# Ambient ozone control in a photochemically active region: short-term despiking or long-term attainment?

Jiamin Ou, Zibing Yuan*, Junyu Zheng*, Min Shao, Hai Guo, and Peter K.K. Louie

## ABSTRACT

China has made significant progress in decreasing ambient concentrations of most air pollutants, with ozone ($O_3$) an exception. $O_3$ mixing ratios during pollution episodes are far higher than its national standards, thus greater evidence-based control efforts are needed for $O_3$ attainment. By using a validated $O_3$ modeling system and the latest regional emission inventory, this study illustrates that control strategies in $O_3$ short-term despiking and long-term attainment might not be concerted in the Pearl River Delta (PRD), a photochemically active region in China with peak $O_3$ levels frequently exceeding the NAAQS. VOC-focused control is more efficient in $O_3$ despiking at urban and industrial areas, but significant reduction on $NO_x$ emissions and the subsequent transition into $NO_x$-limited regime are required for $O_3$ attainment. By tracking $O_3$ changes along the entire path towards long-term attainment, this study suggests to put greater control efforts on $NO_x$ emissions region-wide. Parallel VOCs controls around the port area are necessary in the summertime and should be extended to the urban and industrial areas in fall and be strengthened during $O_3$ episodes. Contingency VOC-focused controls on top of regular $NO_x$-focused controls could hopefully achieve balance between short-term despiking and long-term attainment of $O_3$ pollution in the PRD.

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## INTRODUCTION

Ambient fine particulate matter ($PM_{2.5}$) is the focus of current air quality management in China. Thanks to the implementation of a series of stringent control measures, the increasing trends of $PM_{2.5}$ in recent years have been curbed and even reversed. More than 20% reductions of ambient $PM_{2.5}$ levels were recorded in 2015 as compared with its levels in 2013 at China's three major city clusters, Beijing-Tianjin-Hebei, Yangtze River Delta and Pearl River Delta (PRD).[1] However, ambient $O_3$ levels indeliberately elevated along with the reduction of $PM_{2.5}$ levels. In the PRD, the annual average ground-level $O_3$ mixing ratio increased from 24 ppbv in 2006 to 29 ppbv in 2014.[2] The maximum 1-hour $O_3$ mixing ratio reached 150~220 ppbv on typical $O_3$ episode days in summer and fall in the PRD, and the daily maximum 8-hour standard of 160 $\mu g/m^3$ was violated on about 11% of days in a year.[2] As $O_3$ is associated with significant adverse effect on human health, such an increase negates the benefit attained from $PM_{2.5}$ reduction in a health-based air quality management.

$O_3$ is a type of secondary pollutant that forms when its precursors, mainly nitrogen oxides ($NO_x$) and volatile organic compounds (VOCs), react in the atmosphere in the presence of sunlight. The non-linear relationships between $O_3$, $NO_x$ and VOCs and its dynamic spatial variations often make regional $O_3$ control a complicated issue. For example, $O_3$ formation is generally $NO_x$-limited over most of the Houston and downwind areas, but is VOC-limited in the core area of Houston where $O_3$ concentrations are highest.[3] Although VOC-limited conditions dominated during most rapid $O_3$ formation periods, balanced control on VOC and $NO_x$ is important in reducing $O_3$ levels region-wide.[4] Over California's South Coast Air Basin (SoCAB), $O_3$ levels before 2005 decreased sharply with VOC-focused control, but had leveled off afterwards along with further VOC emission reductions. Although in a more intense VOC-limited regime, strategies focusing primarily on $NO_x$ reductions have been regarded as the best way to achieve long-term $O_3$ and $PM_{2.5}$ attainment objectives, as specified in the recent Air Quality Management Plan of South California Air Quality Management District.[5-7] Such a transition implies discrepancy between short-term and long-term $O_3$ control measures in heavy pollution areas.

Unfortunately, difficulties in $O_3$ controls at both Houston and SoCAB co-exist in the PRD, a photochemically active region with intense precursor emissions and favorable synoptic conditions for photochemistry. $O_3$ formation regimes are spatially intertwined – urban, suburban and industrial areas are more in a VOC-limited regime while rural areas are more $NO_x$-limited.[8-13] As the transition is also dependent on synoptic conditions, $O_3$ control strategies cannot be formulated as simply dichotomous as what science shows; peak $O_3$ levels are far higher than the national standard – control efforts in $O_3$ despiking and attainment might not be concerted. Apart from scientific evidences, practical feasibility is another important factor in consideration when formulating an $O_3$ control strategy. Traditionally, a VOC/$NO_x$ reduction ratio of 3:1 is suggested in urban, suburban and industrial areas of the PRD, as specified in the Guangdong – Hong Kong Joint Emission Reduction Plan (JERP) effective from 1997 to 2010. However, such an ambitious VOC reduction plan is proven not successful, due much to the fact that anthropogenic VOC (AVOC) sources in the PRD are diverse and scattered for an effective control.

In this study, we explore the feasibility in disentangling the puzzles of $O_3$ control issues in the PRD with a WRF/SMOKE-PRD/CMAQ modeling system. A set of control scenarios are designed to investigate the $O_3$-VOC-$NO_x$ relationships and their spatial distributions during $O_3$ episodes in August and October, the two months generally with the most frequent occurrences of $O_3$ episodes in the PRD. $O_3$ responses to different VOC and $NO_x$ co-control schemes are analyzed, and policy implications on $O_3$ controls for short-term despiking and long-term attainment are discussed.

## DATA AND METHODS

### Ozone modeling system

Study domain of the $O_3$ modeling system is the PRD region which is composed of 9 administrative cities in Guangdong Province (Figure 1). Lambert-Conformal projection centered at 28.5 °N 114 °E, with two true latitudes for the projection at 15 °N and 40 °N, is used as the basic projected coordinate in the modeling system.

The Weather Research and Forecast (WRF) model v3.3 is used to provide meteorological data. The $1°\times1°$ global reanalysis data obtained from the National Centers for Environmental Protection (NCEP) and the land use data from Moderate Resolution Imaging Spectroradiometer (MODIS) are adopted. The other physical options in WRF includes the Rapid Radioactive Transfer Model (RRTM) scheme for long wave radiation, the Dudhia scheme for short wave radiation, the Noah Land Surface Model, the Yonsei Planetary Boundary Lay (PBL) scheme, the WRF Single-Moment 6-class (WSM6) scheme for microphysics and the Kain-Fritsch scheme for cumulus parameterization. A three-level nested domain is established for WRF, with horizontal resolutions of 27 km, 9km and 3km, respectively. As illustrated in Figure 1, the coarse domain (D1) covers most parts of East Asia, Southeast Asia and the northern part of Western Pacific, the second domain (D2) covers most of Guangdong province, and the fine domain (D3), the target area in this study, includes the PRD, Hong Kong and Macau. WRF is run with 26 vertical layers with 18 layers under 1000 meters above sea surface level.

The 2010 bulk emission inventories for Hong Kong and the PRD is adopted[14] and transformed by the SMOKE-PRD emission processor into hourly gridded model-ready emission data.[15] The emission inventories cover comprehensive anthropogenic sources with the latest local emission factors, detailed local activity data and updated source classification, including but not limited to power plants, residential combustion, on-road and non-road mobile sources, industrial sources, solvent-use sources, and biomass burning, for pollutants of sulfur dioxide ($SO_2$), carbon monoxide (CO), $NO_x$, VOC and particulates ($PM_{10}$ and $PM_{2.5}$). The Model of Emissions of Gases and Aerosols from Nature (MEGAN) model is used to estimate biogenic VOC emissions.[16] Emissions from D2 and D3 within Guangdong Province are from Guangdong emission inventories.[17,18] The model-ready emission data from the Multi-resolution Emission Inventory for China (MEIC) Model with $1° \times 1°$ resolution (http://www.meicmodel.org/) and Regional Emission inventory in ASia (REAS) are adopted for D1 and D2 but outside Guangdong.

CMAQ v4.7.1 is used to simulate $O_3$ mixing ratios and its relationship with VOC and NOx emissions. Also incorporated in CMAQ model are ISORROPIA v1.7 module for inorganic aerosol simulation, SOAP module for organic aerosol simulation, and Asymmetric Cloud Model 2 (ACM2) PBL scheme for cloud treatment and eddy scheme in PBL. Clean air data provided with CMAQ is employed to generate boundary conditions for D1, and hourly instantaneous mixing ratio file simulated by CCTM for outer domains (D1 and D2) is used to generate boundary conditions for inner domains (D2 and D3).

To eliminate the impact of initial conditions, a 3-day model spin-up is used in each month simulation. Note that the three-nested domains in CMAQ share the same spatial resolution with but are slightly smaller than their WRF counterparts. CMAQ is run with 18 vertical layers from the isobaric surface to 50 mb.

Ground-level meteorological data is used to evaluate the performance of WRF model, while the observed $O_3$ mixing ratios from the PRD regional air quality monitoring network are used to evaluate the simulated $O_3$ mixing ratios. As shown in Tables S1 and S2, the modeling system can reproduce ambient meteorological conditions and $O_3$ mixing ratios fairly well, therefore is reliable for in-depth analysis on the relationships between $O_3$ and its precursors.

## Scenario design for $O_3$-$NO_x$-VOC isopleth

Four areas with different pollutant emission characteristics are selected for scenario analysis, i.e. urban Guangzhou, industrial zone of Dongguan, port area of Nansha, and rural area of Jiangmen. Their locations are shown in Figure 1, and the reasons for selecting them are provided in Supporting Information. $O_3$ elevated days, defined as those days with the maximum 1-hr average $O_3$ mixing ratio over 200 μg/m$^3$ (~102 ppbv), Stage II of China's National Ambient Air Quality Standard (NAAQS), are extracted for analysis, as listed in Table S3.

An emission reduction matrix including 1 base case and 39 emission reduction scenarios is designed to develop $O_3$ isopleth diagrams.[19] The 39 scenarios with different combinations of NOx and AVOC emission reduction in the PRD are shown in Figure S1. For example, the "A" point represents the scenario with both $NO_x$ and AVOC emissions reduced by 10%. Note that emission reduction scenarios are more concentrated around the base case (the up-right corner of the emission matrix), as they are more readily to achieve. $O_3$ isopleth diagrams are then developed by analyzing the responses of $O_3$ mixing ratio to the 40 reduction scenarios.

# RESULTS

## Spatial and seasonal variations of ozone formation regime

Figure 2 shows the $O_3$ isopleth diagrams at the four areas in both months. In an $O_3$ isopleth, the VOC-limited and NOx-limited regimes are separated by the ridge line, which corresponds to the maximum $O_3$ concentration for a given VOC emission to produce. In August, the base case scenarios at Guangzhou, Dongguan and Nansha are above the ridge line, indicating that $O_3$ formation is in a VOC-limited regime in urban, industrial and port areas of the PRD. There is no ridge line at Jiangmen, as the $O_3$ formation is always NOx-limited for any possible VOC-$NO_x$ emission combinations. In October, the base case scenarios at Guangzhou, Dongguan and Nansha keep above but with even longer distance to the ridge line, showing an intensified VOC-limited regime. The ridge line appears in the isopleth at Jiangmen and almost passes through the base case scenario, showing $O_3$ formation in a transitional regime. Table 1 summarizes the $O_3$ formation regimes at the four areas on the $O_3$ elevated days in both months.

The spatial differences in $O_3$ formation regime can be explained by the distribution of total VOC (including biogenic)-to-$NO_x$ emission ratios, as shown in Figure 3. The ratio is the lowest at Nansha, followed by Guangzhou and Dongguan, and the highest at Jiangmen. The lowest ratio at Nansha, mostly below 0.5 or even 0.1, is resulted from the intensive $NO_x$ emissions from the port and the nearby coal-fired power plants. In contrast, most areas in Jiangmen have VOC-to-$NO_x$ emission ratios over 5 or even 10 as a result of significant biogenic VOC emissions in rural area.

The seasonal difference in $O_3$ formation regime can be explained by the seasonal variation of biogenic VOC emissions. Biogenic VOC emissions account for 29% of total VOC emissions and 42% of total $O_3$ forming potentials in the PRD.[14] Biogenic emissions are more intensive in summer as a result of higher temperature and stronger solar radiation. As VOC supply shrinks in fall while NOx emissions change slightly, $O_3$ formation shifts towards VOC-limited in fall, especially in rural areas where biogenic VOC emissions are more significant. $O_3$ formation in fall is more sensitive to changes in VOC emissions than in summer.

### Response of $O_3$ to different precursor reduction schemes

In this section, responses of peak $O_3$ levels to five precursor reduction schemes are examined, including two VOC control-focused schemes (VOC control only, and VOC/$NO_x$ reduction ratio=3:1), a balanced scheme (VOC/$NO_x$ reduction ratio=1:1), and two $NO_x$ control-focused schemes (VOC/$NO_x$ reduction ratio=1:2, $NO_x$ control only). Figure 4 provides a conceptual illustration on the reduction paths of all five schemes.

Figure 5 shows the changes of peak $O_3$ mixing ratio in response to different VOC/$NO_x$ emission reduction schemes. The horizontal axis represents the combined reduction efforts of VOC and $NO_x$ with 10% of VOC or $NO_x$ emission reduction as one unit. For example, reduction effort of 10 in the horizontal axis suggests that the total reduction percentage of VOC and $NO_x$ is 100%, which corresponds to the reduction of VOC and $NO_x$ emissions by 33% and 67%, 50% and 50%, and 75% and 25% in the reduction schemes of VOC/$NO_x$=1:2, 1:1 and 3:1, respectively. The maximum reduction percentage of VOC and $NO_x$ is assumed to be 90% (9 units).

**Guangzhou/Dongguan.** As shown in Figure 5(a-d), Guangzhou and Dongguan share similar characteristics in responses of peak $O_3$ mixing ratios to precursor reductions, thereby are introduced together. In August, $O_3$ mixing ratio decreases the most rapidly for the reduction scheme of 'VOC control only' (brown line), followed by VOC/$NO_x$=3:1 (yellow line). VOC-focused controls are therefore more efficient in short-term $O_3$ despiking. However, $O_3$ attainment cannot be reached until 87% of the VOCs are reduced at Guangzhou, which is not practically feasible considering their diverse and scattered sources. At Dongguan, even if 90% of the VOCs are reduced in both VOC-focused controls, the peak $O_3$ level still exceeds the Stage II of NAAQS of 200μg/m$^3$ (102 ppbv). Therefore, although the VOC-focused controls can efficiently lower the peak $O_3$ level initially, it is likely that the control schemes may fail to bring $O_3$ level into attainment.

Peak $O_3$ mixing ratio shows a slight increase of 1.5% at Guangzhou in the reduction scheme of '$NO_x$ control only' (cyan line), so-called '$NO_x$ disbenefit'. After reducing NOx emissions by 20% (as marked Δ in Figure 5), the VOC-limited regime transfers to NOx-limited regime and $O_3$ mixing ratio decreases sharply in response to the $NO_x$ reduction. $O_3$ attainment at Guangzhou can be reached when 73% of the $NO_x$ are controlled, which is more practically feasible than controlling 90% of VOCs. Interestingly, $O_3$ mixing ratio does not show any increase in 'NOx control only' scheme at Dongguan, and the regime changes when 10% of $NO_x$ emissions are reduced. $O_3$ attainment is achieved when 63% of NOx emissions are reduced.

Parallel control on VOC can avoid the slight increase of $O_3$ mixing ratio at Guangzhou. $O_3$ mixing ratio shows steady decrease in the reduction schemes of VOC/$NO_x$=1:1 (green line) and 1:2 (blue line), but with lower rates after crossing the inflection point. It is also noted that $O_3$ mixing ratio keeps almost constant when 90% of the $NO_x$ emissions are controlled, no matter how much VOC emissions are controlled in parallel. Therefore, $NO_x$-focused controls have higher potential in achieving long-term $O_3$ attainment at Guangzhou. Without $O_3$ increase along its reduction path, $NO_x$-focused controls also favor long-term $O_3$ attainment at Dongguan.

In October, however, the $NO_x$ disbenefit becomes much more seriously when the '$NO_x$ control only' reduction scheme is imposed. $O_3$ mixing ratio increases by 23% when 50% of $NO_x$ emissions are reduced, and returns to its original level only if 78% of $NO_x$ emissions are reduced. In comparison, $O_3$ shows a flatter bulge (6% at Guangzhou and 8% at Dongguan) along the reduction path of VOC/$NO_x$=1:2, and $O_3$ formation changes to $NO_x$-limited regime by reducing 30% of VOC and 60% of $NO_x$ emissions. $O_3$ attainment can be reached when around 40% of VOC and 80% of $NO_x$ emissions are reduced. Although a steady decrease in $O_3$ level is discovered along the reduction path of VOC/$NO_x$=1:1, the reduction efficiency is too low that $O_3$ attainment could only be achieved when more than 70% of VOC and $NO_x$ are reduced, which is not practically feasible. More than 50% of VOC needs to be controlled in the schemes of 'VOC only' and VOC/$NO_x$=3:1 which is not practically feasible either. Therefore, VOC/$NO_x$=1:2 has higher potential in achieving long-term $O_3$ attainment at both sites considering its practical feasibility and the associated slight elevation of $O_3$ level. In terms of short-term $O_3$ despiking, 'VOC control only' is the most effective approach.

**Nansha.** As discussed previously, Nansha is characterized by strong $NO_x$ emissions from the Port and the nearby coal-fired power plant. $O_3$ formation regime, as a result, is VOC-limited in both months. Similar as in Guangzhou/Dongguan, $O_3$ level decreases the most rapidly along with 'VOC control only' approach, but fails to reach attainment, as shown in Figure 5(e-f). $O_3$ level increases along the reduction paths of '$NO_x$ control only', VOC/$NO_x$=1:2 and 1:1, with the maximum increase in peak $O_3$ mixing ratio of 16%, 11% and 6% in August and 20%, 14% and 6% in October, respectively. Although with initial $O_3$ increase, these three reduction schemes can lower the $O_3$ mixing ratio to 110 ppbv in August, very much close to the Stage II of NAAQS of 102 ppbv. In this process, $NO_x$ plays the key role while simultaneous control of VOC functions in restraining $O_3$ elevation along the reduction path. In comparison, the scheme of 'VOC control only' reduces the $O_3$ mixing ratio more efficiently, but has little chance to bring $O_3$ level into attainment. Co-control on $NO_x$ (VOC/$NO_x$=3:1) makes even negative impact that elevates the $O_3$ level in comparison with the 'VOC control only' scheme. Therefore, VOC controls should be the focus for short-term $O_3$ despiking while NOx-focused controls are recommended for its balance between practical feasibility, lower elevation of peak $O_3$ level, and higher chances to bring $O_3$ level into attainment.

**Jiangmen.** As shown in Figure 5(g-h), $O_3$ responses to precursor reductions at Jiangmen are the most straightforward. Due to stronger biogenic emissions and weaker influences from human activities, $O_3$ formation regime is $NO_x$-limited in August and transitional in October. As a result, '$NO_x$ control only' is recommended for $O_3$ attainment in both months. Different from the other three areas, ‘$NO_x$ control only’ is also the most efficient method in short-term despiking at Jiangmen. Due to the exceeding VOC emissions especially from biogenic, control efforts should be paid primarily on $NO_x$ emissions.

## DISCUSSION

Results show that in the urban, industrial and port areas of the PRD, the most efficient way in short-term despiking of peak $O_3$ level is VOC control. This is consistent with VOC-limited $O_3$ formation regimes at these areas. However, the VOC-focused controls cannot bring $O_3$ level into attainment in some areas, i.e. the $O_3$ reduction from VOC control is “short-term efficient but not long-term effective”. $NO_x$-focused controls, instead, have potentials in achieving $O_3$ attainment.

A $NO_x$ control-focused strategy for long-term attainment is based upon an implicit expectation that, with sufficient $NO_x$ reductions, $O_3$ formation would transition from VOC- to $NO_x$-limited $O_3$ formation throughout the PRD and further VOC reductions will not be effective at that point. This is illustrated in Figure 5 that $O_3$ mixing ratios in the three schemes with 90% reduction of $NO_x$ ($NO_x$ only, $VOC/NO_x$=1:2 and 1:1) drop almost to the same level. This indicates that $O_3$ reduction potential is essentially driven by the degree of $NO_x$ control and independent on VOC reductions. Therefore, transition from current VOC-limited to $NO_x$-limited $O_3$ formation regime is the prerequisite for $O_3$ attainment in the urban, industrial and port areas of the PRD. After transition, the effect of $NO_x$ reduction on $O_3$ is even enhanced when greater $NO_x$ emissions have been controlled. The main function of parallel VOC control is to circumvent or lower $O_3$ elevation at the initial stage of $NO_x$ control.

Different approaches between short-term despiking and long-term attainment may complicate the $O_3$ control strategy, let alone they even have conflicting effects and may pose impact to the $PM_{2.5}$ control. For example, short-term VOC control leads to higher availability of OH radical in the atmosphere, which reacts with the abundant $NO_2$ to form nitric acid and further to ammonia nitrate, a significant addition to $PM_{2.5}$.[20] Moreover, VOC control intensifies the limitation of VOC, leading to $O_3$ level more sensitive to the changes of $NO_x$ level in the atmosphere. $O_3$ level would increase in response to the reduction of $NO_x$ emission, a required step for long-term $O_3$ and $PM_{2.5}$ attainment. This probably explains why $PM_{2.5}$ reduction is almost always accompanied by $O_3$ elevation in China.

In addition, the initial increase of $O_3$ would also dampen the desire in adopting $NO_x$-focused controls, especially in fall. Although the magnitude of $O_3$ increase can be alleviated by parallel VOCs control, it is hard to be eliminated due to the poor understanding on the distribution of AVOC sources and thereby difficulties in an accurate VOC control. Therefore, in the process of achieving long-term attainment, a balance needs to be reached between the acceptable level of peak $O_3$ elevation and the efforts paid on VOC reduction. The degree of parallel VOC reduction in a particular area should be determined collectively by the accommodating capacity of $O_3$ elevation, the degree of parallel $NO_x$ reduction, and the practical feasibility in VOC control.

Nevertheless, greater efforts have to be paid on $NO_x$ control for expeditious progress in passing through the $NO_x$-disbenefit period towards $O_3$ attainment. Given the magnitude of these needed emission reductions, it is critical that the PRD maintains its continuing progress and works actively towards achieving as many specific emissions reductions as possible, as specified in the JERP (2015-2020). As $NO_x$ control is also a required step in reducing the ambient $PM_{2.5}$ level, a $NO_x$-focused control may lead to synergistic reduction of $O_3$ and $PM_{2.5}$. The development of the control strategy entails integrated planning to identify, to the extent feasible, co-benefit opportunities in achieving multi-pollutant reductions to meet standards. As such, control measures for attainment of $O_3$ standard can assist in the attainment of $PM_{2.5}$ standard.

In the PRD, $NO_x$ emissions are dominantly contributed by fossil fuel combustion. 53% of total $NO_x$ emissions are from coal-fired power plants, industrial boilers and other stationary sources. They are typically large- to medium-size enterprises under the surveillance of environmental authorities.[21] Their $NO_x$ emissions can be reduced to relatively low levels by denitrification technologies. On-road mobile sources account for 30% of $NO_x$ emissions, which could be reduced by 43% with the implementation of Stage V of the Vehicle Emission Standard in the coming couple of years. 16% of $NO_x$ emissions are contributed by marine emissions, which could be largely reduced by the improvement of fuel for ocean-going vessels and/or setting up emission control areas.[22] This sort of control measures can potentially cut down $NO_x$ emissions by 80%.

It must be pointed out that $NO_x$-focused control strategy for long-term attainment does not mean that VOC controls are negligible. VOC controls are essential in short-term despiking and alleviating $O_3$ increase as a result of $NO_x$ controls. In addition, some VOC species are of higher toxicity therefore detrimental to human health, therefore should be tackled in a health-oriented air quality management. VOC controls, however, are suggested to conduct in a more targeted manner. According to our results, VOC controls are preferentially enhanced around the port area in the summertime and should be extended to the urban and industrial areas in fall. More strengthened VOCs controls should be conducted as contingency measures during high $O_3$ pollution periods for despiking. Practical feasibility is another important consideration when formulating VOC control strategies.

In comparison with $NO_x$, VOC emission controls are much more challenging. 57% of AVOC emissions in the PRD are from industrial solvent usage and industrial process which involve a wide range of industrial sectors and medium- to small-size enterprises.[21] Contributions from solvent use could be even higher considering large amount of fugitive emissions dissipated in the open or semi-open workshops that are failed to collect from chimneys. On-road mobile sources contribute to 28% of AVOCs and the emissions are overlooked in the Stage V of the Vehicle Emission Standard. Therefore, we estimate that at most 40% of VOC emissions can be effectively reduced, making the rough VOC-to-$NO_x$ reduction ratio of 1:2. Such a ratio is adopted in the JERP (2015-2020) due largely to its practical feasibility. This study provides scientific evidences and more detailed refinement on the $NO_x$ control-focused strategies in the PRD.

Similar conundrum on $O_3$ short-term despiking and long-term attainment in the PRD and SoCAB might be partly attributed to the active photochemistry in a sub-tropical climate. In addition, both regions have high vegetation coverage, leading to significant biogenic VOC emissions by relatively high temperature and strong solar radiation. The large amounts of biogenic VOCs are readily involved in the chain reaction for $O_3$ production due to the strong oxidation capacity of the sub-tropical atmosphere. This high

VOC background suppresses the effectiveness of any AVOC-focused controls in lowering $O_3$. The control scenario in August in the PRD can be regarded as an extreme case – with region-wide intense biogenic emissions in summer, $O_3$ level cannot reach attainment even when 90% of AVOC emissions are cut down. In such photochemically active regions with significant biogenic emissions, transition into $NO_x$-limited regime may be the only means for long-term $O_3$ attainment. Such a transition might not be necessary for $O_3$ attainment in areas with temperate climate, e.g. Northern China, where biogenic emissions are weaker and more fluctuating by season. Detailed investigation on the $O_3$-$NO_x$-VOC relationship and the peak $O_3$ responses to different precursor control scenarios along the path towards attainment are required to elucidate the effective $O_3$ control approaches and their spatiotemporal characteristics in these areas.

China has made great determination in tackling its air pollution problem, with some control measures unrealistic to implement in western countries. For example, in order to decrease local emissions during high pollution periods, Beijing issued 'red alert' twice in December 2015. Exceptional control measures during 'red alert' periods included, but were not limited to, car use restriction by odd/even number, shutdown of some industrial plants, and banning of outdoor operations on construction sites. This air quality management philosophy of contingency control on top of regular control sheds light on $O_3$ controls in the PRD. With region-wide $NO_x$ emissions the major regular control focus and more targeted VOCs controls in certain periods and areas, we may hopefully disentangle the conundrum and discrepancy between short-term despiking and long-term attainment in ambient $O_3$ control, and also contribute to the synergistic reduction of $PM_{2.5}$ in the PRD.

## ASSOCIATED CONTENT

Tables, figures, and texts with details of selection of areas for $O_3$ isopleth development and Evaluation of model performance. This material is available free of charge via the Internet at http://pubs.acs.org.

## AUTHOR INFORMATION

### Corresponding Author

*Z.Y.: tel, +86-20-39380021; e-mail, zibing@scut.edu.cn.

*J.Z.: tel, +86-20-39380021; e-mail: zheng.junyu@gmail.com.

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