

Is atmospheric oxidation capacity better in indicating tropospheric O₃ formation?

Peng Wang^{1,2}, Shengqiang Zhu³, Mihalis Vrekoussis^{4,5}, Guy P. Brasseur^{6,7}, Shuxiao Wang (✉)^{8,9},
Hongliang Zhang (✉)^{2,3,10}

¹ Department of Atmospheric and Oceanic Sciences, Fudan University, Shanghai 200438, China

² IRDR ICoE on Risk Interconnectivity and Governance on Weather/Climate Extremes Impact and Public Health, Fudan University, Shanghai 200438, China

³ Shanghai Key Laboratory of Atmospheric Particle Pollution and Prevention, Department of Environmental Science & Engineering, Fudan University, Shanghai 200438, China

⁴ Institute of Environmental Physics, University of Bremen, Bremen D-28359, Germany

⁵ Climate and Atmosphere Research Center (CARE-C), the Cyprus Institute, Nicosia 27456, Cyprus

⁶ Max Planck Institute for Meteorology, Hamburg 20146, Germany

⁷ National Center for Atmospheric Research, Boulder, CO 80307, USA

⁸ State Key Joint Laboratory of Environmental Simulation and Pollution Control, School of Environment, Tsinghua University, Beijing 100084, China

⁹ State Environmental Protection Key Laboratory of Sources and Control of Air Pollution Complex, Beijing 100084, China

¹⁰ Institute of Eco-Chongming (IEC), Shanghai 202162, China

HIGHLIGHTS

- This study summarizes and evaluates different approaches that indicate O₃ formation.
- Isopleth and sensitivity methods are useful but have many prerequisites.
- AOC is a better indicator of photochemical reactions leading to O₃ formation.

ARTICLE INFO

Article history:

Received 22 February 2022

Revised 8 April 2022

Accepted 10 April 2022

Available online 20 May 2022

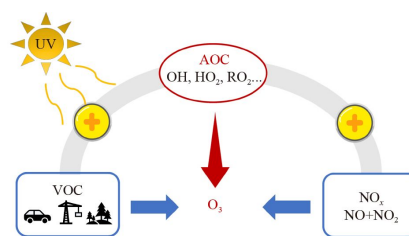
Keywords:

O₃

AOC

O₃ formation regime

GRAPHIC ABSTRACT



ABSTRACT

Tropospheric ozone (O₃) concentration is increasing in China along with dramatic changes in precursor emissions and meteorological conditions, adversely affecting human health and ecosystems. O₃ is formed from the complex nonlinear photochemical reactions from nitrogen oxides (NO_x = NO + NO₂) and volatile organic compounds (VOCs). Although the mechanism of O₃ formation is rather clear, describing and analyzing its changes and formation potential at fine spatial and temporal resolution is still a challenge today. In this study, we briefly summarized and evaluated different approaches that indicate O₃ formation regimes. We identify that atmospheric oxidation capacity (AOC) is a better indicator of photochemical reactions leading to the formation of O₃ and other secondary pollutants. Results show that AOC has a prominent positive relationship to O₃ in the major city clusters in China, with a goodness of fit (R^2) up to 0.6. This outcome provides a novel perspective in characterizing O₃ formation and has significant implications for formulating control strategies of secondary pollutants.

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✉ Corresponding authors

E-mails: shxwang@tsinghua.edu.cn (S. Wang); zhanghl@fudan.edu.cn (H. Zhang)

Special Issue—Frontier Progresses from Chinese-American Professors of Environmental Engineering and Science (Responsible Editors: Xing Xie, Jinkai Xue & Hongliang Zhang)

1 Introduction

Tropospheric ozone (O_3) is considered a key air pollutant that causes, among others, respiratory problems on humans and damages and reduced growth on plants (Lippmann, 1989; Chen et al., 2007; Feng and Kobayashi, 2009; Van Dingenen et al., 2009). It is mainly produced by photochemical reactions of volatile organic compounds (VOCs) and nitrogen oxides (NO_x) from both natural and anthropogenic sources, although transport from the stratosphere is possible (Husain et al., 1977; Steinfeld, 1998). O_3 and its precursors can be transported at great distances (Clarke and Ching, 1983; Lelieveld et al., 2009). Thus, its ambient level at a specific location is impacted by transported O_3 from upwind sources and locally produced O_3 through photochemical reactions.

O_3 formation occurs due to NO_2 photolysis but formed O_3 reacts with NO to regenerate NO_2 without net O_3 accumulation (Steinfeld, 1998). However, O_3 accumulates when hydroperoxyl radical (HO_2) or peroxy radicals (RO_2) formed in VOCs oxidation by the hydroxyl radical (OH) replace O_3 in converting NO back to NO_2 (Kentarchos and Roelofs, 2003; Pollack et al., 2013; Ren et al., 2013; Tan et al., 2018). Thus, O_3 formation depends on the levels of NO_x , VOCs, and oxidants (OH , HO_2 , and RO_2 , Fig. 1(a)). At different atmospheric conditions, O_3 formation varies nonlinearly to different mixtures of NO_x and VOCs (Sillman et al., 1990; Sillman, 1999). In rural areas, where NO_x levels are usually low, O_3 peak concentration decreases when NO_x is further reduced (NO_x -limited regime). Contrary, in urban areas, where NO_x amounts are elevated, a decrease in NO_x at constant VOC levels will increase O_3 peak concentrations (VOC-limited regime). Following this methodology, O_3 formation is usually split into VOC-limited regime, NO_x -limited regime, and transition regime that governing by both NO_x and VOCs (Sillman, 1995; Sillman and He, 2002). Numerical studies have focused on identifying O_3 formation regimes for designing controlling strategies (Feng et al., 2016; Ye et al., 2016;

Lu et al., 2019; Wang et al., 2019b). Xing et al. (2011) investigated the nonlinear response of O_3 to precursor emission changes in China and found that NO_x control appears to be beneficial for O_3 reduction in the downwind areas which usually experience high O_3 levels. Jin and Holloway (2015) investigated the O_3 sensitivity regime from 2005 to 2013 in China. They found that reducing NO_x emissions is an effective way to control O_3 pollution in the Pearl River Delta (PRD). Wang et al. (2019a) reported that the O_3 sensitivity turned into a transition regime in eastern China in recent years, which required more comprehensive emissions control strategies to alleviate O_3 better. Ding et al. (2022) highlighted the necessity of simultaneous VOCs and NO_x emission control in winter while enhancing the NO_x control in the summer. However, most of these studies neglected the importance of atmospheric oxidation capacity (AOC) as the formation regimes are changing. The AOC is a key factor that describes O_3 formation (Kentarchos and Roelofs, 2003; Prinn, 2003; Li et al., 2019b). Generally, AOC is defined as the total oxidation reaction rates of primary pollutants (such as VOCs) by the oxidants (e.g. OH , HO_2 , and NO_3). And the concentrations of these oxidants are used as an indicator to assess the AOC level in the modeling studies. Regardless of the changes in the regime and emissions of NO_x and VOCs, faster reaction rates, indicated by higher levels of oxidants, would lead to enhanced O_3 formation. The following question is then posed: Which is a better indicator when assessing O_3 formation. Here, we discuss different ways to understand O_3 formation and propose that AOC should be additionally considered when designing control policies.

2 Isopleth diagram

As mentioned before, an O_3 isopleth diagram is defined as a contour plot of interpolated maximum O_3 concentrations achieved as a function of VOC and NO_x concentrations (Dodge, 1977). It is used to show the

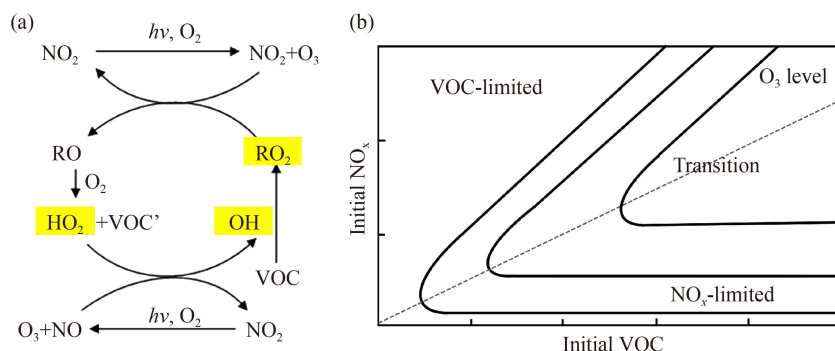


Fig. 1 (a) The O_3 formation mechanism (highlighted parts are the major oxidants) modified from Steinfeld (1998) and (b) a typical O_3 isopleth.

degree of O₃ production by considering the relative abundances of NO_x and VOCs, including constant VOCs composition and meteorological conditions (Milford et al., 1989; Jin and Demerjian, 1993; Menut et al., 2000). These isopleths provide characteristic O₃ ridgelines, which depict the maximum achievable O₃ concentration at the NO_x-limited, VOC-limited and transition regimes (Fig. 1(b)).

O₃ isopleth plots are widely used as a key methodology applied in O₃ control strategies. However, some complex prerequisites are required when interrelating the isopleths. To generate these plots, O₃ maximum concentration has to be predicted from a large number of numerical simulations performed with an atmospheric VOC/NO_x chemical mechanism using varying initial concentrations of VOCs and NO_x. At the same time, all other variables are constant (Qian et al., 2019). In short, the following points need to be considered when interrelating O₃ isopleths:

- 1) A large amount of simulations is required to plot the isopleth;
- 2) The correlation of O₃ with NO_x and VOCs varies greatly on the different assumptions and conditions (such as meteorological parameters), which is partly due to complex atmospheric processes such as regional transport;
- 3) The computation of isopleths is based on constant VOCs composition; however, ambient VOCs composition may vary in time as its total concentration changes;
- 4) Biogenic VOCs (BVOCs) are not considered in most cases as they are not controllable, although they represent a significant fraction of the total VOC budget, especially in suburban and rural areas;
- 5) There are no prescribed common conditions for determining O₃ formation regimes using the isopleths since they depend on multiple factors such as emission inventories, chemical mechanisms, and meteorological conditions;
- 6) Since the isopleths may encounter temporal variability (day-by-day changes), the methodology has limitations to represent a persistent O₃ pollution episode that lasts for several days.

3 Sensitivity methods

State-of-the-art chemical transport models (CTM) are also used to provide sensitivity analysis methods to identify O₃ formation regimes (Sillman et al., 1990). Thereby, NO_x or VOCs are reduced or increased by a certain percentage. Then, the simulated O₃ concentrations are compared with the base case (without NO_x and VOCs changes). A certain difference (e.g. of 5 ppb) is used as a criterion to verify if O₃ formation is sensitive to NO_x or VOCs reduction. In sensitivity methods, NO_x-VOCs indicators from model prediction and ambient

measurements are often used to split O₃ formation to different regimes, which involve secondary species produced concurrently with photochemical O₃ production (Sillman, 1995, 1999; Sillman and He, 2002). These species are relatively long-lived, so they can be transported along with O₃, including peroxides (e.g. H₂O₂), nitric acid (HNO₃), total reactive nitrogen (NO_y = NO_x + HNO₃ + peroxyacetyl nitrates + alkyl nitrates), and NO_x reaction products (NO_z = NO_y - NO_x). The ratios among these species reveal information associated with O₃ formation chemistry. The purpose of deriving these indicators is to build a link of O₃-NO_x-VOC to reduce the peak O₃ by the controllable species. The widely used indicators include, but are not limited to, VOCs/NO_x, H₂O₂/NO_y, H₂O₂/NO_z, H₂O₂/HNO₃, O₃/HNO₃, O₃/NO_y, and O₃/NO_z. Also, productions rates are often used to calculate O₃ formation regimes, such as (P_{H₂O₂} + P_{ROOH})/P_{HNO₃} and P_{H₂O₂}/P_{HNO₃} based on the production rates of H₂O₂, HNO₃, and organic hydroperoxides (ROOH). Some of these indicators are derived from routinely monitored pollutants (e.g. O₃) at observation sites or satellite retrievals (e.g. HCHO and NO₂). Although the above mentioned indicators can be calculated directly from model simulations or satellite data, they are not probing into the complex reactions leading to O₃ formation and having uncertainties in identifying O₃ formation regimes.

In practical implementation, using these indicators to evaluate the O₃ formation regimes requires extensive measurement networks (Jin and Holloway, 2015). Also, results from these indicators should be evaluated separately on a daily even hourly basis, especially for specific hours such as noon to two hours before sunset to maintain effectiveness. Even all these prerequisites are met, the NO_x-VOCs indicators method may have limitations in understanding O₃ changes or identifying O₃ formation regimes when NO_x or VOCs emissions are dramatically changed. For instance, during the COVID-19, O₃ concentrations in northern China increased when large emission reductions occurred due to reduced human activities during the lockdown (Gaubert et al., 2021; Zhu et al., 2021). One potential reason for this change was a shift in the O₃ formation regime due to the reduction in NO_x emissions during the imposed lockdown (Wang et al., 2021b). However, this was concluded mainly based on indicators or isopleth analysis, which may not reflect reality accurately. In particular, during the COVID-19, the O₃ formation regime changed from VOC-limited to NO_x-limited or transition regimes, but the rising O₃ concentrations were found with the NO_x reduction. Table 1 shows the ratios of grid cells attributed to the three O₃ formation regimes (NO_x-limited, VOC-limited and transition) during the COVID-19 lockdown (January and February 2020) under different precursors reductions in China. These regimes are calculated using the Community Multi-scale Air Quality (CMAQ) model.

Table 1 Ratios of grid cells falling in different O₃ formation regimes (VOC-limited, NO_x-limited, and transition regimes) suggested by three different indicators during COVID-19 lockdown (January and February 2020) under different precursors reductions cases. All results are calculated using Community Multi-scale Air Quality (CMAQ) model

Senarios	Indicators	VOC-limited	NO _x -limited	Transition
During COVID-19	HCHO/NO ₂	0.13	0.70	0.17
	O ₃ /NO _y	0.11	0.40	0.49
	H ₂ O ₂ /NO _y	0.42	0.15	0.43
VOCs reduced by 50%	HCHO/NO ₂	0.19	0.65	0.16
	O ₃ /NO _y	0.14	0.39	0.47
	H ₂ O ₂ /NO _y	0.42	0.15	0.43
NO _x reduced by 50%	HCHO/NO ₂	0.02	0.85	0.13
	O ₃ /NO _y	0.03	0.51	0.46
	H ₂ O ₂ /NO _y	0.24	0.19	0.57
VOCs and NO _x reduced by 50%	HCHO/NO ₂	0.04	0.79	0.17
	O ₃ /NO _y	0.03	0.52	0.45
	H ₂ O ₂ /NO _y	0.25	0.19	0.56

Details on the simulation and analysis can be found in Zhu et al. (2021). It is evident that the depending on the selected indicators different results are produced when identifying O₃ formation regimes. The HCHO/NO₂ indicator predicts a higher percentage of grids for the NO_x-limited regime and the O₃/NO_y predicts more for the transition one. Contraty, the H₂O₂/NO_y favors the VOCs-limited regime. In addition, these three indicators show different sensitivities when changes (reductions) in O₃ precursors species emissions are considered. When the VOC emissions decrease by 50%, there are no changes in the formation regimes indicated by the H₂O₂/NO_y ratio. In contrast, an enhancement of the grid percentage corresponding to the VOC-limited regime (~46% increasing rate) is predicted using the HCHO/NO₂ ratio. Consequently, different conclusions can be reached using different indicators.

4 Atmospheric oxidation capacity (AOC)

Reassessing its formation mechanism, O₃ is formed through photochemical reactions. The overall processes are related to the atmospheric oxidation capacity (AOC), which can be characterized by the levels of atmospheric oxidants, mainly including hydrogen oxide radicals (HO_x = OH + HO₂) during daytime, and nitrogen oxide radical (NO₃) (Jacob, 2000; Monks, 2005) during nighttime. There are also other approaches to define the AOC. Elshorbany et al. (2009) identified the AOC as the sum of the explicit oxidation rates of primary pollutants by the oxidants. Liu et al. (2021) calculated the AOC based on electron transfer during the secondary pollutants formation process. The AOC is a fundamental factor in understanding the formation of O₃ and other secondary species. Despite its potential, only a handful of

studies reported the importance of AOC in explaining changes in O₃ formation in China. Li et al. (2019a) found that since 2013, high AOC along with PM_{2.5} reductions is the reason for the reported O₃ increases in China. Since the PM_{2.5} is considered as the sink of the HO_x (a major component of AOC), its reduction leads to the increase of AOC. Wang et al. (2021c) and Zhu et al. (2021) also reported that the unexpectedly rising amounts of O₃ during the COVID-19 were mainly attributed to the enhanced AOC since they had similar variation trends and spatial distributions.

Herewith, we aim at better understanding the interplay between AOC and O₃ formation. Among all oxidants, HO_x concentrations are related to O₃ formation significantly, and even their day-to-day co-variations have been noticed in different cities and episodes (Porter et al., 2017; Chen et al., 2020; Zhu et al., 2020). Zhao et al. (2021) reported that the average day-to-day co-variations between HO_x and O₃ is larger than 0.55 in the PRD. However, there is no further evidence in the relationships between AOC with O₃ concentrations and changes in O₃ concentrations. As a very preliminary test, the results from COVID-19 periods are summarized. Table 2 shows the correlations between the HO_x and O₃ in the major city clusters, including the North China Plain (NCP), the Yangtze River Delta (YRD), and the PRD in China during the COVID-19 (January and February, 2020). O₃ from biogenic source is also considered, since recent studies reported that the BVOCs played an important role in the city clusters due to the urban greening impacts (Ma et al., 2019; Ma et al., 2022). In general, there is a significant positive correlation between non-background O₃ and HO_x in all these three regions. The maximum goodness of fit (*R*) is predicted for the NCP (*R*² = 0.47) where, the most significant increase of O₃ (average increase rate ~54%) was reported (Zhu et al.,

Table 2 The correlation between HO_x and non-background (NB) O₃ and O₃ in the major city clusters (NCP, YRD and PRD regions) in China during COVID-19 under different emission control conditions. The NB O₃ is the sum of O₃ from all emission sources (including both anthropogenic and biogenic sources). Units for NB O₃/O₃ and HO_x are ppb and ppt. Total grid cells are 284, 277, and 158 in the NCP, YRD, and PRD, respectively. Total data points are 10508, 10247, and 5846 in the NCP, YRD, and PRD, respectively

NB	NCP	YRD	PRD
O ₃			
During COVID-19	$O_3 = 3.7*HO_x + 0.2, R^2 = 0.47$	$O_3 = 1.8*HO_x + 0.6, R^2 = 0.40$	$O_3 = 1.2*HO_x + 1.6, R^2 = 0.27$
During COVID-19	$O_3 = 2.1*HO_x + 0.9, R^2 = 0.42$	$O_3 = 2.7*HO_x - 4.0, R^2 = 0.60$	$O_3 = 2.7*HO_x - 7.2, R^2 = 0.43$
NO _x reduced by 50%	$O_3 = 1.5*HO_x + 0.7, R^2 = 0.49$	$O_3 = 2.2*HO_x - 6.4, R^2 = 0.03$	$O_3 = 2.0*HO_x - 9.2, R^2 = 0.55$
VOCs reduced by 50%	$O_3 = 1.3*HO_x + 0.7, R^2 = 0.14$	$O_3 = 2.8*HO_x - 3.4, R^2 = 0.39$	$O_3 = 1.9*HO_x - 7.0, R^2 = 0.05$
VOCs and NO _x reduced by 50%	$O_3 = 1.2*HO_x + 0.6, R^2 = 0.29$	$O_3 = 2.8*HO_x - 6.5, R^2 = 0.69$	$O_3 = 2.3*HO_x - 8.9, R^2 = 0.46$

2021). In addition, O₃ concentrations also show high sensitivity to the changes of AOC (average increase rate ~98%) in the NCP, represented by the higher regression slope (slope = 3.7). Compared to the NCP, the correlation is less strong ($R^2 = 0.27$) for the PRD. The latter is consistent with the findings of previous studies denoting that O₃ concentration remained almost constant during the COVID-19 (Wang et al., 2021a; Zhu et al., 2021). Considering O₃ concentrations (sum of background and non-background O₃), the positive correlations between it and AOC are even more significant with the R^2 up to 0.60 in the YRD during COVID-19 (Table 2). Besides, previous studies also reported that the elevated O₃ was corresponding to the enhanced AOC during the summertime (Li et al., 2019a; Qin et al., 2022), indicating that the AOC may be a better indicator to elucidate the O₃ formation. However, these correlations vary greatly under different emission control strategies in different regions. In the YRD, the R^2 drops from 0.6 to 0.03 when NO_x emissions are reduced by 50%. While in the PRD, the R^2 value is more sensitive to VOC decreases (from 0.43 to 0.05). The AOC levels highly depend on the meteorological parameters and emission conditions. Thus, the correlation between O₃ and AOC changes accordingly to the variations in meteorology and emissions. More comprehensive simulations are required to determine their relationships better under different emissions control scenarios.

5 Summary

In this study, we briefly summarized and evaluated the different methods for indicating the formation of tropospheric O₃. The isopleth diagram and the sensitivity method are two widely used ways to describe O₃ formation. However, both require numerous simulations and the development of complex chemical mechanisms. In addition, they are also affected by multiple environmental factors, which leads to large uncertainties in policymaking decisions. The AOC is regarded as the fundamental factor in the formation of O₃ and other

secondary pollutants in the atmosphere. We suggest that the AOC could serve as a better indicator to characterize O₃ formation. Our results show that AOC and O₃ have a coincident variation trend in key city clusters (NCP, YRD, and PRD regions) in China and the average R^2 between O₃ and AOC is as high as 0.60. As the AOC level could be determined as the sum of the major oxidants, it is important to figure out the budget (generation and remove processes) of these oxidants and then alleviate O₃ pollution via control the key precursors in their generation process. In addition, feasible control strategies should be considered under different meteorological conditions, since AOC highly depend on the meteorological parameters such as temperature. More comprehensive studies should be conducted to investigate the variability of the correlation between O₃ and AOC with the ultimate aim of establishing effective emission control policies in the future.

Acknowledgements This work was supported by the co-funded DFG-NSFC Sino-German Air Changes Project (No. 448720203), the National Natural Science Foundation of China (Nos. 42077194/42061134008/42022023/92044302), and the Shanghai International Science and Technology Partnership Project (China) (No. 21230780200).

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