OH measurements in the coastal atmosphere of South China: Possible missing OH sinks in aged air masses

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Abstract

The hydroxyl radical (OH) is the main oxidant responsible for the removal of many reduced trace gases and the formation of secondary air pollutants. However, due to technical difficulties in measuring OH, the existing measurements of atmospheric OH concentrations are limited, and its sources and sinks are not well understood under low NO_x conditions. In this study, we observed the OH concentrations using chemical ionization mass spectrometry at a coastal site in Hong Kong from October to November 2020. The average noontime OH concentration over the study period was measured at $4.9 \pm 2.1 \times 10^6$ cm^{-3}. We found that a box model with comprehensive observational constraints reproduced the observed daytime OH concentrations when air parcels originated from the continental regions. However, this model overpredicted the observed daytime OH concentrations for coastal air parcels by 142% on average. The missing OH reactivity, which is defined as the OH loss from unmeasured trace gases, is proposed to be the cause of this overprediction. The estimated missing OH reactivity was found in the case of low concentrations of nitrogen oxides (NO_x) and volatile organic compounds, as well as in aged air, and we hypothesize that there could be unmeasured chemical species that cause the model to overestimate OH in aged coastal air parcels. Further studies are needed to find out the exact cause of

the model overestimation and to identify the suspected unmeasured chemical species that contribute to the OH budget, in order to better quantify the formation of secondary air pollutants.

1. Introduction

The hydroxyl radical (OH) dominates atmospheric oxidative capacity and participates in nearly all sunlit tropospheric chemistry. The primary sources of the ambient OH radical include the photolysis of ozone (O_3) and nitrous acid (HONO) and the ozonolysis of alkenes. The OH sinks are mainly the reactions of OH with trace gases, including carbon monoxide (CO), sulfur dioxide (SO_2), nitric oxide (NO), nitrogen dioxide (NO_2), methane, and other volatile organic compounds (VOCs, Fuchs et al., 2018). In reactions with CO and VOCs, peroxy radicals (HO_2 and RO_2) are produced and then recycled back into OH in the presence of NO as a secondary OH source. This interconversion is closely related to photochemical smog production (Stone et al., 2012). The reaction of OH with SO_2 and NO_2 produces H_2SO_4 and HNO_3, contributing to new particle formation and the acidity of rain, fog, and aerosols. OH also plays an important role in the climate system through reactions with the greenhouse gas CH_4 and the sulfate aerosol precursor dimethyl sulfide (DMS)(Berresheim et al., 2002).

Measuring ambient OH is challenging due to its high reactivity, short lifetime (< 1 s), and low environmental concentration (Stone et al., 2012). After decades of efforts, tropospheric OH radicals can now be detected following the development of laser-induced fluorescence (LIF)–fluorescence assay with gas expansion (Heard and Pilling, 2003), chemical ionization mass spectrometry (CIM, Eisele and Tanner, 1991), and open-path differential optical absorption spectrometry (Hausmann et al., 1997). The theory, advantages, and disadvantages of various measuring techniques have been discussed previously (Heard and Pilling, 2003; Mao et al., 2012). Using these techniques, multiple campaigns have been conducted to measure the atmospheric OH concentrations in different regions around the globe. Figure S1 and Table S1 summarise the previous field observations of OH radicals in various environments.

The OH observations are often compared with model simulations to evaluate whether a model has included the major OH sources and sinks. A summary of the results of the most recent studies is shown in Table S1 with the simulation to observation ratios ($R_{S/O}$). As concluded in previous reviews (Stone et

al., 2012; Rohrer et al., 2014; Lu et al., 2019), observed OH concentrations can generally be reproduced by box models under high NO conditions (NO > 1 ppb), such as at urban sites or within polluted air masses (Shirley et al., 2006; Griffith et al., 2016; Slater et al., 2020). However, discrepancies between model predictions and observations have often been found under low NO conditions (NO < 1 ppb). The model typically overpredicts OH concentrations in a low VOC environment and underpredicts them in a high biogenic VOC (BVOC) environment, as discussed below.

The model overestimation of OH has been found in remote marine boundary layers and coastal, urban, and Arctic regions (Table S1), which is attributed to the overestimation of OH sources, missing OH sinks, or the uncertainties inherent in model simulation and observation. For example, model overestimation of OH has been found when dominant sources, such as HONO (in the Antarctic, Kukui et al., 2014a) and HO_2 (in the coastal area Kanaya et al., 2007), are overestimated. In these cases, the overestimation of OH was resolved when these sources were better constrained in the model. Unmeasured VOCs have been proposed as the missing OH sinks, resulting in the overestimation of OH, e.g., in aged air in Idaho Hill (McKeen et al., 1997), in the marine boundary layer (MBL) of Mace Head (Carslaw et al., 1999; Berresheim et al., 2002), in the MBL in Tasmania (Creasey et al., 2003), in Antarctica (Mauldin III et al., 2010), and the urban area of California (Griffith et al., 2016). Other studies have shown evidence of missing OH sinks in various types of environments (Lou et al., 2010; Yang et al., 2016), e.g., in the clean forest (Hansen et al., 2014) and marine (Thames et al., 2020) areas, which is likely resulted from unmeasured organic compounds emitted from biogenic (Kaiser et al., 2016) or oceanic (Thames et al., 2020) sources and their oxidation products. A few studies have shown that the overestimations fall within measurement uncertainties of DOAS, CIMS (McKeen et al., 1997), and LIF, (Carslaw et al., 1999) while others have suggested a possible sampling loss of OH in CIMS (Mauldin III et al., 2010) or a possible calibration bias due to low relative humidity (CIMS, Mauldin III et al., 2001).

Underestimations of OH by models have mostly been found in forest areas with high BVOC emissions and low NO conditions. Few recent studies also found the OH estimation in urban atmospheres when the NO level was below 1ppb (Whalley et al., 2018; Tan et al., 2017, 2019). These underestimations

have usually been attributed to missing OH sources (Tan et al., 2001; Lelieveld et al., 2008; Hofzumahaus et al., 2009; Whalley et al., 2011). To explain the missing sources in forested regions, a series of new OH regeneration reactions under low NO conditions were proposed based on chamber experiments that investigated the oxidation of isoprene by OH. This mechanism, known as the Leuven isoprene mechanism (LIM1; Peeters et al., 2014), includes unimolecular reactions (Peeters et al., 2009; da Silva et al., 2010; Fuchs et al., 2013; Novelli et al., 2020) and isomerization of isoprene and/or its products (Peeters and Müller, 2010; Fuchs et al., 2014). With the adoption of this mechanism, the simulated OH concentration increased by 20% – 30% in the forest region (Lew et al., 2020). Another breakthrough was the development of a new chemical scavenging technique in LIF instruments that were able to determine the interference to the instrument's background. Some studies have shown that the interference in LIF instruments can partly explain the previously observed high OH concentrations (Mao et al., 2012; Hens et al., 2014; Novelli et al., 2014; Feiner et al., 2016; Woodward-Massey et al., 2020). With the adoption of interference scavenging and the LIM1 improved mechanism, measurements using LIF in an Alabama forest (Feiner et al., 2016) and CIMS in Amazon forests (Jeong et al., 2022) agreed with the OH concentration predicted by the model. However, the models in other studies continued to underestimate OH with the improved mechanism (Tan et al., 2019; Lew et al., 2020).

The industrialization of the Pearl River Delta (PRD) region of south China over the past three decades has been accompanied by high anthropogenic emissions of air pollutants (Lu et al., 2013), causing elevated concentrations of surface ozone (Wang et al., 2019b) and particulate matter (Yao et al., 2014). Measurements of OH in the PRD region that were taken using LIF at a forested site (Backgarden) indicated missing OH sources at this BVOC-rich site (Hofzumahaus et al., 2009; Lu et al., 2012). More recently, OH concentrations were measured at a suburban site in Shenzhen during the autumn of 2018 (Wang et al., 2019a, 2021a) using a newly developed LIF instrument. The OH concentrations, which had an average value of 5.3×10^6 cm^{-3} around noon, were briefly presented with no comparison to modeled OH.

In the present study, we measured OH concentrations using quadrupole CIMS from October to November 2020 at a background site in Hong Kong. The study aimed to determine the OH

concentrations in coastal south China and to investigate whether they could be simulated by a state-of-the-art chemical model under different airflow conditions. We first give a brief description of the site and OH measurement procedure, including the working theory of CIMS, calibration, uncertainties, and modelling setup. We then present the overall measurement results for different air masses and compare them with those found in previous studies. After this, we simulate OH concentrations using a box model constrained by comprehensive observations and discuss possible reasons for the model–observation discrepancy. Our measurements add to the limited database of ambient OH radical concentrations, while our analysis sheds light on possible missing OH sinks under low NO_x conditions.

2. Methodology

2.1 The Hok Tsui Supersite

The field campaign was conducted at the Cape D'Aguilar (also known as Hok Tsui, HT) Air Quality Supersite, which is operated by the Hong Kong Environmental Protection Department, between 6 October and 24 November 2020. The HT Supersite (22°12'32" N, 114°15'12" E) is a coastal site located at the south-eastern tip of Hong Kong Island. The site is surrounded by ocean, vegetation, and a country road (Figure 1) and is around 15 km away from the nearest urban center. There is no strong anthropogenic emission source in the surrounding area apart from the ocean-going vessels traveling in nearby waters (Peng et al., 2022). Nonetheless, the site does occasionally receive polluted air masses from mainland China, including air masses from the highly urbanized PRD region (Li et al., 2018; Peng et al., 2022).

We measured OH radicals, O_3, NO_x, CO, HONO, VOCs, oxygenated VOCs (OVOCs), relative humidity, temperature, NO_2 photolysis frequency (J_{NO2}), and aerosol size distribution. Table 1 summarises the measurement technique, resolution, and detection limits. The OH-CIMS was housed in an air-conditioned shelter in yard B together with the time-of-flight (ToF)-CIMS and ozone and NO_x analyzers (Figure 1). J_{NO2} was measured on top of the shelter. The other species and the aerosol size distribution were measured inside the main station building in yard A, which was located around 10 m away from yard B (Figure 1). The backward trajectory was calculated at 1-hour intervals on sampling days at an elevation of 60 m above ground level using the MeteoInfoMap software package (meteothink.org, Wang,

2014, 2019).

2.2 OH radical measurements

OH radical concentrations were indirectly measured using a custom-built quadrupole CIMS instrument (THS Inc, Atlanta). The THS CIMS was originally developed by (Eisele and Tanner, 1991) and improved upon in subsequent works (Eisele and Tanner, 1993; Tanner and Eisele, 1995; Tanner et al., 1997). The ambient OH concentrations were measured by first converting the OH (by addition of SO_2) to sulfuric acid (H_2SO_4) which was further converted to HSO_4^- ion followed by its detection with a quadrupole mass detector.

A schematic diagram of our OH-CIMS instrument is shown in Figure 2. Ambient air was drawn into the stainless steel inlet with a turbulence-reducing scoop by the inlet pump. The central part of the air in the stainless steel inlet was then drawn into the sample inlet, where OH was converted into H_2SO_4 by adding SO_2 to the sample flow (R1 to 3).

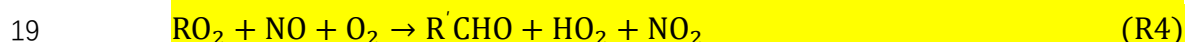
$$OH + SO_2 + M \rightarrow HSO_3 + M \tag{R1}$$

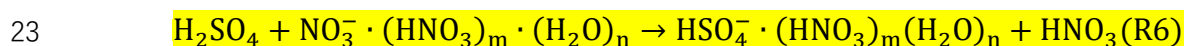
$$HSO_3 + O_2 \rightarrow SO_3 + HO_2 \tag{R2}$$

$$SO_3 + 2H_2O \rightarrow H_2SO_4 + H_2O \tag{R3}$$

The conversion was ended by the addition of scavenger gases (C_3F_6) in the rear flow. The reaction time for OH conversion is 47ms which is short enough to mitigate the HO_2 and RO_2 recycling interference.

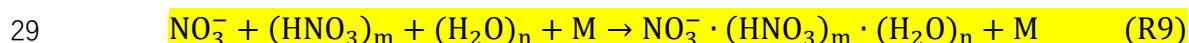
$$RO_2 + NO + O_2 \rightarrow R^{'}CHO + HO_2 + NO_2 \tag{R4}$$

$$HO_2 + NO \rightarrow OH + NO_2 \tag{R5}$$

The converted H_2SO_4 in the sample flow was then reacted with the excess NO_3^- cluster in the sheath flow and converted into an HSO_4^- ion cluster in the ionization chamber (R4).

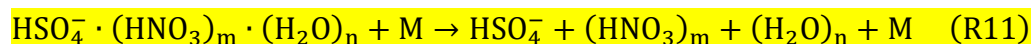
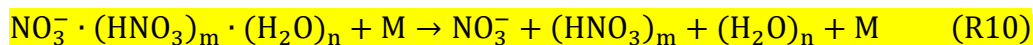
$$H_2SO_4 + NO_3^- \cdot (HNO_3)_m \cdot (H_2O)_n \rightarrow HSO_4^- \cdot (HNO_3)_m(H_2O)_n + HNO_3 \tag{R6}$$

The NO_3^- reagent ion cluster ($NO_3^- \cdot (HNO_3)_m \cdot (H_2O)_n$) with m and n mostly of 0-2 and 0-3 (Berresheim et al., 2000) was generated by passing an HNO_3 containing sheath flow through a [210]Po ion source (R7 to 9).

$$HNO_3 + e^- \rightarrow NO_2^- + OH \tag{R7}$$

$$HNO_3 + NO_2^- \rightarrow NO_3^- + HONO \tag{R8}$$

$$NO_3^- + (HNO_3)_m + (H_2O)_n + M \rightarrow NO_3^- \cdot (HNO_3)_m \cdot (H_2O)_n + M \tag{R9}$$

Where e^- is emitted from the ^{210}Po ion source. The NO_3^- and HSO_4^- ion clusters further dissociated in the collisional dissociation chamber (CDC), refocused in the ion guide chamber (IGC), and were then detected by the detector in the ion detection chamber (IDC).

$$NO_3^- \cdot (HNO_3)_m \cdot (H_2O)_n + M \rightarrow NO_3^- + (HNO_3)_m + (H_2O)_n + M \qquad (R10)$$

$$HSO_4^- \cdot (HNO_3)_m \cdot (H_2O)_n + M \rightarrow HSO_4^- + (HNO_3)_m + (H_2O)_n + M \qquad (R11)$$

The HSO_4^- and NO_3^- were detected by the peak intensities at m/z = 97 (S_{97}) and m/z = 62 (S_{62}). The HSO_4^- ion concentration was determined based on relative signal strength (the S_{97}/S_{62} ratio) rather than absolute signal (S_{97}) (Berresheim et al., 2000).

Apart from ambient OH, some interference gases, such as ambient H_2SO_4, Criegee intermediates, and artificial OH produced by the ion source, can also be converted into HSO_4^- and contribute to the signal S_{97}. To mitigate such interference, the scavenger gas (C_3F_6) and N_2 were added to the sample flow through electrically operated valves (see the pulsed flow in Figure 2) that automatically switched injection positions every 3 min. When a scavenger gas is added to the front injectors, ambient OH radicals are eliminated by the scavenger instead of reacting with SO_2 due to the higher concentration (~100 times) and the faster reaction of C_3F_6 than of SO_2 in the sample flow (Dubey et al., 1996). This allows the background signal (BS_{97}) contributed by the interference gases and instrument noise signal to be determined. When the pulsed flow scavenger gas is switched to the rear injector, the ambient OH radicals and interference gases react with SO_2 to give the total signal (TS_{97}). Then, the ambient OH signal can be obtained by subtracting the signal contributed by interference (BS_{97}) from the total signal (TS_{97}). The measured OH concentration ([OH]) can be calculated using the following equation (E1):

$$[OH] = \frac{1}{C} \times \frac{TS_{97} - BS_{97}}{S_{64}} \ (E1)$$

where C is the calibration factor obtained from calibration that was performed using the calibrator shown in Figure 2. The calibration is based on the production of OH radicals through the photolysis of water vapor by 184.9 nm light in the airflow through the calibrator (SR1). The OH concentration produced by the calibrator is calculated by photon flux (It) and H_2O concentration in the airflow (SE1). Calibration was carried out at least every two days during the campaign, as well as before and after any changes in settings. The difference in calibration factors was included in the calibration accuracy.

The detection limit was calculated by the background signal as shown by the equation in supplementary (SE3). The detection limit is approximately 1.5×10^5 cm^{-3} (signal-to-noise ratio of 2) in the laboratory. Due to variations in the concentrations of H_2SO_4 and other interference gases in the ambient air, the background signal during ambient measurement has a larger variation compared to the lab condition, resulting in a higher detection limit in the ambient condition. During the field study, the daytime and night-time average detection limits in this campaign were 1.0×10^6 cm^{-3} and 0.7×10^6 cm^{-3}, respectively. The overall calibration accuracy was estimated at 38%, by calculation that took into account the uncertainty of all of the parameters measured during the calibration process. The averaged overall uncertainty for this campaign is 44% for OH measurement with consideration of the calibration accuracy and the variations in m/z at 62 (S_{64}, 18%) and at 97 (TS_{97}-BS_{97}, 13%) during observation (SE4 and SE5). The technical details and specifications are in Table S2 and the detailed descriptions of CIMS optimization, calibration process, and calculation of detection limit are in the Supplementary Information.

2.3 Box modeling

The Framework for 0-D Atmospheric Modelling (F0AM) using the Master Chemical Mechanism (MCM) v3.3.1 (Wolfe et al., 2016) was used to simulate OH concentrations. MCM v3.3.1 (http://mcm.leeds.ac.uk/MCM) is a near-explicit chemical mechanism that includes over 17,000 elementary reactions of 6700 primary, secondary, and radical species (Jenkin et al., 2015). The isoprene degradation mechanisms, and in particular the mechanisms OH regenerated by HO_x recycling in low NO_x condition, were improved in MCM v3.3.1. The MCM mechanism has been used in previous studies to investigate OH chemistry in different environments, including forests (Stone et al., 2011), urban areas (Slater et al., 2020), suburban areas (Tan et al., 2018), and coastal regions (Sommariva et al., 2004). In our study, observational data (shown in Table S1) were used to constrain the model. These data included VOCs, OVOCs, SO_2, NO_x, CO, O_3, HONO, photolysis frequency of NO_2 (J_{NO2}), and meteorological parameters (temperature, relative humidity, and pressure). The photolysis frequencies for other species were calculated by the "HYBRID" method in F0AM which is based on Tropospheric Ultraviolet and Visible (TUV v5.2) Radiation Model from National Center for Atmospheric Research. The Ozone column we used for TUV calculation was 240 DU (the Dobson unit) which is the average number from October to November 2020 for the Hok Tsui area according to the worldview website (EOSDIS

 The simulated photolysis frequencies were then scaled by the correction factor obtained from the comparison between observed and modeled J_{NO2}. The first-order physical loss process, with a 24-hour lifetime for all species, was included in the model to represent physical processes (Wolfe et al., 2016; Chen et al., 2022). The physical loss process has a negligible influence on OH simulation because the OH concentrations are controlled by fast *in situ* chemistry.

The heterogeneous uptake of HO_2 by aerosols was included in the model by assuming a pseudo-first-order loss of HO_2 (E2–E4; Jacob, 2000):

$$\frac{d[HO_2]}{dt} = -k_{HO_2}[HO_2] \ (E2)$$

$$k_{HO_2} = \frac{V_{HO_2} \times S_a \times \gamma_{HO_2}}{4} \ (E3)$$

$$V_{HO_2} = \sqrt{\frac{8RT}{\pi \times MM_{HO_2}}} \ (E4)$$

where k_{HO_2} is the first-order loss rate coefficient of HO_2 by aerosol uptake, γ_{HO2} is the effective HO_2 uptake coefficient (0.1 for the base model run; Guo et al., 2019), V_{HO_2} is the mean molecular velocity of HO_2, S_a is the aerosol surface area concentration measured by a scanning mobility particle sizing (SMPS), and MM_{HO_2} (= 17 g/mol) is the molecular mass of HO_2. We assumed in the model that the products of heterogeneous HO_2 loss would not participate in further reactions (Guo et al., 2019).

The observation data were averaged every 10 mins for the model input. Any missing values were calculated assuming linear interpolation. The measured concentrations of NO and NO_2 were used to constrain the model Due to the clean condition of the coastal air, some of the reactive alkenes and long-chain alkanes were below detection limits. For the simulation of those compounds, we used concentrations that were half of the detection limits. The measured VOCs were further divided into those of anthropogenic origin (AVOCs) and biogenic origin (BVOCs). The AVOCs included alkanes (C_2–C_8), alkenes (C_2–C_6) benzene, and TEXs (toluene, ethylbenzene, and xylenes), which covered the dominant species originating from petroleum gas and industrial solvent evaporation (Tang et al., 2008), while the BVOCs included isoprene, terpene, pinene, and limonene. The majority (> 95%) of the measured OVOCs in this study were C_1–C_3 aldehydes, ketones, and acids. For each run, a three-day spin-up was performed with constant photolysis and deposition to create a stable model environment

and to avoid the uncertainty of unconstrained species (Carslaw et al., 1999).

3. Results and Discussion

3.1 Overview of observations

Figure 3 shows the time series of observed OH concentrations, along with the concentrations of other trace gases and the meteorological parameters, during the study period. The weather conditions featured relatively high temperatures, high relative humidity (RH), and strong solar radiation, similar to previous autumn observations at the same site (Li et al., 2018; Peng et al., 2022). The air temperature ranged from 20°C to 30°C and RH ranged from 40% to 96%. The photolysis frequency of NO_2 (J_{NO2}) peaked at 8×10^{-3} s^{-1} around noon on sunny days and decreased to 2×10^{-3} s^{-1} on cloudy days. The observed OH concentrations were mostly above the detection limit during the daytime but fell closer to the detection limit at night. The OH concentrations showed a distinct diurnal pattern and a positive correlation with J_{NO2} and calculated J_{O1D} ($R^2 = 0.68$ and 0.46 for J_{NO2} and calculated J_{O1D}, respectively, Figure S2). The daily maximum OH concentration varied from 2.1×10^6 cm^{-3} on 21 November, accompanying the lowest level of solar radiation, to 15.4×10^6 cm^{-3} on 7 November during a pollution episode. The pollution episode began on the evening of 6 November and featured a maximum concentration of 174.0 ppb O_3, 8.7 ppb NO, 22.7 ppb NO_2, 9.8 s^{-1} total measured VOCs reactivity, and 5.8 s^{-1} total measured OVOCs reactivity. The OH concentration peaked the next day (7 Nov). This suggests abundant OH sources and fast radical propagation under high-NO_x and high-VOC conditions.

Figure 4 shows the average diurnal profiles of OH and other representative species. On average, the maximum OH concentration was $4.9 \pm 2.1 \times 10^6$ (1σ) cm^{-3}. As shown in Table S1, the OH concentrations at our site were comparable to those reported in previous field studies conducted at tropical coastal sites. For example, the reported OH maximum concentration was 4.5×10^6 cm^{-3} in the low-altitude remote tropical troposphere (Brune et al., 2020). In a study conducted in autumn at a suburban site in Shenzhen, approximately 50 km away from our site, an OH diurnal maximum concentration of 5.3×10^6 cm^{-3} was observed (Wang et al., 2021b). The averaged night-time OH concentrations in this study was $5.1 \pm 1.8 \times 10^5$ (1σ) cm^{-3} which was comparable to the previous night-time results (below 10×10^5 cm^{-3}) measured at the PRD region (in Heshan, Tan et al., 2019, and in PKUSZ sites, Yang et al., 2022). The OH

concentration was slightly higher in the evening at $6.8 \pm 1.1 \times 10^5$ (1σ) cm^{-3} than in the morning at $3.7 \pm 0.7 \times 10^5$ (1σ) cm^{-3} which might be due to the higher ozone concentration in the evening which leads to a higher OH production from alkene ozonolysis.

Figure 4 also shows the average diurnal patterns of the other trace gases measured. As a primary source of OH, HONO, peaked in the morning at 0.21 ± 0.09 ppb around 7:00 local time (LT), and O$_3$ peaked in the afternoon at 70 ± 20 ppb at around 16:00 LT. The average NO and NO$_2$ concentrations reached a maximum of 1.2 ± 1.6 ppb at around 10:00 LT and 4.9 ± 3.2 ppb at around 18:00 LT, respectively. Isoprene showed a diurnal pattern similar to that of J_{NO2} and OH, peaking at 0.5 ± 0.4 ppb at noon. The average concentrations of all of the measured species during the campaign are shown in Table S3.

Figure 5 shows the hourly backward trajectories over the whole campaign. Consistent with previous studies conducted at HT in the same season (Li et al., 2018; Peng et al., 2022), the air masses were dominated by continental air masses containing high concentrations of pollutants (Figure 5a) and less polluted coastal air masses (Figure 5c). In this study, we did not encounter oceanic air masses from the south. The average noontime OH concentration was $5.0 \pm 2.2 \times 10^6$ cm^{-3} in the continental air (Figure 5b) and $3.3 \pm 1.6 \times 10^6$ cm^{-3} in the coastal air (Figure 5d).

3.2 Model–observation comparison

To investigate the performance of the MCM box model in simulating OH chemistry at our site, we selected 4 days featuring the continental air mass (8, 21, 22, and 23 Oct) and 4 days featuring the coastal air mass (25–27 Oct, 5 November) (Figure 6). We also selected 10 October as a specific case due to the shifting continental and coastal air masses within the same day during the daytime. These days were selected for model analysis because they comprised relatively complete chemical data that could be used to constrain the model. The below discussions focus on the comparison of the daytime results since the simulated night-time OH concentration was mostly within the measurement uncertainties and the night-time observations for Oct 08, 23, 27 and Nov. 5 were incomplete as shown in Figure 6.

3.2.1 Selected continental air mass cases

Figure 6 shows the comparison between the simulated and observed OH concentrations for the selected cases in the continental and coastal air masses (4 days each). The simulated OH concentrations of the four continental cases (8 October and 21–23 October) were mostly within the OH measurement uncertainty (2σ), with a daytime average $R_{S/O}$ of 1.14 (Figure 7) and a range from 0.99 to 1.18 (Figure 6). High NO_x (~ 5 ppb) and VOCs (~17 ppb) concentrations were measured on these days (Figure 7, Table S3). Therefore, in the continental polluted air mass, the existing MCM mechanism reproduced the observed OH concentrations well. On these days, the reaction between HO_2 and NO was the dominant OH formation pathway (78%), followed by O_3 photolysis (8%), HONO photolysis (6%), the reaction between ozone and HO_2 (2%), and alkene ozonolysis (< 2%; Table 2 and Figure S3). These results are similar to the findings of previous studies in the PRD conducted during autumn under polluted conditions (Tan et al., 2019). The removal of OH occurs mainly through its reaction with non-methane hydrocarbons (NMHCs; ~63%), CO (20%), NO_2 (9%), and CH_4 (4%; Table 2)

The simulated daytime average and peak HO_2 concentration were $2.1 \pm 1.2 \times 10^8$ cm^{-3} and 4.5×10^8 cm^{-3}, respectively, for continental air masses (RUNBase, Figure S4). The peak HO_2 value at our is lower than the result at a clean midlatitude forest area (10×10^8 cm^{-3}, Lew et al., 2020), and the average daytime value is higher than that measured at polluted urban sites in Beijing (0.3 to 0.4×10^8 cm^{-3}, Ma et al., 2019). The ratio between simulated HO_2 and observed OH (HO_{2_SIM}/OH_{OBS}) was 147 on the daytime average in continental cases.

The simulated OH reactivity was 8.1 ± 1.0 s^{-1} on average for continental air masses (Figure S5a), which is comparable to the OH reactivity measured at suburban sites which ranged from 5 to 30 s^{-1} but lower than that measured at the urban sites which ranged from 10 to 100 s^{-1} and mentioned by Yang et al., (2016) and references therein.

3.2.2 Selected coastal air mass cases

In contrast to the continental air mass cases, the diurnal OH patterns in the coastal air mass category (25–27 October and 5 November) were not well reproduced by the model (Figure 6). The simulated results overestimated the observed OH concentration, with the daytime average $R_{S/O}$ of 2.42 (Figure 7)

for these 4 days (range 2.08 to 3.11; Figure 6). The coastal air masses showed statistically significant ($p < 0.05$) lower NO_x (−63%), AVOCs (−47%), BVOCs (−50%), OVOCs (−23%), and CO (−31%) concentrations compared with the continental cases (Figure 7, Table S3). The HO_2 and NO reaction was still the dominant source (69%) of OH in the coastal air masses, like in the continental air mass cases, but in a lower proportion than on continental days due to the lower NO concentration (Table 2 and Figure S3). The other major OH sources were O_3 photolysis (13.8%), HONO photolysis (7%), and the reaction between ozone and HO_2 (4%).

The simulated daytime average HO_2 concentration was $3.4 \pm 1.7 \times 10^8$ cm^{-3} for the coastal cases (RUNBase, Figure S4), which was $\sim 1.2 \times 10^8$ cm^{-3} higher than the value in the continental polluted air mass. The simulated HO_2 level is comparable to the measured value at a rural site in Heshan (3×10^8 cm^{-3}, Tan et al., 2019). The HO_{2_SIM}/OH_{OBS} was 218 in coastal cases, higher than the ratio in continental cases. This could be explained by the lower NO concentration in the coastal cases that slows the recycling reaction of HO_2 back to OH (R4 and R5) (Sommariva et al., 2004; Shirley et al., 2006; Chen et al., 2010).

The simulated OH reactivity was 4.7 ± 0.58 s^{-1} on average for the coastal cases (Figure S5b), which was lower than that of the continental polluted air mass (8.1 ± 1.0 s^{-1}). As discussed below in Section 3.3, low OH reactivity could have been the cause of the model's overestimation of OH concentrations in the coastal cases. The model's overestimation of OH in coastal air masses indicates gaps in our knowledge about the OH budget in relatively clean conditions with low NO_x and VOCs.

3.2.3 The 10 October case day

During the day on 10 October, our site received continental air masses between sunrise and noon and coastal air masses between noon and sunset. This served as another case that could be used to check the model's performance on continental versus coastal air masses within the same day. On 10 October, the $R_{S/O}$ changed from 1.20 in the morning to 2.59 in the afternoon, driven by the air mass drift during continuous measurement without interruption (Figure 8). As with the continental and coastal results shown above, the afternoon of 10 October showed significantly ($p < 0.05$) lower concentrations of NO

(−50%), NO_2 (−68%) and the reactivity of AVOCs (−42%), BVOCs (−27%), and OVOCs (−12%) compared with the morning (Table S3). With lower NO, the fraction of OH produced from HO_2 and NO reaction was also lower in the afternoon (65%) than in the morning (73%; Table 2 and Figure S3). Similarly, the simulated total OH reactivity was lower in the afternoon (7.6 ± 2.3 s^{-1} on average) than in the morning (10.3 ± 1.6 s^{-1} on average; Figure S5c). The simulated HO_2 was $3.6 ± 2.4 × 10^8$ cm^{-3} in the morning when continental air mass dominated and was $5.6 ± 1.9 × 10^8$ cm^{-3} in the afternoon when coastal air mass dominated (RUNBase, Figure S4). The HO_{2_SIM}/OH_{OBS} was 142 in the morning and up to 476 in the afternoon. Again, higher HO_2 concentration and HO_{2SIM}/OH_{OBS} ratio were shown with low NO concentration.

3.3 Discussion on the model–observation discrepancy

As discussed in the introduction, the model's overestimation of OH could have been caused by multiple factors, including uncertainties in OH measurements and modelling, overestimation of OH sources, and underestimation of OH sinks. Below, we discuss possible their roles in the study.

3.3.1 Uncertainties in OH measurement and simulation

The OH measurement uncertainties have been calculated as described in Section 2.2 and are shown as the error bars in Figures 5 and 6. The model's overestimation of OH in coastal air masses exceeded the measurement uncertainties (Figures 6 and 7), and thus, the measurement uncertainty is unlikely to be the main reason for the discrepancy.

Model uncertainties in our study include the uncertainties in photolysis frequencies correction, uncertainties in the constrained VOCs concentrations when they were below detection limits, and uncertainties from not considering halogen chemistry. On the first possibility, we acknowledge that the correction factor for photolysis frequencies due to cloud presence may be different for different species (Walker et al., 2022), thus, using a single correction factor (based on J_{NO2}) may introduce uncertainty in the model simulations. We think such uncertainty should not be significant because the weather was mostly sunny in the coastal cases. Regarding the uncertainty from the VOCs input, we conducted a sensitivity test to show that the treatment of VOCs that were below the detection limits should have a

negligible effect on OH simulation (RUN_{VOC0} and RUN_{VOCDL} in Figure S4). We did not include halogen chemistry in our study as we wanted to compare our results with previous modelling work most of which did not consider halogen chemistry. Our other studies at the same site that did consider the halogen chemistry show a 4% increase in OH concentration from Cl chemistry (Peng et al., 2022) and 2.8% from Br chemistry (Xia et al., 2022), which would even increase the model-measurement in the coastal air mass discrepancy.

3.3.2 Overestimation of OH sources

Our calculated OH budgets show that the main sources of OH in the coastal air masses were the $HO_2 +$ NO reaction (69%), O_3 photolysis (14%), HONO photolysis (7%), and the reaction between ozone and HO_2 (4%). In the simulation, NO, HONO, and O_3 were constrained by observations. Could HO_2 be overestimated which would cause overprediction of OH?

The main HO_2 sources are the VOCs oxidation by OH and the photolysis of OVOCs. In our study, VOCs and OVOCs were more likely under-measured than over-measured, which would underpredict HO_2 rather than overpredicting it. In addition, not including the halogen chemistry would under-simulate HO_2 at this site (Peng et al., 2022; Xia et al., 2022).

We next examine the possibility of the underestimation of HO_2 sinks as the cause of the overprediction of OH. The major sinks of HO_2 include the reaction of NO to recycle OH, self-reaction to form H_2O_2, and heterogeneous loss by aerosol uptake. The first and second pathways have been considered in the MCM. The heterogeneous uptake of HO_2 onto aerosol was also included in our simulations with an uptake coefficient of 0.1. We conducted a sensitivity run by increasing the aerosol uptake of HO_2 ($RUN\gamma_{MAX}$, Figure S4). Even when we set the uptake coefficient to unity (which is unlikely large), the simulated HO_2 concentration would decrease by 34% and the simulated OH $R_{S/O}$ would decrease to 1.73 from 2.42 in the base case. This indicates that the heterogeneous uptake of HO_2 is not the cause of the overestimation of OH in the coastal case. In summary, the discrepancy in modelled and observed OH in coastal cases is unlikely to be due to the overestimated HO_2.

3.3.3 Possible missing OH reactivity.

Based on the above discussions, we propose that the model's overestimation of OH could have been caused by unmeasured species that were not included in the model as OH sinks. We attempt to estimate the magnitude of possible OH sinks and investigate which factors could be important to these sinks. We added an artificial loss reaction into the model with the reactivity of k_{miss} (s^{-1}) and assumed that the reaction product would not participate in further reactions. Assuming a pseudo-steady state of OH during the daytime (P = k[OH]), k_{miss} was calculated as follows:

$$k_{miss} = \frac{P_{constrain}}{[OH_{obs}]} - \frac{P_{constrain}}{[OH_{sim}]} \quad \text{(E9)}$$

where $P_{constrain}$ is the model's calculated OH production rates, with OH constrained by observations; $[OH_{obs}]$ is the observed OH concentration; and $[OH_{sim}]$ is the OH concentration simulated in RUNBase. After introducing the OH sink with k_{miss} into the model, the model better reproduced the observed OH concentrations on the coastal case days, with daytime $R_{S/O}$ close to unity (RUNKmiss Figure S6). The average daytime k_{miss} for the coastal cases was 5.0 ± 2.6 s^{-1}, which larger than the total calculated reactivity in coastal cases (4.7 ± 0.58 s^{-1}). The calculated k_{miss} could be a lower limit of the possible missing source as the products from the reactions of OH with unknown species are most likely to further react with the missing source to produce RO$_2$ and HO$_2$ and recycle back to OH.

We next explored the dependence of k_{miss} on different trace gases. Figure 9a shows the correlation between k_{miss} and NO concentration for the nine case days (including 10 October) between 09:00 and 15:00. At NO > 0.5 ppb, k_{miss} is close to zero. At NO < 0.5 ppb, k_{miss} tended to increase with decreasing NO. Similarly, k_{miss} approached zero at high concentrations of NO$_2$ (> 2.5 ppb), TEXs (> 0.25 ppb), and AVOCs (> 5 ppb; Figure 9) and increased with decreasing concentrations of NO$_2$, TEXs, and AVOCs. High k_{miss} also typically occurred at low toluene/benzene ratios and low C$_2$H$_2$/CO ratios (Figure 9), which are indicators of an aged air mass (Xiao et al., 2007; Kuyper et al., 2020).

Therefore, while we cannot completely rule out other possibilities, we argue that the aged coastal air masses could have contained unmeasured species such as oxygenated organic molecules (OOMs; Nie et al., 2022) and ocean-emitted gases (Thames et al., 2020) that contributed to the missing OH reactivity, causing the model to overestimate OH concentrations on the coastal case days.

4. Summary and conclusion

In this study, we measured OH concentrations using CIMS at a coastal site in Hong Kong in the autumn of 2020 to gain insights into the atmospheric oxidative capacity and to evaluate the performance of a box model in the coastal atmosphere. The daily maximum OH concentration ranged from 2.1 to 15.4 $\times$ 10^6 cm^{-3} over the whole campaign, with an average of 4.9 $\pm$ 2.1 $\times$ 10^6 cm^{-3}. The air masses were categorized into two groups based on their backward air trajectories: (1) continental air masses, which contained high concentrations of NO$_x$ and VOCs, and (2) coastal air masses, which contained low concentrations of NO$_x$ and VOCs. The observed OH concentration in the continental air parcels was on average 52% higher than in the coastal air parcels. The F0AM box model with comprehensive observational constraints generally reproduced the observed OH in the continental cases during the daytime, with a simulated/observed OH ratio (R$_{S/O}$) of 1.14 on average. However, the model significantly overestimated OH concentrations in the coastal cases, with an R$_{S/O}$ of 2.42 on average during the daytime. While we cannot completely rule out other possibilities, we incline to attribute this overestimation to a missing OH reactivity in the aged coastal air parcels that were not accounted for in the model. The lower limit of the missing OH reactivity was estimated at 5.0 $\pm$ 2.6 s^{-1} on average between 09:00 and 15:00 and was especially larger under low NO$_x$, low AVOCs, and aged air conditions. We hypothesize that unknown products from AVOC oxidation or unknown OH-reacting gases emitted from oceans could contribute to the missing OH reactivity in aged coastal air masses. The overestimation of OH in the model could cause an overestimation of the formation of secondary aerosols, such as sulfate and nitrate, while the impacts would be even more complicated if it is due to missing chemical species which participated in ozone formation. Further studies are necessary to pin down the exact cause(s) of the OH overestimation by concurrently measuring HO$_2$ and OH reactivities, VOC oxidation products, and ocean-emitted trace gases.

Data availability. All of the data used to produce this paper can be obtained by contacting Tao Wang (two.wang@polyu.edu.hk).

Supplement. The online supplement for this article is available at:

Author contributions. TW initially conceived the project. TW and ZW planned and organized the overall field campaign at Hok Tsui. ZZ conducted the OH measurements using CIMS, with contributions from TW and ZW. YC performed the aerosol size distribution measurements. YQ performed the OVOC measurements using PTR-MS. MX and YC performed the HONO measurements using ToF-CIMS. YW assisted with HONO calibration. ZZ performed the box model analysis and sensitivity test with contributions from EX and QC. ZZ, TW, and QC analyzed the data and interpreted the results, with contributions from MX. ZZ, TW, and QC wrote the paper. All of the authors reviewed and commented on the paper.

Competing interests. One author (Tao Wang) is a member of the editorial board of Atmospheric Chemistry and Physics. The peer-review process was guided by an independent editor, and the authors have no other competing interests to declare.

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Figures and Tables

Figure 1. The location of the Hok Tsui Air Monitoring Supersite in Hong Kong, South China.

The map is from © Google Earth.

Table 1. Measuring instruments and measured species in the field campaign

Species	Instruments	Time Resolution	Detection Limit	Accuracy (1σ)
NO, NO$_2$	Chemiluminescence/photolytic converter (Thermo, Model 42i)	1 min	60 ppt	NO: ± 5.2% NO$_2$: ± 15.2%
OH	Nitrate-quadrupole chemical ionization mass spectrometer (CIMS)	10 s	Lab: 1.5×10^5 cm^{-3} Daytime: 1×10^6 cm^{-3}	± 44%
Ozone	Ozone analyzer, model 49i, Thermo Scientific	1 min	0.5 ppb	± 6.0%
JNO$_2$	Filter Radiometer, Metcon	1 min	4×10^{-5} s^{-1}	± 10%
HONO	Iodide-Tof-CIMS, Aerodyne Inc	1s	0.2 ppt	± 15 %
SO$_2$	Pulsed Fluorescence SO$_2$ Analyzer (Thermo, Model 43i)	1 min	1 ppb	± 6.1%
CO	Gas Filter Correlation CO Analyzer (Thermo, Model 48i)	1 min	40 ppb	± 7.4%
NH$_3$	Chemiluminescence NH$_3$ Analyzer (Thermo, Model 17i)	2 mins	1 ppb	± 8%
Particle number size distribution	Scanning mobility particle sizer, TSI	5 mins	1 particle cm^{-3}	± 10%
VOCs	GC-MS/FID (GC955 Series 611/811, Syntech Spectras)	1 hour	~10 ppt	± 20%
	PTR-MS (PTR-QMS 500, IONICON Analytik, Austria)	5 mins	20 ppt	± 20%
OVOCs	PTR-Tof-MS, IONICON Analytic;	1 s	~10 ppt	± 15%

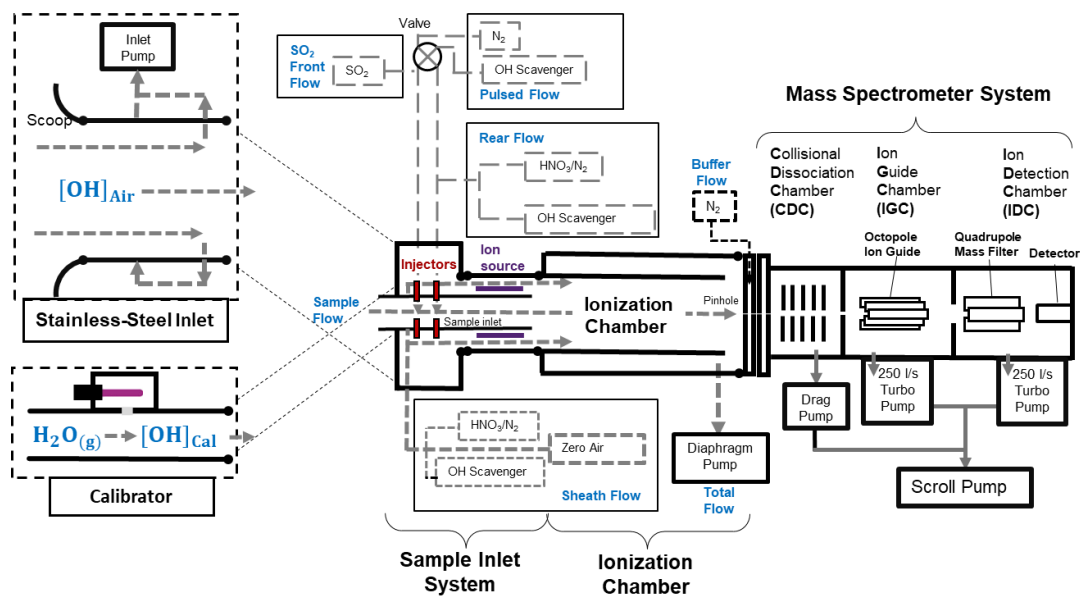



Figure 2. Schematics of the CIMS system which consists of a stainless-steel inlet, a sample inlet, an ionization chamber, a mass spectrometer system, and a calibration unit. The CIMS measures the ambient OH concentration when connecting to the stainless-steel inlet whereas, during calibration, the calibration unit is connected to the CIMS instead. Details of the setup, calibration and optimization of the CIMS can be found in the Supplementary.

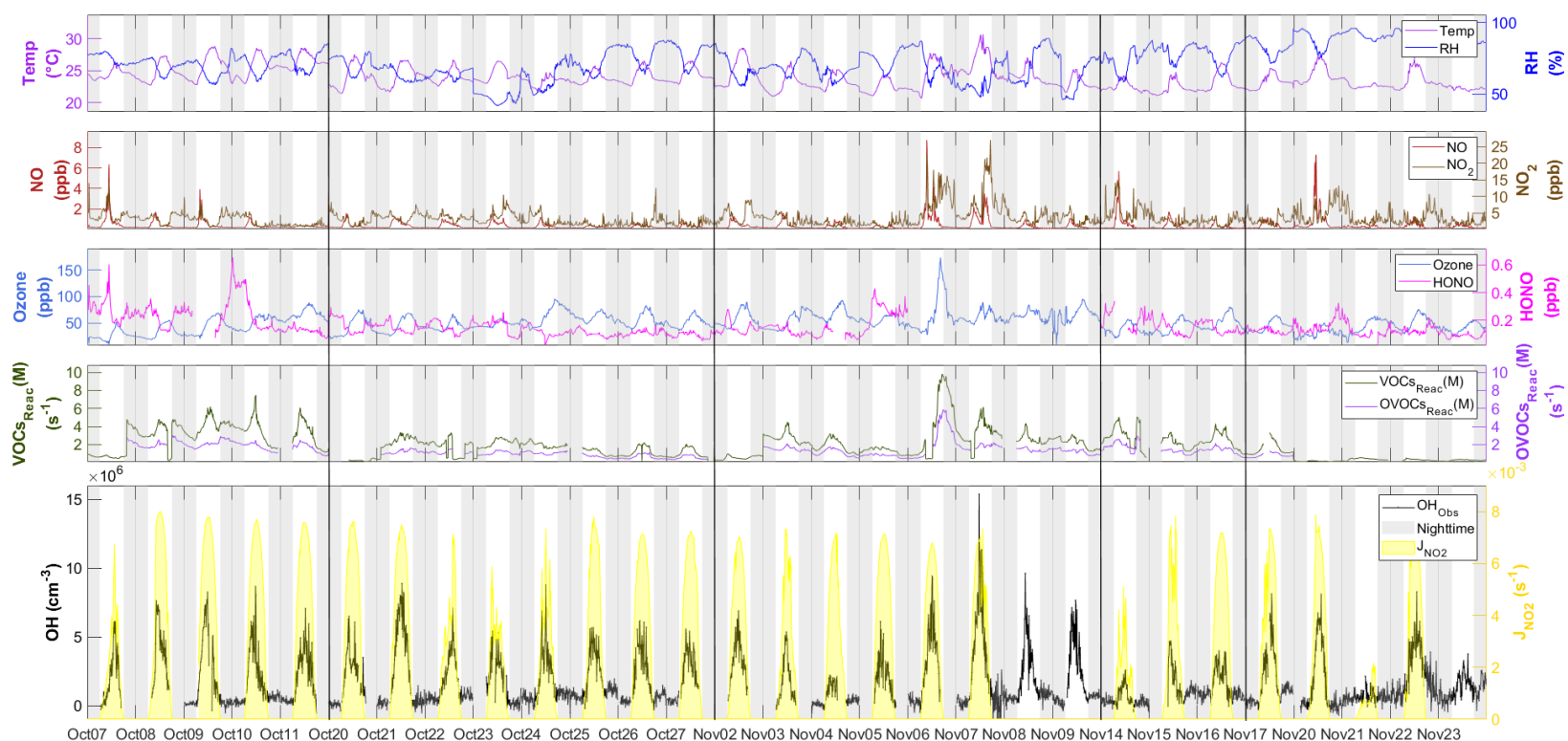



Figure 3. Time series of OH between 7 October and 23 November with measured weather conditions (temperature and RH), OH primary sources (ozone and HONO), NO_x (NO and NO_2), reactivity of measured VOCs and OVOCs ($VOCs_{Reac}(M)$ and $OVOCs_{Reac}(M)$), and photolysis frequency (J_{NO2}). All measurement data shown are 10 min averages. The gaps of the data were due to the calibration or instrument maintenance. The black lines separate the non-continuous days during measurement. The grey shaded area denotes night-time. The time zone was local time (+8 UTC) for the x-axis.

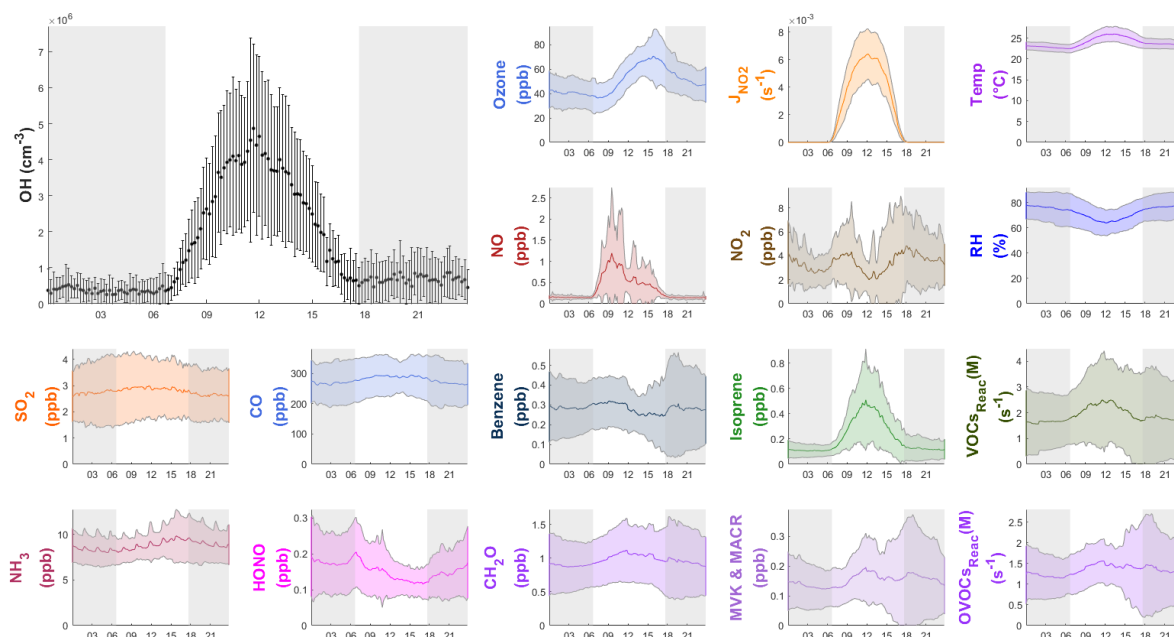



Figure 4. Diurnal profiles of the average (±1σ) concentrations of OH, other chemical species, the measured VOCs reactivity and OVOCs reactivity (VOCs$_{Reac}$(M) and OVOCs$_{Reac}$(M)), and meteorological parameters (T, RH, J_{NO2}) during the field campaign. The grey shaded area denotes night-time. The error bars and shaded error bars are the standard deviation of the averaged data.

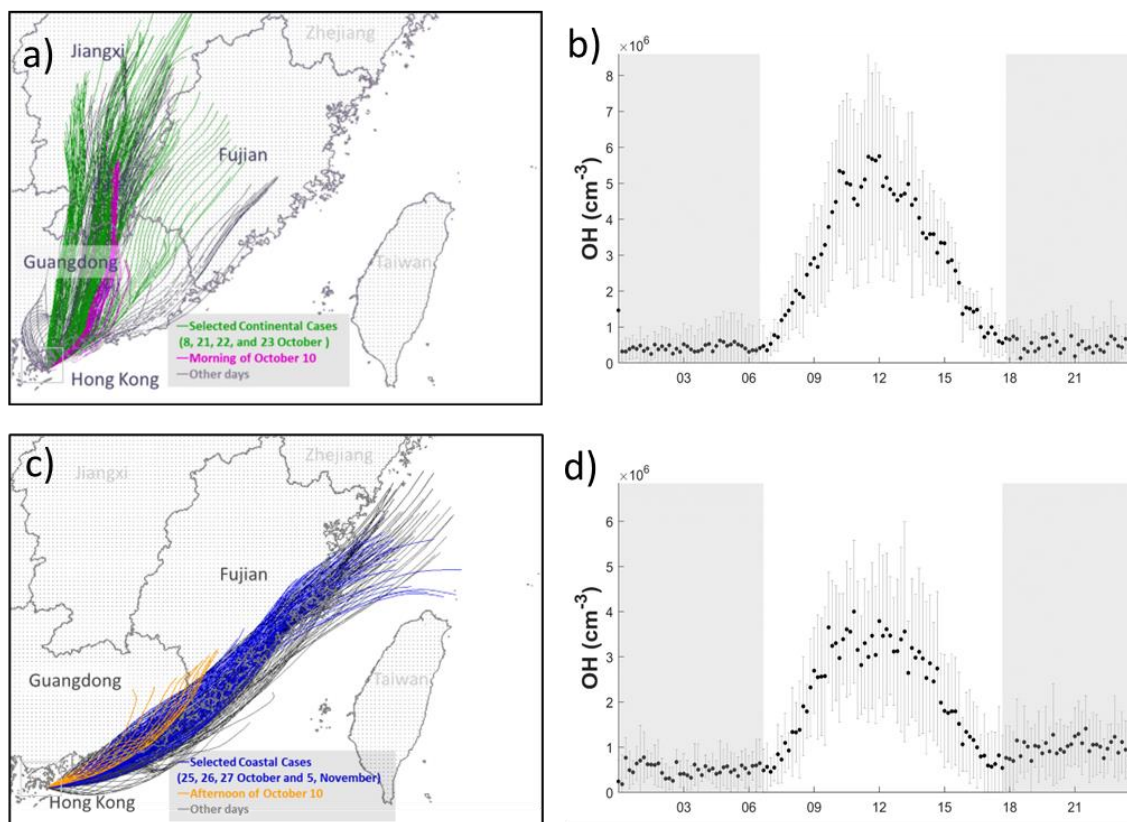
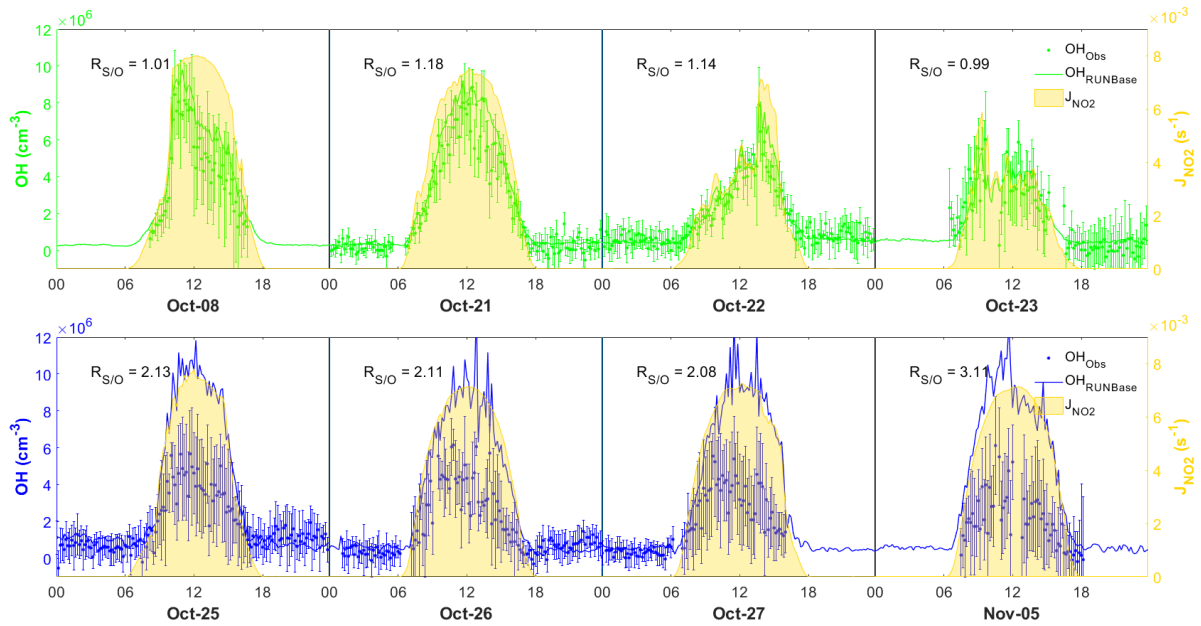



Figure 5. 24 h back trajectories of the continental (a) and coastal (c) cases over the whole measurement

1 period. The selected days for coastal, continental, and mixed cases are labelled in different colours. (b)

2 and (d) show the average concentration of OH with standard deviation in continental and coastal air

3 masses, respectively. The error bars and shaded error bars are the standard deviation of the averaged

4 data.

7 Figure 6. Comparison between observed (dots) and simulated (lines) OH in the four continental cases

8 (top panel) and the four coastal cases (lower panel), also showing measurement uncertainty (error bars)

9 and J_{NO2} measurement (yellow shades). The time zone was local time (+8 UTC) for the x-axis.

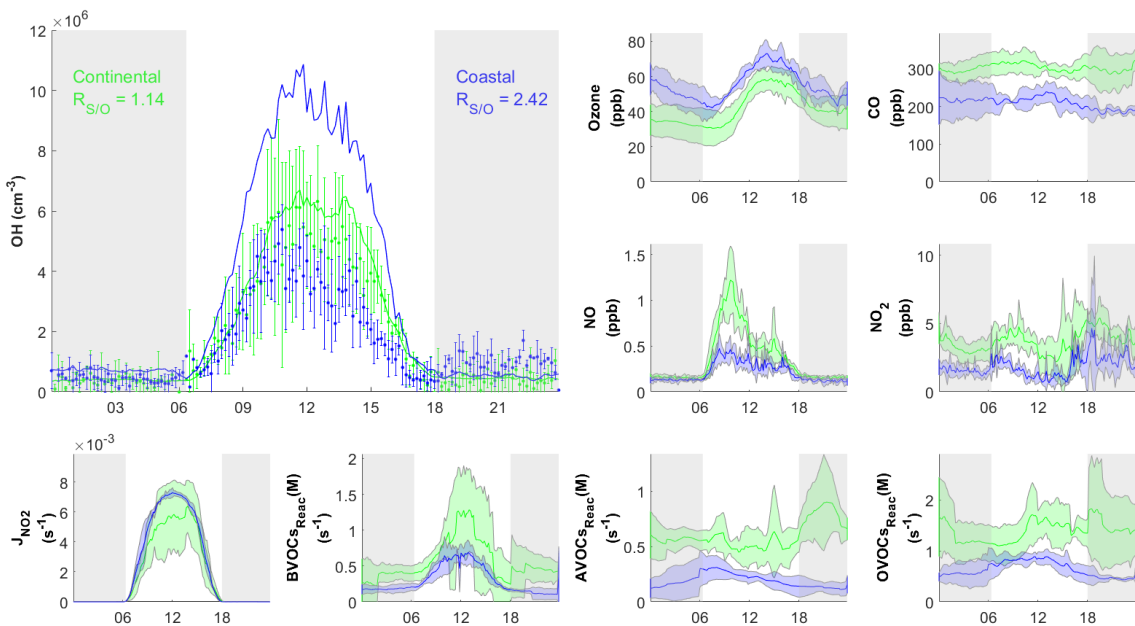



Figure 7. Diurnal profiles of average concentrations of measured (dots) with standard deviation and simulated (RUNBase, line) OH concentration, important trace gases and the measured BVOCs, AVOCs, OVOCs reactivity ($BVOCs_{Reac}(M)$, $AVOCs_{Reac}(M)$ and $OVOCs_{Reac}(M)$) for selected cases in continental (green) and coastal (blue) air masses. The grey shaded area denotes night-time. The error bars and shaded error bars are the standard deviation of the averaged data.

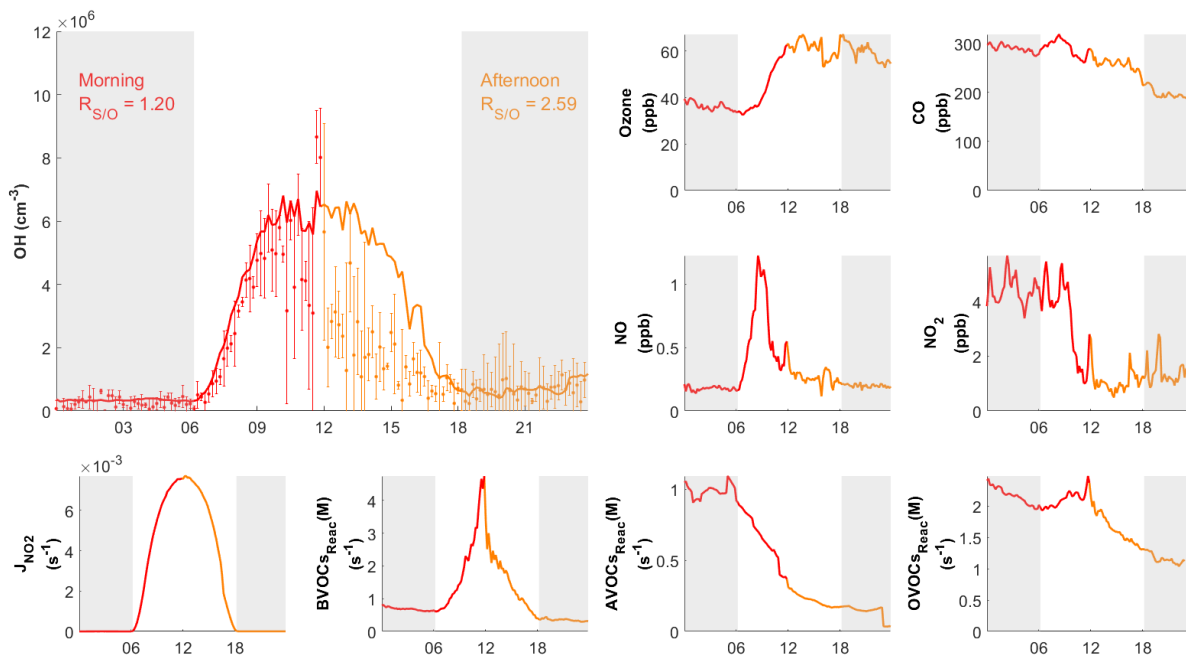



Figure 8. Diurnal profiles of measured (dots) with measurement uncertainty (error bars) and simulated (RUNBase, line) OH on 10 October 2020, with other chemical species and the measured BVOCs, AVOCs, OVOCs reactivity ($BVOCs_{Reac}(M)$, $AVOCs_{Reac}(M)$ and $OVOCs_{Reac}(M)$). The air mass drifted from continental (red) in the morning to coastal (orange) in the afternoon. The grey shaded area denotes night-time. The time zone was local time (+8 UTC) for the x-axis.

1 Table 2. OH budgets for the selected continental and coastal cases, morning and afternoon of 10

2 October.

Continental Case		Coastal Case		Oct 10 Morning		Oct 10 Afternoon	
Production							
$HO_2 + NO$	77.66%	$HO_2 + NO$	69.02%	$HO_2 + NO$	73.17%	$HO_2 + NO$	65.11%
$O^1D + H_2O$	7.98%	$O^1D + H_2O$	13.80%	$O^1D + H_2O$	10.73%	$O^1D + H_2O$	15.04%
HONO + hv	5.78%	HONO + hv	7.32%	HONO + hv	8.65%	HONO + hv	7.16%
$HO_2 + O_3$	1.97%	$HO_2 + O_3$	3.60%	$HO_2 + O_3$	1.70%	$HO_2 + O_3$	3.80%
DM23BU2ENE + O_3	1.59%	ME2BUT2ENE + O_3	1.40%	H_2O_2 + hv	0.52%	H_2O_2 + hv	1.63%
Other	5.02%	Other	4.85%	Other	5.23%	Other	7.25%
Loss							
CO	19.91%	CO	23.39%	C_5H_8	15.96%	C_5H_8	15.38%
NO_2	9.38%	C_5H_8	8.17%	CO	14.68%	CO	13.72%
C_5H_8	9.09%	C_2H_5CHO	7.44%	CH_3CHO	8.76%	C_2H_5CHO	10.64%
C_2H_5CHO	7.96%	CH_3CHO	6.97%	C_2H_5CHO	8.31%	CH_3CHO	7.52%
CH_3CHO	7.94%	NO_2	6.27%	NO_2	5.70%	HCHO	3.44%
CH_4	3.68%	CH_4	5.91%	CH_4	3.04%	NO_2	3.33%
HCHO	2.79%	HCHO	2.50%	HCHO	3.03%	CH_4	3.06%
ACR	1.41%	O_3	2.04%	ACR	1.65%	ACR	1.71%
HOCH2CHO	1.36%	H_2	1.71%	$HOCH_2CHO$	1.61%	$HOCH_2CHO$	1.71%
Other	36.48%	Other	35.61%	Other	37.27%	Other	39.50%

3 Notes: The H_2 concentration were constrained as 550 ppb in the model simulation.

4 The H_2O_2 were simulated by model with averaged concentration at 0.95 ppb.

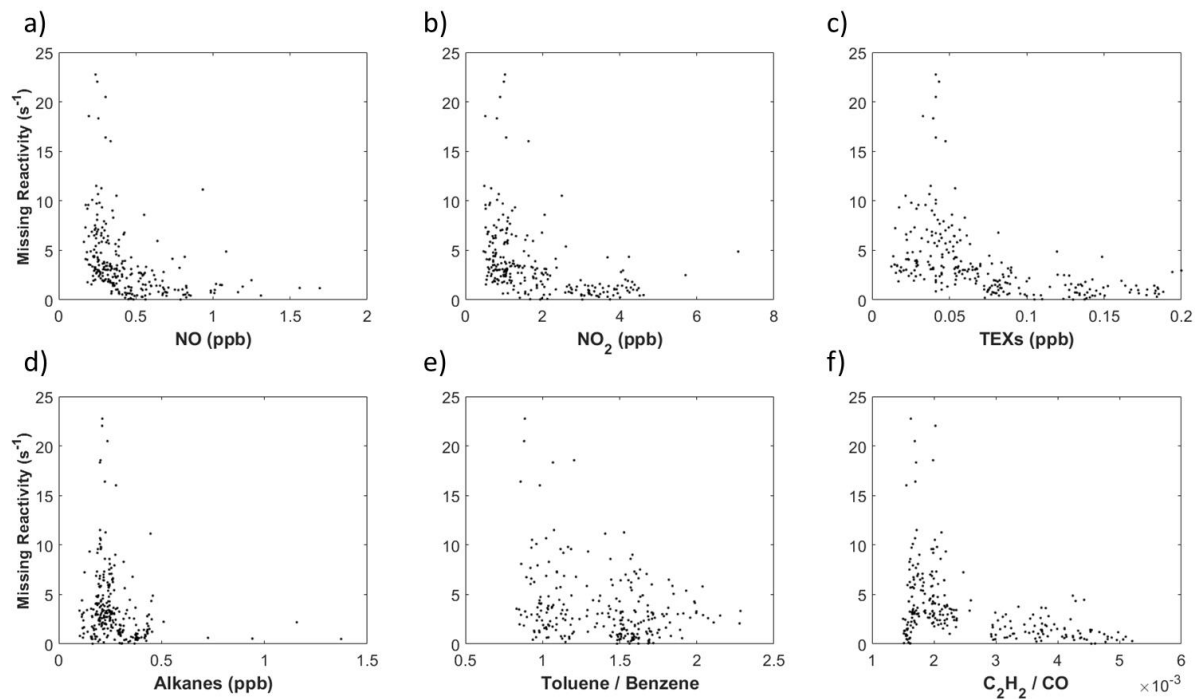
5 ACR- acrolein   HCHO: Formaldehyde

6 C_5H_8: Isoprene $HOCH_2CHO$: Glycolaldehyde

7 C_2H_5CHO: Propanol CH_3CHO: Acetaldehyde

8 ME2BUT2ENE: 2-Methyl-2-butene   DM23BU2ENE: 2,3-Dimethyl-2-butene

9 Other represents the group of the species contribute less than 2% to the total OH reactivities. Most of

10 them were the intermediate species produced by the reaction of OH with VOCs.

2 Figure 9. The dependence of calculated missing reactivity on a) NO, b) NO$_2$, c) TEXs (toluene,

3 ethylbenzene, and xylenes), d) alkanes (C$_2$ to C$_8$), e) the ratio of toluene to benzene, and f) the ratio of

4 C$_2$H$_2$ to CO.

Supplementary Information

3   Figure S1. OH measurements gathered around the world to date.

Table S1. Summary of studies reporting OH and HO$_2$ measurements and comparing them with model predictions (refer to Figure S1 for site locations)

Comparison results (OH only)	Reference	Time	Location in Figure 1	Site types	Measurement notes	OH conc. 10^6 cm^{-3}	HO$_2$ conc. 10^8 cm^{-3}	Ratio notes	OH R$_{S/O}$	HO$_2$ R$_{S/O}$	Other references targeting the same site
Overprediction	Berresheim et al., 2002	June–July 1999	MaceHead	Coast	Mean (All) Peaks (Mean Clean) Peaks (Pollution)	0.12 2.5 18 & 12	N/A	Mean (17 June, Coastal) Mean (30 July, Continental)	2 ~1	N/A	Carslaw et al., 1999; Berresheim et al., 2013, 2014;
Overprediction	Sommariva et al., 2004; Creasey et al., 2003;	Jan–Feb 1999	Tasmania	Coast	Mean (Peaks) Peaks (Range)	3.5 2 to 5.5	2 1 to 2.5	Mean (7–8 Feb) Mean (15–16 Feb)	~1.11 ~1.32	N/A ~2	N/A
Overprediction	Kanaya et al., 2007	September 2003	Rishiri	Island Coast	Peaks (Mean)	2.7	1.45	OH rectified by constrained HO$_2$	1.35	1.89	N/A
Overprediction	Mauldin III et al., 2010	Nov–Jan 2003-04	AmundsenScott	Antarctica	Mean (Range)	1.5 to 2.5	N/A	Mean	~2	N/A	Mauldin III et al., 2001
Overprediction	Kukui et al., 2014	Dec–Jan 2011-2012	Concordia	Antarctica	Mean (All) Peaks (Mean) Mean (range)	3.1 5.2 0.3 to 7.5	0.99* 1.7* 0.1 to 2*	Mean (w/PSS HONO) Mean (w/measured HONO)	0.72 2.19	1.02* 1.84*	N/A
Overprediction	Dusanter et al., 2009a, b;	March 2006	MexicoCity	Urban	Peaks (Range) Peaks (Mean)	2 to 15 4.6	0.56 to 4.5 1.9	Mean (13:00 w/o glyoxal) Mean (Morning, polluted) Mean (11:00–14:30) Mean (After 14:30)	2.4 ~0.5 to ~1 1.7 ~1	1.5 0.2 to ~1 ~1 ~1	N/A
Overprediction	Bloss et al., 2007	Jan–Feb 2005	Halley	Polar	Mean (All) Peak (Mean)	0.39 0.79	2.04 4.03	Peak (S1: Conventional) Peak (S2: S1 + halogen oxides) Peak (S3: S2 + possible VOCs)	0.67 1.64 1.27	N/A	N/A
Overprediction	Holland et al., 2003	Jul–Aug 1998	Pabstthum	Rural	Peaks (Range)	6 to 8	5 to 7.4	Mean (Low NO$_x$)	2	1.4	N/A
Overprediction	Whalley et al., 2018	Jul–Aug 2012	Kensington	Urban	Mean (Noon; S-W air) Mean (Noon; E, polluted air)	~2.2 ~3	~0.2 ~0.5	Mean (Air mass: South-westerly) Mean (Air mass: Easterly, polluted)	1.25 2	~4 10	N/A
Overprediction	Griffith et al., 2016	May–June 2010	CalNexLA	Urban	Peaks (Range) Peaks (Weekdays) Peaks (Weekend)	1.5 to 9 ~4 ~5	0.8* to 10* ~3* ~8*	Mean (Weekend) Mean (Weekday)	1.43 1	0.77* 0.33*	Volz-Thomas et al., 2003b, a

Comparison results (OH only)	Reference	Time	Location in Figure 1	Site types	Measurement notes	OH conc. 10^6 cm^{-3}	HO$_2$ conc. 10^8 cm^{-3}	Ratio notes	OH R$_{S/O}$	HO$_2$ R$_{S/O}$	Other references targeting the same site
Underprediction	Hofzumahaus et al., 2009; Lu et al., 2012;	July 2006	BackGarden	Rural	Peaks (Mean)	15	15	Mean (Range, NO < 1 ppb) Mean (Lu et al., 2012)	0.2 to 0.33 0.5	N/A	N/A
Underprediction	Whalley et al., 2011	Apr–May 2008	DanumValley	Rainforest	Peaks (Mean)	2.5	3	w/C$_5$H$_8$ recycling mechanism (Peeters et al,. 2009)	~0.63	~0.5	Pugh et al., 2010
Underprediction	Liao et al., 2011	May–June 2007 Jun–Jul 2008	Summit	Polar	Mean (2007 spring) Mean (2008 summer)	3.0 4.1	2.7* 4.2*	2007 spring w/o BrO & w BrO 2008 summer w/o BrO & w BrO	0.72 0.78 0.54 0.56	0.87 0.96	Sjostedt et al., 2007
Underprediction	Wolfe et al., 2014	Aug 2010	Manitou	Forest	Peaks (Range)	3 to 10	24.6 to 44.3	Peak	~0.625	0.33	Kim et al., 2013
Underprediction	Tan et al., 2019	Oct–Nov 2014	Heshan	Suburban	Peaks (Mean)	4.5	3	Budget analysis only	N/A	1	N/A
Underprediction	Griffith et al., 2013	Jul–Aug 2008 Jul–Aug 2009	UMBS	Forest	Peak (Mean, 2008) Peak (Mean, 2009)	~3.3 ~1.6	~7 ~4.8	Mean (2008) Mean (2008 w/ISOP mechanisms) Mean (2009) Mean (2009 w/ISOP mechanisms)	~0.4 0.9	~0.57 ~1.3 ~0.6 ~1.5	N/A
Underprediction	Lu et al., 2013	Sept 2006	Yufa	Urban	Peaks (Range) Peaks (Mean)	4 to 17 ~7	2 to 24 ~1.5	Mean (NO < 0.1 ppb) Mean (NO > 1 ppb)	0.38 ~1	~1 ~1	N/A
Underprediction	Mao et al., 2012	Jun–Jul 2009	BFRS	Forest	Peaks (Mean w/ interference) Peaks (Mean w/o interference)	~4.5 ~1.8	N/A	Mean (w/ interference) Mean (w/o interference)	0.32 0.71	N/A	N/A
Underprediction	Tan et al., 2017; Lu et al., 2019	Summer 2014	Wangdu	Rural	Peaks (Range noontime)	5 to 15	3 to 14	Mean (NO > 0.3 ppb) Mean (NO < 0.3 ppb, afternoon)	~1 0.5	10 (NO > 4 ppb) N/A	N/A
Underprediction	Lew et al., 2020	Jul 2015	IURTP	Forest	Peaks (Mean)	4	10	Mean (Daytime) Mean (Evening and morning)	0.83 0.50	1.10 to 1.32	N/A
Underprediction	Lelieveld et al., 2008	Oct 2005	AmazonSuriname	Forest (Flight)	Mean (Forest boundary) Mean (Forest free troposphere) Mean (Atlantic boundary) Mean (Atlantic free troposphere)	5.6 8.2 9.0 10.1	10.5 4.9 6.7 5.5	Mean (w/MIM: Mainz ISOP mechanism) Mean (w/MIM2+: extra 40% to 80% OH recycle)	0.1 to 0.2 ~1	N/A	N/A

Comparison results (OH only)	Reference	Time	Location in Figure 1	Site types	Measurement notes	OH conc. 10^6 cm^{-3}	HO$_2$ conc. 10^8 cm^{-3}	Ratio notes	OH R$_{S/O}$	HO$_2$ R$_{S/O}$	Other reference targeting the same site
Well Matched	Ren, 2003b, a	Jun–Aug 2001	NewYork	Urban	Peaks (Range) Peaks (Mean)	2 to 20 7	0.5 to 6 1	Mean	0.91	0.81	N/A
Well Matched	Ren et al., 2006	Jul–Aug 2002	Whiteface	Forest	Peaks (Mean)	2.6	4.9	Mean	1.22	0.83	N/A
Well Matched	Kanaya et al., 2007b	Jan–Feb & Jul–Aug 2004	Tokyo	Urban	Peaks (Mean, winter) Peaks (Mean, summer)	1.5 6.3	0.27 1.4	Peaks (Mean, winter) Peaks (Mean, summer)	0.99 0.81	0.71 1.22	N/A
Well Matched	Feiner et al., 2016; Kaiser et al., 2016;	Jun–Jul 2013	Alabama	Forest	Peaks (Mean)	1	6.64	Peaks (Mean)	~1	~1	N/A
Well Matched	Jeong et al., 2022	Feb–Mar 2014	AmazonBrazil	Forest	Peaks (Mean 10:00-15:00) Peaks (Range)	1 ~1 to ~2.8	N/A	Mean	1	N/A	N/A
Well Matched	Hens et al., 2014	Summer 2010	Hyytiälä	Forest	Mean (Above-Canopy) Mean (Ground)	3.5 ~1.8 to ~1.2	N/A	Mean	1	0.3	Petäjä et al., 2009; Novelli et al., 2014;
Well Matched	Emmerson et al., 2007	Jul–Aug 2003	WrittleCollege	Urban	Peaks (Range)	1.2 to 7.5	0.16 to 3.3	Mean	1.24	1.07	N/A
Well Matched	Ren et al., 2013	Apr–May 2009	Houston	Urban	Peak (Mean)	~8.8	~6.2	Mean	0.9	1.22	Mao et al., 2010; Chen et al., 2010;
Well Matched	Ma et al., 2019	Nov–Dec 2017	PKU	Urban	Peaks (Mean clean) Peaks (Mean polluted)	2 1.5	0.4 0.3	Mean (clean) Mean (polluted)	~1 ~0.66	~0.66 0.08	N/A
Well Matched with missing source	Whalley et al., 2021	Summer 2017	IAP	Urban	Peak (All)	28	10	Mean (NO < 1 ppb)	~1	1.83	Slater et al., 2020
Well Matched with underpredicted HO$_2$	Zhang et al., 2022b	Nov–Dec 2019	Shanghai	Urban	Peaks (Mean)	2.7	0.8	N/A	N/A	N/A	N/A
No comparison	Kukui et al., 2008	June–July 2007	Grignon	Suburban	Peak (July 6)	~23	~2	N/A	N/A	N/A	N/A
No comparison	Wang et al., 2021	Oct–Nov 2018	PKUSZ	Suburban	Peaks (Mean)	5.3	4.2	N/A	N/A	N/A	Wang et al., 2019
No comparison	Rohrer and Berresheim, 2006	1999–2003	MOHp	Rural	Mean (All)	1.97	N/A	N/A	N/A	N/A	Handisides, 2003; Novelli et al., 2014;
No comparison	Zhang et al., 2022a	Aug–Sept 2019	Chengdu	Urban	Peaks (Range, PKU-LIF) Peaks (Range, AIOFM-LIF)	1.6 to 15 2.1 to 15.9	N/A	N/A	N/A	N/A	N/A

 Notes:

 ISOP: Isoprene.

1	AIOFM:	Laser- induced fluorescence instrument by the Anhui Institute of Optics Fine Mechanics, Chinese Academy of Sciences.
2	Mean:	Campaign average concentration or ratio.
3	Peak:	Campaign maximum concentration or ratio.
4	Peaks (Mean):	Maximum concentration or ratio for the averaged diurnal or averaged cases.
5	Mean (Range):	Daily average concentration or ratio range for the campaign or cases.
6	Peaks (Range):	Maximum concentration or ratio range for the campaign or cases
7	w/ and w/o:	Considered or did not consider the specific mechanism, species, or interference.
8	~:	The result is based on the figure or description, and the exact number is not mentioned in the article.
9	N/A:	Not available in the article
10	*:	The HO_2 result includes some RO_2 species.

Calibration

The calibration was performed by applying the calibrator shown in Figure 3 to the CIMS. The calibration flow passes through the water bubbler and carries H_2O. When the humid calibration flow is exposed to the Pen Ray mercury lamp (Analytik Jena, UVP Pen Ray), the OH radicals produced by H_2O photolysis as shown below:

$$H_2O + hv(184.9\ nm) \rightarrow H + OH \hspace{3cm} (SR1)$$

The OH concentration ([OH]) produced by the calibrator is calculated by SE1.

$$[OH] = [H_2O] * \sigma_{H_2O} * \Phi * It \hspace{3cm} (SE1)$$

[H_2O] is the water concentration in the calibration flow which is calculated from the temperature, saturated water vapor pressure, and relative humidity. σ_{H_2O} (= 7.14×10^{-20} cm^2; (Cantrell et al., 1997) is the photolysis cross-section of water vapor, while Φ represents the photolysis quantum yield and was assumed to be 1 (Kürten et al., 2012). The photon flux (It) was determined using the chemical actinometry method. This method measures the mixing ratio of N_2O and its photolysis products to determine the product It value of the lamp in the calibrator while the N_2O photolysis and H_2O photolysis require the same photon intensity (184.9 nm). The reactions and equations of It determination were presented by (Kürten et al., 2012). In this study, the It values were measured before and after the field campaign and no significant difference was found.

By calculating the [OH]$_{CAL}$ produced by the calibrator, the signal response to OH (TS_{97} - BS_{97}), and reagent ion (S_{62}), the calibration factor (C) can be calculated by following the equation which was transformed from E1.

$$C = \frac{1}{[OH]_{CAL}} \times \frac{TS_{97} - BS_{97}}{S_{64}} \hspace{3cm} (SE2)$$

Detection limit

The detection limit can be calculated as follows,

$$DL = \frac{1}{C} \times \frac{n * \sigma_{BS97}}{S_{64}} \hspace{3cm} (SE3)$$

Where DL is the detection limit in 10^6 molecule/cm^3, C is the calibration factor, and n is the ratio of signal to noise S/N. σ_{BS97} represents the standard deviation of the signal intensity of HSO_4^- at 97 m/z when the scavenger was added through front injectors, and S_{64} represents the

signal intensity of NO_3^- at 64 m/z. Figure 8 shows the concentrations of OH radicals and the corresponding detection limit (S/N=2, average time=6 minutes) in the laboratory. The detection limit was quite stable over the whole day and ranged from 0.08 to 0.20 $\times 10^6$ molecule cm^{-3}, with an average value of approximately 0.15 $\times 10^6$ molecule cm^{-3}.

Uncertainty calculation

The uncertainty of the instrument is calculated by the rules for propagation for the uncertainty.

Propagation Rules for Addition ($y = x_1 + x_2$): $\qquad\qquad e_y = \sqrt{e_{x1}^2 + e_{x2}^2}$ $\qquad\qquad$ (SE4)

Propagation Rules for Multiplication ($y = x_1 \times x_2$): $\quad \dfrac{e_y}{y} = \sqrt{\left(\dfrac{e_{x1}}{x_1}\right)^2 + \left(\dfrac{e_{x2}}{x_2}\right)^2}$ $\qquad$ (SE5)

Where e_y, e_{x1}, e_{x2}, are the absolute uncertainty for y, x_1, and x_2.

Calibration Uncertainties

The calibration uncertainty is calculated by the uncertainties of all the parameters involved in the SE2 which includes the uncertainty of calculated OH radicals concentration and the precision of the measurements of signal at 64 m/z and 97 m/z. Due to the equation SE1, the uncertainty of OH radical ($[OH]_{CAL}$) will further be contributed by the uncertainty of It ~36%, σ_{H_2O} (~5%), ϕ_{H_2O} (<1%, Cantrell et al. 1997), and calculated water concentration based on the measured Temperature and relative humidity (~10%). The precision of the measurements signal at 64 m/z and 97 m/z ($\frac{TS_{97} - BS_{97}}{S_{64}}$) of the CIMS instrument (2σ) was 11% (for 6 min integration time). Considering all the above uncertainties and calculated by the rules (SE3 and SE4), the overall uncertainty for the calibration factor can be calculated by the well-known uncertainty formula. The uncertainty for the calibration factor was about 38% in this study.

Sensitivity optimization

The sensitivity (S) of the CIMS instrument to the OH radicals depends on the conversion efficiency of OH to H_2SO_4 in the chemical conversion region (E_{Conv}), the ionization efficiency of H_2SO_4 to HSO_4^- in chemical ionization region (E_{Ion}), and the ion-transmitted efficiency of HSO_4^- from sample inlet to mass spectrometer system (E_{Trans}):

$$S \sim E_{Conv} \cdot E_{Ion} \cdot E_{Trans}$$

E_{Conv} is dependent on the reaction time and the SO_2 concentration of the conversion reactions (R1-3). However, the conversion time has to be relatively short (<1s) to avoid the interference of HO_2 recycling as mentioned by Berresheim et al. (2000). E_{Ion} is affected by the flow dynamics, which determines the mixing of flows, and the electric field inside the ionization region, which forces the $NO_3^- \cdot (HNO_3)_m \cdot (HO_2)_n$ primary ions to the center of the region for H_2SO_4 ionization. E_{Trans} is related to the N_2 buffer and induces an electric field in the pinhole area. On the other hand, E_{Trans} is proportional to the transmission of the neutral molecule and particles from sampling air to the mass spectrometer system which deteriorates the measurement and damages the mass spectrometer. Thus, the optimization should take both transmission efficiency and protection function into consideration.

In this study, the CIMS was optimized before the field campaign. The detailed specification was shown in Table S1. To maximize the E_{Conv}, 5 sccm SO_2 was added from the front injectors to the sample flow and the $[SO_2]$ was around 12 ppm in the sample flow. The sample flow was 3727 sccm and the sample flow rate was 55 cm/s which means the reaction time for OH conversion is around 47 ms.

The reaction time affects the positive bias of OH arising from HO_2 + NO in the inlet. To estimate this bias, Tanner et al., (1997) calculated the OH produced by the HO_2 recycling reaction under different NO conditions (from < 60 ppt to 1-2 ppb) in the inlet by a box model. Their results showed that the positive bias of less than 0.5×10^6 cm^{-3} with a 60 ms conversion time, and the bias does not increase with the increase of NO concentration. Thus, the conversion time of 47 ms in our study should further reduce such positive bias.

Compared to C_3F_6, propane (C_3F_8) has a higher elimination rate. However, the purity of the C_3F_8 from most of the suppliers is not high enough for elimination of the artificial OH, we thus chose C_3F_6 due to its stable quality. These parameters taking the E_{Conv} and the HO_2 interference mentioned above into consideration. Similarly, the sample/sheath flow ratio was adjusted to 0.3 and the voltages different between sample and sheath flow were adjusted to 48 V to achieve the maximum E_{Ion}. Finally, the buffer flow was 440 sccm and the Pinhole voltage difference was 30 V for a better E_{Trans} and to prevent neutral molecules enter the mass

1   spectrometer system as the same time.

 Table S2. Technical details and specifications of the OH-CIMS

Efficiency Related	Parameters	Gas	Values	Units	Specification for Measurement	Values	Units
	Front Injection	SO_2 (0.9%)	5	sccm	Sample Flow [SO_2]	12	ppm
E$_{Conv}$	**Pulse Valve**	N_2	2	sccm	Cycle Duration (OH)	6	mins
		C_3F_6 (99.9%)	2	sccm	Elimination Rate (OH)	92%	
	Rear Injection	C_3F_6 (99.9%)	2	sccm	Sample Flow [C_3F_6]	1072	ppm
		HNO_3	10	sccm	Reaction Time	47	ms
	Sample Flow		3.7	slpm	Sample Flow Speed	55	cm/s
E$_{Ion}$	**Sheath Flow**	Zero Air	12.6	slpm	Reynolds Number in Ionization Chamber	>4000 Turbulent flows	
		HNO_3	10	sccm			
		C_3F_6 (99.9%)	2	sccm	Sheath Flow [C_3F_6]	159	ppm
	Total Flow		16.8	slpm	Sheath Flow Speed	25	cm/s
	Sheath Voltages		-80	V	Voltages Difference for ionization	48	V
	Sample Voltages		-32	V			
E$_{Trans}$	**Buffer Gas**	N_2	440	sccm	Voltages Difference for transmission	80	V
	Buffer Voltages		-70	V			
	Pinhole Voltages		-40	V			
Cal	**Calibration Flow**		10	slpm	Calibration Factor (Reagent ion: NO_3^-)	$1.21*10^{-8}$	OH·cm^3/Hz
	Flow Speed		65	cm/s			
	Product It Value		$8.8*10^{10}$	photon/cm			
Uncertainties	**Sigma (σ)**		2		**Detection Limit**	In lab	1.5
	Calibration		38%			Daytime	10
	Overall		44%			Nighttime	7.7

2 Notes:
3 sccm – Standard cubic centimeters per minute.   slpm - Standard liter per minute.
4 ppm – Parts per million   V – Voltage
5 The zero air was produced by Model 111 Zero Air Supply (Thermo Fisher Scientific) with an air
6 compressor.
7 Suppliers for N_2, SO_2, and C_3F_6: Scientific Gas Engineering Co. Ltd., HK.

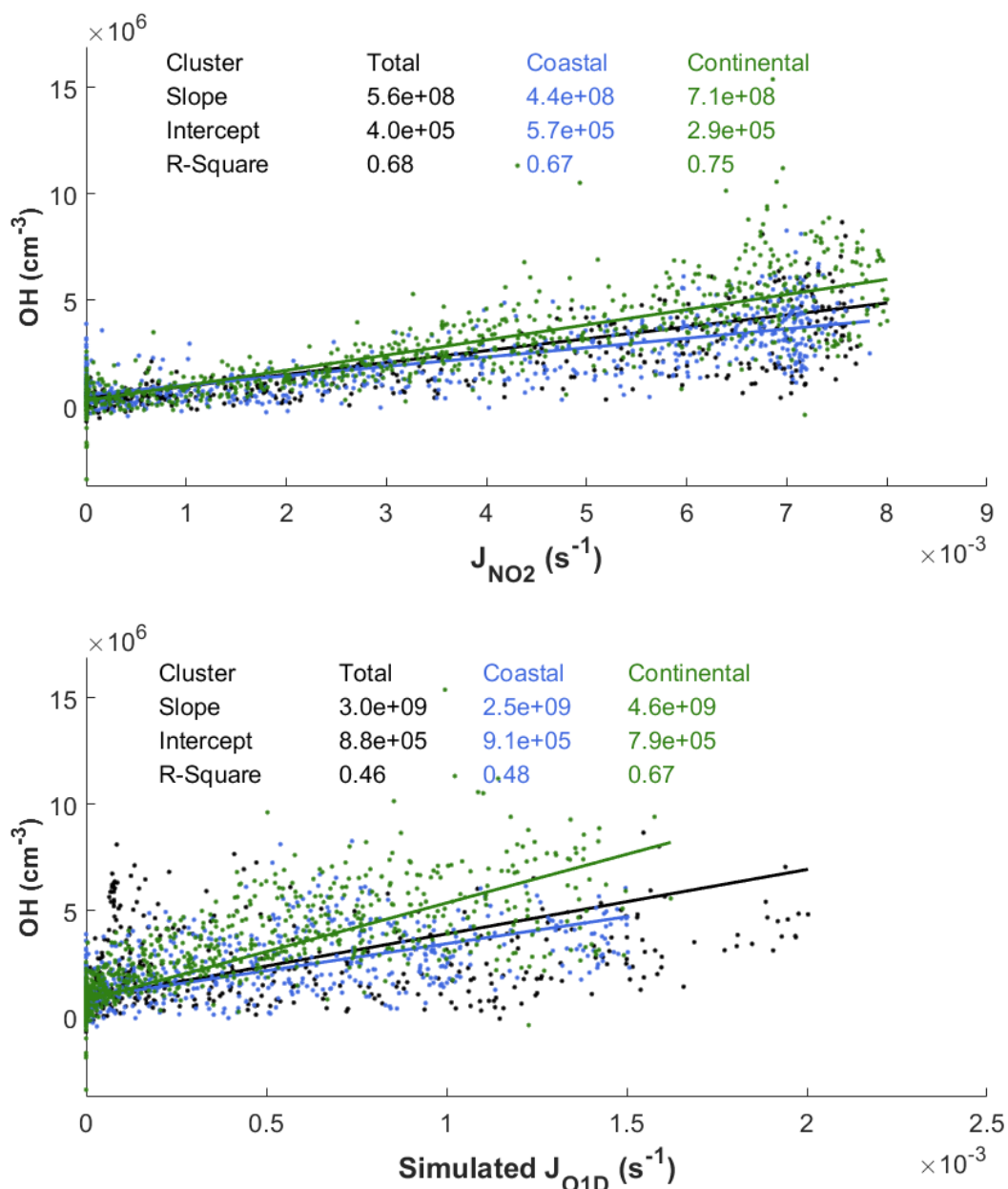



Figure S2. Correlation between observed OH concentration and a) photolysis frequency of NO$_2$ (J$_{NO2}$), and b) model simulated photolysis frequency O$_3$ (Simulated J$_{O1D}$). The linear regressions with respect to total, coastal, and continental cases are labelled in black, blue, and green. Note that the coastal and continental cases are reported as correlations for all cases in different clusters, not only the selected cases in the Figure 8 comparison.

1   Table S3. Average concentration with the standard deviations of measured species with respect to

2   different cases.

Species Abb.	Species Name	Total	Coastal	Continental	Oct10M	Oct10A	Episode
OH 10^6 (cm^{-3})	Hydroxyl radical	2.4±1.9	2.5±1.4	3.1±1.7	3.7±2.1	1.8±1.5	4.2±2.8
OH_DL 10^6 (cm^{-3})	Detection limit of hydroxyl radical	1.0±0.5	0.8±0.3	0.9±0.3	1.2±0.5	1.5±0.7	1.0±0.5
OH_Err 10^6 (cm^{-3})	OH Measurement Uncertainty	1.5±1.0	1.8±0.5	1.7±0.6	0.9±0.8	1.0±0.9	2.5±1.7
PM_Num 10^3 ($\#/cm^3$)	Number of particulate matters	3.8±1.9	4.1±1.7	4.9±1.4	NaN	NaN	5.6±2.0
*PM_Sur 10^7 (nm^2/cm^3)	Surface of particulate matters	19.7±9.0	15.0±2.3	26.8±4.3	NaN	NaN	31.5±14.2
PM_Vol 10^9 (nm^3/cm^3)	Volumn of particulate matters	7.6±3.8	4.9±0.7	10.5±1.5	NaN	NaN	12.0±5.9
*RH (%)	Relativie humidity	70.1±10.1	69.9±4.5	64.2±2.8	69.3±4.6	63.7±3.7	61.6±9.6
*CO2 (ppm)	Carbon dioxide	426.7±14.8	412.8±1.2	426.3±2.4	424.1±2.8	425.2±2.5	428.0±10.8
WindDi (°)	Wind direction	45.9±35.7	49.3±0.9	53.3±24.0	30.7±5.5	48.5±3.3	125.7±90.1
WindSp (m/s)	Wind speed	4.3±1.6	5.2±0.9	3.9±0.6	4.0±0.5	3.0±0.5	2.4±1.5
*Temp (°C)	Temperatuer	23.3±3.5	24.7±0.9	25.5±1.4	25.3±1.6	27.4±0.9	26.7±2.1
[†]SO2	Sulfur dioxide	2.6±1.2	3.2±0.2	3.4±0.1	3.5±0.2	3.2±0.1	4.4±0.8
[†]CO	Carbon monoxide	304.9±72	217.4±10.9	318.0±8.5	291.3±16.3	258.4±14.1	329.0±74.6
NH3	Ammonia	8.8±1.8	8.9±0.4	9.5±0.6	9.7±0.2	9.2±0.6	10.6±3.0
[†]NO	Nitrogen Monoxide	0.9±1.4	0.3±0.1	0.7±0.4	0.6±0.3	0.3±0.1	1.4±1.3
[†]NO2	Nitrogen Dioxide	3.9±3.5	1.6±0.7	4.5±1.1	3.4±1.4	1.1±0.5	10.1±5.6
[†]NOx	Nitrogen Oxides	4.8±4.4	1.9±0.7	5.2±1.2	4.0±1.6	1.4±0.5	11.4±6.2
[†]O3	Ozone	49.9±20.6	59.5±10.1	54.7±14.5	44.2±9.9	61.2±3.8	70.4±33.5
[†]JNO2 10^{-3} (s^{-1})	Photolysis rate constant of NO2	3.6±2.5	4.7±2.4	4.0±2.0	4.8±2.5	5.0±2.6	4.3±2.2
^HONO	Nitrous acid	0.15±0.069	0.15±0.019	0.16±0.035	0.29±0.101	0.14±0.015	NaN
*C2H4	Ethene	1.4±1.3	0.5±0.1	0.7±0.1	0.6±0.1	0.3±0.1	0.9±0.2
*C2H6	Ethane	1.9±0.9	1.4±0.1	2.1±0.1	2.0±0.1	1.7±0.1	2.3±0.5

*C3H8	Propane	1.7±0.9	1.1±0.2	1.5±0.2	1.3±0.1	0.8±0.1	2.1±1.7
*C3H6	Propene	0.10±0.05	0.07±0.01	0.11±0.02	0.18±0.06	0.06±0.01	0.12±0.04
*C2H2	Ethyne	1.63±0.65	0.97±0.03	1.42±0.23	1.07±0.08	NaN	1.39±0.48
*IC4H10	i-Butane	0.55±0.44	0.22±0.04	0.61±0.14	0.44±0.09	0.23±0.07	1.02±1.04
*NC4H10	n-Butane	0.76±0.60	0.27±0.06	0.88±0.19	0.67±0.13	0.32±0.08	1.53±1.62
*TBUT2ENE	But-2-ene	0.06±0.01	0.05±0.00	0.06±0.00	0.05±0.00	NaN	0.06±0.01
*BUT1ENE	But-1-ene	0.08±0.03	NaN	0.10±0.01	0.08±0.01	NaN	NaN
*IC5H12	i-Pentane	0.40±0.22	0.18±0.04	0.42±0.05	0.46±0.03	0.28±0.11	0.60±0.36
*NC5H12	n-Pentane	0.24±0.12	0.13±0.02	0.24±0.02	0.33±0.05	0.17±0.04	0.29±0.21
*C4H6	Buta-1,3-diene	0.06±0.01	NaN	0.06±0.00	NaN	NaN	0.06±0.00
*M2PE	2-Methyl pentane	0.31±0.14	NaN	0.28±0.05	0.30±0.04	0.20±0.00	0.36±0.27
*NC6H14	n-Hexane	0.15±0.11	0.08±0.01	0.15±0.04	0.10±0.03	0.05±0.00	0.28±0.28
*IC8H18	i-Octane	0.02±0.02	NaN	0.02±0.01	NaN	NaN	0.05±0.06
*NC7H16	n-Heptane	0.03±0.01	NaN	0.07±0.00	NaN	NaN	0.07±0.00
*NC8H18	n-Octane	0.03±0.00	NaN	0.03±0.00	NaN	NaN	0.03±0.00
*EBENZ	Ethyl Benzene	0.05±0.04	0.02±0.01	0.05±0.01	0.05±0.02	0.01±0.00	0.08±0.09
*MXYL	m-Xylene	0.03±0.03	0.01±0.00	0.03±0.01	0.03±0.01	0.01±0.00	0.02±0.02
*OXYL	o-Xylene	0.04±0.03	0.01±0.00	0.03±0.01	0.03±0.01	0.01±0.00	0.03±0.03
**CH2O2	Formic acid	1.02±0.44	0.58±0.08	1.03±0.19	1.16±0.20	1.55±0.11	1.54±0.47
**C2H4O2	Acetic acid	2.76±1.46	1.59±0.34	3.03±0.68	4.54±0.35	3.19±0.61	4.38±3.25
**C2H8O2	Ethylene dihydrate	0.06±0.02	0.06±0.00	0.06±0.01	0.05±0.00	0.04±0.00	0.09±0.06
**C5H8	Isoprene	0.31±0.24	0.16±0.06	0.36±0.14	0.69±0.46	0.56±0.33	0.54±0.25
**C4H6O	Methyl Vinyl Ketone + Methacrolein	0.16±0.10	0.06±0.01	0.22±0.06	0.26±0.05	0.15±0.06	0.32±0.19
**C3H4O2	Acrylic acid	0.12±0.05	0.06±0.01	0.13±0.03	0.16±0.02	0.13±0.02	0.19±0.10
**C3H6O2	Propanoic acid/ Hydroxy acetone	0.90±0.43	0.57±0.15	0.97±0.23	1.26±0.03	1.01±0.11	1.45±0.93
**C6H6	Benzene	0.28±0.13	0.12±0.03	0.33±0.03	0.43±0.04	0.25±0.05	0.38±0.21
**C6H12	Cyclohexane	0.02±0.01	0.01±0.00	0.03±0.00	0.03±0.01	0.02±0.01	0.04±0.03
**C3H4O3	Pyruvic acid	0.05±0.02	0.03±0.00	0.05±0.01	0.07±0.01	0.07±0.00	0.06±0.03
**C7H8	Toluene	0.38±0.27	0.20±0.10	0.46±0.11	0.50±0.08	0.24±0.04	0.69±0.67
**C8H10	Xylene	0.25±0.22	0.09±0.08	0.35±0.07	0.49±0.17	0.07±0.05	0.41±0.34
**C10H16	Monoterpene	0.05±0.03	0.03±0.00	0.06±0.01	0.10±0.06	0.09±0.04	0.07±0.03
**CH2O	Formaldehyde	1.03±0.41	0.62±0.05	1.17±0.11	1.72±0.10	1.59±0.17	1.17±0.42
**C2H4O	Acetaldehyde	1.88±0.90	0.98±0.13	2.10±0.41	2.74±0.16	1.96±0.36	3.17±1.98
**C3H6O	Acetone	3.88±1.60	2.18±0.31	4.43±0.74	5.64±0.49	5.91±0.47	5.92±2.85
**C3H4O	Acrolein	0.25±0.11	0.14±0.02	0.29±0.05	0.39±0.04	0.33±0.05	0.39±0.19
**C4H8O	MEK + Butanals	0.45±0.30	0.24±0.04	0.53±0.16	0.59±0.05	0.44±0.05	0.87±0.86

**C8H8O	Methyl benzaldehyde	0.04±0.03	0.02±0.00	0.05±0.01	0.06±0.00	0.04±0.01	0.08±0.06
&BVOC	Biogenic VOCs	0.3±0.4	0.2±0.1	0.4±0.1	1.1±0.6	0.8±0.4	0.7±0.5
&AVOC	Anthropogenic VOCs	7.1±3.6	4.0±0.7	7.6±0.9	7.7±0.9	4.4±0.7	11.1±8.7
&OVOC	Oxygenated VOCS	7.2±7.4	7.0±1.0	9.2±1.5	18.6±1.3	16.4±1.9	14.9±12.8
&Arom	Aromatic compounds	0.6±0.6	0.4±0.2	0.8±0.1	1.5±0.3	0.6±0.1	1.2±1.3
&Alkane	Alkane	6.5±3.4	3.6±0.5	6.8±0.8	6.3±0.6	3.8±0.6	9.9±7.5
&Alkene	Alkene	2.5±1.9	0.5±0.1	2.2±0.2	2.6±0.2	1.0±0.5	2.5±1.0
&Aldehyde	Aldehyde	4.4±4.5	4.2±0.5	5.7±0.8	11.4±0.8	10.4±1.1	9.1±7.6
&Acid	Acid	2.8±2.9	2.8±0.5	3.4±0.6	7.2±0.5	5.9±0.8	5.8±5.2

1   Notes:

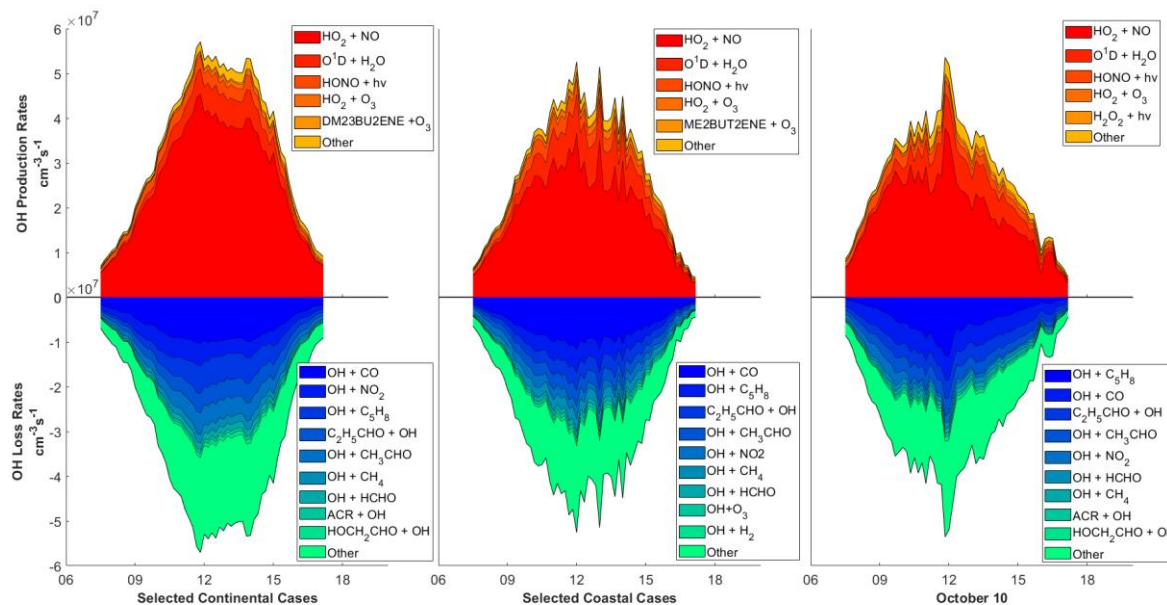
2   The concentration unit is presented in the bracket in the 'Species Abb.'.

3   The unit for other species is in ppb.

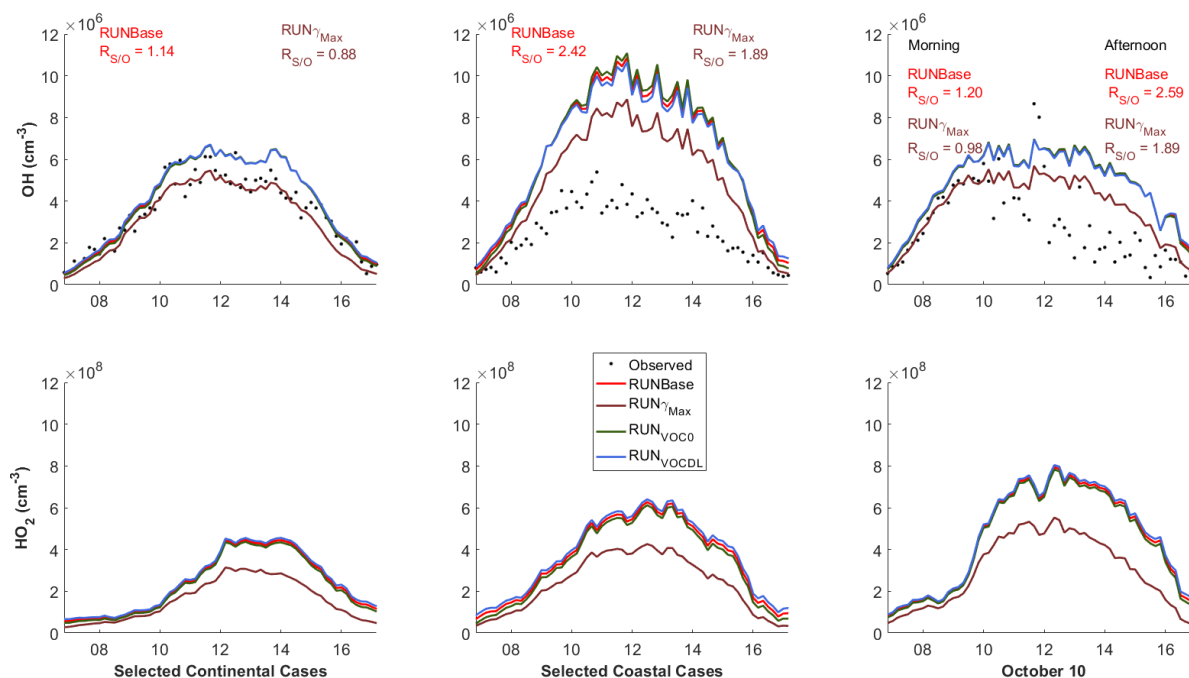
4   * Species measured by GC-MS and constrained by the model

5   ** Species measured by PTR-MS and constrained by mode.

6   † Species measured by instrument specified in Table 1.

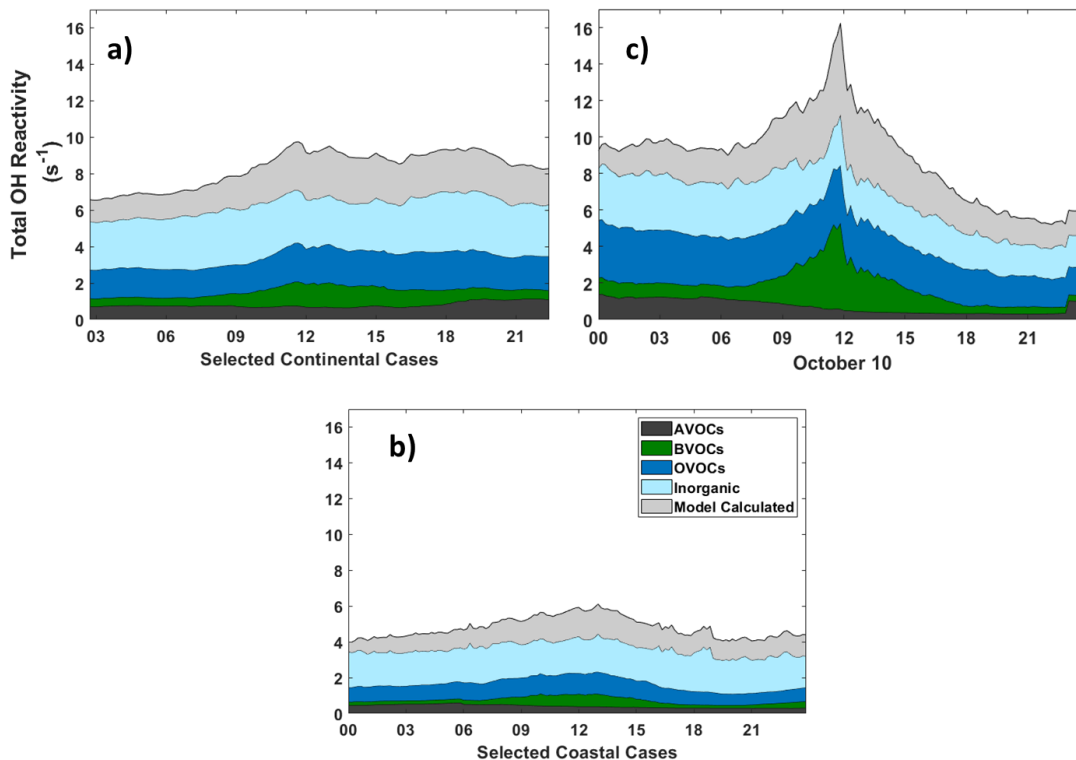
7   & Different VOCs functional groups.

2 Figure S3. OH radical budgets for the continental cases, coastal cases, and 10 October. Where

3 DM23BU2ENE and ME2BUT2ENE represent 2,3-Dimethyl-2-butene and 2-Methyl-2-butene

4 respectively.

7 Figure S4. Sensitivity tests for the simulated OH and HO_2 in continental and coastal cases and on 10

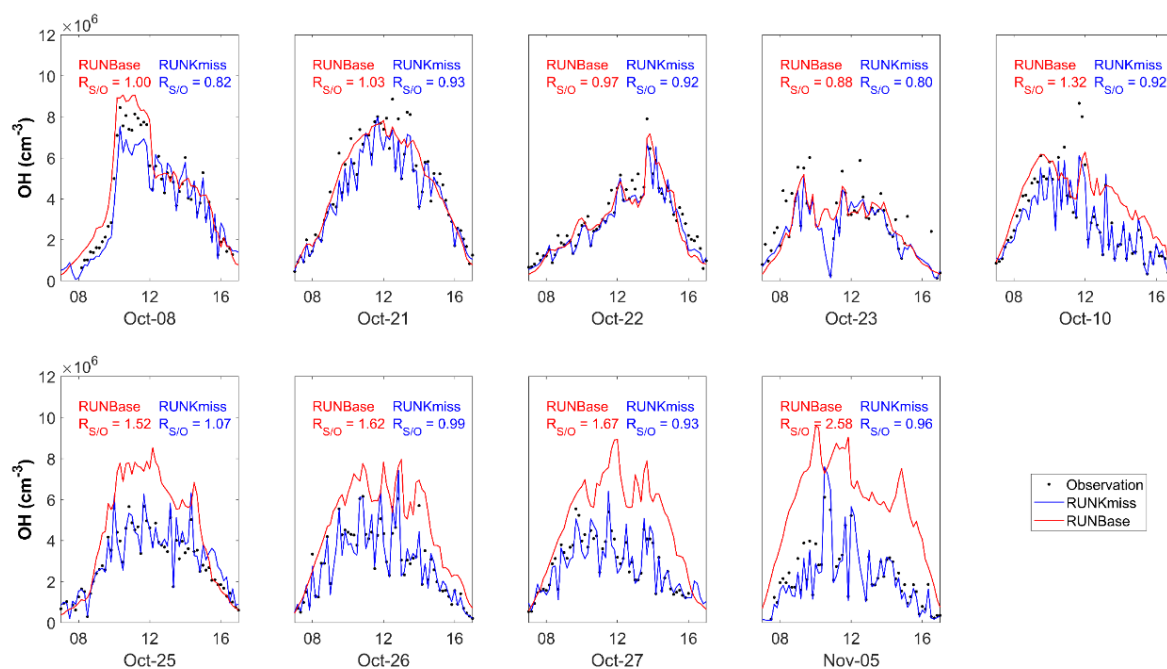
8 October. $RUN\gamma_{MAX}$ shows the simulated results for the maximum heterogeneous uptake effect of HO_2

9 ($\gamma = 1$). The RUN_{VOC0} and RUN_{VOCDL} show the simulated results that constraints "0" and the detection

 limit value as the concentration of VOCs when their concentration were below detection limits.

3 Figure S5. Simulated reactivity for continental cases (a), coastal cases (b), and 10 October (c). The

4 AVOCs, BVOCs, OVOCs, and Inorganic demostrates the reactivity calculated from the measured

5 species and the Model Calculated represtens the reactivity calculated by the derived species simulated

6 by model.

1 Figure S6. Nine-day comparison between observed OH and simulated OH with (RUNBase) and without

2 (RUNKmiss) addition reactivity.

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