Intensive photochemical oxidation in the marine atmosphere: Evidence from direct radical measurements

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Abstract: Comprehensive observations of hydroxyl (OH) and hydroperoxy (HO₂) radicals were conducted in October 2019 at a coastal continental site in the Pearl River Delta (YMK site, 22.55°N, 114.60°E). The average daily maximum OH and HO₂ concentrations were (4.7–9.5) × 10⁶ cm⁻³ and (4.2–8.1) × 10⁸ cm⁻³, respectively. The synchronized air mass transport from the northern cities and the South China Sea exerted a time-varying influence on atmospheric oxidation. Under a typical ocean-atmosphere (OCM), reasonable measurement model agreement was achieved for both OH and HO₂ using a 0-D chemical box model incorporating the regional atmospheric chemistry mechanism version 2-Leuven isoprene mechanism (RACM2-LIM1). Land mass (LAM) influence promoted more active photochemical processes, with daily averages of 7.1 × 10⁶ cm⁻³ and 5.2 × 10⁸ cm⁻³ for OH and HO₂, respectively. Intensive photochemistry occurred after precursor accumulation, allowing local net ozone production comparable with surrounding suburban environments (5.52 ppb/h during the LAM period). The rapid oxidation process was accompanied by a higher diurnal nitrous acid (HONO) concentration (> 400 ppt). After a sensitivity test, HONO-related chemistry elevated the ozone production rate by 33% and 39% during the LAM and OCM periods, respectively, while the nitric acid and sulfuric acid formation rates were 52% and 35% higher, respectively. The simulated daytime HONO and ozone concentrations were reduced to a low level (~70 ppt and ~35 ppb) without the HONO constraint. This work challenges the conventional recognition of the MBL in a complex atmosphere. For coastal cities, the particularity of the HONO chemistry in the MBL tends to influence the ozone-sensitive system and eventually magnifies the background ozone. Therefore, the promotion of oxidation by elevated precursor concentrations is worth considering when formulating emission reduction policies.

Keywords: FAGE-LIF; OH and HO₂ radicals; Atmospheric oxidation; Marine boundary layer; Precursors;
1 Introduction

The marine boundary layer (MBL) occupies 71% of the planetary boundary layer, is a massive active carbon sink on Earth, and plays an irreplaceable role in coping with global climate change (Stone et al., 2012; Woodward-Massey et al., 2022b; Liu et al., 2022a). As a typical background atmosphere on the Earth, the MBL is equivalent to a natural smog chamber with limited anthropogenic emissions and is characterized by low NOx (the sum of nitric oxide (NO) and nitrogen dioxide (NO₂)) and non-methane hydrocarbons (NMHCs) under a layer of clean air (Woodward-Massey et al., 2022b). The lifetime of OH radical, a key oxidant, is on the order of a few hundred milliseconds (Fuchs et al., 2012). Due to the scarcity of oxidation precursors, including nitrous acid (HONO), formaldehyde (HCHO), and NMHCs, the reaction between O¹D and water vapor generally dominates the radical initiation pathway in the marine environment. For example, in a tropical boundary layer observation experiment (reactive halogens in the marine boundary layer, RHaMBLe), ozone photolysis was found to account for 70% of the OH radical source based on the master chemical mechanism (MCM) (Whalley et al., 2010). The vital role of ozone photolysis is contrasting with typical polluted and semi-polluted areas investigated in a series of field campaigns, in which the propagation routes were found to dominate the radical source (Yang et al., 2021; Tan et al., 2019a). Therefore, studying the radical chemistry in the MBL provides a valuable opportunity to test the current understanding of atmospheric oxidation mechanisms in a natural setting.

Since the earliest observations off the coast of northern Norfolk in the Weybourne Atmospheric Observatory Summer Experiment in June 1995 (WAOSE95), more observations and simulations of radical chemistry in the MBL environment have been conducted using ground-based, airborne, and shipborne instruments (Qi et al., 2007; Kanaya et al., 2002; Kanaya et al., 2001; Mallik et al., 2018; Woodward-Massey et al., 2022a; Carpenter et al., 2011; Grenfell et al., 1999; Brauers et al., 2001; Whalley et al., 2010). Most field measurements have yielded well-reproduced OH and HO₂ concentration profiles via chemical mechanisms, with differences of within ~20%.
However, the base model is not sufficient to describe the radical chemistry in some exceptional cases, especially in regard to the HO$_2$ radical. Considering the practical association between halogen (Cl, Br, and I) chemistry and heterogeneous chemistry in marine new particle formation, particularly the involvement of heterogeneous iodine-organic chemistry, exploring the synchronous influence of these mechanisms on HOx (OH and HO$_2$) radical chemistry in the MBL region is a worthy endeavor (Xu et al., 2022; Huang et al., 2022). The mixing of air masses of continental and marine origins can lead to more variability in radical concentrations. During seasonal measurements of both OH and HO$_2$ in the Atlantic Ocean, variance analysis indicated that around 70% of the variance of OH and HO$_2$ was due to diurnal behavior (in the form of photolysis frequency), while the remaining variance was attributed to long-term seasonal cycles (in the form of the changes in O$_3$, CO and air mass contribution) (Vaughan et al., 2012).

The Chinese economy has undergone rapid development in recent years, and the co-occurrence of primary and secondary regional pollution has become a severe problem (Lu et al., 2019; Liu et al., 2022c). The interactions between air pollutants from upwind cities, shipping vessels, and other anthropogenic emissions lead to precursor accumulation (Sun et al., 2020; Zeren et al., 2022). The background ozone concentration in key regions of China has increased year by year, highlighting the significant influence of anthropogenic activities on the atmospheric oxidation in background regions in China (Wang et al., 2009; Chen et al., 2022). However, little research has been dedicated to the radical chemistry and oxidation mechanism in regions with both coastal and continental features. To fill this research gap, in this study, a field campaign was conducted on photochemistry in the MBL at a coastal site in the Pearl River Delta. The OH and HO$_2$ radicals associated with other related species were measured in October 2019, and the radical-related oxidation process was identified to determine the photochemical efficiency in the marine atmosphere.

2 Materials and methods
2.1 Site description

As shown in Fig. 1(a), this observation campaign lasted for 11 days from October 18 to October 28, 2019, in Yangmeikeng (YMK, 22.55° N, 114.60° E), a coastal site in Shenzhen, Pearl River Delta. As the core city of the Greater Bay Area, Shenzhen is bordered by Dongguan to the north, Huizhou to the east, and Hong Kong to the south. The YMK site is on the Dapeng Peninsula, to the southeast of Shenzhen, between Mirs Bay and Daya Bay. As it is adjacent to the port of Hong Kong, precursors from ship emissions may influence the atmospheric chemistry. The site is approximately 35 m above sea level, and the sea is approximately 150 m to the east. No apparent local emissions exist, and the surrounding forest is lush (Fig. 1(b)). In addition to anthropogenic and vegetation emissions, the site is also affected by the synchronization of plumes from northern cities and the South China Sea (Niu et al., 2022; Xia et al., 2021). Due to its significant time-varying pollution characteristics, this area is an ideal site for studying the effects of plume transport on atmospheric oxidation.

2.2 Instrumentation

2.2.1 HOx radical measurements

The OH and HO$_2$ radicals were measured via laser-induced fluorescence (LIF).
The OH radical can be directly measured by exciting the fluorescence using a 308-nm laser. HO₂ is converted into the OH radical via chemical transformation and then detected in the form of OH radical. The self-developed instrument, the Anhui Institute of Optics Fine Mechanics-LIF (AIOFM-LIF), was used to conduct the measurements (Zhang et al., 2022a; Wang et al., 2021; Wang et al., 2019). This system has been used in key regions of China, including the Yangtze River Delta, Pearl River Delta, and Chengdu-Chongqing region, and achieved good performance in a comparison experiment with a LIF system jointly developed by Forschungszentrum Jülich and Peking University (PKU-LIF) (Zhang et al., 2022b).

The system and detection interference process have been described in detail in previous studies (Zhang et al., 2022a). Briefly, the system consists of a laser output module, a radical detection module, and a control and data acquisition module. These modules are integrated into a sampling box with constant temperature and humidity control (Fig. 1(c)). The laser output module is a union of an Nd:yttrium-aluminum-garnet (YAG) solid-state laser, a 532-nm laser output, and a tunable dye laser. In the radical detection module, the OH and HO₂ fluorescence cells are combined in parallel and share a common axial optical path. The 308-nm laser is introduced into the HO₂ cell first and then into the OH cell via an 8-m fiber. To maintain the detection efficiency, the power in the OH fluorescence cell should be at least 15 mW. In the detection process, a set of lenses was deployed and positioned in front of the microchannel plate detector (MCP) to boost the fluorescence collection capacity. Each MCP detector contains a timing control instrument to optimize the signal-to-noise ratio (SNR) of the fluorescence detection. Efficient ambient air sampling was achieved using an aluminum nozzle (0.4 mm orifice), and the pressure in the chamber was maintained at 400 Pa via a vortex vacuum pump (XDS35i, Edwards) to avoid fluorescence quenching.

A wavelength modulation for the background measurement that periodically switches from an on-resonant state to a non-resonant state has been widely used to obtain spectral zero. The ozone photolysis interference was subtracted according to
laboratory experiments. An OH measurement comparison with an interference-free instrument, PKU-LIF, was conducted in a real atmosphere in a previous study (Zhang et al., 2022b). The ozonolysis interference on the measurement consistency of both systems was excluded under high-NOx and high-NMHC conditions, confirming the general applicability under complex atmospheric pollution. For HO2 measurement, the NO concentration corresponding to a conversion efficiency of ~15% was selected to avoid RO2→HO2 interference (especially from RO2 radicals derived from long-chain alkanes (C ≥ 3), alkenes, and aromatic hydrocarbons).

A standard HOx radical source based on the simultaneous photolysis of H2O/O2 by a 185 nm mercury lamp was used to complete the calibration of the detection sensitivity (Wang et al., 2020). During the observation campaign, the instrument was calibrated every 1 or 2 days (except for shutdown during rainy periods), and the sensitivity used for the data processing was an average of all of the calibration results. Considering the system error and calibration error, the detection limits of the OH and HO2 radicals were 3.3 × 10^5 cm^-3 and 1.1 × 10^6 cm^-3 (60 s, 1σ), respectively, at a typical laser power of 15 mW, and the measurement errors were 13% and 17%, respectively.

2.2.2 Supporting measurements

In addition to measuring the HOx radicals, an extensive suite of relevant species was also measured close to the LIF instrument to improve the analysis of the radical photochemistry. Detailed information about the measurement instrument is presented in Table S1, including the meteorological parameters (wind speed (WS), wind direction (WD), temperature (T), relative humidity (RH), pressure (P), and solar radiation (J-values)), conventional pollutants (ozone (O3), carbonic oxide (CO), and sulfur dioxide (SO2)), secondary pollution precursors (HONO, NO, NO2, HCHO, and NMHCs), and destruction products (particulate matter (PM2.5)). In addition to HCHO, other volatile organic compounds (VOCs) were detected using a gas chromatograph coupled with a flame ionization detector and mass spectrometer (GC-FID-MS). Ninety-nine types of VOCs, including C2–C11 alkanes, C2–C6 alkenes, C6–C10...
aromatics, halohydrocarbons, and some oxygenated VOCs (OVOCs), were observed using the GC-FID-MS at a 1-h time interval. Only isoprene was considered as a representative of biogenic VOCs (BVOCs). All of the instruments were located close to the roof of the fourth floor, nearly 12 m above the ground to ensure that all of the pollutants were located in a homogeneous air mass.

2.3 Model description

A 0-D chemical box model incorporating a condensed mechanism, the regional atmospheric chemistry mechanism version 2-Leuven isoprene mechanism (RACM2-LIM1), was used to simulate the radical concentrations and the generation of radical-related secondary pollution (Stockwell et al., 1997; Griffith et al., 2013; Tan et al., 2017). The meteorological parameters, conventional pollutants, and precursor concentrations mentioned in Section 2.2.2 were input into the model as boundary conditions. All of the constraints were unified to a temporal resolution of 15 min through averaging or linear interpolation. The overall average during the observations was substituted for large areas of missing data due to instrument maintenance or failure. Three days of data were entered in advance as the spin-up period, and a synchronized time-dependent dataset was eventually generated. The hydrogen (H$_2$) and methane (CH$_4$) concentrations were set to fixed values of 550 ppb and 1900 ppb, respectively. The physical losses of species due to processes such as deposition, convection, and advection were approximately replaced by an 18 h atmospheric lifetime. According to the measurement accuracy, the simulation accuracy of the model for the OH and HO$_2$ radicals was 50% (Zhang et al., 2022a).

Considering the environmental characteristics of the MBL, the gas-phase mechanisms for bromine (Br$_2$) were introduced into the base model to diagnose the impacts of the reactive bromine chemistry at the field site. The details of the mechanisms involved are listed in Tables S2 and S3. The halogen species were not available in the YMK site, so the Br$_2$ concentration during the same season at a coastal site in the Pearl River Delta was used as a reference value (average daytime concentration of 3–5 ppt at a coastal ground site in Hong Kong, China).
3 Results

3.1 Meteorological and chemical parameters

3.1.1 Data overview

Fig. S1 presents the time series of the main meteorological parameters and pollutants during the observation period at the YMK site. Except for on 2 days, October 26 and 28, the meteorological characteristics of the other days were generally stable. The daily maximum T, RH, and J-values did not vary significantly. The suitable temperature (20–30°C) and humidity (50–80%) conditions promoted the stable oxidation of the diurnal photochemistry. The peak j(O¹D) value was approximately $2.0 \times 10^{-5}$ s$^{-1}$, exhibiting the typical characteristics of intense light radiation in autumn in the Pearl River Delta region (Yang et al., 2022a; Tan et al., 2022).

As typical marine air components, the concentrations of NOx, CO, PM$_{2.5}$, and other pollutants were lower than those detected in other observation campaigns in both urban and suburban areas in the Pearl River Delta region (Tan et al., 2019b; Lu et al., 2012; Yang et al., 2022b). The PM$_{2.5}$ and CO concentrations exhibited good consistency and even mild pollution features on some dates, reflecting the influence of human activities. Contrary to the conventional belief that marine ozone is a global background setting, the ozone concentration in the YMK site was always at the critical value of the updated Class I standard (GB3095-2012, average hourly O$_3$ of 81 ppb at 25°C and 1013 kPa). The occurrence of fewer emissions reduced the titration effect, resulting in the ozone exhibiting no apparent diurnal trend on some of the dates and a high background value at night (67.3 ± 7.6 ppb). The NOx concentrations also maintained typically low levels on most dates. The daily maximum NMHC concentration peaked at 19.3 ± 3.0 ppb, and the maximum value of ~40 ppb occurred on October 27. Local biological emissions significantly affected the NMHC composition of the site, and isoprene, a representative BVOC, achieved a noon maximum of 0.82 ± 0.16 ppb. Neither anthropogenic alkenes nor aromatic
hydrocarbons were abundant, and OVOCs accounted for approximately 50% of the total. As a photochemical indicator, formaldehyde peaked at ~4 to ~8 ppb on October 18, 19, and 27, suggesting a more vigorous oxidation process. HONO exhibited a grooved distribution with high daytime (0.49 ± 0.097 ppb) and low nighttime (0.20 ± 0.11 ppb) concentrations. This unique distribution of HONO has been observed in remote environments in several previous observation campaigns (Jiang et al., 2022; Crilley et al., 2021). An extremely high daytime HONO concentration will significantly affect the chemical composition of the atmosphere and the secondary pollution generation.

Table 1. Summary of radical concentrations and related species concentrations at MBL. All data are listed as the average in noontime (10:00–15:00).

<table>
<thead>
<tr>
<th>Campaign</th>
<th>Location</th>
<th>Date</th>
<th>OH (10^6/cm^3)</th>
<th>HO_2 (10^6/cm^3)</th>
<th>HCHO (ppb)</th>
<th>HONO (ppb)</th>
<th>NOx (ppb)</th>
<th>O_3 (ppb)</th>
<th>Ref</th>
</tr>
</thead>
<tbody>
<tr>
<td>WAOSE95</td>
<td>Weybourne, UK</td>
<td>1995 (Jun)</td>
<td>5.0</td>
<td>-</td>
<td>1.50</td>
<td>0.10</td>
<td>&lt;2.0</td>
<td>40.0</td>
<td>(Grenfell et al., 1999)</td>
</tr>
<tr>
<td>ALBATROSS</td>
<td>Atlantic Ocean</td>
<td>1996 (Oct-Nov)</td>
<td>7.0</td>
<td>-</td>
<td>0.50</td>
<td>-</td>
<td>-</td>
<td>25.0</td>
<td>(Brauers et al., 2001)</td>
</tr>
<tr>
<td>EASE96</td>
<td>Mace Head, Ireland</td>
<td>1996 (Jul-Aug)</td>
<td>2.3</td>
<td>2.6</td>
<td>-</td>
<td>-</td>
<td>~1.0</td>
<td>45.0</td>
<td>(Carslaw et al., 1999)</td>
</tr>
<tr>
<td>EASE97</td>
<td>Mace Head, Ireland</td>
<td>1997 (Apr-May)</td>
<td>1.8</td>
<td>1.0</td>
<td>0.70</td>
<td>-</td>
<td>0.95</td>
<td>46.0</td>
<td>(Creasey et al., 2002)</td>
</tr>
<tr>
<td>ORION99</td>
<td>Okinawa Island, Japan</td>
<td>1999 (Aug)</td>
<td>4.0</td>
<td>4.3</td>
<td>-</td>
<td>0.20</td>
<td>6.3</td>
<td>23.0</td>
<td>(Kanaya et al., 2001)</td>
</tr>
<tr>
<td>RISOTTO</td>
<td>Rishiri Island, Japan</td>
<td>2000 (June)</td>
<td>7.4</td>
<td>3.1</td>
<td>-</td>
<td>-</td>
<td>0.45</td>
<td>-</td>
<td>(Kanaya et al., 2002)</td>
</tr>
<tr>
<td>RISFEX</td>
<td>Rishiri Island, Japan</td>
<td>2003 (Aug)</td>
<td>2.7</td>
<td>1.5</td>
<td>-</td>
<td>-</td>
<td>0.2</td>
<td>28.0</td>
<td>(Qi et al., 2007)</td>
</tr>
<tr>
<td>RHMBLe</td>
<td>Cape Verde, Atlantic Ocean</td>
<td>2007 (May-Jun)</td>
<td>9.0</td>
<td>6.0</td>
<td>0.30</td>
<td>-</td>
<td>0.014</td>
<td>35.0</td>
<td>(Whalley et al., 2010)</td>
</tr>
<tr>
<td>SOS</td>
<td>Cape Verde, Atlantic Ocean</td>
<td>2009 (Jun-Sep)</td>
<td>9.0</td>
<td>4.0</td>
<td>1.9</td>
<td>-</td>
<td>0.050</td>
<td>40.0</td>
<td>(Carpenter et al., 2011)</td>
</tr>
<tr>
<td>CYPHEX</td>
<td>Mediterranean</td>
<td>2014 (Jul)</td>
<td>5.8</td>
<td>6.3</td>
<td>~1.0</td>
<td>~0.080</td>
<td>&lt;1.0</td>
<td>69.0</td>
<td>(Mallik et al., 2018)</td>
</tr>
<tr>
<td>ICOZA (NW-SE)</td>
<td>North Norfolk, UK</td>
<td>2015 (Jul)</td>
<td>3.0</td>
<td>1.4</td>
<td>0.9</td>
<td>0.052</td>
<td>2.0</td>
<td>39.0</td>
<td>(Woodward-Massey et al., 2022b)</td>
</tr>
<tr>
<td>ICOZA (SW)</td>
<td>North Norfolk, UK</td>
<td>2015 (Jul)</td>
<td>4.1</td>
<td>1.0</td>
<td>1.1</td>
<td>0.097</td>
<td>3.0</td>
<td>31.0</td>
<td>(Woodward-Massey et al., 2022b)</td>
</tr>
<tr>
<td>HT</td>
<td>Hok Tsui, China</td>
<td>2020 (Oct-Nov)</td>
<td>4.9</td>
<td>-</td>
<td>1.0</td>
<td>0.15</td>
<td>~4.0</td>
<td>65.0</td>
<td>(Zou et al., 2022)</td>
</tr>
<tr>
<td>YMK (Land Mass)</td>
<td>Shenzhen, China</td>
<td>2019 (Oct)</td>
<td>7.1</td>
<td>5.2</td>
<td>3.4</td>
<td>0.66</td>
<td>6.4</td>
<td>75.6</td>
<td>This work</td>
</tr>
<tr>
<td>YMK (Ocean Mass)</td>
<td>Shenzhen, China</td>
<td>2019 (Oct)</td>
<td>4.5</td>
<td>4.9</td>
<td>1.2</td>
<td>0.48</td>
<td>3.0</td>
<td>78.1</td>
<td>This work</td>
</tr>
</tbody>
</table>

3.1.2 Influences of different air masses

During the YMK observation campaign, the wind direction was mainly easterly...
and southerly, and the wind speed was below 3 m/s. The conventional wind direction is insufficient to reflect the air mass trajectory at a slightly higher altitude due to the mountain-valley breeze (Niu et al., 2022). Using the hybrid single-particle Lagrangian integrated trajectory (HYSPLIT) model, the 24-h backward trajectories on special days were obtained (Fig. S2). In Fig. S2, the red, blue, and green trajectories represent the results at altitudes of 100, 500, and 1000 m above ground level, respectively. Two typical transportation pathways dominated the air parcels. One originated from the northern megacities in the Pearl River Delta (defined as the land mass, LAM), especially on October 18, 19, and 27. In contrast, a clean air mass from the east or northeast was mainly transported to the observation site from the ocean (defined as the ocean mass, OCM), with representative episodes on October 22, 25, and 26.

Several observation campaigns have discovered the relationship between wind direction and radical chemistry (Lu et al., 2012; Fuchs et al., 2017; Niu et al., 2022). Although there was no apparent wind speed condition, the dominant air mass still influenced the pollutant concentrations due to the particularity of the marine site. During the OCM period, the NOx and HCHO concentrations exhibited relatively clean characteristics that were consistent with those previously reported (Table 1). However, both the HONO and O₃ concentrations were twice as high as those of the other components, and their daily average values (10:00–15:00) reached 0.48 ppb and 78.1 ppb, respectively. Compared with the OCM period, the meteorological conditions (T, RH, and J-values) changed greatly during the LAM episode. The pollutants were accumulated due to the transport of the plume from the northern cities (Fig. 2). Both NO and NO₂ peaked at around 10:00, exhibiting prominent pollution characteristics. The diurnal peaks of the HONO and HCHO concentrations were much higher than those of the Integrated Chemistry of Ozone in the Atmosphere (ICOZA) Project observations (a pollution period dominated by a southwest wind direction) (Woodward-Massey et al., 2022b). The HONO concentration was 6.8 times higher than when the wind direction was southwest in the ICOZA observations, while the HCHO concentration was 3.1 times higher. The abundance of oxidation precursors
(HONO, HCHO, O₃, and NMHCs) reflected the unique atmospheric conditions in the marine environment in China, which originated from the complex atmospheric pollution.

Fig. 2. Mean diurnal profiles of measured trace gases parameters during Land mass and Ocean mass episodes. The coloured shadows denote the 25 and 75% percentiles. The grey areas denote nighttime.

3.2 HOx radical concentrations and modeled OH reactivity

Fig. 3(a) and (b) shows the time series of the simulated and observed OH and HO₂ radical concentrations during the observation campaign. The time series of the simulated OH reactivity ($k_{OH}$) is presented in Fig. 3(c). The observed OH and HO₂ radicals exhibited significant diurnal trends. The average daily maximum OH and HO₂ values were $(4.7–9.5) \times 10^6$ cm$^{-3}$ and $(4.2–8.1) \times 10^8$ cm$^{-3}$, respectively. The peak $k_{OH}$ value was commonly less than $10 \text{ s}^{-1}$. Due to human activities, the simulated $k_{OH}$ reached more than $15 \text{ s}^{-1}$ on some days. The radical concentrations and reactivity exhibited similar trends, which differed from reports on urban and semi-urban areas where inorganic species (NOx and CO) were the dominant controllers of
$k_{OH}$ (Zhang et al., 2022a; Tan et al., 2019b; Lou et al., 2010).

Fig. 3. Timeseries of the observed and modelled parameters for OH, HO$_2$ and $k_{OH}$ during the observation period. (a) OH, (b) HO$_2$, (c) $k_{OH}$.

The OH and HO$_2$ concentrations were calculated using a base model incorporating the RACM2-LIM1 mechanism. Overall, the observed OH and HO$_2$ concentration data were both well reproduced by the base model (Fig. 4(a)–(b)). The base model slightly overestimated the OH radical, suggesting that a radical removal pathway was missing. Halogen species have been recognized as potent oxidizers that can boost photochemistry (Xia et al., 2022; Peng et al., 2021). A sensitivity test was performed by imposing ~3 ppt Br$_2$, a typical mixing ratio reported for a coastal site in the Pearl River Delta, into the base model to diagnose the impact of the halogen chemistry on the troposphere chemistry (Xia et al., 2022). The details of the mechanisms involved are listed in Tables S2 and S3. In this scenario (Fig. 4(a)–(b), green line), the simulated OH was 11.6% lower than in the base model, and no significant effect on the HO$_2$ radical was identified. The daily maximum calculated total OH reactivity was 9.9 s$^{-1}$ (Fig. 4(c)). Regarding the contributions of the inorganic species, the contributions of CO and NOx were close at 18.0% and 14.8%, respectively. Nearly 70% of the reactivity was accounted for by the organic species, among which the OVOCs were the largest contributor (30.6%). The anthropogenic alkanes, alkenes, and aromatic hydrocarbons contributed less than 10% to the reactivity in the marine environment. The BVOCs emitted by the surrounding forest
could not be ignored, accounting for 15.7%.

Fig. 4. Median diurnal profiles of the observed and modelled parameters for OH, HO$_2$ and $k_{OH}$ during the observation period. (a) OH, (b) HO$_2$, (c) $k_{OH}$.

The regional transport of radicals was generally impossible due to their short lifetimes. However, the air mass transport of the precursors increase the ROX primary sources. Under the linkage of NO concentration, this leads to accelerated cycling efficiency of the radicals, promoting the accumulation of photochemical products. The effects can be seen directly in the changes to the oxidation level. Isoprene is discussed as an example. The prevailing wind direction experienced a series of southerly-easterly shifts from 8:00 to 18:00 on October 18 (Fig. 5(a)). The growth and decline of the isoprene concentration were highly correlated with the changes in the wind direction (Fig. 5(b)), and the maximum concentration (2.1 ppb) occurred at 17:00 under the southwest wind. Correspondingly, the sensitive LIF instrument captured the decrease in the concentration at noon. The base model simulated the fluctuations in the OH concentration, but the solar radiation did not vary, indicating that the change in the precursor accelerated the instantaneous OH $\rightarrow$ HO$_2$ propagation (Fig. 5(c)). In addition, the evolution of the air mass composition inhibited the
conversion of HO$_2$ to OH and maintained the high HO$_2$ level during the afternoon (Fig. 5(d)).

Therefore, it is worth comparing the concentrations and reactivities of the radicals by classifying the predominant air mass (Fig. 6). During the OCM period, the observed OH and HO$_2$ radicals could be reflected by the base chemical mechanism, with daily averages of $4.5 \times 10^6$ cm$^{-3}$ and $4.9 \times 10^8$ cm$^{-3}$, respectively. Compared to other campaigns (Table 1), the observed maximum values were within reasonable ranges (OH: $2-9 \times 10^6$ cm$^{-3}$; HO$_2$: $1-6 \times 10^8$ cm$^{-3}$). Despite low NOx levels during the OCM period, the HO$_2$ radical was not overestimated using the base model, which was dissimilar to many MBL observations. The heterogeneous uptake pathway did not need to be further investigated due to the low PM$_{2.5}$ concentration during the OCM period ($<25$ µg/m$^3$). However, both the OH and HO$_2$ radical concentrations reached higher levels during the LAM-dominant period, indicating a more active photochemical process. The diel averages for the OH and HO$_2$ radicals were $7.1 \times 10^6$ cm$^{-3}$ and $5.2 \times 10^8$ cm$^{-3}$, respectively, which were notably higher than the levels reported in the ICOZA observations (Woodward-Massey et al., 2022b). The base model underestimated both the OH and HO$_2$ concentrations between 10:00 and 15:00, and the observation-to-model ratio was greater than 1.2. Compared with the OCM-
dominant episode, the higher reactivity during the LAM period indicated the occurrence of efficient recycling during the ROx propagation (12.4 s\(^{-1}\) vs. 8.8 s\(^{-1}\)). The higher contributions of the BVOCs (only isoprene was considered, 15.6%) and OVOCs (30.2%) to the reactivity reflected the diverse composition of the VOCs in the forest environment. The more reactive atmosphere did not introduce a missing OH source in the afternoon, but radical cycling under enhanced photochemistry is worth discussing (Hofzumahaus et al., 2009). As a representative of the OVOCs, HCHO reflects the photochemical level to a certain extent. As shown in Fig. S3, a solid positive dependence between the OH\(_{\text{obs}}\)-to-OH\(_{\text{mod}}\) ratio and HCHO was observed (the daytime data were restricted according to j(O\(^1\)D) > 5 \times 10\(^{-6}\) s\(^{-1}\)). Considering the essential contributions of the OVOCs and BVOCs during ROx recycling, the other unmeasured species (mono-terpenes and reactive halogens) involved in the oxidation cycle were responsible for the elevated photochemistry. Obtaining the full magnitude of the radical-related parameters is necessary to compensate for the discrepancy in the concentration closure experiments.

Fig. 6. Median diurnal profiles of the observed and modelled OH, HO\(_2\), k\(_{\text{OH}}\) during LAM and OCM episodes. The coloured shadows for OH and HO\(_2\) radicals denote the 25 and 75% percentiles. The grey areas denote nighttime.

4 Discussion

4.1 Experimental radical budget balance
4.1.1 OH radical

A process-oriented experiment was conducted to investigate the photochemistry progress from a budget balance perspective (Woodward-Massey et al., 2022a; Tan et al., 2019b; Yang et al., 2021). The OH was in a photostationary steady state due to its short lifetime. The total OH removal rate was directly quantified from the union of the OH concentration and the reactivity (R (1)):

\[ D(OH) = [OH] \times k_{OH}. \] (1)

The total production rate of the OH radical was the sum of the primary sources (O3/HONO photolysis and ozonolysis reactions) and secondary sources (HO2 + NO) (R (2)):

\[ P(OH) = j_{HONO}[HONO] + \varphi_{OH}(O^3D)[O_3] + \Sigma i \{ \varphi_{OH} k_{Alkenes + O_3}[Alkenes][O_3] \} + (k_{HO2+NO}[NO] + k_{HO2+O3}[O_3])[HO_2]. \] (2)

The diel profiles of the experimental OH budget during the LAM and OCM periods are shown in Fig. 7. Both the observed OH and HO2 radicals were introduced into the budget calculations. Because \( k_{OH} \) was not measured during the observation experiment, the simulated value was used as the lower limit to analyze the removal rate (Yang et al., 2022b). During the OCM period, the HO2 + NO reaction accounted for ~50% of the OH yield. The maximum of 6.6 ppb/h occurred at around 12:00. The photolysis reactions could increase the daytime contributions of HONO and O3 to 1.52 ppb/h and 0.84 ppb/h, respectively (10:00–15:00). The contribution of the non-photolytic radical source (ozonolysis reactions) was almost negligible.
Fig. 7. The diurnal profiles of the experimental OH budget during (a) Land mass and (b) Ocean mass episodes. The blue line denotes the OH destruction rate([OH]×kOH). The grey areas denote nighttime.

Compared with other marine observations, the calculated OH generation rate was approximately twice that reported in the ICOZA Project and five times that obtained in the RHaMBLe Project (Woodward-Massey et al., 2022a; Whalley et al., 2010).

During the LAM period, the OH generation rate reached a maximum of 12.6 ppb/h, accompanied by a secondary source contribution of 67% (from the reaction between HO₂ and NO) during the daytime, which was close to several observations related to polluted plumes (Woodward-Massey et al., 2022a; Tan et al., 2019b; Lu et al., 2012; Yang et al., 2022b). No additional OH radical source was needed when the simulated kOH was introduced into the experimental budgets. The difference between P(OH) and D(OH) was less than 2 ppb/h, indicating the absence of a nontraditional OH recycling pathway (X mechanism) under low NO concentration conditions (Hofzumahaus et al., 2009).

4.1.2 Total ROx radicals

The budget analysis of the HO₂ and RO₂ radicals could not be performed well due to the lack of RO₂ radical observation data. The diurnal profiles of the ROx production (P(ROx)) and termination rate (L(ROx)) for the different air masses are shown in Fig. 8. The P(ROx) could reach 3.36 ppb/h with an ocean plume. HONO photolysis controlled nearly half of the primary sources (45.7%), and the daily distribution was consistent with that of solar radiation. The ozone-related
contributions from photolysis and ozonolysis were approximately 25.1% + 11.5%. The remaining contribution was from the photolysis of carbonyls (HCHO and OVOCs) (15.0%). The anthropogenic contribution to the radical chemistry was not ignorable, and the ROx source in this observation was exponentially higher than that in other MBL observations (Woodward-Massey et al., 2022a; Stone et al., 2012; Whalley et al., 2010; Mallik et al., 2018). The P(ROx) of the LAM was close to that in Shenzhen (~4 ppb/h) but was significantly lower than that in Yufa (~7 ppb/h) and the BackGarden (~11 ppb/h) (Tan et al., 2019b; Lu et al., 2012; Yang et al., 2022b). The reactions between ROx and NOx and self-combination were the main pathways of radical termination (~70%). The contribution of the formation of peroxynitrite to the L(ROx) could not be ignored in the daytime.

Fig. 8. The diurnal profiles of ROx budget during Land mass and Ocean mass episodes. The pie chart denotes proportions in different parts during the daytime (10:00-15:00). The grey areas denote nighttime.

Due to the high HONO concentration during the daytime, the photolysis reaction made daytime contributions of 1.52 ppb/h and 2.19 ppb/h during the OCM and LAM periods, respectively. As the only known gas-phase source, OH + NO accounted for a negligible proportion of the HONO loss. Considering the location of the YMK site, HONO from cruise ship emissions is a possible component of the primary anthropogenic source (Sun et al., 2020). Other active tropospheric HONO sources
(heterogeneous reactions with NO$_2$ and $p$(NO$_3^-$) photolysis) are worthy of consideration and significantly contribute to the atmospheric oxidation in the MBL area (Zhu et al., 2022; Crilley et al., 2021).

### 4.2 Local ozone production rate

Peroxyl radical chemistry is the essential photochemical source of tropospheric ozone (F(Ox), R (3)):

$$F(O_x) = k_{HO_2+NO}[NO][HO_2] + \sum_i k_{RO_2+NO}[NO]RO_2^i$$  \hspace{1cm} (3)

NO reacts with HO$_2$ and RO$_2$ radicals to form NO$_2$, and then, photolysis occurs to form O$_3$ under solar radiation. NO$_2$ and ozone are the two sides of the oxidation reservoir. The effect of local emissions on the photodynamic equilibrium can be avoided by characterizing the photochemical production of the total oxidants (Tan et al., 2019b). Ox is mainly photochemically removed through ozone photolysis, ozonolysis, radical chain propagation (OH/HO$_2$ + O$_3$), and chain termination (OH + NO$_2$) reactions in the troposphere (D(Ox), R (4)):

$$D(O_x) = \varphi_{OH}(O^1D)[O_3] + \sum_i [k_{Alkenes+O_3}[Alkenes][O_3]] + (k_{O_3+OH}[OH] + k_{O_3+NO_2}[HO_2])[O_3] + k_{OH+NO_2}[OH][NO_2].$$  \hspace{1cm} (4)

The net formation rate (P(Ox)) can be calculated by subtracting D(Ox) from F(Ox):

$$P(O_x) = F(O_3) - D(O_3).$$  \hspace{1cm} (5)

The simulated RO$_2$ radical concentration was introduced into the F(Ox) calculation. The diurnal variations in the ozone generation in the different air masses are shown in Fig. 9. The contribution of the HO$_2$ radical to F(Ox) was approximately 60%. The RO$_2$ radicals consisted of various types such as methyl peroxyl (MO$_2$), acetyl peroxy radicals (ACO$_2$/RCO$_3$), and other radicals derived from alkanes (ALKAP), alkenes (ALKEP), and isoprene (ISOP), which accounted for an additional 40% of the F(Ox). On a daytime basis, the maximum F(Ox) reached 7.4 ppb/h at around 12:00 in the OCM period, while a persistent-high value (maximum of 12.5 ppb/h at 10:00–14:00) occurred in the LAM period. A vast amount of Ox was consumed in the nitric acid (OH + NO$_2$) formation pathways, i.e., higher than the ozonolysis removal. The daily averaged ozone production rates were 5.52 and 2.76 ppb/h during the LAM and OCM periods, respectively.
4.3 Relationship between precursors and oxidation rates

Despite the low level of human activities, oxidation precursors have an extended lifetime in the stable atmosphere of coastal areas. Intensive photochemical reactions occur after the accumulation of precursors, resulting in local net ozone production comparable to that in the surrounding suburban environments (Zeren et al., 2022). Simultaneous observations of both urban and coastal settings in Shenzhen have indicated that the oxidation rates are comparable (Xia et al., 2021). The coupling of precursor transport and local photochemical processes in marine areas makes it meaningful to explore secondary pollution generation (Fig. 10(a), (b), and (c)). No obvious radical source was missing during the LAM and OCM periods, and the oxidation level was that expected from the base model. On a daytime basis, the mean diurnal profile of the P(Ox) reached ~7 ppb/h in the LAM period, and the average nitric acid (P(HNO$_3$)) and sulfuric acid (P(H$_2$SO$_4$)) production rates were ~1.6 and ~0.11 ppb/h, respectively. The P(HNO$_3$) production rate was similar to the average of observations in the Pearl River Delta region (~1.3 ppb/h), while that of the P(H$_2$SO$_4$) was only half the average level (~0.24 ppb/h) (Lu et al., 2013; Tan et al., 2019b; Yang et al., 2022b). During the OCM period, the characteristics of the ocean air mass alleviated the photochemical process, and the production rates of the secondary pollutants decreased by approximately half and were close to the average levels in
winter (Ma et al., 2019).

Fig. 10. The calculated reaction rates based on the observed concentrations for Land mass and Ocean mass episodes (a) P(Ox), (b) P(HNO₃), (c) P(H₂SO₄), (d) The observed and modelled O₃ concentration with a first-order loss term. The deposition process was equivalent to a lifetime of 15 hours to all species. All the rates and concentration are averaged for the daytime period between 10:00 and 15:00.

Contrary to numerous ocean observations, in the YMK site, intensive oxidation was accompanied by a high diurnal HONO level (higher than 400 ppt) (Fig. 11). The ozone levels were consistent with the Grade I air quality standard and far exceeded the global background concentration (~40 ppb). Daytime photolysis reactions of HONO contributed 1.52 ppb/h and 2.19 ppb/h to P(ROₓ) during the OCM and LAM periods, respectively, which were much higher than the values in several megacities during the photochemically polluted season (Tan et al., 2019a). Given the significance of HONO photolysis in driving atmospheric chemistry, a sensitivity test was conducted without constraints on HONO (i.e., w.o HONO) to specifically quantify the contribution of HONO-induced secondary pollution. Only the homogeneous reaction (OH + NO) participated in the formation of HONO in the default mode without HONO input (Liu et al., 2022b). After evaluation, the P(Ox) was found to be 33% and 39% lower during the LAM and OCM periods, respectively, while the nitric acid and sulfuric acid formation rates were 52% and 35% lower, respectively. The sensitivity test identified the privileged role of the HONO-related mechanisms in the OH
chemistry, which resulted in a correlation between the efficient radical recycling and secondary pollution.

A time-dependent box model was used to test the association between the HONO chemistry and the local ozone generation (Fig. 10(d)). In order to isolate the the \( \text{O}_3 \) photochemical production, the impacts of vertical entrainment and horizontal advection were in general ignored. On the basis of the base scenario run, constraint of the observed ozone concentration was removed, and the deposition process was equivalent to a lifetime of 15 hours to all species. The observed and modelled \( \text{O}_3 \) concentrations in Fig. 10(d) are averaged for the daytime period between 10:00 and 15:00. The observed diurnal ozone concentrations were 75.7 ppb and 78.6 ppb during the LAM and OCM periods, respectively. The daytime ozone was well reproduced by the time-dependent box model, and the deviation of the simulation was less than 20% (Fig. 10(d)). After removing the HONO constraint, the simulated ozone concentrations were 38.2 and 26.3 ppb, i.e., 48% and 58% lower, during the LAM and OCM periods, respectively. Both the HONO and ozone concentrations were reduced to a low level (~70 ppt and ~35 ppb) and were close to several ocean observations (Fig. 11) (Woodward-Massey et al., 2022b; Zhu et al., 2022; Xia et al., 2022). The elevated daytime HONO had an additional effect on the oxidation in the background atmosphere. For coastal cities, the particularity of the HONO chemistry in the MBL tends to influence the ozone-sensitive system and eventually magnifies the ozone background. Therefore, the promotion of oxidation by elevated precursor
concentrations is worth considering when formulating emission reduction policies.

## 5 Conclusions

Comprehensive observations of HOx radicals and other relevant species were conducted in October 2019 at a coastal site in the Pearl River Delta (the YMK site, 22.55°N, 114.60°E). The overall air pollutants exhibited typical coastal features due to the scarce anthropogenic emissions. The average daily maximum OH and HO₂ concentrations were \((4.7-9.5) \times 10^6\) cm\(^{-3}\) and \((4.2-8.1) \times 10^8\) cm\(^{-3}\), respectively. The base RACM2-LIM1 model satisfactorily reproduced both the observed OH and HO₂ radical concentrations, but a slight overestimation of the OH radical occurred. The daily maximum calculated total OH reactivity was 9.9 s\(^{-1}\), and nearly 70% of the reactivity was contributed by organic species.

In addition to anthropogenic and vegetation emissions, the synchronized air mass transport from the northern cities and the South China Sea exerted a time-varying influence on radical photochemistry and atmospheric oxidation. During the OCM period, the observed OH and HO₂ radical concentrations could be reflected by the base chemical mechanism, with daily average values of \(4.5 \times 10^6\) cm\(^{-3}\) and \(4.9 \times 10^8\) cm\(^{-3}\), respectively. The more active photochemical process during the LAM period promoted the underestimation of the radical concentrations. Unmeasured reactive species involved in oxidation propagation were responsible for elevated photochemistry.

In the episode that was dominated by ocean mass, the HO₂ + NO reaction accounted for ~50% of the primary OH yield. A higher OH generation rate was found(12.6 ppb/h) during the LAM period, and the secondary source accounted for 67% of the total, which was similar to several observations in polluted plumes. Reactions between ROx and NOx and self-combination were the main pathways of radical termination (~70%), and the contribution of peroxynitrite formation to the L(ROx) could not be ignored in the daytime.

Intensive photochemical reactions occur after the accumulation of precursors,
resulting in local net ozone production comparable to that in the surrounding suburban environments. The daily average ozone production rates were 5.52 and 2.76 ppb/h in the LAM and OCM periods, respectively. The rapid oxidation process was accompanied by a higher diurnal HONO concentration (higher than 400 ppt). A non-HONO-constrained sensitivity test was performed to quantify the HONO-induced contribution to secondary pollution. After evaluation, the P(Ox) values were 33% and 39% lower during the LAM and OCM periods, respectively, while the nitric acid and sulfuric acid formation rates were 52% and 35% lower, respectively. The simulated daytime HONO and ozone concentrations were reduced to a low level (~70 ppt and ~35 ppb, respectively). For coastal cities, the particularity of the HONO chemistry in the MBL tends to influence the ozone-sensitive system and eventually magnifies the ozone background. Therefore, the promotion of oxidation by elevated precursor concentrations is worth considering when formulating emission reduction policies.

Financial support

This work was supported by the National Natural Science Foundation of China (62275250, U19A2044, 61905003), the Natural Science Foundation of Anhui Province (No. 2008085J20), the National Key R&D Program of China (2022YFC3700301), and the Anhui Provincial Key R&D Program (202210720022).

Data availability

The data used in this study are available from the corresponding author upon request (rzhu@aiofm.ac.cn).

Author contributions

WQ Liu, PH Xie, RZ Hu contributed to the conception of this study. GX Zhang and RZ Hu performed the data analyses and manuscript writing. All authors contributed to measurements, discussed results, and commented on the paper.
Competing interests

The contact author has declared that none of the authors has any competing interests.
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