https://doi.org/10.5194/acp-2021-764
Preprint. Discussion started: 29 October 2021

Atmospheric Chemistry and Physics Discussions
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Atmospheric oxidation capacity and ozone pollution mechanism in a coastal city of Southeast China: Analysis of a typical photochemical episode by Observation-Based Model

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Abstract:

A typical multi-day ozone (O_3) pollution event was chosen to explore the atmospheric oxidation capacity (AOC), OH reactivity, radical chemistry, and O_3 pollution mechanism in a coastal city of Southeast China, with an Observation-Based Model coupled to the Master Chemical Mechanism (OBM-MCM). The hydroxyl radical (OH) was the predominant oxidant (91±23%) for daytime AOC, while NO_3 radical played an important role for AOC during the nighttime (64±11%). Oxygenated volatile organic compounds (OVOCs, 30±8%), NO_2 (29±8%) and CO (25±5%) were the dominant contributors to OH reactivity, accelerating the production of O_3 and recycling of ROx radicals (ROx=OH+HO_2+RO_2). Photolysis of nitrous acid (HONO, 33±14%), O_3 (25±13%), formaldehyde (HCHO, 20±5%), and other OVOCs (17±2%) were the important primary sources of ROx radicals, which played initiation roles in atmospheric oxidation processes. O_3 formation was VOC-sensitive, and controlling emissions of aromatics, alkenes, and long-chain alkanes were benefit for ozone pollution mitigation. Combined with regional transport analysis, the reasons for this O_3 episode were the accumulation of local photochemical production and regional transport. The results of sensitivity analysis showed that VOCs were the limiting factor of radical recycling and O_3 formation, and the 5% reduction of O_3 would be achieved by decreasing 20% anthropogenic VOCs. The findings of this study have significant guidance for emission reduction and regional collaboration on future photochemical pollution control in the relatively clean coastal cities of China and similar countries.

Keywords: Atmospheric oxidation capacity; Radical chemistry; O_3 formation mechanism; OH reactivity; OBM-MCM

1 Introduction

Tropospheric ozone (O_3) is mainly produced by photochemical reactions of anthropogenic and natural emitted volatile organic compounds (VOCs) and nitrogen oxides (NOx), and is an important factor resulting in regional air pollution (Zhu et al., 2020; Lu et al., 2018). The elevated O_3 concentrations enhance the atmospheric oxidation capacity (AOC) and have harmful effects on global climate change, ecosystems, and human health (Liu et al., 2019a; Fowler et al., 2009). The formation mechanisms of O_3 pollution are extremely difficult to figure out, due to the complex types and sources of its precursors (Simon et al., 2015). O_3 formation is affected by multiple factors such as temporal & spatial distribution, meteorological conditions, atmospheric oxidation processes and regional transport (Gong and Liao, 2019; Chang et al., 2019). To effectively control the tropospheric O_3 pollution, exploration of the photochemical mechanism and judgment on the control factors of O_3 formation become extremely important for scientific community (Chen et al., 2020; Li et al., 2018).

The atmospheric oxidation capacity reflects the essential driving force in tropospheric chemistry, and plays an important place in the destruction rates of primary components and production rates of secondary pollutants (Elshorbany et al., 2008). Generally, the AOC levels in the polluted regions are much higher than those at the background sites or remote regions (Geyer et al., 2001; Xue et al., 2016). ROx radicals, including hydroxyl radical (OH), hydro peroxy radical (HO_2) and organic peroxy radical (RO_2), are very important indicators in atmospheric photochemistry and dominate the atmospheric oxidative capacity (Li et al., 2018). Meanwhile, radical chemistry drives the transformation and recycling of O_3 through initiating atmospheric oxidation processes (Wang et al., 2020). Among these radicals, the OH radical accounts for the majority of AOC over 90% during the daytime, thus the OH reactivity (i.e., OH loss) indicates the primary contribution of individual pollutant (Wang et al., 2018a; Mao et al., 2010). Hence, atmospheric oxidation capacity, OH reactivity, and radical chemistry are crucial aspects for understanding the complex atmospheric photochemistry processes (Li et al., 2018). For example, the major primary ROx sources are the photolysis reaction of O_3, formaldehyde (HCHO), other oxygenated volatile organic compounds (OVOCs), nitrous acid (HONO) and the reactions of O_3 with unsaturated VOCs (Volkamer et al., 2010). The dominant ROx sources at some rural sites were O_3 photolysis and O_3 reactions with VOCs (Li et al., 2018; Martinez et al., 2003), and those at many urban sites were HONO and OVOCs photolysis (Xue et al., 2016; Liu et al., 2012; Emmerson et al., 2005). For oil and gas field

https://doi.org/10.5194/acp-2021-764
Preprint. Discussion started: 29 October 2021

sites, there were highly abundant VOCs to promote the formations of O_3, and the contribution of OVOCs photolysis was 2-5 times higher than that in urban areas (Chen et al., 2020; Edwards et al., 2013, 2014). The HONO photolysis was a very important primary ROx source at the high-altitude or background sites. (Acker et al., 2001; Jiang et al., 2020).

Current studies of atmospheric O_3 photochemical pollution observations have been conducted at the urban, suburban, rural and remote sites around the world (Smith et al., 2006; Eisele et al., 1997; Kanaya et al., 2001; Hofzumahaus et al., 2009; George et al., 1999; Emmerson et al., 2005; Kanaya et al., 2007; Michoud et al., 2012). In China, O_3 photochemical pollution events have been reported in some megacities, such as Beijing, Shanghai, Guangzhou, and Chengdu (Liu et al., 2012; Tan et al., 2019; Zhu et al., 2020; Wang et al., 2020; Liu et al., 2019b; Ling et al., 2017). Few studies on O_3 photochemical pollution in cities with low O_3 precursor emissions have been reported, and the air quality in these areas usually depends on the change of meteorological conditions. The coastal region of Southeast China is influenced by the East Asian monsoon and acts as an important transport path between the Yangtze River Delta (YRD) and the Pearl River Delta (PRD) (Hu et al., 2019; Liu et al., 2020a; Liu et al., 2020b), which is a good 'laboratory' to further explore O_3 photochemical pollution and formation mechanism with relatively low O_3 precursors and complex meteorological conditions (Zhang et al., 2020b; Hu et al., 2020b).

The Observation-Based Model (OBM) is widely used to investigate O_3-VOCs-NOx relationships and radical chemistry (Wang et al., 2018a; Tan et al., 2019). The O_3 sensitivity reveals the non-linear relationship between O_3 and its precursors (i.e., VOCs and NOx), which was conducted to investigate O_3 formation mechanism and control strategies (Wang et al., 2020). The OBM combined with the Master Chemical Mechanism (V3.3.1) (OBM-MCM) has been applied to explore the O_3 photochemical pollution mechanism in different environmental conditions (Chen et al., 2020; Li et al., 2018; Xue et al., 2016; Wang et al., 2018). In this study, we chose a typical multi-day O_3 pollution event in the coastal city Xiamen (Fig. S1). Based on the OBM-MCM analyses, the study aims to clarify (1) the pollution characteristics of O_3 and its precursors, (2) the atmospheric oxidation capacity and radical chemistry, and (3) the O_3 formation mechanism and sensitivity analysis. The results are expected to enhance the understanding of O_3 formation mechanism with low O_3 precursor levels, and provide scientific evidence for O_3 pollution control in the coastal cities.

2 Materials and methods

2.1 Study area and field observations

Xiamen is a coastal city in the southeast area of China, to the west coast of the Taiwan Strait. The

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field campaigns were carried out at the Atmospheric Environment Observation Supersite (24.61° N, 118.06° E) on the rooftop of around 70 m high building in the Institute of Urban Environment, Chinese Academy of Sciences. The supersite was equipped with complete monitoring instruments, including gas and aerosol species compositions, O_3 precursors, meteorological parameters, and photolysis rate. Criteria air pollutants of O_3, SO_2, NO-NO_2-NOx, and CO were monitored by commercial instruments TEI 49i, 43i, 42i, and 48i (*Thermo Fisher Scientific, USA*), respectively. The meteorological parameters of wind speed (WS), wind direction (WD), air temperature (T), pressure (P), and relative humidity (RH) were measured by an ultrasonic atmospherium (*150WX, Airmar, USA*). HONO was measured with an analyzer for Monitoring Aerosols and Gases in Ambient Air (*MARGA, ADI 2080, Applikon Analytical B.V., the Netherlands*). A gas chromatography-mass spectrometer (GC-FID/MS, *TH-300B, Wuhan, CN*) was used for atmospheric VOCs concentrations monitoring, involving about 103 species of VOCs with a 1-hour time resolution. Photolysis frequencies were measured by a photolysis spectrometer (*PFS-100, Focused Photonics Inc., Hangzhou, China*). The photolysis rate constants include $J(O^1D)$, $J(NO_2)$, $J(H_2O_2)$, J(HONO), J(HCHO), and $J(NO_3)$. Strict quality assurance and quality control were applied, and the detailed descriptions of the monitoring procedures were documented in our previous studies (Zhang et al., 2020b; Wu et al., 2020; Liu et al., 2020a; Liu et al., 2020b; Hu et al., 2020a).

2.2 Observation-based chemical box model

In this study, the Observation-Based Model (OBM) combined with the latest version 3.3.1 of MCM (MCM v3.3.1; http://mcm.leeds.ac.uk/MCM/), involving 142 non-methane VOCs and more than 17000 elementary reactions of 6700 primary, secondary and radical species (Jenkin et al., 2003; Saunders et al., 2003), was used to explore the atmospheric oxidation processes and O_3 formation mechanisms. The physical process of deposition within the boundary layer height (BLH), which varied from 300 m during nighttime to 1500 m during the daytime in autumn (Li et al., 2018), was considered in the model. Therefore, the dry deposition velocity was utilized to simulate the deposition loss of some reactants in the atmosphere, which avoided continuous accumulation of pollutant concentrations in the model (Zhang et al., 2003; Xue et al., 2016).

The observation data of the gaseous pollutants (i.e., O_3, CO, NO, NO_2, HONO, SO_2, and VOCs), meteorological parameters (i.e., T, P, and RH), and photolysis rate constants ($J(O^1D)$, $J(NO_2)$, $J(H_2O_2)$, J(HONO), J(HCHO), and $J(NO_3)$) were input into the OBM-MCM model as constraints. The photolysis rates of other molecules such as OVOCs were parameterized by solar zenith angle and then scaled by the measured $J(NO_2)$ (Saunders et al., 2003). We pre-ran for 5 days before running the model to initialize the unmeasured compounds and radicals (Xue et al., 2014).

OBM-MCM is mainly used to simulate in situ atmospheric photochemical processes and quantify the O_3 production rate, AOC, OH reactivity, and ROx radical budgets. Among them, primary sources of ROx, including the photolysis reactions of O_3, HONO, formaldehyde (HCHO), and other OVOCs as well as reactions of VOCs with O_3 and NO_3 radicals, are important (Xue et al., 2016). The termination reactions of ROx are controlled by cross-reactions with NOx (under high NOx conditions) and ROx (under low NOx conditions) to form nitric acid, organic nitrates, and peroxides (Liu et al., 2012; Xue et al., 2016). The production rate of O_3 ($P(O_3)$) includes HO_2+NO and RO_2+NO reactions (Eq. 1), and the destruction of O_3 ($D(O_3)$) involves reactions of O_3 photolysis, O_3+OH, O_3+HO_2, O_3+VOCs, NO_2+OH, and NO_3+VOCs (Eq. 2). The net O_3 production rate ($Pnet(O_3)$) is calculated by $P(O_3)$ minus $D(O_3)$ as equation 3.

$$P(O_3) = k_1[HO_2][NO] + \sum(k_{2i}[RO_2][NO]) \quad (1)$$

$$D(O_3) = k_3[O_1D][H_2O] + k_4[O_3][OH] + k_5[O_3][HO_2] + k_6[NO_2][OH] + \sum(k_{7i}[O_3][unsat.VOCs]) + 2\sum(k_{8i}[NO_3][unsat.VOCs]) \quad (2)$$

$$Pnet(O_3) = P(O_3) - D(O_3) \quad (3)$$

where *ki* is the related reaction rate constant. Detailed descriptions of the chemistry calculation can be found elsewhere (Chen et al., 2020; Wang et al., 2018a; Xue et al., 2014).

Relative incremental reactivity (RIR), an index to diagnose the sensitivity of O_3 formation to precursors, is defined as the ratio of the differences in O_3 production rate to the difference in precursor concentrations (Chen et al., 2020). Here, the $\Delta X/X$ in the OBM-MCM represents the percentage reduction in the input concentrations of each targeted O_3 precursor group and this value is adopted as 20% (Liu et al., 2020c).

$$RIR = \frac{\Delta P(O_3)/P(O_3)}{\Delta X/X} \quad (4)$$

2.3 Meteorological data and back trajectory calculation

The backward trajectories of air masses arriving at the observation site were calculated by the MeteoInfo during the episode (Wang *et al*., 2014). The backward trajectories with 72-h were run with the time resolution of 3 hours at 100 m height above ground level, and starting time was 0:00 LT and the ending time was 23:00 LT. Meteorological data were provided by NOAA ARL (ftp://arlftp.arlhq.noaa.gov/pub/archives/gdas1). The Final Operational Global Analysis data (FNL) is

https://doi.org/10.5194/acp-2021-764
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from the Global Data Assimilation System and analyzes results with the model which is also used by the National Center for Environmental Prediction (NCEP) in the Global Forecast System (GFS) (https://rda.ucar.edu/datasets/ds083.2/). The weather charts were conducted using Grid Analysis and Display System (GrADS) with the specific programmed script files. A detailed description of the synoptic information was shown in our previous study (Wu et al., 2019).

3 Results and discussion

3.1 Overview of observations

The O_3 pollution events frequently appeared in the coastal city Xiamen during autumn time, related to the West Pacific Subtropical High (WPSH), carrying high temperature, low RH, and stagnant weather conditions, encouraging the formation and accumulation of O_3 in the southeast coastal area (Wang et al., 2018a). The daily maximum 8-h-average O_3 concentrations (MDA8h O_3) from 20 to 29 Sep, 2019 ranged from 53 to 85 ppbv, partly exceeding the Grade II of China's National Ambient Air Quality Standard of 75 ppbv. The time series and descriptive statistics of air pollutants and meteorological parameters during this multi-day O_3 pollution event are shown in Fig. 1 and Table 1. During this period, the dominant wind direction was northeast, with an average wind speed of 1.8±0.9 $m \cdot s^{-1}$. The maximum hourly temperature was as high as 35 °C, and the average RH was 56.4±12.6%. Solar radiation intensity and $J(NO_2)$ were strong, compared to those of the Yellow River Delta (Chen et al., 2020), Shanghai (Zhu et al., 2020) and Hong Kong (Xue et al., 2016). In general, these meteorological parameters were conducive to the production and accumulation of O_3. In addition, O_3 concentrations at nighttime kept relatively high (Fig.1), indicating the influence of regional transport and little NO titration (Zhang et al., 2020a; Wu et al., 2020). Figure S2 shows the 72 h back trajectories at the monitoring site. Among them, 80% of the air masses came from the Yellow Sea, and the other 20% air masses originated from the northeast China through long-range transport.

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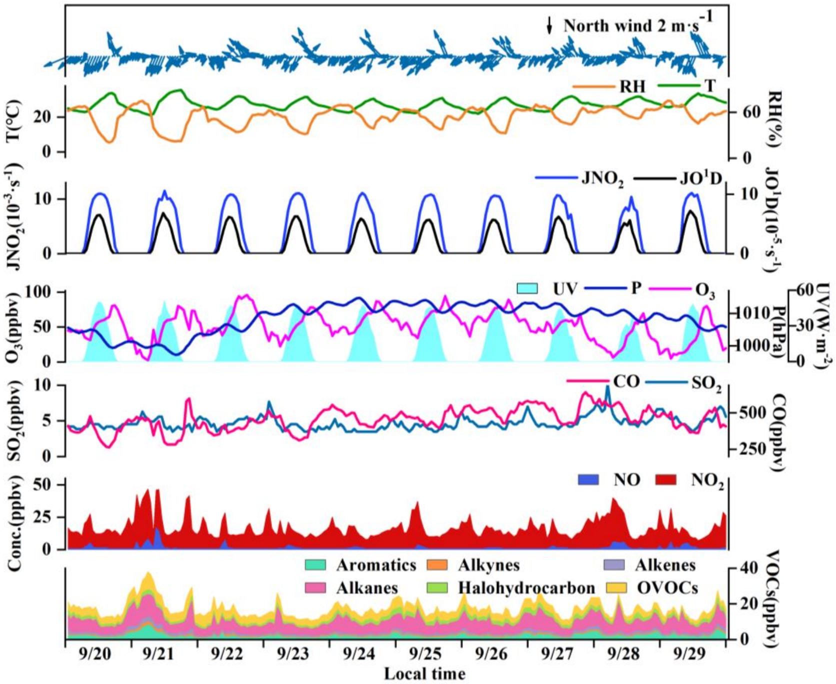

Figure 1. Time series of major trace gases, photolysis rate constants, and meteorological parameters during 20-29 Sep. 2019 in Xiamen.

Table 1. Descriptive statistics of major trace gases (ppbv) and meteorological parameters during 20-29 Sep. 2019

Parameters	Mean±SD	Median	Max
MDA8h O_3	67.4±17.2	52.6	89.3
TVOCs	17.2±4.8	16.1	38.0
CO	452±77.3	454	641
NO	1.4±1.3	0.8	17.1
NO_2	15.4±6.9	13.6	40.9
SO_2	4.7±0.9	4.6	10.2
T (°C)	27.3±3.21	26.9	35.6
RH (%)	56.4±12.6	56.6	75.0
P (hPa)	1008±4.57	1010	1015
UV ($W \cdot m^{-2}$)	46.4±1.12	0	51.1
Wind speed ($m \cdot s^{-1}$)	1.8±0.9	1.6	3.8
Wind direction (◦)	90.8±90.4	45.0	337

Table 2. Measured VOCs concentrations during 20-29 Sep. 2019 in Xiamen (Units: pptv)

Chemicals	Mean±SD	Chemicals	Mean±SD
Aromatics	**2131±1236**	**Alkanes**	**6970±2325**
toluene	995±632	ethane	1552±342
m/p-xylene	392±326	propane	1546±608
benzene	236±95	iso-pentane	930±316
o-xylene	154±121	n-butane	844±365
ethylbenzene	138±94	n-dodecane	618±101
styrene	76±65	iso-butane	494±201
1,2,4-trimethylbenzene	75±37	n-pentane	254±157

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m-ethyltoluene	16±11	n-hexane	134±184
p-ethyltoluene	10±6	3-methylhexane	116±93
iso-propylbenzene	5±3	n-heptane	104±78
1,3,5-trimethylbenzene	8±6	3-methylpentane	82±48
o-ethyltoluene	8±5	2-methylhexane	67±38
1,2,3-trimethylbenzene	7±5	2-methylpentane	56±46
n-propylbenzene	7±4	2,3-dimethylbutane	54±33
Halocarbons	**1951±572**	cyclohexane	42±15
dichloromethane	998±392	n-undecane	33±35
1,2-dichloroethane	499±210	n-octane	24±15
chloromethane	294±75	n-nonane	15±13
1,2-dichloropropane	88±34	2,2-dimethylbutane	15±7
bromomethane	47±23	n-decane	14±11
trichloroethene	15±6	**Alkenes**	**1205±464**
1,4-dichlorobenzene	9±3	ethene	671±361
OVOCs	**4246±1263**	propene	207±116
acetone	2802±750	isoprene	171±232
2-butanone	799±430	trans-2-pentene	105±62
2-propanol	343±283	1-butene	16±21
2-methoxy-2-methylpropane	169±97	cis-2-butene	12±12
acrolein	66±22	1-pentene	10±7
4-methyl-2-pentanone	16±15	1,3-butadiene	8±7
2-hexanone	12±3	trans-2-butene	4±4
		Acetylene	**674±290**

Table 2 lists the detailed VOCs concentrations during the observation period. Alkanes (6970±2325 pptv) were the predominant components of total VOCs, followed by OVOCs (4246±1263 pptv), aromatics (2131±1236 pptv), halocarbons (1951±572 pptv), alkenes (1205±464 pptv), and acetylene (674±290 pptv). The ratio of ethene/ethane (0.4±0.2) was significantly ($p<0.05$) lower than that in Hong Kong (0.7±0.1) with significant aged air masses, indicating that the high O_3 in Xiamen might be partially attributed to the aged air masses (e.g., transport of air from polluted regions or intense atmospheric oxidation) (Wang et al., 2018a). The concentration of TVOCs in Xiamen (17.2±4.8 ppbv) was much lower than that in the developed areas with large anthropogenic emissions (i.e., Beijing (65.6 ppbv), Hangzhou (55.9 ppbv), Guangzhou (47.3 ppbv), Nanjing (43.5 ppbv), Hong Kong (26.9 ppbv) and Shanghai (29.7 ppbv), but was higher than that at the background site (i.e., Mt. Wuyi, 6.1 ppbv) (Li et al., 2019; Hong et al., 2019). Figure S3 shows the contributions of top 10 VOCs species (including alkenes and aromatics) to the total ozone formation potential (OFP), which was calculated by the localized maximum incremental reactivity in China (Zhang et al., 2021). The key VOCs species with the highest OFP was ethene (3.6±2.0 $\mu g\cdot m^{-3}$), m/p-xylene (2.2±1.9 $\mu g\cdot m^{-3}$), toluene (2.2±1.5 $\mu g\cdot m^{-3}$), propene (1.3±0.8 $\mu g\cdot m^{-3}$) and isoprene (1.3±1.7 $\mu g\cdot m^{-3}$).

The O_3 formation process depends on its precursors and related environmental conditions, while the

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photochemical reactions during the daytime are the basis for O_3 changes. Figure 2 shows the diurnal patterns of major trace gases and meteorological parameters during 20-29 Sep. 2019. The O_3 concentration maintained at relatively low levels from night to 07:00 LT, then rose and reached its maximum at around 17:00 LT. O_3 peak in the afternoon was related to the accumulation of both local photochemical reaction and potential regional transport (including O_3 and its precursors in the upwind direction to the observation site), and the detailed analysis will be shown in Section 3.3.2. The reduction of observed O_3 (ΔO_3) in the early morning rush hour caused by NO titration did not appear, verifying the impacts of regional transport (Liu et al., 2019b; Zeren et al., 2019; Chen et al., 2020). The diurnal patterns of VOCs and NOx were similar, with the highest concentrations at around 08:00 LT and then decreasing during 9:00~16:00 LT and increasing at night, which is related to the human activities emissions (including vehicle exhaust and industry emission), photochemical reaction and the variations of boundary layer (Elshorbany et al., 2008; Hu et al., 2020b).

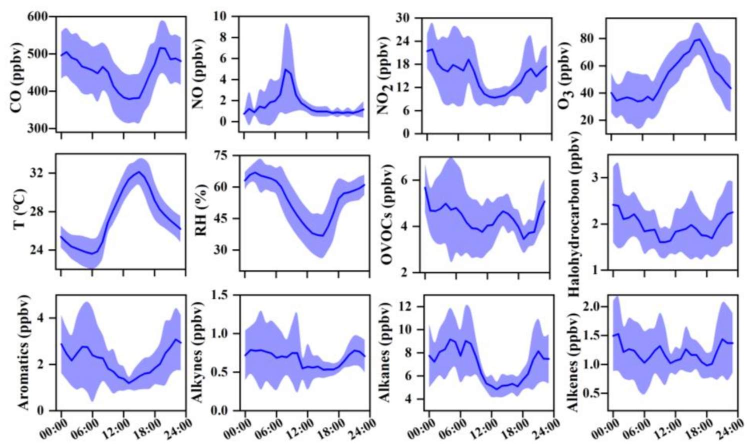

Figure 2. Average diurnal patterns of major trace gases and meteorological parameters during 20-29 Sep. 2019 in Xiamen. The error bar is the standard error.

3.2 Atmospheric oxidation and radical chemistry

3.2.1 Atmospheric oxidation capacity (AOC)

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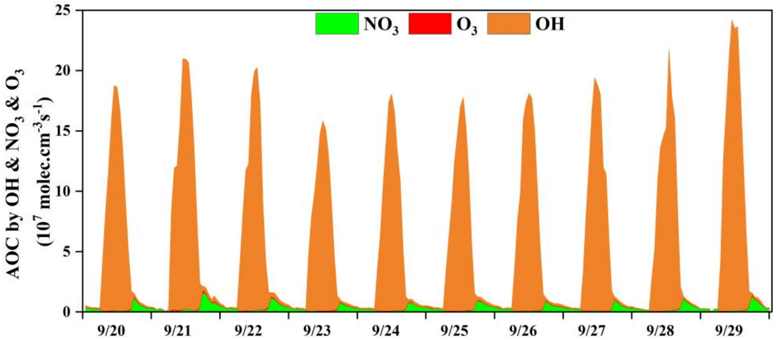

Figure 3. Time series of the model-calculated Atmospheric Oxidation Capacity (AOC) in Xiamen during 20-29 Sep. 2019.

Figure 3 shows the time series of the model-calculated AOC during the O_3 pollution period. The AOC determines the removal rate of primary pollutants and the production rate of secondary pollutants, and was the basis for reflecting atmospheric photochemical pollution (Geyer et al., 2001). AOC is calculated as the sum of oxidation rates of various primary pollutants (CO, NOx, VOCs, etc.) by the major oxidants (i.e., OH, O_3, NO_3) (Chen et al., 2020; Xue et al., 2016; Xue et al., 2014). In this study, the average daytime AOC was 10.0×10^7 molecules cm^{-3} s^{-1}, which was comparable to Hong Kong (6.3×10^7 molecules cm^{-3} s^{-1}), higher than those in Shanghai (3.5×10^7 molecules cm^{-3} s^{-1}) and a rural site of Berlin (1.4×10^7 molecules cm^{-3} s^{-1}), but lower than that in Santiago (3.2×10^8 molecules cm^{-3} s^{-1}) (Li et al., 2018; Chen et al., 2020; Xue et al., 2016; Geyer et al., 2001; Zhu et al., 2020). The results of AOC characteristics in different regions were decided by the precursor concentrations/types and photochemical environment.

According to the diurnal patterns of the AOC contributed by OH, O_3, and NO_3, the predominant oxidant was OH (91±23%) during the daytime, followed by NO_3 (8±20%) and O_3 (1±2%). Meanwhile, the diurnal characteristics of AOC were consistent with the profile of the model-calculated OH (Fig. S4) and the observed photolysis rate constants (Fig.1) (Zhu et al., 2020). Meanwhile, NO_3 (64±11%) played the most important role in the oxidant capability during the nighttime, followed by OH (29±12%) and O_3 (6±1%). In particular, the contribution of NO_3 to AOC reached the maximum of 80% at around 18:00 LT, when the concentrations of O_3 and NO_2 were relatively high and accelerated the formation of NO_3 (Fig.2). In addition, solar radiation was woken during the nighttime, which resulted in the accumulation of NO_3 due to the cease of photolysis of NO_3 (Rollins et al., 2012; Chen et al., 2020). AOC contributed by O_3 was negligible, owing to the relatively low concentration of alkenes at the monitoring site (Fig.1 and Table 2), since O_3 contributed to the oxidation capacity through alkenes ozonolysis (Xue et al., 2016). In

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summary, the OH radical dominated the AOC in Xiamen, and it was necessary to further explore the partitioning of OH reactivity among different precursor groups.

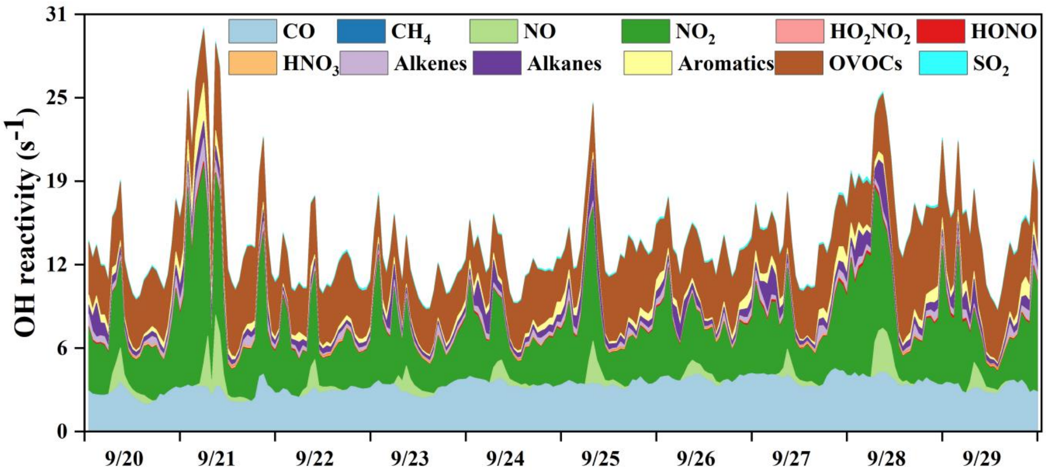

Figure 4. Time series of model-calculated OH reactivity and its partitioning to the major reactants in Xiamen during 20-29 Sep. 2019.

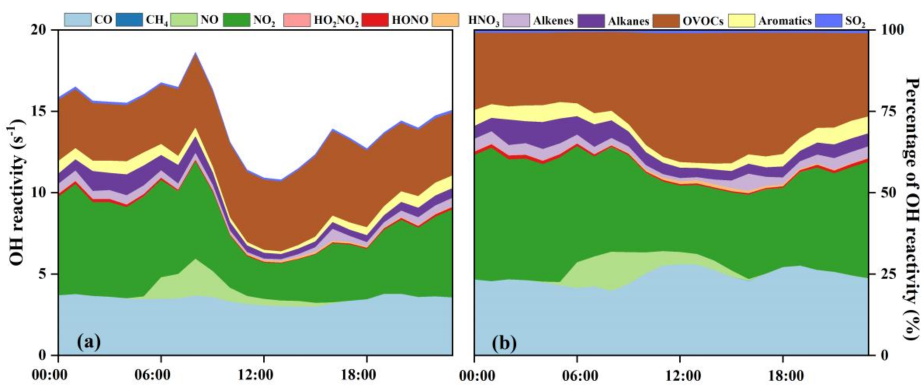

Figure 5. (a) Diurnal patterns and (b) percentage of model-calculated OH reactivity and its partitioning to the major reactants

The OH reactivity is an indicator for the OH chemical loss frequency, computed as the reaction rates of OH with CO, NOx, SO_2, HONO, HNO_3, HO_2NO_2, and VOCs (Whalley et al., 2016; Chen et al., 2020). Zhu et al. (2020) found that unmeasured species and unknown secondary products contributed considerably to the actual OH reactivity. Time series and diurnal patterns of model-calculated OH reactivity as well as its partitioning to the major reactants during the episode are shown in Fig. 4 and Fig.

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5. The OH reactivity reached the peak (18.6±4.8 s^{-1}) at around 8:00 LT, mainly caused by the reaction of OH with NOx, since vehicle exhaust emitted large amounts of NOx during rush hours. The average daily OH reactivity was 14.4±3.83 s^{-1}, which was much lower than those in some polluted regions in Santiago (42 s^{-1}) and the PRD (50 s^{-1}), comparable to that at a rural site in Nashville (11 s^{-1}), but higher than that at a mountain site in Pennsylvania (6 s^{-1}) (Elshorbany et al., 2008; Lou et al., 2010a; Lou et al., 2010b; Kovacs et al., 2003; Ren et al., 2005). Figure 5 shows the diurnal variations and percentage of model-calculated OH reactivity to the major reactants during the episode. As shown in Fig. 5b, OVOCs (30±8 %) and NO_2 (29±8%) were the dominant contributors to OH reactivity, followed by CO (25±5%), alkanes (5±3%), aromatics (3±2%), alkenes (3±1%), and NO (2±4%). The partitioning of OH reactivity elucidated the inherent photochemical processes and major reactants in Southeast China. High OH reactivity of OVOCs, NO_2, and CO would promote the production of ROx radical. Therefore, the investigation of detailed chemical budget of the ROx, recycling, and termination reaction is meaningful to figure out the complex atmospheric photochemistry (Li et al., 2018; Lou et al., 2010b).

3.2.2 Radical chemistry

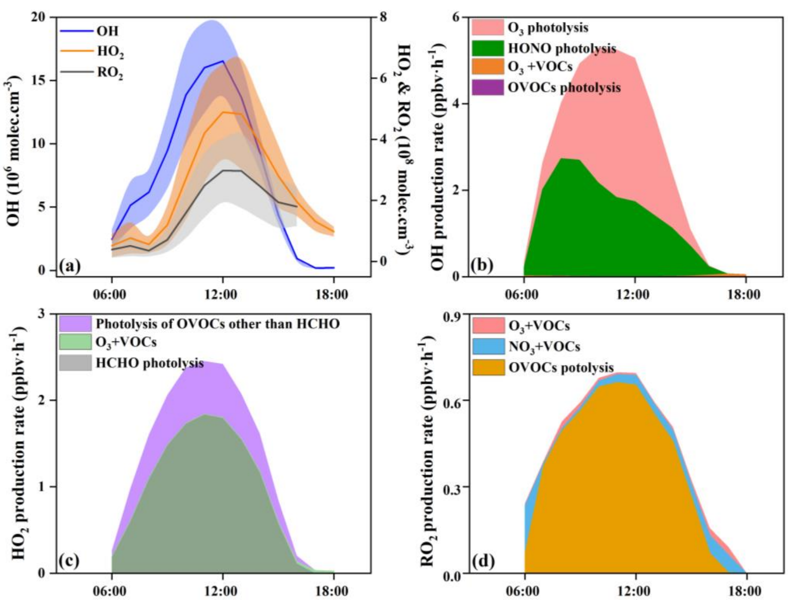

Figure 6. Model-simulated daytime average diurnal variations in (a) OH, HO_2, and RO_2 concentrations, and average primary production rates of (b) OH, (c) HO_2, and (d) RO_2 during 20-29 Sep. 2019 in Xiamen.

With the influence of NOx and VOCs, OH, HO_2, and RO_2 undergo efficient recycling and produce secondary pollutants, such as O_3 and OVOCs (Sheehy et al., 2010). Figure 6 shows the model-simulated OH, HO_2, and RO_2 concentrations and their primary sources. The detailed time series of ROx

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concentrations and chemical budget are summarized in Fig. S4. Figure 6a shows the diurnal variations of the simulated OH, HO_2, and RO_2. The maximum daily values of OH, HO_2, and RO_2 concentrations were 2.4×10^7, 7.9×10^8 and 4.7×10^8 molecules cm^{-3}, with the daytime average concentrations of 7.4×10^6, 2.4×10^8 and 1.7×10^8 molecules cm^{-3}, respectively. Model-predicted concentrations of OH in Xiamen were higher than that in the the Yellow River Delta (an oil field with high VOCs emission), while the concentrations of HO_2 and RO_2 showed a reverse trend (Chen et al., 2020). The ROx recycling of $OH\rightarrow RO_2$ was mainly controlled by the reaction of OH+VOCs, and the $RO_2\rightarrow HO_2$ and $HO_2\rightarrow OH$ depended on the reactions with NO (Fig.7). Combined with the ratio of VOCs/NOx (1.1±0.4), it was convinced that NOx would not be the limiting factor in the radical recycling processes. Hence, efficient conversions of radical propagation of $RO_2+NO\rightarrow HO_2$ and $HO_2+NO\rightarrow HO$ were expected, and $OH+VOCs\rightarrow RO_2$ reaction was the rate-depended step of the radical recycling in our study. The detailed radical chemistry would be further discussed as follows.

Figure 6b shows the daytime average diurnal variations of primary OH sources. HONO photolysis reached the maximum of 2.7 ppb h^{-1} at around 8:00 LT, which occupied 56±19% of the total OH primary production rates. The second source of OH primary production was O_3 photolysis (42±21%), and the percentages of O_3+VOCs and OVOCs photolysis were minor. The highest HONO photolysis rate appeared in the morning rush hour, suggesting the influence from vehicle emissions and nocturnal accumulation of HONO (Hu et al., 2020a). Considering the recycling of radicals, the reaction of HO_2+NO (8.0±6.2 ppb h^{-1}) dominated the total production of OH (Fig. S4a). Meanwhile, OH-initiated oxidations of VOCs (4.9±3.3 ppb h^{-1}) consumed OH most during the daytime, followed by OH+CO (2.6±1.9 ppb h^{-1}), $OH+NO_2$ (2.4±1.1 ppb h^{-1}), OH+NO (0.6±0.3 ppb h^{-1}), and $OH+O_3$ (0.2±0.1 ppb h^{-1}).

In this study, HCHO photolysis was identified as the most important source for HO_2 primary formation, with an average production rate of 1.1±0.6 ppb h^{-1} (Fig.6c), followed by the other OVOCs photolysis (0.4±0.2 ppb h^{-1}). The rate of OVOCs photolysis in Xiamen was much lower than that in some megacities, such as Beijing (Liu et al., 2012) and Hong Kong (Xue et al., 2016). The reaction of OH+CO (2.6±2.2 ppb h^{-1}) and RO_2+NO (2.5±1.5 ppb h^{-1}) were also important sources of HO_2 (Fig. S4b). The main sinks of HO_2 were HO_2+NO (7.9±6.2 ppb h^{-1}), while HO_2+HO_2 and HO_2+RO_2 were negligible.

In Fig. 6d, OVOCs photolysis contributed most to primary RO_2 production with a rate of 0.5±0.2 ppb h^{-1}, accounting for 85±20% of total RO_2 primary production. The reactions of unsaturated VOCs and NO_3 were the second important source, accounting for 11±18 % of the total primary RO_2. The radical

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recycling rate of OH+VOCs was 8.4 times higher than the sum of RO_2 primary production. The consumption reaction of RO_2 was mainly caused by RO_2+NO (3.7±2.9 ppb h^{-1}), and the cross-reactions by ROx themselves were limited.

The daytime average ROx budget and its recycling were also demonstrated (Fig. 7). For the ROx primary sources, the photolysis of HONO (33±14%), O_3 (25±13%), HCHO (20±5%) and other OVOCs (17±2%) were the major contributors. For ROx recycling, CO and VOCs reacted with OH producing HO_2 and RO_2 with the average rate of 4.0 and 4.4 ppbv h^{-1}, respectively. RO_2+NO and HO_2+NO enhanced the production of RO (3.6 ppbv h^{-1}) and OH (7.9 ppbv h^{-1}), with O_3 formed as a by-product. For the termination processes, the reactions of ROx with NOx were approximately 2-5 times faster than the cross-reactions of ROx.

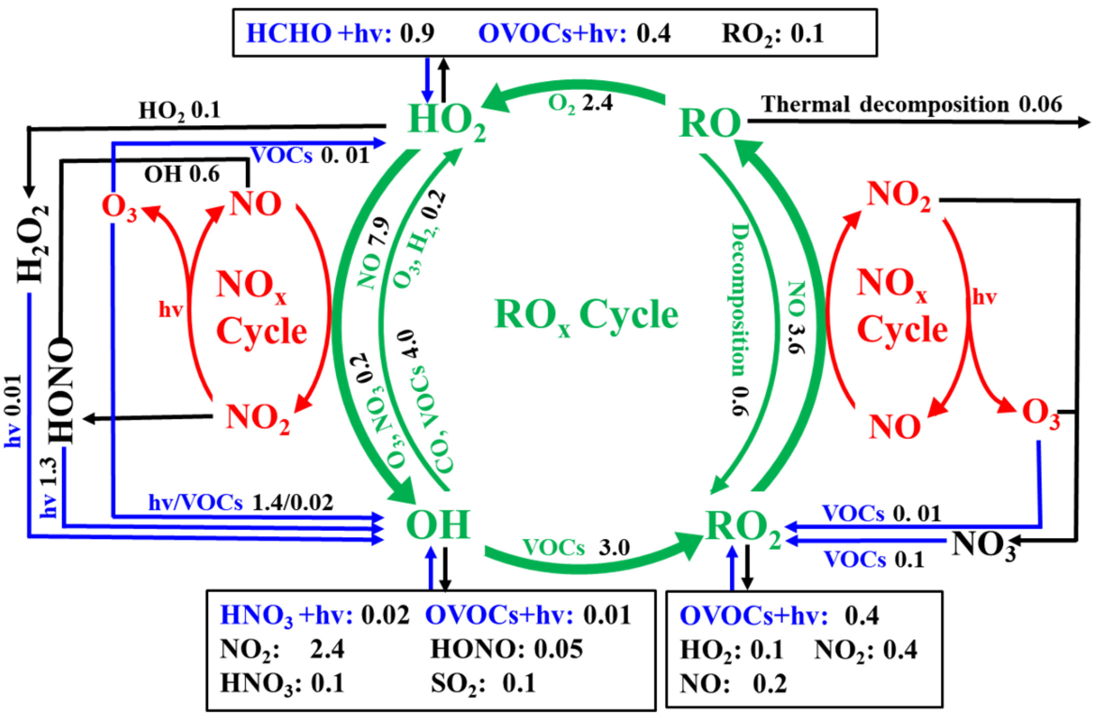

Figure 7. Daytime ROx budget during 20-29 Sep. 2019 in Xiamen. The unit is parts per billion per hour. The blue, black, and green lines and words indicate the production, destruction, recycling pathways of radicals, respectively.

3.3 O_3 formation mechanism

3.3.1 Chemical budget and sensitivity analysis of O_3 production

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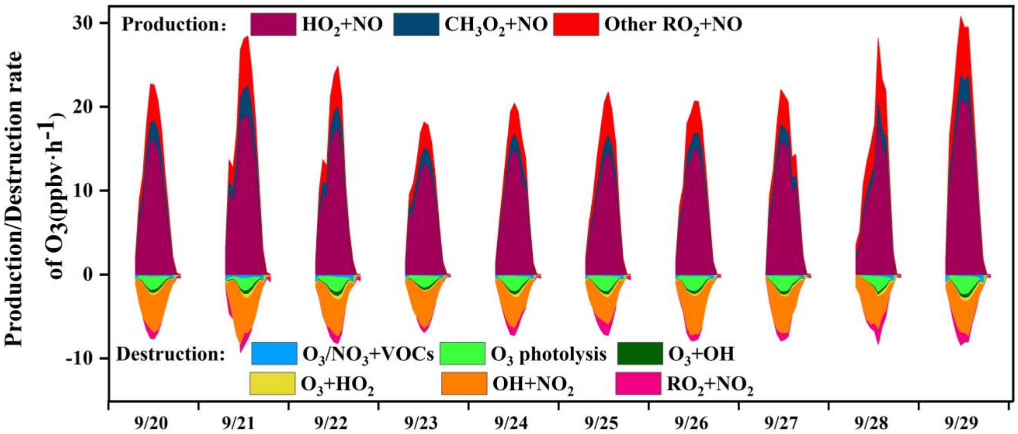

Figure 8. Time series of model-simulated O_3 chemical budgets during 20-29 Sep. 2019 in Xiamen.

The in situ O_3 production mechanism was examined, and the detailed reaction weights are shown in Fig. 8. The daytime rate of HO_2+NO was 7.9±6.2 ppb h^{-1}, accounting for 68±4% of the total O_3 production. This result was consistent with that in section 3.2.2. The OH radical was the initiator of photochemical O_3 formation, and the main sources of OH from HO_2+NO was also the dominant pathway to produce O_3 (Liu et al., 2020c). The second pathway of O_3 production was RO_2+NO (3.6±2.0 ppb h^{-1}). The reaction of RO_2+NO contained more than 1000 types of RO_2 radicals, and the pathway of CH_3O_2+NO (34±6%) contributed the most among them. In contrast, the contributors of O_3 destruction were OH+NO_2 (61±18%), followed by O_3 photolysis (18±9%), RO_2+NO_2 (9±10%), O_3+HO_2 (4±4%), and O_3+OH (4±2%), while the other pathways of O_3+VOCs as well as NO_3+VOCs, contributed limitedly. In addition, the net O_3 production (9.1±5.7 ppb h^{-1}) in Xiamen was ~2-5 times lower than that derived from the metropolis of Shanghai (26 ppb h^{-1}), Lanzhou (23 ppb h^{-1}) and Guangzhou (50 ppb h^{-1}), reflecting the influence of O_3 precursors emissions and photochemical conditions (Xue et al., 2014).

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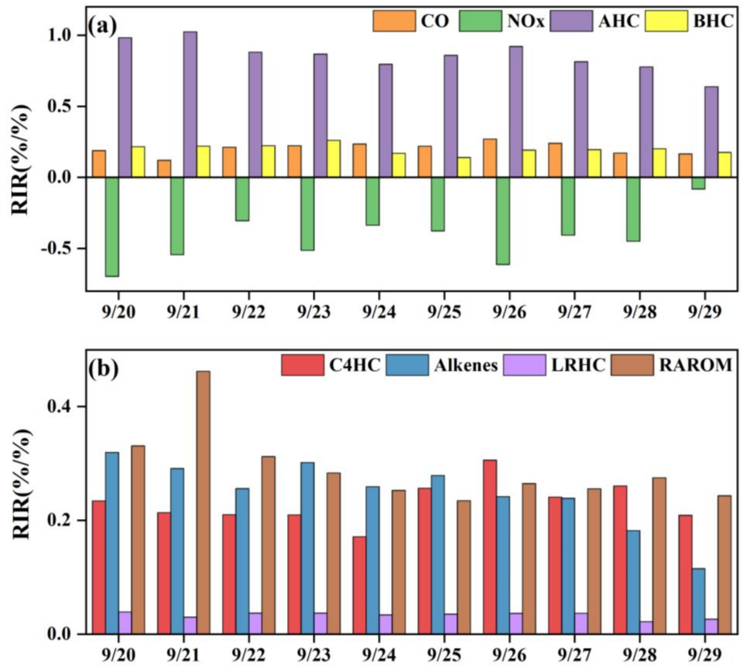

Figure 9. The model-calculated RIRs for (a) major O_3 precursor groups and (b) the AHC sub-groups during high O_3 daytime (06:00-18:00 LT) (AHC: anthropogenic hydrocarbons; BHC: biogenic hydrocarbons; RAROM: aromatics except for benzene; LRHC: low reactivity hydrocarbons; C4HC: alkenes, and alkanes with ≥4 carbons).

In this study, we also calculated the relative incremental reactivity (RIR) to diagnose the sensitivity of O_3 formation to its precursors. Figure 9 shows the RIR values for major groups of O_3 precursors. Around 50 types of VOCs were classified as anthropogenic hydrocarbons (AHC), and the isoprene was categorized into biogenic hydrocarbons (BHC), with AHC further divided into four groups of reactive aromatics (RAROM, including aromatics except for benzene), low reactivity hydrocarbons (LRHC, including methane, ethane, acetylene, propane, and benzene), alkenes, and alkanes with ≥4 carbons (C4HC). The in situ O_3 production was highly VOCs-sensitive, especially for AHC-sensitive (0.63–1.02 %/%) (Fig. 9a), followed by CO (0.17–0.27 %/%) and BHC (0.14–0.26 %/%), indicating the impacts from anthropogenic activities and flourishing vegetation emissions (Liu et al., 2020a; Lin et al., 2020). The RIRs were NOx-negative ranging from -0.70 to -0.08. As shown in Fig. 9b, the contributors of AHC sub-groups to RIRs were RAROM (0.24–0.46 %/%), C4HC (0.17–0.30 %/%), alkenes (0.11–0.32 %/%), and LRHC (0.03–0.04 %/%). Therefore, the reduction of aromatics, alkenes, and longer alkanes effectively decreased O_3 production, and the reduction of NOx might aggravate O_3 pollution.

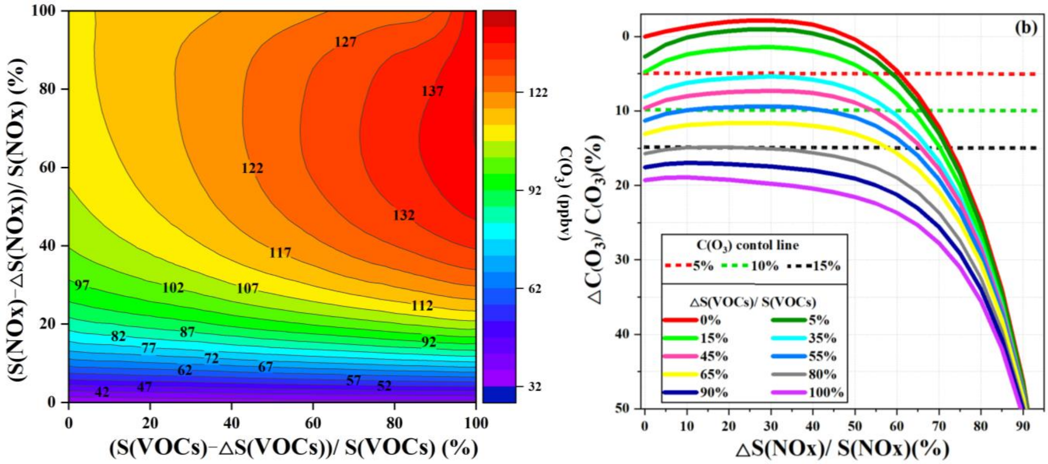

Figure 10 (a) Isopleth diagrams of modeled O_3 production potential (C(O_3)) on S(VOCs) and S(NOx) remaining percentages (i.e., (S(VOCs)-S(VOCs))/(S(VOCs)) and (S (NOx)-S(NOx))/(S(NOx)); (b) Relationship of C(O_3) increment percentage (△C(O_3)/C(O_3)) with S(NOx) and S(VOCs) reduction percentages (△S(NOx)/S(NOx) and △S(VOCs)/S(VOCs)). Note: C(O_3), S(NOx), and S(NOx) represent the concentrations of corresponding pollutants.

In order to investigate the O_3 control strategies in the relatively clean coastal city, the scenario analysis with reduction by 0-100% at intervals of 5% for the reduction of anthropogenic VOCs (△S(VOCs)/S(VOCs) and NOx (△S(NOx)/S(NOx)) were conducted using the OBM-MCM. According to the Empirical Kinetic Modeling Approach (EKMA) and scenario analysis, O_3 formation was in the NO-titration regime (Fig. 10), in accordance with those of RIR analysis. The maximum value of MDA8h O_3 during the monitoring period was 85 ppbv, exceeding the national air quality standard of 75 ppbv for O_3 by 13%. Hence, the O_3 reductions of 5%, 10%, and 15% were set to discuss the reduction schemes of anthropogenic VOCs and NOx. As shown in Fig. 10b, achieving the 5% control target were 1) S(VOCs) is reduced by 15%, while S(NOx) remains unchanged; 2) S(VOCs) is reduced larger than 35%; 3) S(NOx) reduction is higher than 60%. In addition, the 10% of O_3 control target was achieved by the 45% reduction of S(VOCs), and the S(NOx) keeps original emission. In view of the long-term control strategy of NOx and VOCs, S(VOCs) reduced by 55% and 80% could decrease 10% and 15% O_3 concentrations, respectively. Although VOCs and NOx control measures were drastically implemented, it is still challenging to achieve the 15% O_3 control goals in urban areas with relatively low precursor emissions. Meanwhile, as the O_3 sensitivity changed under the implementation of control measures, it is necessary to adjust timely the reduction of VOC and NOx policies.

3.3.2 O_3 from local photochemical production and regional transport

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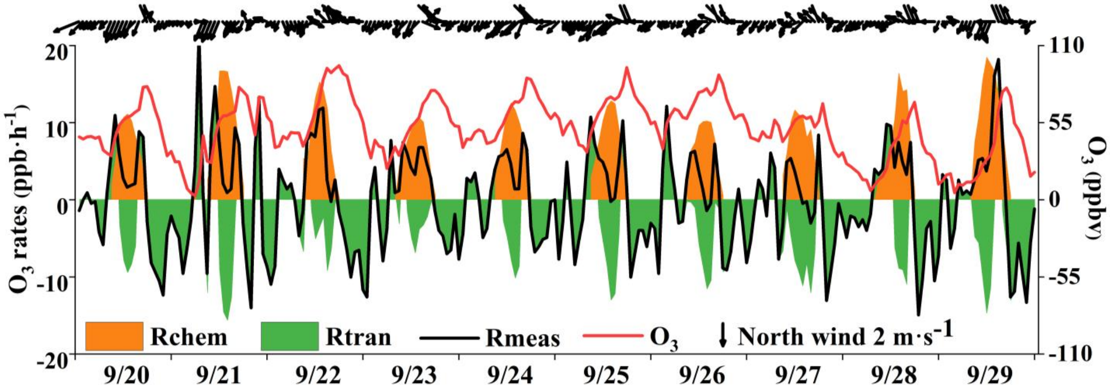

Figure 11. O_3 accumulation and contributions from local photochemical production and regional transport, and Rchem, Rtran, and Rmeas in figure caption represent local O_3 photochemical production, regional transport and observed O_3 formation rate, respectively.

Previous studies have found that the variation of O_3 mixing ratios was mainly influenced by chemical and physical processes (Xue et al., 2014; Tan et al., 2018). Figure 11 shows the time series of O_3 accumulation and contributions from local photochemical production and regional transport. The observed rate of change in O_3 (Rmeas) was calculated by the derivative of the observed O_3 concentrations (Rmeas=d(O_3)/dt). The local O_3 production (Rchem) was calculated by Equation 3, and computed hourly by the OBM as described in Section 2.2. The regional transport (Rtran) was calculated by the equation of Rtran=Rmeas−Rchem, including horizontal and/or vertical transport, deposition and so on. The positive values of Rtran represented the O_3 import of regional transport, while the negative values indicated the O_3 export and deposition. We quantified the contributions of local photochemical formation and regional transport to the observed O_3, and figured out the reasons for the O_3 pollution process.

As shown in Fig. 11, two regular O_3 import phenomenon with positive values of Rtran were observed, and the curve of the Rmeas showed the "M" trend during the daytime. The first transient intense O_3 import happened in the early morning, which was mainly attributed to the residual ozone from the day before. The O_3 export was remarkable at around 10:00-15:00, indicating the potential impacts on air quality in downwind areas. When the near-surface wind direction changed from northeast to southeast, the second O_3 import phenomenon occurred in the afternoon (16:00-19:00 LT) in four days (20, 25 27 and 29 Sep.). Due to the Rtran in the afternoon, the daily maximum O_3 values appeared at around 17:00 LT. However, the maximum daily value of O_3 at this observation site generally appeared at around 15:00 LT without regional transport (Wu et al., 2019). Under the conditions of southeast wind direction, downtown area with high density vehicles would make O_3 and its precursors transmitting to our observation site, consistent with the diurnal patterns of NO_2, OVOCs, alkanes, and aromatic in the early morning and

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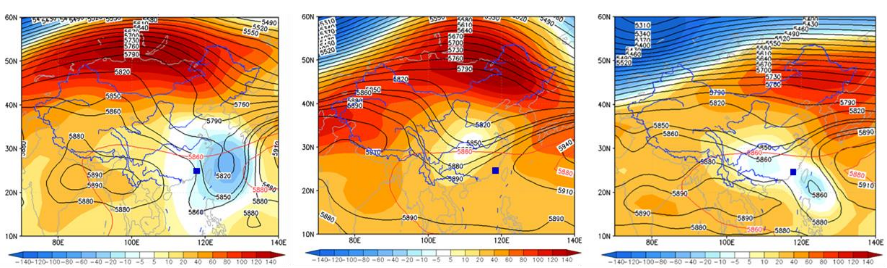
afternoon (Fig. 2) to match with the "M" trend of Rmeas. This result indicated that the sudden changes of near-surface winds corresponding to the variation in the transport of the urban plume.

According to photochemical parameters including UV, JNO_2, JO^1D and the synoptic situations (Fig. 1, Fig. S5 and Fig.12), the environmental conditions also favored the O_3 pollution process during the observation periods. The contribution of Rchem (daily maximum: ranged from 10.2 to 19.1 ppb h^{-1}) during the daytime was observed (Fig.11). In Fig. S5abc, the monitoring site was continuously affected by the northerly O_3 polluted airflow from YRD, due to the typhoon 'Tapah' from 20 to 22 Sep. 2019. The transport of O_3 import appeared on 21 Sep. (7.1±7.0 ppb h^{-1}), which resulted in the accumulation of O_3 (the MDA8h O_3: 85 ppbv) on 22 Sep. When the influence of typhoon disappeared, the direction of airflow turned from northerly into southwest with humid and warm at 500hPa (Fig. S5d), the surface wind on Sep. 23 was affected by the control of the cold northerly airflow (Fig. S5ef). Meteorological conditions including continental high pressure during 23 to 27 Sep. were favorable to the accumulation of air pollutants (Fig. 12). The isoline of 5880 gpm moved from north to the Yangtze River (Fig. 12a,b), indicating the subtropical high pressure was significantly strengthened during 23-27 Sep. 2019. As a result, meteorological conditions such as high temperature, low RH, strong solar radiation, and weak wind speed were conducive to the formation and accumulation of O_3. The transport rate of O_3 export (5.4±3.4 ppb h^{-1}) on 24-26 Sep. was lower than that on other days (6.3±4.0 ppb h^{-1}). Hence, under the combined effects of stable atmospheric conditions and strengthened WPSH, the MDA8h O_3 exceeded the standard of 75 ppbv during 24-26 Sep. Previous studies had found that severe multi-day O_3 pollution appeared under the WPSH control (Wang et al., 2018a). Overall, the results indicate that local photochemical production and synoptic situations caused high O_3 concentrations, and regional transport aggravated the O_3 pollution process.



(a)500 hPa 20-22 sep. (b)500 hPa, 23-27 sep. (c)500 hPa, 28-29 sep.

Figure 12. Synoptic situations of continental high pressure from 20 to 29 Sep. 2019. The gradient color area indicates the WPSH over the map and the contour line was from the characteristic isoline of 5880 gpm to the center isoline of 5920 gpm. The blue square is the study site.

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4 Conclusions

In the present study, we analyzed a typical high O_3 event during 20-29 Sep. 2019 in a coastal city of Southeast China. We clarified the characteristics of AOC, OH reactivity, and radical chemistry, as well as O_3 formation mechanisms using the OBM-MCM model. The predominant oxidant for AOC during the daytime and nighttime was the OH and NO_3, respectively. During the period of O_3 pollution process, OVOCs, NO_2, and CO consumed OH most. Meanwhile, the photolysis of HONO, O_3, HCHO, and other OVOCs were the most important primary sources of ROx, which played the initiation roles in atmospheric oxidation processes. The radical termination reactions were governed by cross-reactions between ROx and NOx. The RIRs and EKMA results showed that the O_3 formation in autumn in coastal city was VOCs-sensitive, and the VOCs were the limited factor of radical recycling and O_3 formation. The reduced emissions of aromatics, alkenes, and long-chain alkanes were benefit for ozone pollution control. The local photochemical production and synoptic situations caused the high concentrations of O_3, and the regional transport aggravated the pollution of ozone. Overall, the results clarified the O_3 pollution process with relatively low local precursor emissions, and implied the fact that O_3 pollution control in coastal cities needs to be further studied.

Authorship Contribution Statement

Taotao Liu and Youwei Hong contributed equally to this work. Jinsheng Chen and Likun Xue designed and revised the manuscript. Taotao Liu collected the data, contributed to the data analysis. Taotao Liu and Youwei Hong performed chemical modeling analyses of OBM-MCM and wrote the paper. Jinsheng Chen supported funding of observation and research. Lingling Xu, Mengren Li, Chen Yang, Yangbin Dan, Yingnan Zhang, and Min Zhao contributed to discussions of results. Zhi Huang and Hong Wang provided meteorological conditions in Xiamen.

Acknowledgment

This study was funded by the Cultivating Project of Strategic Priority Research Program of Chinese Academy of Sciences (XDPB1903), the FJIRSM&IUE Joint Research Fund (RHZX-2019-006), the Center for Excellence in Regional Atmospheric Environment, CAS (E0L1B20201), the Xiamen Youth Innovation Fund Project (3502Z20206094), the foreign cooperation project of Fujian Province (2020I0038) and Xiamen Atmospheric Environment Observation and Research Station of Fujian Province.

Reference:

Acker, K., Möller, D., Wieprecht, W., Auel, R., Kalaß, D., and Tscherwenka, W.: Nitrous and nitric acid measurements inside and outside of clouds at Mt. Brocken, Water Air Soil Pollut., 130, 331–336, 2001.

Chang, L., Xu, J., Tie, X., and Gao, W.: The impact of Climate Change on the Western Pacific Subtropical High and the related ozone pollution in Shanghai, China, Sci Rep, 9, 16998, 10.1038/s41598-019-53103-7, 2019.

Chen, T., Xue, L., Zheng, P., Zhang, Y., Liu, Y., Sun, J., Han, G., Li, H., Zhang, X., Li, Y., Li, H., Dong, C., Xu, F., Zhang, Q., and Wang, W.: Volatile organic compounds and ozone air pollution in an oil production region in northern China, Atmos. Chem. Phys., 20, 7069-7086, 10.5194/acp-20-7069-2020, 2020.

Edwards, P. M., Brown, S. S., Roberts, J. M., Ahmadov, R., Banta, R. M., Degouw, J. A., Dubé, W. P., Field, R. A., Flynn, J. H., Gilman, J. B., and Graus, M.: High winter ozone pollution from carbonyl photolysis in an oil and gas basin, Nature, 514, 351, https://doi.org/10.1038/nature13767, 2014.

Edwards, P. M., Young, C. J., Aikin, K., deGouw, J., Dubé, W. P., Geiger, F., Gilman, J., Helmig, D., Holloway, J. S., Kercher, J., Lerner, B., Martin, R., McLaren, R., Parrish, D. D., Peischl, J., Roberts, J. M., Ryerson, T. B., Thornton, J., Warneke, C., Williams, E. J., and Brown, S. S.: Ozone photochemistry in an oil and natural gas extraction region during winter: simulations of a snow-free season in the Uintah Basin, Utah, Atmos. Chem. Phys., 13, 8955–8971, https://doi.org/10.5194/acp13-8955-2013, 2013.

Eisele, F. L., Mount, G. H., Tanner, D., Jefferson, A., Shetter, R., Harder, J. W., and Williams, E. J.: Understanding the production and interconversion of the hydroxyl radical during the Tropospheric OH Photochemistry Experiment, J. Geophys. Res., 102, 6457–6465, 1997.

Elshorbany, Y. F., Kurtenbach, R., Wiesen, P., Lissi, E., Rubio, M., Villena, G., Gramsch, E., Rickard, A. R., Pilling, M. J., and Kleffmann, J.: Oxidation capacity of the city air of Santiago, Chile, Atmos. Chem. Phys., 9, 2257–2273, https://doi.org/10.5194/acp-9-2257-2009, 2009.

Emmerson, K. M., Carslaw, N., and Pilling, M. J.: Urban Atmospheric Chemistry During the PUMA Campaign 2: Radical Budgets for OH, HO_2 and RO_2, J. Atmos. Chem., 52, 165-183, 10.1007/s10874-005-1323-2, 2005.

Fowler, D., Pilegaard, K., Sutton, M. A., Ambus, P., Raivonen, M., Duyzer, J., Simpson, D., Fagerli, H., Fuzzi, S., Schjoerring, J. K., Granier, C., Neftel, A., Isaksen, I. S. A., Laj, P., Maione, M., Monks, P. S., Burkhardt, J., Daemmgen, U., Neirynck, J., Personne, E., Wichink-Kruit, R., Butterbach-Bahl, K., Flechard, C., Tuovinen, J. P., Coyle, M., Gerosa, G., Loubet, B., Altimir, N., Gruenhage, L., Ammann, C., Cieslik, S., Paoletti, E., Mikkelsen, T. N., Ro-Poulsen, H., Cellier, P., Cape, J. N., Horváth, L., Loreto, F., Niinemets, Ü., Palmer, P. I., Rinne, J., Misztal, P., Nemitz, E., Nilsson, D., Pryor, S., Gallagher, M. W., Vesala, T., Skiba, U., Brüggemann, N., Zechmeister-Boltenstern, S., Williams, J., O'Dowd, C., Facchini, M. C., de Leeuw, G., Flossman, A., Chaumerliac, N., and Erisman, J. W.: Atmospheric composition change: Ecosystems–Atmosphere interactions, Atmos. Environ., 43, 5193-5267, 10.1016/j.atmosenv.2009.07.068, 2009.

George, L. A., Hard, T. M., and O'Brien, R. J.: Measurement of free radicals OH and HO_2 in Los Angeles smog, J. Geophys. Res., 104, 11643–11655, 1999.

Geyer, A., Alicke, B., Konrad, S., Schmitz, T., Stutz, J., and Platt, U.: Chemistry and oxidation capacity of the nitrate radical in the continental boundary layer near Berlin, J. Geophys. Res., 106, 8013-8025, 10.1029/2000jd900681, 2001.

Gong, C., and Liao, H.: A typical weather pattern for the ozone pollution events in North China, Atmos. Chem.

https://doi.org/10.5194/acp-2021-764
Preprint. Discussion started: 29 October 2021

Atmospheric Chemistry and Physics Discussions

Phys., 10.5194/acp-2019-263, 2019.

Hofzumahaus, A., Rohrer, F., Lu, K. D., Bohn, B., Brauers, T., Chang, C. C., Fuchs, H., Holland, F., Kita, K., Kondo, Y., Li, X., Lou, S. R., Shao, M., Zeng, L. M., Wahner, A., and Zhang, Y. H.: Amplified Trace Gas Removal in the Troposphere, Science, 324, 1702–1704, 2009.

Hong, Z., MengzeLi, HongWang, LinglingXu, Hong, Y., Chen, J., Chen, J., Zhang, H., Zhang, Y., Wu, X., Hu, B., and Li, M.: Characteristics of atmospheric volatile organic compounds (VOCs) at a mountainous forest site and two urban sites in the southeast of China, Sci Total Environ, 10.1016/j.scitotenv.2018.12.132, 2019.

Hu B, Liu T, Yang Y, Hong Y, Li M, Xu L, Wang H, Chen N, Wu X, Chen J: Characteristics and Formation Mechanism of Surface Ozone in a Coastal Island of Southeast China: Influence of Sea-land Breezes and Regional Transport. Aerosol Air Qual. Res., 19(8):1734-1748, 2019.

Hu, B., Duan, J., Hong, Y., Xu, L., Li, M., Bian, Y., Qin, M., Fang, W., Xie, P., and Chen, J.: Exploration of the atmospheric chemistry of nitrous acid in a coastal city of southeastern China: Results from measurements across four seasons, Atmos. Chem. Phys. Discuss. [preprint], https://doi.org/10.5194/acp-2020-880, 2020a.

Hu, B., Liu, T., Hong, Y., Xu, L., Li, M., Wu, X., Wang, H., Chen, J., and Chen, J.: Characteristics of peroxyacetyl nitrate (PAN) in a coastal city of southeastern China: Photochemical mechanism and pollution process, Sci Total Environ, 719, 137493, 10.1016/j.scitotenv.2020.137493, 2020b.

Jenkin, M. E., Saunders, S. M., Wagner, V., and Pilling, M. J.: Protocol for the development of the Master Chemical Mechanism, MCM v3 (Part B): tropospheric degradation of aromatic volatile organic compounds, Atmos. Chem. Phys., 3, 181–193, https://doi.org/10.5194/acp-3-181-2003, 2003.

Jiang Y, Xue L, Gu R, Jia M, Zhang Y, Wen L, Zheng P, Chen T, Li H, Shan Y et al: Sources of nitrous acid (HONO) in the upper boundary layer and lower free troposphere of the North China Plain: insights from the Mount Tai Observatory. Atmos. Chem. Phys., 20(20):12115-12131, 2020.

Kanaya, Y., Cao, R. Q., Akimoto, H., Fukuda, M., Komazaki, Y., Yokouchi, Y., Koike, M., Tanimoto, H., Takegawa, N., and Kondo, Y.: Urban photochemistry in central Tokyo: 1. Observed and modeled OH and HO_2 radical concentrations during the winter and summer of 2004, J. Geophys. Res., 112, D21312, doi:10.1029/2007JD008670, 2007.

Kanaya, Y., Matsumoto, J., Kato, S., and Akimoto, H.: Behavior of OH and HO_2 radicals during the Observations at a Remote Island of Okinawa (ORION99) field campaign 2. Comparison between observations and calculations, J. Geophys. Res., 106, 24209–24223, 2001.

Kovacs, T. A., Brune, W. H., Harder, H., Martinez, M., Simpas, J. B., Frost, G. J., Williams, E., Jobson, T., Stroud, C., Young, V., Fried, A., and Wert, B.: Direct measurements of urban OH reactivity during Nashville SOS in summer 1999, J. of Environ. Monitor., 5, 68-74, 10.1039/b204339d, 2003.

Li, B., Ho, S. S. H., Gong, S., Ni, J., Li, H., Han, L., Yang, Y., Qi, Y., and Zhao, D.: Characterization of VOCs and their related atmospheric processes in a central Chinese city during severe ozone pollution periods, Atmos. Chem. Phys., 19, 617-638, 10.5194/acp-19-617-2019, 2019.

Li, N., He, Q., Greenberg, J., Guenther, A., Cao, J., & Wang, J., Liao H., Zhang Q.: Impacts of biogenic and anthropogenic emissions on summertime ozone formation in the Guanzhong Basin, China, Atmos. Chem. Phys., 2018a.

Li, Z., Xue, L., Yang, X., Zha, Q., Tham, Y. J., Yan, C., Louie, P. K. K., Luk, C. W. Y., Wang, T., and Wang, W.: Oxidizing capacity of the rural atmosphere in Hong Kong, Southern China, Sci Total Environ, 612, 1114-1122, 10.1016/j.scitotenv.2017.08.310, 2018.

https://doi.org/10.5194/acp-2021-764
Preprint. Discussion started: 29 October 2021

Atmospheric Chemistry and Physics Discussions

Lin, H., Wang, M., Duan, Y., Fu, Q., Ji, W., Cui, H., Jin, D., Lin, Y., and Hu, K.: O_3 Sensitivity and Contributions of Different NMHC Sources in O_3 Formation at Urban and Suburban Sites in Shanghai, Atmosphere, 11, 295, 10.3390/atmos 11030295, 2020.

Ling, Z., Zhao, J., Fan, S., and Wang, X.: Sources of formaldehyde and their contributions to photochemical O_3 formation at an urban site in the Pearl River Delta, southern China, Chemosphere, 168, 1293-1301, 10.1016/j.chemosphere. 2016.11.140, 2017.

Liu, J., Wang, L., Li, M., Liao, Z., Sun, Y., Song, T., Gao, W., Wang, Y., Li, Y., Ji, D., Hu, B., Kerminen, V.-M., Wang, Y., and Kulmala, M.: Quantifying the impact of synoptic circulation patterns on ozone variability in northern China from April to October 2013–2017, Atmos. Chem. Phys., 19, 14477-14492, 10.5194/acp-19-14477-2019, 2019a.

Liu, T., Hu, B., Xu, X., Hong, Y., Zhang, Y., Wu, X., Xu, L., Li, M., Chen, Y., Chen, X., and Chen, J.: Characteristics of $PM_{2.5}$-bound secondary organic aerosol tracers in a coastal city in Southeastern China: Seasonal patterns and pollution identification, Atmos. Environ., 237, 117710, 10.1016/j.atmosenv. 2020.117710, 2020a.

Liu, T., Hu, B., Yang, Y., Li, M., Hong, Y., Xu, X., Xu, L., Chen, N., Chen, Y., Xiao, H., and Chen, J.: Characteristics and source apportionment of $PM_{2.5}$ on an island in Southeast China: Impact of sea-salt and monsoon, Atmos. Res., 235, 104786, 10.1016/j.atmosres.2019.104786, 2020b.

Liu, X., Lyu, X., Wang, Y., Jiang, F., and Guo, H.: Intercomparison of O_3 formation and radical chemistry in the past decade at a suburban site in Hong Kong, Atmos. Chem. Phys., 19, 5127-5145, 10.5194/acp-19-5127-2019, 2019b.

Liu, X., Wang, N., Lyu, X., Zeren, Y., Jiang, F., Wang, X., Zou, S., Ling, Z., and Guo, H.: Photochemistry of ozone pollution in autumn in Pearl River Estuary, South China, Sci Total Environ, 754, 141812, 10.1016/j.scitotenv.2020.141812, 2020c.

Liu, Z., Wang, Y., Gu, D., Zhao, C., Huey, L., Stickel, R., Liao, J., Shao, M., Zhu, T., Zeng, L., Amoroso, A., Costabile, F., Chang, C., and Liu, S.: Summertime photochemistry during CARE Beijing-2007: RO_{x</s ub> budgets and O< sub>3} formation, Atmos. Chem. Phys., 12, 7737-7752, 10.5194/acp-12-7737-2012, 2012.

Lou, S., Holland, F., Rohrer, F., Lu, K., Bohn, B., Brauers, T., Chang, C. C., Fuchs, H., Haeseler, R., Kita, K., Kondo, Y., Li, X., Shao, M., Zeng, L., Wahner, A., Zhang, Y., Wang, W., and Hofzumahaus, A.: Atmospheric OH reactivities in the Pearl River Delta - China in summer 2006: measurement and model results, Atmos. Chem. Phys., 10, 11243-11260, 10.5194/acp-10-11243-2010, 2010a.

Lou, S., Holland, F., Rohrer, F., Lu, K., Bohn, B., Brauers, T., Chang, C.., Fuchs, H., Häseler, R., Kita, K., Kondo, Y., Li, X., Shao, M., Zeng, L., Wahner, A., Zhang, Y., Wang, W., and Hofzumahaus, A.: Atmospheric OH reactivities in the Pearl River Delta – China in summer 2006: measurement and model results, Atmos. Chem. Phys., 10, 11243-11260, 10.5194/acp-10-11243-2010, 2010b.

Lu, X., Hong, J., Zhang, L., Copper. O. R., Schultz, M. G., Xu, X., Wang, T., Gao, M., Zhao, Y., Zhang, Y. Severe Surface Ozone Pollution in China: A Global Perspective. Environ. Sci. Technol. Lett., 5, 487-494, 2018.

Mao, J., Ren, X., Chen, S., Brune, W. H., Chen, Z., Martinez, M., Harder, H., Lefer, B., Rappenglück, B., Flynn, J., and Leuchner, M.: Atmospheric oxidation capacity in the summer of Houston 2006: Comparison with summer measurements in other metropolitan studies, Atmos. Environ., 44, 4107-4115, 10.1016/j.atmosenv.2009.01.013, 2010.

Martinez, M.: OH and HO_2 concentrations, sources, and loss rates during the Southern Oxidants Study in Nashville,

https://doi.org/10.5194/acp-2021-764
Preprint. Discussion started: 29 October 2021

Atmospheric Chemistry and Physics Discussions

Tennessee, summer 1999, J. Geophys. Res., 108, 10.1029/2003jd003551, 2003.

Mazzuca, G. M., Ren, X., Loughner, C.P., Estes, M., Crawford, J. H., Pickering, K. E., Weinheimer, A. J., Dickerson, R. R.: Ozone production and its sensitivity to NOx and VOCs: results from the DISCOVER-AQ field experiment, Houston 2013. Atmos. Chem. Phys. 16, 14463–14474, 2016.

Michoud, V., Kukui, A., Camredon, M., Colomb, A., Borbon, A., Miet, K., Aumont, B., Beekmann, M., Durand-Jolibois, R., Perrier, S., Zapf, P., Siour, G., Ait-Helal, W., Locoge, N., Sauvage, S., Afif, C., Gros, V., Furger, M., Ancellet, G., and Doussin, J. F.: Radical budget analysis in a suburban European site during the MEGAPOLI summer field campaign, Atmos. Chem. Phys., 12, 11951-11974, 10.5194/acp-12-11951-2012, 2012.

Ren, X., Brune, W. H., Cantrell, C. A., Edwards, G. D., Shirley, T., Metcalf, A. R., and Lesher, R. L.: Hydroxyl and peroxy radical chemistry in a rural area of Central Pennsylvania: Observations and model comparisons, J. Atmos. Chem., 52, 231-257, 10.1007/s10874-005-3651-7, 2005.

Rollins, A. W., Browne, E. C., Min, K. E., Pusede, S. E., Wooldridge, P. J., Gentner, D. R., Goldstein, A. H., Liu, S., Day, D. A., Russell, L. M., and Cohen, R. C.: Evidence for NOx Control over Nighttime SOA Formation, Science, 337, 1210–1212, 2012.

Saunders, S. M., Jenkin, M. E., Derwent, R. G., and Pilling, M. J.: Protocol for the development of the Master Chemical Mechanism, MCM v3 (Part A): tropospheric degradation of nonaromatic volatile organic compounds, Atmos. Chem. Phys., 3, 161–180, doi:10.5194/acp-3-161-2003, 2003.

Sheehy, P. M., Volkamer, R., Molina, L. T., and Molina, M. J.: Oxidative capacity of the Mexico City atmosphere – Part 2: A RO_x radical cycling perspective, Atmos. Chem. Phys., 10, 6993-7008, 10.5194/acp-10-6993-2010, 2010.

Simon, H., Reff, A., Wells, B., Xing, J., and Frank, N.: Ozone trends across the United States over a period of decreasing NOx and VOC emissions, Environ. Sci. Technol., 49, 186-195, 10.1021/es504514z, 2015.

Smith, S. C., Lee, J. D., Bloss, W. J., Johnson, G. P., Ingham, T., and Heard, D. E.: Concentrations of OH and HO_2 radicals during NAMBLEX: measurements and steady state analysis, Atmos. Chem. Phys., 6, 1435–1453, doi:10.5194/acp-6-1435-2006, 2006.

Tan, Z., Lu, K., Jiang, M., Su, R., Dong, H., Zeng, L., Xie, S., Tan, Q., and Zhang, Y.: Exploring ozone pollution in Chengdu, southwestern China: A case study from radical chemistry to O_3-VOC-NOx sensitivity, Sci Total Environ, 636, 775-786, 10.1016/j.scitotenv.2018.04.286, 2018.

Tan, Z., Lu, K., Jiang, M., Su, R., Wang, H., Lou, S., Fu, Q., Zhai, C., Tan, Q., Yue, D., Chen, D., Wang, Z., Xie, S., Zeng, L., and Zhang, Y.: Daytime atmospheric oxidation capacity in four Chinese megacities during the photochemically polluted season: a case study based on box model simulation, Atmos. Chem. Phys., 19, 3493-3513, 10.5194/acp-19-3493-2019, 2019.

Volkamer, R., Sheehy, P., Molina, L. T., and Molina, M. J.: Oxidative capacity of the Mexico City atmosphere – Part 1: A radical source perspective, Atmos. Chem. Phys., 10, 6969-6991, 10.5194/acp-10-6969-2010, 2010.

Wang, H., Lyu, X., Guo, H., Wang, Y., Zou, S., Ling, Z., Wang, X., Jiang, F., Zeren, Y., Pan, W., Huang, X., and Shen, J.: Ozone pollution around a coastal region of South China Sea: interaction between marine and continental air, Atmos. Chem. Phys., 18, 4277–4295, 10.5194/acp-18-4277-2018, 2018a.

Wang, H., Tan, S., Wang, Y., Jiang, C., Shi, G., Zhang, M., Che, H.: A multisource observation study of the severe prolonged regional haze episode over eastern China in January 2013. Atmos. Environ. 89, 807–815, 2014.

Wang, M., Chen, W., Zhang, L., Qin, W., Zhang, Y., Zhang, X., and Xie, X.: Ozone pollution characteristics and

https://doi.org/10.5194/acp-2021-764
Preprint. Discussion started: 29 October 2021

sensitivity analysis using an observation-based model in Nanjing, Yangtze River Delta Region of China, J Environ Sci (China), 93, 13-22, 10.1016/j.jes.2020.02.027, 2020.

Wang, Y., Guo, H., Zou, S., Lyu, X., Ling, Z., Cheng, H., and Zeren, Y.: Surface O_3 photochemistry over the South China Sea: Application of a near-explicit chemical mechanism box model, Environ Pollut, 234, 155-166, 10.1016/j.envpol.2017.11.001, 2018b.

Whalley, L. K., Stone, D., Bandy, B., Dunmore, R., Hamilton, J. F., Hopkins, J., Lee, J. D., Lewis, A. C., and Heard, D. E.: Atmospheric OH reactivity in central London: observations, model predictions and estimates of in situ ozone production, Atmos. Chem. Phys., 16, 2109-2122, 10.5194/acp-16-2109-2016, 2016.

Wu, X., Li, M., Chen, J., Wang, H., Xu, L., Hong, Y., Zhao, G., Hu, B., Zhang, Y., Dan, Y., and Yu, S.: The characteristics of air pollution induced by the quasi-stationary front: Formation processes and influencing factors, Sci Total Environ, 707, 136194, 10.1016/j.scitotenv.2019.136194, 2020.

Wu, X., Xu, L., Hong, Y., Chen, J., Qiu, Y., Hu, B., Hong, Z., Zhang, Y., Liu, T., Chen, Y., Bian, Y., Zhao, G., Chen, J., and Li, M.: The air pollution governed by subtropical high in a coastal city in Southeast China: Formation processes and influencing mechanisms, Sci Total Environ, 692, 1135-1145, 10.1016/j.scitotenv.2019.07.341, 2019.

Xue, L. K., Wang, T., Gao, J., Ding, A. J., Zhou, X. H., Blake, D. R., Wang, X. F., Saunders, S. M., Fan, S. J., Zuo, H. C., Zhang, Q. Z., and Wang, W. X.: Ground-level ozone in four Chinese cities: precursors, regional transport and heterogeneous processes, Atmos. Chem. Phys., 14, 13175-13188, 10.5194/acp-14-13175-2014, 2014.

Xue, L., Gu, R., Wang, T., Wang, X., Saunders, S., Blake, D., Louie, P. K. K., Luk, C. W. Y., Simpson, I., Xu, Z., Wang, Z., Gao, Y., Lee, S., Mellouki, A., and Wang, W.: Oxidative capacity and radical chemistry in the polluted atmosphere of Hong Kong and Pearl River Delta region: analysis of a severe photochemical smog episode, Atmos. Chem. Phys., 16, 9891–9903, 10.5194/acp-16-9891-2016, 2016.

Zeren, Y., Guo, H., Lyu, X., Jiang, F., Wang, Y., Liu, X., Zeng, L., Li, M., and Li, L.: An Ozone "Pool" in South China: Investigations on Atmospheric Dynamics and Photochemical Processes Over the Pearl River Estuary, J. Geophys. Res., 124, 12340-12355, 10.1029/2019jd030833, 2019.

Zhang L , Brook J R , Vet R . A revised parameterization for gaseous dry deposition in air-quality models. Atmos. Chem. Phys., 3(2), 2067-2082, 2003.

Zhang, Y., Hong, Z., Chen, J., Xu, L., Hong, Y., Li, M., Hao, H., Chen, Y., Qiu, Y., Wu, X., Li, J.-R., Tong, L., and Xiao, H.: Impact of control measures and typhoon weather on characteristics and formation of $PM_{2.5}$ during the 2016 G20 summit in China, Atmos. Environ., 224, 117312, 10.1016/j.atmosenv.2020.117312, 2020a.

Zhang, Y., Xu, L., Zhuang, M., Zhao, G., Chen, Y., Tong, L., Yang, C., Xiao, H., Chen, J., Wu, X., Hong, Y., Li, M., Bian, Y., and Chen, Y.: Chemical composition and sources of submicron aerosol in a coastal city of China: Results from the 2017 BRICS summit study, Sci Total Environ, 741, 140470, 10.1016/j.scitotenv.2020.140470, 2020b.

Zhang, Y. , Xue, L. , Carter, W. , Pei, C. , and Wang, W.: Development of Ozone Reactivity Scales for Volatile Organic Compounds in a Chinese Megacity, Atmos. Chem. Phys., 10.5194/acp-2021-44, 2021

Zhu, J., Wang, S., Wang, H., Jing, S., Lou, S., Saiz-Lopez, A., and Zhou, B.: Observationally constrained modeling of atmospheric oxidation capacity and photochemical reactivity in Shanghai, China, Atmos. Chem. Phys., 20, 1217-1232, 10.5194/acp-20-1217-2020, 2020.