART, downloaded from https://www.acom.ucar.edu/wrf-chem/mozart.shtml) were conducted. Fig. S5 shows that in the high O$_3$ generation regions in northern, eastern and southeast China, using the MOZART leads to less scrutiny in future studies. The source contributions to O$_3$NOx and uncertain (Wang et al., 2018), thus this conclusion requires more urban areas. VOC emission rates from transportation sources are rather emissions to O$_3$VOC are small, on the order of a few percent in most versions of the MEIC emission inventory, contributions from tra China is from the biogenic and industrial sectors. Based on the current version of the MEIC emission inventory, contributions from traffic emissions to O3 VOC are small, on the order of a few percent in most urban areas. VOC emission rates from transportation sources are rather uncertain (Wang et al., 2018), thus this conclusion requires more scrutiny in future studies. The source contributions to O3NOx and O3VOC for each province can be found in Tables S2 and S3, respectively.

Table 1 summarizes the monthly average 8-hr total and non-background O$_3$ and source contributions to non-background O$_3$ for each province. The overall regional source contributions (O$_3$NOx + O$_3$VOC) to monthly average 8-hr O$_3$ are shown in Fig. 2, with fractional contribution shown in Fig. S4. Due to its high contributions to both O$_3$NOx and O$_3$VOC, the industrial sector has the highest concentrations and contributions to O$_3$ in large areas, particularly in the south part of the Hebei province, the traditional industrial regions in northeast China and SCB, and urban and industrial regions along the east coast. For transportation and power plants sectors, their contributions to O$_3$VOC are small, so their overall regional contributions are similar to those in Fig. 1. The overall contributions of biogenic sources to O$_3$ are 8–14 ppb, or 12–20%, in areas in central and east China, and in SCB. The background O$_3$ is highest (~50 ppb) in high elevation areas in Tibet, Xinjiang and part of the Inner Mongolia. It accounts for almost 100% of the total O$_3$ concentrations in these areas. In east and southeast China, a background concentration of ~25 ppb is predicted.

A sensitivity simulation using boundary conditions derived from the Model for Ozone and Related Chemical Tracers (MOZART, downloaded from https://www.acom.ucar.edu/wrf-chem/mozart.shtml) were conducted. Fig. S5 shows that in the high O$_3$ generation regions in northern, eastern and southeast China, using the MOZART leads to less
O₃ on high O₃ (8-h O₃ > 80 ppb) and low O₃ (40 ppb < 8-h O₃ ≤ 80 ppb) days are investigated. From Fig. 4a, areas experienced at least one high O₃ day are mainly located at the BTH region and LiaoNing, Shanxi, Henan and Jiangsu and Shanghai. In Shanghai and south Jiangsu the average 8-h O₃ on high O₃ days is over 140 ppb, which is approximately 1.75 times that of the Class II daily maximum 8-h average O₃ standard of 160 μg m⁻³ (or approximately 75 ppb under 273K and 1 atm) required by the Ministry of Environmental Protection (MEP) of China (MEP, 2012). For days with 8-h O₃ less than 80 ppb, higher average concentrations occur in north and central China with an average concentration of approximately 60–70 ppb (Fig. 4b).

Average relative source contributions to non-background 8-h O₃ on low and high O₃ days are compared in Fig. 5. While O₃ concentrations attributed to all major source sectors increase during high O₃ days (Fig. S6), source contributions to non-background O₃ from biogenic sources on low O₃ days in August are generally higher than on high O₃ days. The decrease in biogenic contributions leads to increase in contributions due to anthropogenic sources, most noticeably in the industrial and power plants sectors. Since the emissions of anthropogenic sources in the same month in this study only have weekday-weekend differences but biogenic emissions are calculated based on meteorological conditions, the decrease in biogenic relative contributions is likely due to decrease in biogenic emissions on high O₃ days. If changes in anthropogenic emissions due to meteorological conditions had also been considered properly (e.g. increase of power plants emissions on high temperature days due to higher energy demand), the relative contributions of biogenic emissions would have been even lower.

5. Discussion

5.1. Compare with the two-regime source apportionment results

The source apportionment results in previous sections are based on the 3R approach. The 2R and 3R approaches only affect concentrations of non-reactive O₃ tracers but the sum of non-background ozone from the two approaches are the same because they use the same chemical mechanism, and thus the have the same amount of net ozone formation in each model time step. The source apportionment results are compared with those from the traditional 2R approach as shown in Fig. 6 for industries, transportation, power plants and biogenic sectors for monthly average 8-h O₃ concentrations. The 3R approach leads to higher contributions of O₃ NOₓ and lower contributions of O₃ VOC by as much as 8–10 ppb in urban areas where the 2R approach classifies them as VOC-limited, but the 3R approach classifies them as transition. Since the industrial sector accounts for a larger fraction of NOₓ than the power plants and transportation sectors, it has the biggest difference by up to 4 ppb in O₃ NOₓ. The transportation and power plants sectors show a difference of 1–2 ppb O₃ NOₓ each. For O₃ VOC, the 3R approach predicts lower contributions than the 2R approach. The biggest differences are in the industrial and biogenic sectors, by as much as 2 and 4 ppb, respectively.

Fig. 7 compares source apportionment of monthly 8-h O₃ using the 2R and 3R approaches for the four cities discussed in Fig. 3. The two approaches lead to relatively large differences in the total O₃ VOC and O₃ NOₓ estimations. For example, in Chengdu the 2R approach estimates that O₃ VOC is slightly higher while the 3R approach estimates that O₃ NOₓ is almost two times of O₃ VOC. The relative source contributions to O₃ VOC and O₃ NOₓ between the two approaches are very similar but the overall source apportionment shows bigger differences. In general, the overall source contributions determined by the 3R approach are higher than the 2R approach for anthropogenic sources but are lower for the biogenic sector.

5.2. Source attribution functions for NOₓ and VOCs

Another uncertainty in O₃ source apportionment comes from the source apportionment functions. Fig. 8 shows the VOC source apportionment factors (equations (7) and (7)’) for industry and biogenic sectors based on monthly average concentrations and conversion rates during the hours for 8-hr O₃ calculations. For the industry sector, the attribution factors based on MIR weighted concentrations (equation (7)’) are usually higher than those based on the NO to NO₂ conversion rates (equation (7’)), with a difference of 5–10%. The trend is opposite for the biogenic sector. The MIR-based approach leads to a smaller fraction of 5–10%. Differences for other source sectors are generally small (Fig. S7). The differences in NOₓ apportionment factors, arising from equations (6) and (6)’ are generally small and are not expected to cause major differences in source apportionment estimations for O₃ NOₓ (Figs. S8 and S9). As the MIR value for sesquiterpenes are not available, a sensitivity calculation using equation (7)’ was performed to include sesquiterpenes (model species SESQ), assuming its MIR value is the same as TERP (likely over-estimated based on personal communication with W.P.L Carter). However, this does not lead to significant differences in the calculated source attribution factors due to low concentrations of SESQ. In conclusion, using the source apportionment functions in traditional O₃ source apportionment techniques are expected to cause significant differences in source apportionment estimations in areas where O₃ VOC is high, and are significantly influenced by industrial and/or biogenic VOC emissions.

The complexity in the current treatment is to expand the mechanism to track sources of RO₂. Although this is theoretically more accurate in attributing VOC source contributions to O₃ than the MIR based approach, the difference is relatively small (10–15%). A simplified source apportionment method that includes the 3R treatment in O₃ attribution but based on the concentration weighted MIR to apportion O₃ to VOC emission sources can be developed. This will significantly simplify the mechanism and allows simultaneous ozone source apportionment for multiple sources.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.atmosenv.2019.05.006.

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