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Identification of close relationship between atmospheric oxidation and ozone formation regimes in a photochemically active region

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A R T I C L E   I N F O
Article history:
Received 5 July 2020
Revised 28 September 2020
Accepted 29 September 2020
Available online 21 October 2020

Keywords:
Atmospheric oxidation
O₃ formation regimes
WRF-CMAQ
Photochemically active region

A B S T R A C T
Understanding ozone (O₃) formation regime is a prerequisite in formulating an effective O₃ pollution control strategy. Photochemical indicator is a simple and direct method in identifying O₃ formation regimes. Most used indicators are derived from observations, whereas the role of atmospheric oxidation is not in consideration, which is the core driver of O₃ formation. Thus, it may impact accuracy in signaling O₃ formation regimes. In this study, an advanced three-dimensional numerical modeling system was used to investigate the relationship between atmospheric oxidation and O₃ formation regimes during a long-lasting O₃ exceedance event in September 2017 over the Pearl River Delta (PRD) of China. We discovered a clear relationship between atmospheric oxidative capacity and O₃ formation regime. Over eastern PRD, O₃ formation was mainly in a NOₓ-limited regime when HO₂/OH ratio was higher than 11, while in a VOC-limited regime when the ratio was lower than 9.5. Over central and western PRD, an HO₂/OH ratio higher than 5 and lower than 2 was indicative of NOₓ-limited and VOC-limited regime, respectively. Physical contribution, including horizontal transport and vertical transport, may pose uncertainties on the indication of O₃ formation regime by HO₂/OH ratio. In comparison with other commonly used photochemical indicators, HO₂/OH ratio had the best performance in differentiating O₃ formation regimes. This study highlighted the necessities in using an atmospheric oxidative capacity-based

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https://doi.org/10.1016/j.jes.2020.09.038
1001-0742/© 2020 The Research Center for Eco-Environmental Sciences, Chinese Academy of Sciences. Published by Elsevier B.V.
Introduction

Tropospheric ozone (O₃) pollution is of great concern due to its adverse effects on human health, vegetation growth, and climate change (Swackhamer, 1993; Ainsworth et al., 2012; Zhang et al., 2016; Westervelt et al., 2019). In the troposphere, O₃ is generated by a series of photochemical reactions between its precursors, volatile organic compounds (VOCs) and nitrogen oxides (NOₓ, sum of nitric oxide (NO) and nitrogen dioxide (NO₂)), under conducive meteorological conditions such as high temperature, strong solar radiation, weak winds, and stable atmospheric boundary layer Logan (1989). Reduction of O₃ should be achieved by emission controls on VOCs, NOₓ, or both.

However, due much to the complex chemical reactions leading to O₃ formation, O₃ responses nonlinearly to precursor changes under different O₃ formation regimes Sillman (1999). For instance, when O₃ forms in a VOC-limited regime, VOCs control decreases O₃ level while NOₓ reduction would lead to O₃ increase, so-called ‘NOₓ disbenefits’, due to the reduced titration in removing O₃. Significant increases in O₃ mixing ratio and atmospheric oxidation capacity in response to the sharp decrease of NOₓ emissions in the recent Corona Virus Disease 2019 (COVID-19) outbreak over northern China provided a perfect illustration on NOₓ disbenefits under a VOC-limited regime (Huang et al., 2020; Le et al., 2020; Sicard et al., 2020; Wang et al., 2020). The maximum daily 8 h average (MDA8) O₃ concentration had increased by 18% over the PRD due to the COVID-19 lockdown in China (Zhao et al., 2020).

Extensive studies have been conducted to investigate O₃-precursor nonlinearity using different methods, including photochemical indicators (e.g. Sillman et al., 1996; Sillman, 1995; Kleinman et al., 1997; Jaegle et al., 1998), Observation-Based Model (OBM) (e.g., Cardelino and Chameides, 1995; Kumar and Russell, 1996; Cheng et al., 2010), and Emission-Based Model (EBM) (e.g., Ou et al., 2016; Sharma and Khare, 2017). Due much to its simplicity, the photochemical indicator approach has been widely applied to identify O₃ formation regimes. A series of photochemical indicators were proposed and their values quantified to separate O₃ formation regime into VOC-limited and NOₓ-limited, including but not limited to, VOCs/NOₓ ratio of 8 (Sillman, 1995; Sillman, 1999), H₂O₂/NOₓ of 0.07–0.3 and O₃/NOₓ of 4–6 (Sillman and He, 2002), O₃/NOₓ of 2, O₃/NOₓ of 18–22 and H₂O₂/NOₓ of 2.5–3 Jiménez and Baldassano (2004), and H₂O₂/NOₓ of 0.2–2.4 (Liu et al., 2010). Note that a majority of these indicators were derived from routinely monitored pollutants due to the availability of monitoring data. Although simple and direct, they cannot delineate the complex photochemical process leading to O₃ formation, posing adverse impact on the accuracy of indicating O₃ formation regime. The role of atmospheric oxidation, the core driver of O₃ formation, was largely neglected.

Atmospheric oxidation plays a critical role in O₃ and secondary fine particles production. The hydroxyl radical (OH) and hydroperoxyl radical (HO₂), called HOₓ, are commonly used to characterize atmospheric oxidation. A series of studies have been performed to investigate the relationship between atmospheric oxidation and O₃ production (e.g. Monks, 2005; Mao et al., 2010; Ren et al., 2013). Previous studies have demonstrated that HOₓ oxidizing NO to produce NO₂ dominates O₃ production in late spring and summer of 2003 at Waliguan of China (Xue et al., 2013), and higher O₃ production was generally associated with greater OH production in the summer of 2006 at Houston (Mao et al., 2010). Although the impact of the atmospheric oxidation on O₃ production have been extensively studied, the impacts of atmospheric oxidation on O₃-precursor nonlinearity and O₃ formation regimes, the essential indicators for O₃ pollution control, remain a large knowledge gap.

In this study, we selected Pearl River Delta (PRD) of China as our research target area to investigate the interplay between atmospheric oxidation and O₃-precursor nonlinearity. Located in southern China, PRD is one of the most photochemically active regions in the world due to its warm weather, strong solar radiation and intense VOCs and NOₓ emissions attributed to rapid urbanization and industrialization (Chan and Yao, 2008; Lu et al., 2019). PRD has been suffering from significant and worsening O₃ pollution. The annual 90th percentile of MDA8 O₃ concentration had increased by 2.1% per year since 2013 and reached 176 μg/m³ in 2019, exceeding the national tier-II standard of 160 μg/m³. Such a dramatic increase is largely driven by the high oxidative capacity over the region. OH and HO₂ average concentration of 0.63 pptv and 63 pptv, respectively, were measured in the summer of 2006 (Hofzumahaus et al., 2009), which are the highest OH and HO₂ levels ever recorded in the world. Such a high HOₓ radical concentration poses great challenges on O₃ control, and may potentially impact O₃ formation regime. Studies showed that PRD was generally in a VOC-limited regime, but with significant diurnal and inter-episode variations (Zhang et al., 2008; Shao et al., 2009; Wang et al., 2011; Li et al., 2013; Zou et al., 2015). In general, VOCs control is the most effective way to reduce peak O₃ levels but a shift to NOₓ-limited regime with stringent NOₓ control is required for O₃ attainment in the long term (Ou et al., 2016). Hence, the mechanism of atmospheric oxidation, especially the role of HOₓ radicals in shaping O₃ formation regimes over the PRD, deserves detailed investigation.

In this study, we applied a two-way coupled Weather Research and Forecasting – Community Multi-scale Air Quality (WRF-CMAQ) modeling system to investigate the relationship between oxidative capacity and O₃ formation regime
in September 2017, a month with long-lasting O3 pollution episode over the PRD. Emission reduction scenario analysis was performed to identify the O3 formation regime on each day. We demonstrated that HO2/ OH is a better indicator for O3 formation regime in the PRD, and process analysis (PA) can explain the underlying reasons of the relationship between HO2/OH ratio and O3 formation regime. We thereby recommended using the HO2/OH ratio for signaling O3 control strategies over the PRD and other photochemically active regions worldwide alike.

1. Methodology and data

1.1. Modeling system and configurations

The version 5.0.2 of WRF-CMAQ modeling system was used in this study. The modeling domains were configured using the Lambert projection, with a triple-nested grid centered at 28.5°N 114°E and two true latitudes for the projection at 15°N and 40°N as the basic projected coordinate. In order to avoid interference of meteorological boundary fields during model simulation, the WRF simulation domain (Table S1) was slightly larger than the CMAQ simulation domain (Table S2 and Fig. S1a). The outermost domain (D1) covers much of East Asia, Southeast Asia and the northwestern Pacific with a resolution of 27 km, the middle domain (D2) covers most of Guangdong province with a resolution of 9 km, and the innermost domain (D3) covers most of the PRD region with a resolution of 3 km. There are 46 vertical levels from surface to the 50-hPa level. The height of the lowest vertical layer is about 44 m above the ground level.

In WRF simulation, the Final Operational Global Analysis data (FNL) at an interval of 6 h with the horizontal resolution of 1° × 1° provided by the National Centers for Environmental Prediction (NCEP) were used for initial and boundary conditions. The land use data was retrieved from Moderate Resolution Imaging Spectroradiometer (MODIS) observation. The specific WRF parameterization scheme can be found in Table S3.

Anthropogenic emissions in Guangdong Province were generated based on the 2017 latest emission inventory and transformed by the SMOKE-PRD emission processor into hourly gridded model-ready emission data to be used in the WRF-CMAQ modeling system. This localized inventory included emissions from sources of power plants, fixed combustion, on-road mobile, shipping, industrial process, solvent use, and biomass burning, for pollutants of sulfur dioxide (SO2), carbon monoxide (CO), NOx, anthropogenic VOCs (AVOCs), black carbon (BC), organic carbon (OC) and particulates (PM10 and PM2.5). Biogenic VOCs (BVOCs) emissions were calculated by the Model of Emissions of Gases and Aerosols from Nature (MEGAN) (Guenther et al., 2012). Multi-resolution Emission Inventory for China (MEIC) Model with a 1° × 1° resolution (http://www.meicmodel.org) and Regional Emission inventory in Asia (REAS) with a 0.25° resolution were adopted for areas in D1 and D2 outside Guangdong (Zhang et al., 2009; Kurokawa et al., 2013).

In CMAQ simulation, CB-05 gas-phase chemical mechanism and AER aerosol mechanism were used. Also incorporated in the CMAQ model were JRPRC module for clear-sky photolysis rate calculation, initial condition (ICON) module for initial chemical conditions, boundary condition (BCON) module for dynamic boundary conditions of the modeling domain, and CCTM module for continuous atmospheric chemical simulation. The specific CMAQ information can be obtained from Ou et al. (2016). Simulation was conducted for the entire month of September 2017 with significant O3 pollution. The first three-day simulation was treated as spin-up time and the model outputs were not included in the analysis.

The hourly observations on atmospheric temperature, wind speed and O3 concentration at seven sites across the PRD, including Jiangmen, Foshan, Guangzhou, Zuhai, Shenzhen, Zhongshan, and Huizhou, were used to evaluate model performance on replicating meteorological variables and ambient O3 level. Fig. S1b shows the geographical locations of the seven sites. Correlation coefficient (R) and mean bias (MB) between observed and simulated values were calculated, as shown in Tables S4 and S5.

1.2. Identification of O3 formation regime

As shown in Fig. S2, an emission reduction matrix, including 1 base case and 39 emission reduction scenarios with AVOCs and NOx emission reductions in various degrees (% change in gram), was designed to examine O3 changes in response of AVOCs and NOx reductions (Kinosian, 1982; Ou et al., 2016). Emission reductions were only conducted for D3, and only AVOCs were considered as BVOCs emissions are uncontrollable. O3 isopleth diagrams were plotted by interpolating O3 concentrations at different AVOCs and NOx reductions and were used to identify O3 formation regime on each day in September 2017.

In order to quantitatively identify O3 formation regime, we calculated T which is the ratio between O3 change in response to 10% reduction of NOx emission and that in response to 10% reduction of AVOCs emission. A T value less than 0.5 indicates AVOCs-limited O3 formation regime, 0.5 to 2 for a transitional regime, and higher than 2 for a NOx-limited regime (Sillman and West, 2009; Li et al., 2018).

1.3. Process analysis

We applied PA to estimate contributions to a particular species from different physical and chemical processes at each integration time step over each grid (Zhao et al., 2019). The WRF-CMAQ model calculates the time rates of change in chemical species concentrations (ci) by using the following mass continuity equation,

\[
\frac{\partial c_i}{\partial t} = - \left( u \frac{\partial c_i}{\partial x} + v \frac{\partial c_i}{\partial y} \right) - w \frac{\partial c_i}{\partial z} + \frac{\partial}{\partial z} \left( K_e \frac{\partial c_i}{\partial z} \right)_{\text{cloud}} + R + D + E
\]

where \( u, v, \) and \( w \) denote the components of wind speed in the three directions, respectively, and \( K_e \) is turbulent diffusivity. The seven terms on the right-hand side in Eq. (1) represent horizontal advection, vertical advection, vertical diffusion, cloud processes, chemical reactions \( (R) \), dry deposition \( (D) \), and source emission rate \( (E) \), respectively. PA was per-
formed over D3 at 11:00–16:00 every day when O₃ peaks occurred Liu and Roy (2015).

1.4. Indicator evaluation metrics

In this section, we developed a method to evaluate the performance of indicators in distinguishing O₃ formation regime. By identifying the O₃ formation regime and indicator values on each day of September 2017, we may calculate the value ranges of all indicators under the three O₃ formation regimes in the entire month. The performance of indicators was evaluated by two factors, the percentage of overlap between the three regimes and the number of the days in the overlap. The percentage of overlap, P, for a specific indicator was quantified using the following equation:

\[ P = \frac{O_{\text{max}} - O_{\text{min}}}{T_{\text{max}} - T_{\text{min}}} \]  

where \(O_{\text{max}}\) and \(O_{\text{min}}\) represent the maximum and minimum value of the overlap range, and \(T_{\text{max}}\) and \(T_{\text{min}}\) denote the maximum and minimum value of the indicator, respectively. The smaller the percentage of overlap and the number of days in the overlap are, the better the indicator in distinguishing O₃ formation regimes.

2. Results and discussion

2.1. General characteristics of O₃ episode in September 2017

Fig. 1 depicts the hourly averaged O₃ concentrations at the seven sites over the PRD during September 2017. There were 21 days with MDA8 O₃ concentration over the national tier-II standard of 160 ppb/m³ (~80 ppbv), indicating a continuous and long-lasting O₃ elevation event. The most significant O₃ episode occurred during 15–19, with the MDA8 O₃ exceeding 300 ppbv at some stations. The highest hourly O₃ concentration of 336 ppbv was recorded at Foshan on 18. This O₃ episode was associated with three synoptic patterns, i.e., approaching of a tropical cyclone on 15–16, eastward movement of a high pressure ridge on 17, and extension of Western Pacific Subtropical High (WPSH) on 18–19, as shown in the weather maps of Fig. S3 (Jian et al., 1998; Shen et al., 2015). On 15–16 when a tropical cyclone was located 500–800km to the PRD, PRD was controlled by the subsidence air in the outskirt of the tropical cyclone, leading to strong solar radiation, high temperature and a stabilized atmospheric structure. The background winds were weak and the dispersion capacity was largely hindered, favoring local pollutant accumulation and photochemical reaction. On 17 when PRD was located in front of a ridge, the coupling between upper-level convergence and low-level divergence led to vertical downward movement, which favored transport of O₃ from upper level. On 18–19, PRD was gradually controlled by the westward extension of WPSH. Located between WPSH and a low pressure system over Gulf of Tonkin, PRD was prevailed by easterly wind due to pressure gradient, favoring horizontal O₃ transport.

We conducted meteorology and O₃ simulations for the entire September. In terms of meteorology, better model performance in temperature than wind speed simulation was discovered, as shown in Table S4. Relatively poorer simulation of wind speed was largely due to the kind of outdated land use information which cannot well capture land use changes in the rapid urbanization process in the past decade. A comparison between O₃ observations and simulation is presented in Fig. S4, and the statistics is provided in Table S5. Overall, the model had a good performance in O₃ simulation, with correlation coefficient (R) of 0.71 and mean bias (MB) of 4.7, which were well above the recommended values by US EPA (Emery et al., 2017). The model was able to capture diurnal variation of O₃ at different sites, but underestimated O₃ peak levels during O₃ episode and overestimated O₃ levels at night. The under-prediction of O₃ peaks during daytime is mainly related to the uncertainties of emissions and over-predicted wind speed (Zhao et al., 2019). The nighttime over-predictions of surface O₃ might be collectively caused by inaccuracies in nighttime NOx chemistry Dimitroulopoulos and Marsh (1997) and meteorological inputs such as boundary layer height and vertical motion (Zhao et al., 2019), as well as uncertainties in emissions of O₃ precursors.

2.2. Atmospheric oxidation during O₃ episode

As explained in Section 1, HO₂ radicals play a critical role in atmospheric oxidation and O₃ production. In this section, we in-
vestigated the relationship between HO\textsubscript{x} radicals and O\textsubscript{3} budget.

Fig. 2 compares simulated HO\textsubscript{x} with observed O\textsubscript{3} concentrations during the entire month of September 2017. The simulated daily peak OH and HO\textsubscript{2} values were in the range of 0.15-0.65 pptv and 21-65 pptv, respectively, during the entire month of September 2017. Due much to the fact that the OH and HO\textsubscript{2} observational data is very scarce, we further compare the CMAQ-simulated concentrations of HO\textsubscript{x} radicals with a set of earlier studies (Hofzumahaus, et al., 2009; Mao et al., 2010; Ren et al., 2013), as shown in Fig. S5. A similar diurnal variation with same magnitude of HO\textsubscript{x} radicals was found. The results indicate that the model was comparable to those published. These values were higher than those in the other regions worldwide, such as 0.6 pptv for OH and 40 pptv for HO\textsubscript{2} in Houston and 0.35 pptv for OH and 10 pptv for HO\textsubscript{2} in New York City (Ren et al., 2013; Mao et al., 2010), and were comparable with those observed over the PRD in the summer of 2006 (Hofzumahaus et al., 2009). Diurnally, both OH and HO\textsubscript{2} had maxima in the afternoon with peaking time around 14:00-16:00 and minima at night. Day-to-day co-variations between HO\textsubscript{x} and O\textsubscript{3} concentrations can be also noticed. Correlation coefficients were higher than 0.55 at all sites.

Similar spatial distributions of HO\textsubscript{x} and O\textsubscript{3} concentrations was also revealed, as shown in Fig. S6 using the 15-19 episode as an example. A HO\textsubscript{x} and O\textsubscript{3} concentration hotspot was noted over central FRD, which further indicated that HO\textsubscript{x} radicals play a critical role in O\textsubscript{3} production. In addition, a clear relationship between large-scale circulation and accumulation and transport of O\textsubscript{3} was noticed. On 15-16, typhoon Taili in the South China Sea brought about stabilized atmospheric structure, weak surface winds, strong solar radiation and high temperature over the FRD, which were conducive to the formation and accumulation of O\textsubscript{3}. Afterwards, a northward movement of O\textsubscript{3} and HO\textsubscript{x} hotspot areas from central FRD were noticed, which corresponded to the eastward movement of a strengthened ridge on 17 and extension of WPSH on 18-19. Thus, the strengthened O\textsubscript{3} and HO\textsubscript{x} episode over the PRD were mainly driven by the variation of large-scale circulation.

2.3. Impact of atmospheric oxidation on O\textsubscript{3} formation regimes

In the previous section, we discovered a clear connection between atmospheric oxidation and O\textsubscript{3} production over the PRD. The O\textsubscript{3} production rate is essentially driven by the production
rate of NO2 which is closely associated with two main reactions (H2O2 + NO and RO2 + NO). When O3 formation is in the VOC-limited regime, higher amount of HO2 favors transformation from NO to NO2, accelerating NOx cycle and leading to O3 formation. Abundant NO is ready to convert HO2 to OH, lowering HO2/OH ratio. In the NOx-limited regime, OH reacts with VOCs to produce organic peroxy radicals (RO2). RO2 oxidizes NO to produce NO3, and the photolysis of NO3 produces O atom and further reacts with O3 to form O3. Excessive HO2 radical is generated by the RO2+O2 and OH+VOCs reactions, elevating HO2/OH ratio. Thus, we expect that the HO2/OH ratio have a close relationship with O3 formation regime, which is examined in this section.

By doing a set of sensitivity study described in Section 2.2, we developed O3 isopleth diagram to identify O3 formation regime at different sites over the PRD. The shapes of O3 isopleths varied greatly on the different days, indicating varied O3 formation regimes under the base condition. For example, at Zhuhai site during the 15-19 episode, O3 formation regime fluctuated between VOC-limited, and NOx-limited regimes, as illustrated in Fig. S7. This highlighted significant variation in O3 formation mechanisms over the PRD, even within a single O3 pollution event.

We further examined the co-variations of HO2/OH and O3 formation regime during the entire month of September. A clear correspondence was found, as shown in Fig. 3. As expected, HO2/OH was higher when O3 formation regime shifted to NOx-limited and lower when O3 formation regime shifted to VOC-limited. However, there was a spatial heterogeneity of HO2/OH threshold ratios for O3 formation regime differentiation, as indicated in Table 1. The cities were generally split into two clusters, with Huizhou, Zhongshan, Shenzhen and Zhuhai having HO2/OH threshold values around 9–12 and Guangzhou, Jiangmen and Foshan around 5–6. The mis-matching ratios of VOC- and NOx-limited regimes inferred from HO2/OH ratios and scenario analysis were less than 16%, indicating HO2/OH is a good indicator for O3 formation regime. The mis-matching ratios of transitional regime were a bit higher due much to the limited number of days falling within this regime.

To better identify the underlying reason for the spatial heterogeneity of HO2/OH threshold ratios for O3 formation regime, we further investigated the spatial distribution of NOx and VOC emissions over the PRD, as shown in Fig. S8. We noticed that these three sites (i.e. Jiangmen, Foshan, and Guangzhou) located at red hotspot area with the NOx emission intensity of 0.20, 0.32, and 0.25 mole/sec, respectively (Table S6). For the other four sites, relatively lower NOx emission intensity was found (0.08 mole/sec for Zhuhai, 0.10 mole/sec for Shenzhen, 0.11 mole/sec for Zhongshan, and 0.03 mole/sec Huizhou). Previous studies have demonstrated that the model always underestimated HO2 at high NO levels in most ground-based campaigns, which may cause a lower HO2/OH ratio over central and western PRD (Martinez et al., 2003; Ren et al., 2006). Ren et al., (2003) also noticed a similar under-predicted HO2 under high NO concentration with NCAR chemical ionization mass spectrometer (CIMS). Their results further proved that the uncertainties in the model at high NOx is responsible for the under-predicted HO2.

We further compared O3 formation regimes estimated by both HO2/OH ranges listed in Table 1 and scenario analysis during the 15–19 episode, as shown in Fig. 4. Good consistency in O3 formation regimes were discovered. This highlighted the powerfulness of using HO2/OH to indicate O3 formation.

Table 1 – Distribution of HO2/OH values for different O3 formation regime and the percentages of mis-matches during the entire month

| Site     | NOx-limited | Transitional | VOC-limited |
|----------|-------------|--------------|-------------|
| Jiangmen | >5.5 (12%)  | 5-5.5 (0%)   | <5 (9%)     |
| Foshan   | >5.2 (5%)   | 4.2-5.2 (50%)| <4.2 (0%)   |
| Guangzhou| >2.5 (0%)   | 2.25-2.5 (50%)| <2 (16%)   |
| Zhuhai   | >10 (14%)   | 9.5-10 (25%) | <9.5 (8%)  |
| Shenzhen | >10 (0%)    | 9.7-10 (0%)  | <9.7 (0%)  |
| Zhongshan| >10.8 (8%)  | 9.9-10.8 (0%)| <9.9 (0%)  |
| Huizhou  | >12 (0%)    | 10-12 (0%)   | <10 (0%)   |

Fig. 3 – Time series of HO2/OH ratio at each site (curve) and number of sites in three O3 formation regimes (bar) during September 2017. Bars in red, green and blue represent NOx-limited, transitional, and VOC-limited regime, respectively.
regime, even in the context of drastically changing O$_3$ formation mechanisms as a result of a wide span of large-scale circulation patterns occurred during this episode. Only exceptions were revealed at Guangzhou on 17 and 18 and Zhuhai on 19 when HO$_2$/OH and scenario analysis inferred different O$_3$ formation regimes. HO$_2$/OH indicator suggested NO$_x$-limited regime for all three cases while scenario analysis estimated transitional on 17 at Guangzhou and VOC-limited on 18 at Guangzhou and 19 at Zhuhai. We will examine the underlying reason for such discrepancies in the following section.

2.4. Identification of underlying reasons of the relationship between O$_3$ formation and atmospheric oxidation

To better identify the underlying factors for the relationship between HO$_2$/OH and O$_3$ formation regime, we performed PA to retrieve physical and chemical contributions to O$_3$ increase during the 15-19 episode, as listed in Table 2. The PA results listed in Table 2 represent a domain average. Chemical processes contributed predominantly to O$_3$ increase on all days, as a result of favorable meteorological conditions. Physical processes, including horizontal transport and vertical advection, posed substantially less or even negative contributions to O$_3$ increase.

We further investigated physical and chemical contributions to O$_3$ changes at each site during this episode, as shown in Fig. 5. The PA results presented in Fig. 5 represent a closest grid to each site. We noticed that overall, chemical reaction contributed predominantly to O$_3$ changes. Exceptional cases with higher physical than chemical contributions, i.e. Guangzhou on 17 and 18 and Zhuhai on 19, are highlighted by yellow boxes. Interestingly, these three cases coincided exactly with those having discrepancies in O$_3$ formation regimes inferred by HO$_2$/OH and scenario analysis. This likely indicated a causal relationship between greater physical contribution and discrepancies in O$_3$ formation regimes. Extending this analysis to the entire September, we found that about 95% (18 out of 19) of discrepancy cases were associated with larger physical than chemical contributions, which gave further weight to the causal relationship. As an indicator essentially delineating atmospheric oxidation capacity, HO$_2$/OH is
transport subsidence significant port Guangzhou, and calculation to underscored signaling cases HO precursor reactions. Fig. 380 Huizhou Shenzhen Guangzhou Jiangmen River Table quantify HO2/OH2 by percentage played physical role in the necessity of the regime of the O3 formation. The chemical transport variations in the horizontal transport were transported to Guangzhou and Zuhai through easterly winds. Our analysis revealed that horizontal and vertical transport contributed differently in the mismatching cases under different large-scale circulation types, which indicated that the large-scale circulation played an important role in shaping O3 formation regime over the PRD.

Since a few uncertainties remain in HO2/OH2 indicator, a long-period simulation together with more observations are needed to quantify the threshold of HO2/OH2 indicator in different sites. Besides, the results also indicate the great importance of promoting measurement of atmospheric radicals to gain insight in atmospheric processes leading to O3 pollution.

2.5. Comparison between HO2/OH2 and other indicators in indicating O3 formation regime

In this section, we compared the performance of a series of photochemical indicators with a same criterion at each site, including HO2/OH2, H2O2/HNO3, H2O2/NO2, H2O2/NO2.

Table 3 – Percentage of overlap and number of the days in the overlap for all indicators at the seven sites across the Pearl River Delta

| Site      | HO2/OH | H2O2/HNO3 | H2O2/NO2 | H2O2/O2 | O3/HNO2 | O3/NO2 | O2/NO2 |
|-----------|--------|-----------|----------|---------|---------|--------|--------|
| Jiangmen  | 2.7% (5) | 49.9% (28) | 36.3% (23) | 48.9% (25) | 66.9% (29) | 98.6% (28) | 37.5% (21) |
| Foshan    | 0.3% (2) | 24.5% (29) | 30.3% (19) | 55.0% (25) | 46.6% (28) | 100% (30) | 87.6% (26) |
| Guangzhou | 56.3% (13) | 100% (30) | 88.6% (26) | 100% (30) | 99.2% (29) | 97.1% (29) | 49.1% (24) |
| Zuhai     | 34.8% (20) | 100% (30) | 100% (30) | 65.6% (29) | 38.2% (28) | 89.3% (27) | 47.7% (26) |
| Shenzhen  | 0% (0) | 93.7% (23) | 60.9% (12) | 94.9% (25) | 85.5% (18) | 60.5% (8) | 86.4% (20) |
| Zhongshan | 10.4% (5) | 15.9% (23) | 64.3% (25) | 52.4% (25) | 4.0% (15) | 100% (30) | 10.5% (15) |
| Huizhou   | 0% (0) | 65.7% (28) | 24.5% (11) | 7.5% (11) | 43.0% (29) | 99.3% (29) | 6.7% (6) |
O$_2$/HNO$_3$, O$_3$/NO$_2$ and O$_3$/NO$_2$ in indicating O$_3$ formation regimes. First, we developed O$_3$ isopleth diagram to identify O$_3$ formation regime at different sites over the PRD as described in Section 2.2. Second, we investigate the distribution of the ratio of each indicator under the three O$_3$ formation regimes. And finally, as described in Section 2.4, the percentage of overlap and the number of the days in the overlap were used to evaluate the performance, as listed in Table 3.

It is noted that at Jiangmen, Foshan, Zhuhai, Shenzhen and Huizhou, HO$_2$/OH showed the best performance with the lowest percentage of overlap and the number of the days in the overlap. In particular, there was no overlap at Shenzhen and Huizhou, meaning HO$_2$/OH can indicate O$_3$ formation regimes with 100% accuracy. At Guangzhou and Zhongshan, although the percentage of overlap of HO$_2$/OH was the second lowest (56.3% for HO$_2$/OH vs. 49.1% for O$_3$/NO$_2$ at Guangzhou and 10.4% for HO$_2$/OH vs. 4.0% for O$_3$/HNO$_3$ at Zhongshan), the number of days was the lowest and much smaller than the second lowest value (13 for HO$_2$/OH vs. 24 for O$_3$/NO$_2$ at Guangzhou and 5 for HO$_2$/OH vs. 15 for O$_3$/HNO$_3$ and O$_3$/NO$_2$ at Zhongshan).

Therefore, we believe HO$_2$/OH is the best indicator to distinguish O$_3$ formation regimes over the PRD. This also highlights the fact that atmospheric oxidation is the core driver of O$_3$ formation regimes in a photochemically active region. Using HO$_2$/OH to identify O$_3$ formation regimes circumvents the time-consuming sensitivity analysis by numerical models which very often involves tens of scenarios, thereby providing a simple and direct way for fast identification of O$_3$ formation regimes which is essential to formulate contingency control strategies to mitigate O$_3$ pollution during episode.

3. Conclusions

PRD has been suffering from significant and worsening O$_3$ pollution which is largely driven by the high oxidative capacity over the region. A set of studies have been performed to investigate the impact of the atmospheric oxidation on O$_3$ production, but the impacts of atmospheric oxidation on O$_3$ precursor nonlinearity and O$_3$ formation regimes, the essential indicators for O$_3$ pollution control, still remain a large knowledge gap. In this study, a comprehensive air quality model (WRF-CMAQ) was used to investigate the relationship between atmospheric oxidation and O$_3$ formation regimes during the entire month of September 2017 with 21 days with MDAB O$_3$ concentration over the national tier-II standard.

A detailed investigation of the mechanism of atmospheric oxidation, especially the role of HO$_2$ radicals in shaping O$_3$ formation regimes is required over the PRD. We discovered a clear relationship between oxidative capacity and O$_3$ formation regime over the PRD. The O$_3$ formation is dominated by NO$_2$-limited regime when the HO$_2$/OH ratio is approximately higher than 11 and lower than 9.5 when dominated by VOC-limited over eastern PRD. Over central and western PRD, an HO$_2$/OH ratio higher than 5 and lower than 2 was indicative of NO$_2$-limited and VOC-limited regime, respectively.

PA results denote that the HO$_2$/OH indicator exhibits a good performance on O$_3$ formation judgment when the chemical reaction contributed predominantly to O$_3$ changes. Physical contribution, including horizontal transport and vertical transport, may pose uncertainties on the indication of O$_3$ formation regime by HO$_2$/OH ratio. Substantial transport of O$_3$ would change the O$_3$-precursor nonlinearity, thereby negating the relationship between HO$_2$/OH and O$_3$ formation regime. As only 9% of cases with higher physical than chemical contributions in the entire month, we believe HO$_2$/OH is a good indicator in signaling O$_3$ formation regime over the PRD. In comparison with other commonly used photochemical indicators, the HO$_2$/OH indicator showed a lower range of the percentage of overlap and the limited number of the days in the overlap at each site. Thus, HO$_2$/OH ratio had the best performance in differentiating NO$_2$-x, transition, and VOC-limited regimes.

Due much to the fact that the observational data of HO$_2$ and OH is very scarce, we would currently recommend using the model simulation to obtain the HO$_2$/OH ratio. Although there are some uncertainties in simulation results, it is a simple and direct way for fast identification of O$_3$ formation regimes.

This study has an important implication on understanding the relationship between atmospheric oxidation and O$_3$ formation regimes during O$_3$ episodes. Using HO$_2$/OH to identify O$_3$ formation regimes circumvents the time-consuming sensitivity analysis by numerical models, thereby providing a simple and direct way for fast identification of O$_3$ formation regimes which is essential to formulate contingency control strategies to mitigate O$_3$ pollution during episode. The results also underscored the importance of characterizing behaviors of radicals to gain insight in atmospheric processes leading to O$_3$ and other secondary pollution over a photochemically active region.

Acknowledgement

This work is sponsored by the National Natural Science Foundation of China (Nos. 91644221, 41575009).

Appendix A. Supplementary data

Supplementary material associated with this article can be found, in the online version, at doi:10.1016/j.jes.2020.09.038.

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